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# Self-Assembly, Luminescence Properties and Excited State Interactions of Block Copolymers that Contain Ruthenium tris(bipyridine)

By

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A thesis submitted to McGill University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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## Abstract

## Self-Assembly, Luminescence Properties, and Excited State Interactions of Block Copolymers that Contain Ruthenium Tris(bipyridine)

This thesis describes the examination of novel block copolymers that  $contain Ru(bpy)_3^{2+}$  complexes incorporated into one block of diblock copolymers made by ROMP. With the intent of exploring the potential usefulness of these interesting materials in applications such as light-harvesting and sensing, a systematic study of the solution self-assembly, luminescence properties, and the ability of the metal complex to engage in electron and energy transfer reactions has been conducted.

The solution self-assembly of block copolymers that contain  $Ru(bpy)_3^{2+}$  complexes was examined first. Using a series of these block copolymers, a detailed study of the effects of block length, block ratio, polymer concentration and solution conditions on the copolymer self-assembly is presented. Using TEM, a number of morphologies were reproducibly observed including star micelles, large compound micelles, tubules, and interestingly, vesicles. These structures all contain the metal complex Ru(bpy)\_3^{2+} within their core domains.

The luminescence properties of two block copolymers containing  $Ru(bpy)_3^{2+}$  were examined: one polymer self-assembled into star micelles, the other into vesicles. Comparison of the unassembled polymer chains and the self-assembled polymers indicated that self-assembly, and confinement of the  $Ru(bpy)_3^{2+}$  complexes into the core domains of the aggregates, did not seriously adversely affect the luminescence properties of the metal complex. Measurement of the luminescence lifetime decay of the polymers suggested that energy



migration occurred among the metal complexes along the polymer chain. The ability of the metal complexes within self-assembled structures to participate in electron transfer reactions with small molecules was also explored. It was found that from within the core domains of self-assembled structures, the  $Ru(bpy)_3^{2+}$  complexes could still engage in electron transfer reactions with molecules on the outsides or the insides of the aggregates, likely a result of energy migration.

The ability of  $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$  complexes within the cores of micelles to participate in energy transfer was explored. Micelles were formed in aqueous solutions using polymers that possessed both the metal complex and a water-soluble block. Several methods were attempted to encapsulate two molecules, a derivative of coumarin 2 and an Os(bpy)\_3^{2^+}-based molecule, inside these micelles. It was observed that  $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$  could act as an energy acceptor from the coumarin derivative, and could act as an energy donor to the osmium-based complex. Encapsulation of the small molecules greatly enhanced the efficiency of energy transfer, by non-covalently bringing the small molecules in close proximity to the Ru(bpy)\_3^{2^+} complexes.

Polymers were synthesized that contained a  $Ru(bpy)_3^{2^+}$ -based block and were terminated with the molecular recognition unit biotin. These polymers, upon self-assembly, formed micelles with biotin groups on their periphery. The addition of the protein streptavidin, which has a strong binding affinity for biotin, resulted in the aggregation of the self-assembled structures. This established the potential for self-assembled metal-containing aggregates to form higher-order structures.

Early work is presented in Appendix A involving block copolymers that contain hydrogen-bonding groups. Several methods were attempted to elucidate the solution morphologies of these polymers, namely IR, <sup>1</sup>H NMR, DLS, and pyrene fluorescence. The transition of this initial work to polymers that contain the  $Ru(bpy)_3^{2+}$  complex is also described.

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#### Résumé

# L'auto-assemblage, les propriétés luminescentes et les interactions à l'état excité de copolymères à blocs contenant le tris(bipyridine) ruthénium

Cette thèse décrit l'examen de nouveaux copolymères à blocs contenant des complexes de  $\text{Ru}(\text{bpy})_3^{2+}$  incorporés dans un bloc de copolymères diblocs. Ayant pour intention d'explorer les utilisations potentielles de ces matériaux intéressants pour divers applications, pouvant être utilisés comme collecteur de lumière et senseur par exemple, une étude systématique de l'auto-assemblage en solution, des propriétés luminescentes et l'habileté du complexe métallique à s'engager dans des réactions de transfère d'électrons et d'énergie a été effectuée.

L'auto-assemblage en solution de copolymères à blocs contenant des complexes de  $Ru(bpy)_3^{2+}$  a été examiné en premier lieux. En utilisant une série de ces copolymères à blocs, une étude détaillée de l'effet de la longueur et du ratio des blocs, de la concentration du polymère et des conditions de l'auto-assemblage du copolymère en solution est présentée. En utilisant le MET, de nombreuse morphologies ont été observées de manière reproductible incluant des micelles étoilées, de larges composés fait de micelles, des tubules et, encore plus intéressant, des vésicules. Ces structures contiennent tous le complexe métallique  $Ru(bpy)_3^{2+}$  dans leurs domaines centraux.

Les propriétés luminescentes de deux copolymères à blocs contenant du  $Ru(bpy)_3^{2+}$  ont été examinées ; un des polymères s'auto-assemblant en micelles étoilées et l'autre en vésicules. La comparaison des chaines de polymères non assemblées avec celles auto-assemblées indique que l'auto-assemblage et le confinement du complexe  $Ru(bpy)_3^{2+}$  dans le domaine centrale des agrégats

n'influencent pas de manière défavorable les propriétés luminescentes du complexe métallique. La mesure de la réduction de la durée de vie luminescente des polymères suggère qu'une migration d'énergie se produit parmi les complexes métalliques qui sont attachés aux chaines de polymères. L'habilité des complexes métalliques insérés dans des structure auto-assemblées à participer aux réactions de transfère d'électrons avec de petites molécules a aussi été explorée. Il a été découvert que parmi les domaines centraux de la structure auto-assemblée, les complexes fait de Ru(bpy)<sub>3</sub><sup>2+</sup> peuvent s'engager dans des réactions de transfère d'électrons avec des molécules à l'extérieur ou à l'intérieure des agrégats. Ceci est probablement dû à la migration de l'énergie.

L'habilité des complexes de  $Ru(bpy)_3^{2^+}$  situés au centre de micelles à participer au transfère d'énergie a été exploré. Des micelles ont été formées dans une solution aqueuse en utilisant des polymères possédant un complexe métallique et un bloc soluble dans l'eau. Plusieurs méthodes ont été utilisées pour encapsuler deux molécules, c'est-à-dire un dérivé de coumarine 2 et une molécule faite à base de Os(bpy)\_3<sup>2+</sup>, à l'intérieur des ces micelles. Il a été observé que le  $Ru(bpy)_3^{2^+}$  peut agir comme un accepteur d'énergie provenant de la molécule faite à base de coumarine et peut agir comme un donneur d'énergie aux complexes fait d'osmium. L'encapsulation de ces petites molécules accroît considérablement l'efficacité du transfère d'énergie en rapprochant de manière non covalente les petites molécules des complexes de  $Ru(bpy)_3^{2^+}$ .

Des polymères ayant pour bloc le complexe métallique fait de  $Ru(bpy)_3^{2+}$  et étant terminés par la molécule de reconnaissance biotine ont été synthétisés. Lors de l'auto-assemblage, ces polymères forment des micelles ayant à leur périphérie les groupes biotines. L'addition de la protéine surnommée streptavidine, qui a une grande affinité de liaison avec la biotine, a pour effet d'agréger la structure autoassemblée. Cette protéine a en fait le potentiel de créer l'auto-assemblage d'agrégats contenant des métaux et par le fait même de produire une structure ayant un degré d'organisation plus élevé.

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Des travaux préliminaires relatif aux copolymères à blocs contenant des groupes hydrogènes liant sont présentés dans l'Appendice A. Plusieurs méthodes ont été utilisées afin d'élucider la morphologie en solution de ces polymères, incluant l'infrarouge, la RMN du <sup>1</sup>H, la diffraction dynamique de la lumière et la fluorescence par pyrènes. L'application de ces travaux initiaux aux polymères contenant le complexe Ru(bpy)<sub>3</sub><sup>2+</sup> est aussi décrite.

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## **Contributions of Authors**

Two of the Chapters included in this thesis include work previously published.

Chapter 2. The author of this thesis is the sole author on the related publication (besides Dr. Sleiman), and performed all the self-assembly experiments and the TEM and DLS analysis. The author also synthesized all the monomers and polymers for this study, excluding polymers 4a and 4b, which were synthesized by Bingzhi Chen.

Chapter 5. The author of this thesis contributed to the self-assembly experiments and analysis of the polymers described in this Chapter. The synthesis was performed by Bingzhi Chen.

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## List of Abbreviations

A	Acceptor
ATRP	Atom transfer radical polymerization
CHCl <sub>3</sub>	Chloroform
$CH_2Cl_2$	Dichloromethane
D	Donor
DAP	Diamidopyridine
DLS	Dynamic light scattering
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
GPC	Gel permeation chromatography
НОМО	Highest occupied molecular orbital
IR	Infrared
LED	Light emitting diode
LCM	Large compound micelle
LUMO	Lowest unoccupied molecular orbital
MeCN	acetonitrile
MLCT	Metal-to-ligand charge transfer
MWCO	Molecular weight cut-off
NQ	Naphthquinone
NMR	Nuclear magnetic resonance
PAA	Poly(acrylic acid)
PDI	Polydispersity index
PEG	Poly(ethylene glycol)
PMMA	Poly(methyl methacrylate)
PS	Poly(styrene)
PTZ	Phenothiazine

ROMPRing opening metathesis polymerizationSDSSodium dodecasulfateTEMTransmission electron microscopy

THF Tetrahydrofuran

# Chapter 1: Introduction

## **Chapter 1: Introduction**

With the pressing need to develop new energy sources, the improvement of systems that can harvest the sun's energy is becoming increasingly important. Traditional designs to convert light energy into electrical or chemical energy include solar cells based on silicon or other inorganic or organic materials.<sup>1</sup> One approach to light-harvesting systems is to use specific molecules (such as  $Ru(bpy)_3^{2+}$ ) to mimic particular functions of natural photosynthetic systems. The molecular components of these designs must be capable of absorbing visible light from the sun, forming a charge-separated state and, through electron transfer reactions, shuttling positive and negative charges away from each other and towards active centers where they can be used to participate in reactions or generate a current. In such designs, the precise arrangement of chromophores and other active molecules is often critical to ensure that the positive and negative charges are shuttled in the right directions and that they do not recombine. Polymer backbones can act as scaffolds to arrange the various components of these systems, and thus polymers are increasingly examined for light-harvesting applications, as well as for designs for light-emitting, catalyst, and sensor materials.

A variety of polymer systems that incorporate the  $Ru(bpy)_3^{2+}$  complex have been designed for these applications, but there have, until recently, been no reports of block copolymers that contain a dense arrangement of this luminescent and redox-active metal complex. Block copolymers can spontaneously selfassemble under controlled conditions into predictable structures, and thus may have potential to organize various components in a predetermined manner. The development of these well-defined block copolymers that can self-assemble into predictable morphologies may result in a new class of materials. Thorough examination of the photophysical properties of these new polymers and their selfassembled structures could determine the feasibility of using these systems for

applications including light-harvesting and light-emitting materials, sensors and catalysts.

This thesis describes the synthesis and solution self-assembly of novel ROMP block copolymers that contain ruthenium tris(bipyridine), their excited state interactions with other small molecules, and the development of polymer systems that possess molecular recognition capability.

## 1.1. Properties of Ru(bpy)<sub>3</sub><sup>2+</sup>

#### 1.1.1. Excited state features

Upon irradiation at 450 nm, an electron is promoted from the metal to a ligand  $\pi^*$  orbital (a singlet metal-to-ligand-charge transfer (<sup>1</sup>MLCT) excited state). Intersystem crossing to the emissive <sup>3</sup>MLCT occurs within approximately 100 fs of excitation in acetonitrile solution<sup>2</sup> with a quantum yield of unity (Scheme 1.1). Femtosecond spectroscopy has indicated that upon initial absorption and promotion of the electron, the negative charge is delocalized on all three bpys, and that localization on one of the bipyridine ligands takes about 60 fs in acetonitrile. This corresponds to the inertial response of the solvent; the solvent dipoles must reorient with respect to the new dipole of the complex, thus this time scale for charge localization increases with the inertial mass of the solvent. Because the time scale for population of the <sup>3</sup>MLCT state is so much faster than the emission, in the excited, charge-separated, emissive state, the promoted electron is considered to be localized on one of the three bipyridyl ligands, and not delocalized over all three ligands.<sup>3</sup>

Scheme 1.1. Energy diagram for  $Ru(bpy)_3^{2+}$ .



From the <sup>3</sup>MLCT excited state, relaxation occurs by radiative and nonradiative processes (Scheme 1.1). Emission occurs from a set of three closely-spaced energy levels ( $\Delta E = 10$  and 61 cm<sup>-1</sup>), which at room temperature are in equilibrium.<sup>4</sup> This "average" excited state is considered to be mostly triplet in nature, with singlet character imparted by spin-orbit coupling due to the heavy metal center. Because the emitting state is predominantly triplet in character, the lifetime of the excited state is relatively long (500 ns - >1 µs). Due to the partial singlet character of this state, emission is not technically called "phosphorescence", and thus the term "luminescence" is often used to describe Ru(bpy)<sub>3</sub><sup>2+</sup> emission.

Nonradiative decay processes include relaxation through vibrational pathways with solvent and thermal population of a metal-centered <sup>3</sup>d-d state. The <sup>3</sup>d-d state lies slightly higher in energy than the <sup>3</sup>MLCT bands, but at room temperature it is thermally accessible and is a major decay pathway in all solvents.<sup>5</sup> It may decay without emission to the ground state or, as it results in

significant distortions along the Ru-N bond, may undergo photochemistry and ligand loss.

#### **1.1.2. Tuning Excited State Properties**

One of the attractive features of ruthenium polypyridyl complexes is that emission properties, such as the emission wavelength and lifetime, can be modified to some degree. Methods to tune the emission of the complex include changing or modifying the ligands or adjusting the solvent polarity or rigidity.

#### 1.1.2.1. Ligand Modification

By modifying or changing the ligands attached to the ruthenium, the emission wavelength can be tuned to cover a range from below  $600 \text{ nm}^6$  to into the near IR (1400 nm).<sup>7</sup> Both the acceptor and auxiliary ligands can affect the emission wavelength.

The acceptor ligand is obviously important because excitation promotes an electron into an orbital on a single ligand. One way to tune the emission of the complex is to derivatize the accepting ligand with electron donating or electron accepting groups. This changes the reduction potential of the accepting ligand and affects the emission energy. Another way to adjust the energy of the acceptor ligand (and thus affect the emission wavelength) is to modify its conjugation. Increasing the conjugation can lower the energy of the acceptor ligand without significantly decreasing its sigma donation ability.<sup>7</sup> As well, with more rigid acceptor ligands, structural changes between the ground state and the excited state are decreased and the acceptor energy can increase. This can cause a decreased rate of non-radiative decay and longer luminescence lifetimes. However, there is a delicate balance involved because with higher energy acceptors, thermal population of the <sup>3</sup>d-d metal-centered states is increased, and therefore the emission lifetime is decreased.

The acceptor ligand is not the only important factor toward controlling the energy of the excited state; the auxiliary ligands are relevant as well. The energy of the MLCT excited state also depends on the oxidation potential of the metal, which is affected by the electron donating and accepting properties of all the ligands. The +3 charge, or hole, that forms on the metal upon excitation of the ruthenium complex, is stabilized by electron donation from electron rich ligands.<sup>7</sup>

The complex relationships between the metal, the accepting ligands, and the auxiliary ligands must all be considered when trying to adjust the ligands to tune the emission properties of ruthenium polypyridyl complexes. Large adjustments of the excited state energy can be made by changing the ligand itself, while substitutions on the ligand rings can allow fine-tuning.<sup>6</sup>

Scheme 1.2. Polydentate ligands. (a) Adapted from reference 8b; (b) Adapted from reference 8d.



Polydentate, rather than simply bidentate, ligands have also been shown to affect the emission properties of ruthenium complexes. For example, the synthesis of hexadentate cage ligands has been reported<sup>8</sup> (Scheme 1.2). The use of such cage ligands can significantly increase the lifetime and quantum yield of

the ruthenium complexes because the rigidity of the cage prevents significant distortions of the nuclear configurations that are required for some non-radiative decay processes. As well, the activation energy for cross-over to the <sup>3</sup>dd state is increased. The rate of non-radiative decay, which in ruthenium polypyridyl complexes is usually much more significant than the radiative decay rate, is therefore decreased.

#### **1.1.2.2.** Solvent Effects

The emission properties of ruthenium polypyridyl complexes can also be tuned by adjusting the polarity of the solvent environment. The excited state responsible for the emission of the complex is a charge separated state, and thus the polarity of the surrounding solvent affects the excited state energy, and therefore its lifetime and quantum yield.

The excited state decays by radiative and non-radiative processes. Changing the solvent does not affect the rate of formation of the <sup>3</sup>MLCT excited state, but does result in changes in emission energy.<sup>9</sup> According to the Energy Gap Law, the rate of non-radiative decay ( $k_{nr}$ ) increases exponentially as the energy gap or emission energy decreases. It has been demonstrated that changing the solvent does not greatly affect the rates of radiative decay, but more profoundly influences the rate of non-radiative decay.<sup>9</sup> Since the rate of non-radiative decay is generally much greater than the radiative decay rate and largely determines the overall decay rate, solvent adjustments can have a noticeable effect on  $Ru(bpy)_3^{2+}$  emission. In less polar solvents, the excited state is less stabilized, and the energy gap increases, thus decreasing the rate of non-radiative decay. In general,  $Ru(bpy)_3^{2+}$  complexes can therefore have longer decay times and higher quantum yields in non-polar solvents (equations 1.1 and 1.2).

$$\phi = \frac{k_r}{k_r + k_{nr}}$$
(Eq. 1.1)  
$$\tau = \frac{1}{k_r + k_{nr}}$$
(Eq. 1.2)

#### 1.1.2.3. Rigidity of the medium

Controlling the rigidity of the environment surrounding ruthenium complexes is another way to tune their emission properties. When Ru(bpy)<sub>3</sub><sup>2+</sup> is incorporated into rigid media (like films<sup>10</sup> or sol-gels<sup>11</sup>), the stability of the complex, as well as the lifetime, quantum yield, and emission energy can increase. Increasing the rigidity of the matrix has several effects on the photochemistry of the excited state that contribute to increased stability of the complex. For one, there is a decrease in surface crossing from the <sup>3</sup>MLCT to the <sup>3</sup>dd state, and the reactivity of the <sup>3</sup>dd state is decreased. This <sup>3</sup>dd state is responsible for ligand loss, and is thermally accessible from the <sup>3</sup>MLCT in all solvents at room temperature.<sup>9,12</sup> Finally, in rigid media, there is a cage effect that promotes ligand rebinding should one of the bipyridine nitrogens become dissociated from the ruthenium.<sup>12</sup>

In addition to these direct influences on the physical stability of the complex, the rigidity of the environment can influence the emission behavior in other ways. Upon excitation in fluid solution, solvent dipoles reorient according to the newly formed charge-separated configuration of the excited state, stabilizing the excited state somewhat prior to emission. In rigid media, however, the medium is at least partially frozen on the time scale for excited state decay, so the surrounding solvent dipoles are orientated more like those that surround the ground state complex. Since the solvent does not stabilize the excited state before emission, emission occurs at a higher energy (blue shifted) in rigid media than in fluid solution.<sup>13</sup> The greater emission energy can also result in longer lifetimes and higher quantum yields in accordance with the energy gap law.
### 1.1.3. Excited State Reactivity

The absorbance and luminescence properties of ruthenium polypyridyl complexes, and the ability to tune these features, are not the only reasons that these complexes have been utilized for many applications. Perhaps most useful is that the  $Ru(bpy)_3^{2+}$  excited state is capable of participating in bimolecular electron transfer and energy transfer reactions with quencher molecules Q (Scheme 1.3).

Scheme 1.3. Excited state reactions of  $Ru(bpy)_3^{2+}$ 

Energy transfer:	* $Ru^{2+} + Q \longrightarrow Ru^{2+} + *Q$
Electron transfer (oxidative):	$*Ru^{2+} + Q \longrightarrow Ru^{3+} + Q^{-}$
Electron transfer (reductive):	* $Ru^{2+} + Q \longrightarrow Ru^+ + Q^+$

This is because the excited state is of relatively high energy, and since it is reasonably long-lived (500 ns->1  $\mu$ s), interaction with other molecules is possible within the lifetime of the excited state.<sup>14</sup> In addition, in the excited state, with an electron localized on one of the bpy ligands, bimolecular association of a quencher molecule with the edge of the aromatic bipyridine ligand gives an efficient pathway for energy or electrons to flow from the \*Ru(bpy)<sub>3</sub><sup>2+</sup> to a guencher.<sup>15</sup>

#### 1.1.3.1. Electron transfer

The result of the metal-to-ligand charge transfer transition is that there is an electron missing from the  $t_{2g}$  orbital of the metal center (a hole), and an electron in the  $\pi^*$  orbital of a ligand. Therefore, the excited state can act as both an oxidizing

and reducing agent. The excited state has an overall higher energy content than the ground state complex, and thus it is a stronger oxidant and reductant than the ground state species (Scheme 1.4).

Scheme 1.4. Redox properties of  $Ru(bpy)_3^{2+}$  relevant for electron transfer reactions.



According to the Marcus theory, the rate of electron transfer between two reactants is described by  $k = v_N \kappa exp^{-\Delta G^{\neq}/RT}$ ,<sup>16</sup> where  $v_N$  is the effective nuclear frequency and  $\kappa$  is the electronic transmission coefficient.  $\Delta G^{\neq}$  is the free energy of activation, and can be expressed as  $\Delta G^{\neq} = \left(\frac{\lambda}{4}\right) \left(1 + \frac{\Delta G^0}{\lambda}\right)^2$ . In this equation,  $\lambda$  is the reorganizational energy, and is the sum of two components: the inner (bond lengths and angles for the two reactants) and outer (solvent reorganization around the reactants) modes.  $\Delta G^0$  is the free energy change for the reaction.

This equation predicts a bell-shaped curve for a plot of log k vs  $\Delta G^0$  in which there are three regions<sup>16</sup> (Scheme 1.5). There is a "normal" region for endoergonic and slightly exergonic reactions, in which log k increases with increasing driving force. For  $-\Delta G^0 = \lambda$ ,  $\Delta G^{\neq} = 0$  and the reaction becomes barrierless. Finally, for highly exergonic reactions, log k decreases with increasing driving force in the "inverted" region. In other words, as  $\Delta G^0$  becomes more negative, the rate of electron transfer increases to a maximum;

when  $\Delta G^0$  becomes too negative, the rate decreases, even though the reaction becomes more thermodynamically favoured.<sup>17</sup>



Scheme 1.5. Energy diagrams for electron transfer with  $Ru(bpy)_3^{2+}$ .

The ability of ruthenium polypyridyl complexes to participate in electron transfer reactions has been utilized in applications such as light-emitting materials, solar energy harvesting and water splitting. For example, electron transfer studies with  $Ru(bpy)_3^{2+}$  attached to soluble polymers have been aimed towards the generation of multiple redox equivalents for solar energy conversion.<sup>18</sup>

#### 1.1.3.2. Energy Transfer

Ruthenium polypyridyl complexes are also able to engage in energy transfer reactions. Depending on the system, the complex can act as either the energy acceptor or the energy donor. The two main mechanisms for energy transfer are the Coulombic, or dipole-dipole, mechanism, and the exchange, or collisional, mechanism. The two mechanisms are pictured in Scheme 1.6.<sup>19</sup>

**Scheme 1.6.** Coulombic and Exchange mechanisms for energy transfer. The numbered circles represent the "active" electrons involved in the transitions, while the solid circles represent "passive" electrons. Adapted from reference 19.

Coulombic (Förster, dipole-dipole) mechanism:



Exchange (Dexter) mechanism:



$$k_{ET}(Coulombic) = k \frac{\kappa^2 k_D^0}{R_{DA}^6} J(\varepsilon_A)$$
 (Eq. 1.3)

$$k_{ET}(exchange) = KJexp^{\left(-2R_{DA}/L\right)}$$
 (Eq. 1.4)

In the dipole-dipole, or Coulombic mechanism, the orbital motions (oscillations) of electron 1 in the excited donor D\* cause perturbation of the orbital motions of electron 2 in the HOMO of the ground state acceptor A. If there is resonance, energy transfer may occur resulting in electron 1 relaxing its motion (becoming de-excited) and electron 2 being set into motion (becoming excited). With the Coulombic mechanism, resonance between D\* and A occurs via the electromagnetic field, and thus physical contact between D\* and A is not necessary.

The rate of Coulombic energy transfer is given in equation  $(1.3)^{19}$  In this equation, *k* is a constant related to experimental conditions such as concentration and the index of refraction of the solvent,  $\kappa^2$  is the orientation factor between two oscillating dipoles (equal to 2/3 in random systems) and  $k_D^0$  is the pure radiative rate of the donor D\*.  $R_{DA}$  is the distance between D\* and A, and  $J(\varepsilon_A)$  is similar to the spectral overlap integral but includes the extinction coefficient of the acceptor. The rate of Coulombic (dipole-dipole) energy transfer is greatest when there is: a) a large overlap integral J between the D\* emission and the A absorbance, b) the radiative rate constant of the donor is large, c) the magnitude of  $\varepsilon_A$  is large, and d) there is small separation between D\* and A. The D\*-A separation at which the rate of energy transfer is equal to the inherent rate of decay of D\* is called the Förster distance,  $R_0$ . If the donor and the acceptor are closer than the Förster distance, energy transfer dominates; if they are farther apart than  $R_0$ , D\* decay dominates.

In the exchange mechanism, there is overlap between electron 1 in the excited state of D\* and the LUMO of the ground state of A, and overlap between electron 2 in the HOMO of A and the HOMO of D\*. Energy transfer occurs when electron 1 is transferred to the acceptor A, and electron 2 is transferred to the donor D. In this mechanism, electrons actually exchange between D\* and A, and therefore overlap of electron clouds and physical contact is required.

The rate of energy transfer by the exchange mechanism is given in equation (1.4).<sup>19</sup> Here, K is related to specific orbital interactions, J is the spectral overlap

integral that is normalized to the extinction coefficient of the acceptor, and  $R_{DA}$  is the D\*-A separation relative to their van der Waals radii, L.

One difference between the Coulombic and exchange mechanisms is that in the exchange mechanism, the overlap integral J is normalized for  $\varepsilon_A$  so it does not depend on the magnitude of  $\varepsilon_A$ . This means that the rate of Coulombic energy transfer is related to the absorbance characteristics of the acceptor, but the rate of energy transfer by the exchange mechanism does not. Another key difference between the two mechanisms is the dependence of the energy transfer rate on the distance between D\* and A. The rate of dipole-dipole energy transfer decreases as R<sup>-6</sup>, while the rate of energy transfer decreases as  $\exp(-2R_{DA}/L)$ . Therefore, the rate of energy transfer by the exchange mechanism essentially becomes negligible (relative to the donor lifetime) as R becomes larger than 1 or 2 molecular diameters, or 5 – 10 Å. The dominant mechanism of energy transfer can be determined by measuring the rate of energy transfer as a function of donor -acceptor separation.<sup>20</sup>

# **1.2.** Applications involving $Ru(bpy)_3^{2+}$ photophysics:

As a result of its photophysical and electrochemical properties, ruthenium polypyridyl complexes have been used in a range of applications, including sensors, light-emitting materials and solar cells.

## 1.2.1 Ru(bpy)<sub>3</sub><sup>2+</sup>-based complexes in sensors

Various designs for sensors have exploited the ability of ruthenium-based complexes to engage in energy transfer and electron transfer reactions, the influence of the local environment on the emission properties, and the effects that ligand modifications have on the absorbance and emission features. Ruthenium polypyridyl complexes have been studied as sensors for oxygen,<sup>21</sup> pH,<sup>22</sup> glucose,<sup>23</sup> peroxide,<sup>24</sup> DNA damage<sup>25</sup> or mismatches,<sup>26</sup> ions such as F<sup>-27</sup> and

 $K^{+\ 28},$  enzyme activity,  $^{29}$  and even the environment inside mesoporous clay hosts.  $^{30}$ 

Most ruthenium polypyridyl-based sensors for oxygen rely on the oxygen quenching of the MLCT excited state, and involve using the metal complex embedded in a matrix such as a sol-gel or gas-permeable membrane. This matrix is then exposed to a sample and the luminescence intensity or lifetime decay is measured. The decrease in either intensity or lifetime as a result of quenching by oxygen can then be compared to a calibration curve to determine the amount of oxygen in a sample. Some more complex sensor designs involve ruthenium complexes attached to other molecules that experience a change in absorption properties as a function of a particular analyte. In the case of the sensor for potassium ions listed above,<sup>28</sup> if the analyte is present, energy transfer occurs from the ruthenium complex to the molecule attached to it, resulting in decreased lifetimes of the ruthenium complex.

Some of the advantages of using ruthenium-based complexes as sensors, particularly for oxygen, is that the complexes do not consume oxygen, they have short response times, and they can be used for measuring O<sub>2</sub> concentrations in gaseous, aqueous, and organic phases. They also have long lifetimes, which can be particularly useful for sensing involving samples that may have their own background fluorescence.<sup>21j</sup> In many sensing applications, the metal complex is embedded into a matrix such as a gel. One advantage of this method is that the more rigid environment of the matrix can increase the complex's luminescence lifetime, thus improving the sensitivity of assays.<sup>22b</sup> However, a main disadvantage of incorporating the complex into a matrix is that the weak interactions holding the complex in place, such as van der Waals forces or hydrogen bonding, may not be able to control the aggregation of the emitting species. This can lead to a heterogenous dispersion of the complexes and result in complicated decay kinetics and Stern-Volmer quenching curves. Another problem is that the complexes can, with time, leach out of a matrix.<sup>21j</sup> Fortunately, another feature of ruthenium polypyridyl complexes is the ease of

derivatizing the ligands, and so these complexes can be grafted to the matrix or to polymers, thus decreasing the uncontrolled aggregation of the complexes. Several sensor systems in which the ruthenium moieties are attached covalently to a polymer chain have been developed.<sup>31</sup>

## 1.2.2. $Ru(bpy)_3^{2+}$ -based complexes in light emitting materials

The unique properties of ruthenium polypyridyl complexes have also been harnessed in the design of light-emitting materials. In such devices, an applied electrical potential results in the emission of light. Ruthenium-based complexes are appropriate for light-emitting materials because they are relatively chemically, photochemically, electrochemically, and thermally stable.<sup>32</sup> It is also possible to achieve high-brightness and high-efficiency emission using low driving voltages with solid-state electrochemiluminescence (ECL) cells based on ruthenium complexes.<sup>33</sup> In addition, relatively simple modification of the ligands allows tuning of the redox and emission properties as well as the film-forming and polymerization ability.

Many of these systems<sup>34</sup> take advantage of the disproportionation reaction

$$\operatorname{Ru}(\operatorname{bpy})_{3}^{3+} + \operatorname{Ru}(\operatorname{bpy})_{3}^{+} \leftrightarrow \operatorname{Ru}(\operatorname{bpy})_{3}^{2+} + \operatorname{Ru}(\operatorname{bpy})_{3}^{2+}$$

\*Ru(bpy)<sub>3</sub><sup>2+</sup>  $\rightarrow$  Ru(bpy)<sub>3</sub><sup>2+</sup> + hv

The 1+ and 3+ ruthenium species can be produced at different electrodes, or at the same electrode by applying a cyclic square potential wave between the reduction and oxidation potentials of the ruthenium complex. Reaction of the +1 and +3 species results in the generation of an excited state  $Ru(bpy)_3^{2+}$  complex, which then emits red light. Other systems<sup>35</sup> incorporate a semiconductive polymer as the host material for the electrochemiluminescent (ECL) devices, ie, the semiconductive polymer is doped with the metal complex. Energy transfer then occurs from the semiconductive host polymer to the ruthenium species, resulting in red-coloured emission. In the design of such systems, it is important to consider the excited state lifetime of the conducting polymer (energy donor); it must be long enough for energy transfer to the Ru(bpy)<sub>3</sub><sup>2+</sup> to occur. Another important factor is the compatibility of the host polymer with the Ru(bpy)<sub>3</sub><sup>2+</sup> complex. Aggregation of the ruthenium species within the polymer host would prevent the metal complexes from being in close proximity to the host polymer molecules and result in decreased energy transfer.

In many of these designs for light-emitting devices, the metal complexes are mixed with a host polymer or other substrate (doping of the host polymer) and layered with electrodes in a device. Mixing the metal complex with a host polymer can help to decrease triplet-triplet annihilation and self-quenching reactions among the ruthenium complexes and thus improve device lifetime. However, doping the metal complex into a host polymer can result not only in problems associated with rapid decay of device efficiency with an increase in current density, but in problems with long-term storage and operation due to complex aggregation over time. Attaching the metal complex directly to the host polymer can combat these problems.<sup>36</sup>

# 1.2.3. $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$ -based complexes in solar cells.

Not only have ruthenium complexes been used to emit red light upon the application of an electric current, but they have also been applied to solar cells, in which production of electricity is the result of irradiation with sunlight. Traditional solar cells use silicon-based materials, but problems associated with these systems include loss of energy as heat, recombination of charges to create an upper limit to efficiency, and the high cost of silicon.<sup>37</sup> Since O'Regan and

Grätzel first described a ruthenium dye-sensitized solar cell (DSSC),<sup>38</sup> there has been a flurry of research<sup>39</sup> into variations of these "Grätzel cells".

A typical Grätzel cell has several main components (Scheme 1.7). On the top is a transparent anode, such as tin oxide doped with fluorine, deposited on a glass plate. Attached to the surface of the conductive plate is a highly porous layer of titanium dioxide (TiO<sub>2</sub>) particles (or film) coated with the sensitizing dye. The dye is typically a derivative of a ruthenium polypyridyl complex. Also in the cell is an electrolyte that is usually composed of  $\Gamma/I_3^-$ . The cell is completed with a conductive sheet or counter electrode (such as platinum metal).

When sunlight enters the cell through the transparent  $SnO_2$ :F layer, it excites the ruthenium-based dye that coats the TiO<sub>2</sub> surface. Electrons are "injected" from the excited dye into the conduction band of the TiO<sub>2</sub>, and from there move to the anode. The dye is then reduced by the iodide in the electrolyte solution, forming triiodide, I<sub>3</sub>. This occurs faster than the rate of recombination between the TiO<sub>2</sub> and the oxidized dye. I<sub>3</sub> is reduced back to I at the counter electrode.<sup>40</sup>





DSSC's are efficient, low-cost alternatives to traditional solar cells.<sup>41</sup> Ruthenium-based complexes are well-suited to solar cell applications because they absorb in the visible region, they have suitable oxidation and reduction potentials, are relatively stable in their oxidized and reduced forms, and their photophysical and electrochemical properties can be tuned by modifying the ligands.<sup>42</sup> However, they do have some limitations, including the limited range of absorption and relatively low molar extinction coefficients of ruthenium polypyridyl complexes.<sup>41a</sup>

While some studies have examined the effects of adjusting the electrode material<sup>43</sup> and the electrolyte composition,<sup>44</sup> the majority of work has focused on modifying the ruthenium dye.<sup>45</sup> For example, replacing the carboxylic acids on one bipyridine with alkyl chains (9 carbons) can help reduce/prevent water absorption onto the TiO<sub>2</sub> and thus improves device stability<sup>46</sup> and decreases the rate of recombination with  $I_3$ .<sup>47</sup> One of the challenges is that the LUMO and HOMO of the dye must be maintained so that both electron transfer from the dye into the conduction band of the TiO<sub>2</sub> as well as regeneration of the dye by iodide can occur efficiently.<sup>41a</sup> The photophysical properties of ruthenium complexes are dependent on the ligands, and thus variation of the ligands to enhance the absorbance range and extinction coefficient may improve the efficiency of these devices. The ruthenium complex used in the early Grätzel cell is shown in Scheme 1.8.

**Scheme 1.8.** The ruthenium complex used in the early Grätzel cells: cis-bis(4,4'-dicarboxy-2,2'-bipyridine)-bis(isothiocyanato)ruthenium(II) dye, or N3.



There have also been limited studies on the use of ruthenium-containing polymers in solar cells.<sup>48</sup> Using metal-based polymers can result in lower-cost fabrication procedures while maintaining high accuracy control of the thickness of the dye layer.<sup>49</sup>

#### **1.3. Other metal complexes**

There are a number of metal complexes besides ruthenium polypyridyl species that have been examined for sensing and light emitting applications. Several lanthanide complexes based on Eu(III),<sup>50</sup> Tb(III),<sup>50b</sup> Nd(III),<sup>51</sup> and Yb(III)<sup>52</sup> have luminescence arising from f-f transitions.<sup>53</sup> While these complexes generally have uncomplicated spectra and some have long lifetimes<sup>50b,54</sup> (up to ms), they generally do not absorb visible light and have to be excited via energy transfer from the ligands to the metal center.<sup>51,52,55</sup> There are also Re(I),<sup>56</sup> Rh(III),<sup>57</sup> and Ir(III)<sup>58</sup> complexes that have been shown to have useful emission properties. Using a range of complexes of these metals, emission wavelengths can span much of the visible region, quantum yields vary from almost zero to 0.5, and lifetimes can be as long as several hundred microseconds. Some of these

complexes were once synthetically challenging, but are becoming increasingly available.<sup>58c</sup>

While metal complexes other than ruthenium polypyridyl-based ones are reported more and more frequently, Ru(bpy)-based complexes are still very well-represented in the literature. One reason for this is that Ru(bpy)<sub>3</sub><sup>2+</sup> can still outperform other metal complexes, particularly in light-emitting applications.<sup>56b,c,57b</sup> The other important reason for the use of Ru(bpy)-related complexes is that they possess a very favourable *combination* of useful properties,<sup>59</sup> including visible absorption, large Stokes shift, tunable emission, long lifetime, a mid-range quantum yield (compared to some other metal complexes) and stability (photochemical, thermal). Ru(bpy)-based complexes also have favourable electrochemical properties and excited state reactivity that encourages their use in light harvesting applications.

# 1.4. Polymers containing Ru(bpy)<sub>3</sub><sup>2+</sup>

Because of their useful properties and functions in different applications, ruthenium polypyridyl complexes have been incorporated into a variety of polymer systems. Attaching  $Ru(bpy)_3^{2+}$  directly to a polymer backbone can minimize or eliminate several disadvantages associated with simply doping a polymer matrix with the metal complex, such as expensive fabrication processes<sup>60</sup> and problems associated with phase behavior (complex aggregation) that become a more significant with long-term storage and operation.<sup>61</sup> The polymer backbone can also be used as a "chemical scaffold" to arrange the metal complexes.<sup>62</sup>

Most commonly, polymers containing pendant  $Ru(bpy)_3^{2^+}$ -based complexes are generated by adding the complex to a preformed polymer backbone, often either poly(styrene)<sup>63</sup> or acrylate-related backbones.<sup>64</sup> In some cases, direct copolymerization of a Ru-containing monomer has been performed.<sup>65</sup> One of the advantages of directly polymerizing a metal-containing monomer is that higher loading, or a higher  $Ru(bpy)_3^{2^+}$  content in the final polymer, can be achieved.<sup>65d</sup>

The main disadvantage is that the final metal containing polymer can be more difficult to characterize by GPC methods.<sup>66</sup>

There have been very few examples of *living* polymerization of rutheniumcontaining monomers. M. Weck reported the ring-opening metathesis polymerization (ROMP) of a  $Ru(bpy)_3^{2+}$ -based monomer to form a homopolymer,<sup>67</sup> and the Sleiman group demonstrated the living ROMP of a ruthenium-based monomer into well-defined homopolymers and block copolymers.<sup>68</sup>

A variety of different polymer architectures that contain the complex have been synthesized and studied. In some cases, the ruthenium complex comprises the centre of a star-shaped polymer. For example, in the lab of C. Fraser,<sup>69</sup> the bipyridine ligands of the  $Ru(bpy)_3^{2+}$  complex were functionalized for polymerization by ATRP, and polymer or block copolymer arms were "grown" from the centre metal complex (Scheme 1.9). The combination of biocompatible polymers like poly(acrylic acid) and poly(lactic acid),<sup>70</sup> or DNA-binding polymers like poly(ethylenimine)<sup>71</sup> with the  $Ru(bpy)_3^{2+}$  complex yields a multifunctional system for vector localization or drug delivery (in cell culture) with optical imaging.<sup>70</sup>

Scheme 1.9. Star-shaped polymers from the Fraser lab. (a) Adapted from reference 70; (b) Adapted from reference 69e.



Scheme 1.10. Star-shaped antenna polymers. Adapted from reference 72a.



Other star-shaped polymers that have ruthenium polypyridyl complexes at the centre have been developed in the lab of K.P. Ghiggino as light harvesting or antenna systems (Scheme 1.10).<sup>72</sup> These polymers have an energy gradient from the periphery to the core, and when light is absorbed by these systems, an energy cascade occurs from acenaphthenyl moieties at the ends of the arms, to coumarin complexes and finally to the Ru(bpy)<sub>3</sub><sup>2+</sup>-based cores.

Scheme 1.11. Polymers with ruthenium as a junction between polymer chains. (a) Adapted from reference 75b; (b) Adapted from reference 75a.





Some polymers contain ruthenium polypyridyl complexes at the junction between polymer chains.<sup>73</sup> For example, research in the group of U.S. Schubert<sup>74</sup>,<sup>75</sup> has included the synthesis and supramolecular chemistry of block copolymers that possess a ruthenium terpyridine complex at the interface between polymer blocks (Scheme 1.11). Polymer chains are derivatized at one end (or both ends) with a terpyridine molecule, and two (or more) different derivatized polymer blocks can be attached by coordination to ruthenium. This allows for the very specific placement of functional metal complexes within polymer chains. Self-assembly of these chains leads to aggregates where the complexes are located in a particular domain of a self-assembled polymer structure.<sup>75</sup> The driving force behind this work has been the creation of materials with new and interesting properties including reversibility, optical and electrical properties, and film formation.

Ruthenium polypyridyl complexes have also been incorporated into conjugated polymers<sup>76</sup> (Scheme 1.12). Conjugated polymers themselves are attractive for a number of applications due to their solution processability, mechanical flexibility, color tunability, and low operating voltage.<sup>77</sup> Adding phosphorescent groups, such as metal complexes, to conjugated polymers can potentially result in improved charge carrier ability.<sup>78</sup> as well as higher electroluminescence efficiencies because the final material could have both triplet and singlet emission.<sup>77,79</sup> In addition, conjugated polymers containing metals in the main chain may also exhibit non-linear optical behavior and liquid crystallinity.<sup>80</sup> The main goal of research in this area is to create metal-organic hybrid materials that have unique and useful optical and/or electrical properties, and to potentially tune the physical properties of the resulting materials. Ruthenium-containing conjugated polymers are studied for applications such as LED's, laser damage protection, electronic or optical signaling.<sup>81</sup> and photoconducting materials.<sup>80</sup>

Scheme 1.12. Conjugated polymers containing  $\text{Ru}(\text{bpy})_3^{2^+}$ . (a) Adapted from reference 80; (b) Adapted from reference 76a.



Among polymers containing multiple ruthenium complexes, those generated by the group of T.J. Meyer over the past 20 years are perhaps the most thoroughly examined. This research has generally explored the ability of soluble polymers to facilitate a build-up of redox equivalents through a combination of electron transfer and energy transfer reactions. One of the goals of this work has been to create polymers for artificial photosynthesis applications, where the ability of the polymer components to engage in energy transfer and electron transfer reactions would be highly advantageous.

The polymers created in the Meyer lab have predominantly been based on poly(styrene) backbones that are polymerized by either free radical polymerization or living anionic polymerization techniques.<sup>82</sup> Both methods generate random copolymers, often consisting of styrene and derivatized styrene (such as chloromethyl styrene, to which the metal complexes are attached) and in all cases, the metal complexes are added to the pre-formed polymer backbone. This method has the disadvantage that precise spatial distribution of complexes and other components along the polymer chain is not possible. The metal

complexes, such as  $\text{Ru}(\text{bpy})_3^{2^+}$  or  $\text{Os}(\text{bpy})_3^{2^+}$ , attached to these polymers possess the PF<sub>6</sub> counterion and are soluble in acetonitrile solutions.

Among the most important findings to emerge from this research relates to the effects of incorporating multiple ruthenium-based complexes along a polymer backbone. One concern is the likelihood of electron transfer quenching of \*Ru(bpy)<sub>3</sub><sup>2+</sup> by Ru<sup>3+</sup>, (Eq. 1.5) which forms upon electron transfer quenching of \*Ru<sup>2+</sup> with an electron acceptor. This would limit the ability of these polymers to accumulate multiple redox equivalents, especially considering that mechanisms like energy migration would bring \*Ru<sup>2+</sup> and Ru<sup>3+</sup> to adjacent sites (see below).<sup>83</sup> Fortunately, the electron transfer reaction between \*Ru<sup>2+</sup> and Ru<sup>3+</sup> is not major problem for these soluble polymers because the reaction is in the Marcus inverted region.

\*
$$Ru^{II} + Ru^{III} \longrightarrow Ru^{III} + Ru^{II}$$
 (Eq. 1.5)

In addition, polymers with multiple  $Ru(bpy)_3^{2+}$  units often display nonexponential, or at least bi-exponential, decay. There are two main reasons for The first is that \*Ru – Ru energy migration can occur, a phenomenon in this. which the ruthenium excited state migrates among the complexes within the polymer chain (random walk, Scheme 1.13a). Second, with multiple chromophores along a polymer chain, it is possible to have multiple photons absorbed and thus multiple excited complexes per polymer chain. This can have two main effects. The first is that with multiple excited states in a polymer sample, not all are going to be in the exact same environment. Closely related to this is that when one complex is excited, the solvent dipoles around it reorganize to accommodate the newly formed excited state dipole. The environment surrounding nearby complexes is thus slightly more polar, decreasing their excited state energy.  $Ru(bpy)_3^{2+}$  emission is sensitive to environmental factors, and thus a range of excited state energies and decay times exist across the whole

polymer. As well, triplet-triplet annihilation between excited state complexes can occur (Scheme 1.13b). These can all contribute to non-exponential decay.

Scheme 1.13. (a) Energy migration via random walk of the excited state, and (b) triplet-triplet annihilation along a polymer chain containing multiple  $\text{Ru(bpy)}_3^{2+}$  complexes.



It might be advantageous to have a soluble polymer system with multiple excited complexes per chain. This could have implications in terms of the multielectron transfer requirements of small molecule reactions such as the reduction of  $CO_2$  or the oxidation of  $H_2O$ . In one study,<sup>84</sup> it was demonstrated that it was possible to achieve up to 7 excited states on a single polymer chain.

Other important information gained from work in the Meyer lab regards the importance of the nature of the linkage between the metal complex and the polymer backbone (Scheme 1.14).

Scheme 1.14. Polymers with the  $Ru(bpy)_3^{2+}$  complex attached to the polymer backbone by (a) an ether linkage, or (b) an amide bond.



Earlier work focused on polymers in which the metal complex is attached to the polymer backbone by an ether linkage, such as in Scheme 14a.<sup>85</sup> Ru(bpy)<sub>3</sub><sup>2+</sup> and Os(bpy)<sub>3</sub><sup>2+</sup> complexes were attached to the polymer backbone, and the efficiency of energy transfer from the Ru(bpy)<sub>3</sub><sup>2+</sup> to the Os(bpy)<sub>3</sub><sup>2+</sup> complexes was measured. Depending on the metal content of the polymer, energy transfer occurred at a relatively fast rate (k>2x10<sup>8</sup>). However, only those Ru(bpy)<sub>3</sub><sup>2+</sup> complexes directly adjacent to the Os(bpy)<sub>3</sub><sup>2+</sup> moieties participated in energy transfer, because \*Ru-Ru energy migration processes in ether-linked polymers were slow (k<1x10<sup>6</sup>).<sup>85b</sup>

Later work resulted in the creation of amide-linked polymers (Scheme 1.14b).<sup>86</sup> When polymers with this structure contained both ruthenium and osmium complexes, energy transfer from  $Ru(bpy)_3^{2+}$  to  $Os(bpy)_3^{2+}$  was observed, as in the ether-linked polymers. However, in this case, \*Ru-Ru energy migration was 200x faster than in the ether-linked polymers, and this resulted in more efficient energy transfer and sensitization of the Os(bpy)\_3^{2+} complexes.<sup>87</sup> Energy

transfer between the complexes along the polymer chains is believed to proceed via a through-space interaction.

In terms of energy transfer and energy migration processes, the important difference between the amide-linked and the ether-linked polymers is the orientation of the excited state dipole. Upon excitation of Ru(bpy)<sub>3</sub><sup>2+</sup> complexes, one of the bipyridyl ligands is reduced and a dipole is formed. In the ether linked polymer (Scheme 1.14a), the bipyridyl ligand attaching the complex to the polymer backbone contains an electron donating group; it is therefore less easily reduced and so it is one of the other two bipyridine ligands that receives the electron density. The dipole formed in the excited state is therefore oriented *away* from the polymer backbone. In the (electron withdrawing) amide-linked polymers (Scheme 1.14b), the excited state electron density lies on the bipyridine that attaches the complex to the polymer backbone. In this case, the excited state dipole is pointed *towards* the polymer backbone and also towards neighbouring complexes; it is believed that this is the reason for the enhanced rates of energy migration processes observed in the amide-linked polymers compared to the ether linked species.

The Meyer lab has also investigated the effect of incorporating, or embedding,  $Ru(bpy)_3^{2+}$ -containing polymers into rigid media such as polymer films or SiO<sub>2</sub> sol-gels.<sup>88</sup> Energy migration and energy transfer processes had been demonstrated for polymers in fluid solution, but, particularly in terms of device fabrication, the determination of the efficiency of these processes in a rigid environment was warranted.

In some experiments,<sup>88a</sup> both monomeric model compounds and polymers were embedded in poly(methyl methacrylate) (PMMA) films about 1 mm thick. While it was assumed that the individual polymer chains would adopt extended rod-like structures in the PMMA like they do in acetonitrile solutions, there would likely be some important differences. One was that in the absence of the highly polar solvent molecules of acetonitrile, the electrostatic interactions between neighbouring complexes would be greater, and this might result in an increase in

the average distance between the peripheries of adjacent complexes. The second difference was that the  $PF_6$  counterions would be more closely associated with the polymer chains, since the PMMA has a low dielectric constant.

The model monomer complexes, upon incorporation into PMMA films, exhibited a blue-shifted emission and higher quantum yield as a result of the increased rigidity of the film environment (see Section 1.1.2.3). When poly(styrene)-based Ru(bpy) $_{3}^{2+}$  (20 units) or Os(bpy) $_{3}^{2+}$  (20 units) homopolymers or mixed  $Ru(bpy)_3^{2+}$ :Os(bpy)\_3^{2+}(17:3) copolymers were embedded in the PMMA films, they did not show the same features as the monomer samples. In general, detailed analysis became more complicated in PMMA films than for the same samples in fluid solution because of a more heterogeneous environment. There was no increase in quantum yield for the polymers when they were incorporated into the films. It was also determined that while energy transfer from  $Ru(bpy)_3^{2+}$ to  $Os(bpv)_3^{2+}$  in the mixed polymer could still occur in the rigid PMMA, it was not as efficient as in acetonitrile. This is likely due to a decreased rate of energy migration among ruthenium complexes, which is in turn caused by decreased fluctuations and motion along the polymer chain and the formation of energy "traps".

In the work from the Meyer lab described above, the potential of  $Ru(bpy)_3^{2+}$  polymer systems to function in designs for artificial photosynthesis was demonstrated. The drawback of these systems is that there is no way to control the overall spatial positioning of chromophores or other molecules on the poly(styrene) polymers. However, specific chromophore arrangement and directionality of electron- or energy transfer reactions are of fundamental importance in light harvesting designs. To gain precise control over the placement of metal complexes and other molecules,  $Ru(bpy)_3^{2+}$  complexes and electron donors and acceptors were attached to proline residues. Oligoprolines can adopt a helical conformation, and therefore this allowed for the generation of well controlled "polymers" containing complexes in predetermined spatial arrangement.<sup>89</sup>

Scheme 1.15. (a) Oligoprolines containing  $Ru(bpy)_3^{2+}$  complexes separated from phenothiazine quenchers by oligoproline residues. Adapted from reference 89c. (b) Phenothiazine (electron donor) and anthroquinone (electron acceptor) separated by a  $Ru(bpy)_3^{2+}$  complex along an oligoproline chain. Adapted from reference 89b.





Some experiments varied the number of proline residues (bonds) that separated a  $Ru(bpy)_3^{2+}$  complex and the reductive quencher phenothiazine (Scheme 1.15a).<sup>89c</sup> Because of the helical structure of the oligoproline, increasing the number of bonds between the metal and the quencher did not necessarily increase the through-space distance between them. Based on the rates of electron transfer, the predominant mechanism was through-space, rather than through

bond. In other studies, an electron donor and an electron acceptor were separated by a ruthenium complex (Scheme 1.15b). Through electron transfer reactions, the metal could facilitate charge separation to form a fully redox separated state; back electron transfer then occurred directly between the positively charged electron donor and the negatively charged acceptor (not via the  $Ru(bpy)_3^{2+}$  complex). If additional ruthenium complexes were added between the electron donor and acceptor, energy migration among the  $Ru(bpy)_3^{2+}$  complexes allowed for the formation of the redox separated state, but back electron transfer was slowed.

In general, a variety of different polymer architectures that contain  $Ru(bpy)_3^{2+}$ -related species have been created that have utilized the interesting properties of the metal complex. Many detailed studies have demonstrated the ability of polymer-bound  $Ru(bpy)_3^{2+}$  complexes to absorb and emit visible light, transport excited state energy, engage in excited state reactions such as energy-and electron transfer, and facilitate charge separation. The potential of these metal-containing polymers to function in applications such as sensing, light harvesting and energy conversion, and light emitting is thus highly anticipated and these systems are continually developed.

### 1.5. Ring-Opening Metathesis Polymerization with Grubbs Catalyst

The ruthenium-based ROMP catalysts 1-3 have become indispensible for the polymerization of cyclic olefin species. One of the main reasons for their increased popularity is their functional group tolerance. The ruthenium group's preference for "soft" Lewis bases, like olefins, over "hard" bases, such as oxygen, is responsible for the high tolerance of these catalysts towards air and water, and has made possible the polymerization of monomers possessing a rich array of functional groups. In addition, ROMP is a living polymerization, ie, chain termination mechanisms are minimized. This allows for the synthesis of block copolymers, thereby further expanding the range of properties of polymers made by the ROMP technique.



#### 1.5.1. Mechanism

The general mechanism of ROMP can be demonstrated using the generalized Grubbs catalyst ([Ru]) as an example (Scheme 1.17). First, in the initiation step, dissociation of a phosphine ligand results in a coordinatively unsaturated species (14-electron for 1 and 2; dissociation of a bromopyridine ligand results in a 16-electron species for 3). The second step involves coordination of an electron-rich olefin to the metal. In the third step, a 2+2 cycloaddition results in a metallocyclobutane species that can then undergo a retro 2+2 reaction to generate a new alkylidene product (the propagating polymer chain). The overall catalytic activity of the catalyst depends on the relative rates of three processes: phosphine dissociation (initiation)  $k_1$ , phosphine recoordination  $k_{-1}$ , and olefin binding  $k_2$ .<sup>90</sup>

Scheme 1.17. (a) Mechanism of Grubbs catalyst [Ru]. L=PCy<sub>3</sub> (generation 1) or N-heterocyclic carbene (generations 2 and 3); X = Cl. Adapted from reference 90; (b) ROMP reaction for generation of polymers.<sup>91</sup>



35

[Ru]

Ph

#### **1.5.2.** Catalyst features

There are three ruthenium-based Grubbs catalysts that have been frequently used, referred to as generations 1 (1), 2(2) and 3(3) (sometimes referred to as a modified generation 2 catalyst). These catalysts are discussed below.

The first generation catalyst 1 has found widespread use as it leads to polymers with low PDI's (polydispersity index; a PDI of 1.0 means that all polymer chains have exactly the same number of monomer units, while higher numbers indicate a broader distribution of molecular weights). However, this catalyst suffers some disadvantages. While it is air stable in the solid state, in solution it reacts rapidly with air. The catalyst also decomposes in the presence of coordinating solvents like acetonitrile, DMSO and DMF, and reacts slowly with methanol. It is also unstable in the presence of CO and primary amines.<sup>92</sup> In addition, it is not very effective at polymerizing bulky monomers.<sup>93</sup>

In the second generation catalyst **2**, an N-heterocyclic carbene (NHC) replaces one of the phosphine ligands. This ligand is a stronger  $\sigma$ -donor, is bulkier, and is less labile. The increased activity for the second generation catalyst, compared to the first generation, is related not to increased phosphine exchange rates, as first thought, but to an increased preference for binding the more  $\pi$ -accepting olefins over phosphines. The phosphine exchange rates were actually found to be slower for the second generation, so the initiation rate k<sub>i</sub> is slower but since the catalyst, with its preferred binding for olefins, remains in the catalytic cycle longer the overall rate of catalysis is high. Because of the strong donor ability of the NHC ligand, this generation of the Grubbs catalyst is more effective than the previous version for more highly substituted (bulkier) olefins and for electron-poor olefins.<sup>94</sup> However, because the rate of propagation (k<sub>p</sub>) is increased greatly compared to the initiation rate k<sub>i</sub>, use of the second generation catalyst can result in uncontrolled polymerizations that yield polymers with high PDI's.<sup>93</sup>

The third generation catalyst (3) also contains an N-heterocyclic carbene group, but instead of a phosphine ligand possesses two bromo-pyridine groups. The change results in improved initiation rates, and thus the third generation catalyst possesses many of the advantages of the second generation catalyst (including high activity with a range of monomers), but also yields polymers with improved PDI's.<sup>95</sup>

#### **1.5.3. Examples of ROMP polymers**

Because of the very good functional group tolerance of the series of ruthenium-based ROMP initiators, these catalysts have been used to polymerize a wide variety of monomers into polymers with interesting functionality and applications. There are many examples in which ROMP monomers that possess biologically relevant moieties have been incorporated into polymers for biomedical applications. These include biodegradable polymers,<sup>93</sup> polymers with drugs covalently attached to the backbone,<sup>96</sup> polymers with zwitterionic functionality,<sup>97</sup> and even polymers to which MRI contrasting agents (Gd(III)) can be attached.<sup>98</sup> In addition, ROMP polymers have been made that incorporate biorecognition or molecular recognition elements.<sup>99</sup> Many of these polymers are developed for biodetection assays or are designed to be stimuli-responsive.

One interesting example of a functional polymer made by ROMP, and of the functional group tolerance of the ruthenium-based ROMP catalysts, involves the synthesis of a triblock copolymer designed for battery materials (Scheme 1.18).<sup>100</sup> This polymer consists of a cobalt-containing block (polymerization of a cobalt-containing monomer), a block of poly(ethylene oxide) (PEO), and a block of poly(norbornene-dicarboxylic acid), which contains polar functionalities that can incorporate metal salts (particularly Li). In this polymer, the cobalt block was the anode, the PEO was the electrolyte, and the third block was the cathode.



Scheme 1.18. Polymer made by ROMP for battery materials. Adapted from reference 100.



Photoresponsive polymers,<sup>101</sup> polymers for packing in columns for separation applications,<sup>102</sup> and solid polymer electrolytes<sup>103</sup> are other examples of the materials generated by the ring-opening metathesis technique.

The monomers used to create these polymers often possess a variety of functional groups or include metal complexes.<sup>104</sup> As well, monomers with large or bulky substituents<sup>105</sup> can be polymerized, and thus the use of the ROMP technique has greatly increased the range of functional polymeric materials that can be generated.

#### 1.6. Self-Assembly of Block Copolymers in Solution

Block copolymers are polymers that contain a string of one monomer attached to a string of a different monomer, in the general form A-A-A-A-A-B-B-B-B-B, or poly(A)-*block*-poly(B). They are ideal for the construction of nanoscale materials because of their inherent dimensions, their general ease of synthesis, their processability, and the degree of control over their architecture.<sup>106</sup> Particularly, they are able to self-assemble, both in bulk and in solution, into a variety of morphologies.<sup>107</sup> As a result of these desirable properties, block copolymers have been studied for use in a range of applications including drug delivery, catalysis, and cosmetics.<sup>108</sup> Self-assembly is the process by which the polymers aggregate in solution as a result of a thermodynamic driving force (such as the incompatibility of one block with solvent) to minimize the interfacial energy of the system. In general, for a diblock copolymer in which one block is soluble in a particular solvent but the other block is not, self-assembly results in the insoluble block forming the "core", (which is hidden from the solvent), and the soluble block forming the "corona." If the core-forming block is small relative to the solubilizing coronaforming block, aggregates that form are generally termed "star micelles." If, on the other hand, the core-forming block is large relative to the corona, the structures that form are generally called crew-cut morphologies. While star-like micelles are spherical, crew-cut morphologies can encompass a range of structures. Spherical crew-cut micelles, rods, and vesicles are all considered thermodynamic crew-cut morphologies (Scheme 1.19).<sup>109</sup>





Crew-cut morphologies

There are three components to the free energy of aggregation for block copolymer systems: core-chain stretching, interfacial energy, and chain-chain repulsion within the corona.<sup>110</sup> Core-chain stretching relates to the polymer block that forms the core region of the aggregate. As the core size increases, the

polymer chains inside it must stretch out, and at some point this becomes entropically unfavourable for the polymer chains. The interfacial energy refers to the compatibility of the core-forming block with the solvent environment; the less compatible the solvent is with the core block, the greater the interfacial energy. Coronal chain-chain repulsion refers to steric or electrostatic interactions among the polymer chains that form the soluble corona of an aggregate. If the corona chains become too crowded or there are too many unfavourable electrostatic interactions, this becomes energetically unfavourable. Depending on the balance between these various forces, polymer chains within an aggregate might rearrange to form a structure in which at least one of these components is eased and the overall energy of the system is relaxed.

Several factors can affect the sometimes delicate balance of these three forces, and therefore affect the morphology of the aggregates that form. These factors include the method used to induce self-assembly, the nature of the solvents used and the amount of selective solvent added, the relative block lengths of the core and corona-forming blocks, the total block length (molecular weight) of the polymer, the initial concentration of the polymer, and the polydispersity index (PDI) of the polymer.

Perhaps the most thorough studies on the solution self-assembly of block copolymers, particularly crew-cut systems, have been conducted by the group of A. Eisenberg. For the purpose of continuity, the factors listed above will be illustrated using examples from this work, namely crew-cut poly(styrene)-*b*-poly(acrylic acid) (PS-*b*-PAA) polymers. In these examples, the block length of poly(styrene) is much longer than the poly(acrylic acid) block length.



#### 1.6.1. Factors affecting block copolymer solution self-assembly

#### 1.6.1.1. Method of inducing self-assembly

Solution self-assembly experiments are typically conducted in one of two ways. The first is direct dissolution of the polymer in the desired solvent. This is generally only possible when the soluble, corona-forming block is much larger than the core-forming block, as in some star micelle-forming systems.<sup>111</sup> The second method, particularly useful for crew-cut polymers, is to dissolve the polymer sample in a solvent in which both blocks are soluble. A second solvent, compatible with (i.e., selective for) only one of the blocks can then be added to induce aggregation. This method is commonly used when the polymer is not directly soluble in the final solvent content because the insoluble block is too long. For the (PS)-*b*-(PAA) example, the polymers that have a long PS block compared to a shorter PAA block are dissolved in an organic solvent in which both blocks are soluble. Water is then added, in which the PS block is insoluble, and self-assembly occurs.

In cases where both methods can be used on the same polymer, different final morphologies can be obtained.<sup>112</sup> Often, if directly dissolving the polymer is possible, the morphologies can be more complicated.<sup>111</sup> When the two-solvent method is used and selective solvent (water in the PS-*b*-PAA example) is slowly added to a polymer solution, chain exchange, particularly at low water contents, is more rapid and thermodynamically stable morphologies are more likely to form. At higher water contents chain mobility is decreased. In this scenario, the rate of addition may also be relevant.<sup>111, 112b</sup>

#### **1.6.1.2.** Nature of the common solvent

In the two-solvent method, the initial, common solvent can affect the morphologies obtained.<sup>113</sup> In one study, PS-*b*-PAA polymers were dissolved in either DMF, THF or dioxane before water was added to induce self-assembly. At

the same final water content, the morphology obtained for the polymer samples varied with the initial solvent used. The initial solvent affects the dimensions of the aggregate cores at the onset of micellization, the core sizes increasing with the compatibility of the solvent with the core-forming block. The stretching of the core chains, if it becomes too great, can become entropically unfavourable and result in a change in morphology. The common solvent can also affect the chain-chain repulsion within the corona, particularly if the corona chains are charged, and this can also affect the morphologies that form.

#### 1.6.1.3. Amount of selective solvent added

The amount of selective solvent added to the system also contributes to the morphologies obtained.<sup>114</sup> Again, the well-studied PS-*b*-PAA system in water can be used as an example. As the water content increases, the interfacial energy increases because the solvent becomes worse for the core block. The system thus decreases the total interfacial area by decreasing the number of aggregates and increasing the aggregate core size (more polymer chains are incorporated into a particular structure). This in turn results in increased stretching for the core chains and greater repulsion among corona chains, both of which make the structure energetically unfavourable at some point. The result is a transition from spheres, which initially form, to rods to vesicles or lamellae as the water content increases. For example, the transition from spheres to rods reduces the entropic cost of the core-chain stretching in the spherical micelle core.

#### 1.6.1.4. Block ratio

The effect of the relative block lengths of the core- and corona forming blocks can be illustrated using a series of crew-cut PS-*b*-PAA polymers as an example.<sup>115</sup> For these samples the PS block is longer than the hydrophilic PAA block, and thus the polymers are dissolved in a solvent that is good for both

blocks, such as dioxane, and then water (selective for PAA) is added slowly. As the ratio of the insoluble PS block increases, the core volume, and hence aggregate size, increases. For spherical crew cut micelles, if the spheres become too large as a result of the increased core size, the stretching within the core becomes unfavourable and a transition to rods with a smaller core diameter can result.

In contrast, if the proportion of the soluble PAA block increases, so does the repulsion between chains within the corona. This tends to decrease the radius of curvature of the aggregate (increase the curvature of the surface) and can lead to a change in morphologies from vesicles to rods to spheres in crew-cut systems.<sup>115</sup> As well, for a series of polymers in which the PS length is constant but the PAA length varies, the onset of micellization occurs at higher water contents for polymers with a longer soluble PAA block. This is due to the increased solubility of the polymer chains.<sup>116</sup>

### **1.6.1.5.** Polymer length

The total block length of the polymer is also important, as can be demonstrated using the same PS-*b*-PAA example.<sup>116</sup> For a series of three "crew-cut" polymers that all had the same block ratio (PAA content of 13%) but different overall polymer lengths, it was found that decreasing the overall polymer size resulted in an increase in the water required before the onset of self-assembly. The transitions between different morphologies (ie, spheres to rods) were also shifted to higher water contents as the overall polymer length decreased. This shift to higher water contents occurs because as the length of the insoluble PS block deceases, the interfacial tension between the core and solvent decreases.

#### 1.6.1.6. Polymer concentration

The initial concentration of the polymer is also a determinant in the final morphologies observed.<sup>117</sup> The concentration of the polymer has been found to be proportional to the aggregation number (number of polymer chains per aggregate). As the concentration increases, so does the aggregation number and this results in both increased repulsion among corona chains and increased stretching for chains in the core. As seen in the examples above, this eventually becomes energetically unfavourable, and results in a change from spheres to rods to bilayer structures (such as vesicles) as the polymer concentration increases.

#### **1.6.1.7.** Polymer polydispersity

Other work from the Eisenberg group using PS-*b*-PAA in water demonstrated the effect of the polymer polydispersity on the morphology of the aggregates that form.<sup>117,118</sup> A series of polymers were generated that had similar core-forming PS blocks, but varied soluble PAA blocks. These polymers were mixed to generate samples with artificially varied PDI's. The PDI's in these studies ranged from 1.1 (polymer chains had similar lengths) to 3.3 (a large distribution of chains lengths).

With low PDI samples, a mixture of primary spherical micelles and large compound micelles (LCM's) was obtained; the short soluble PAA blocks were small enough to form small pockets of inverse micelles within the PS phase (LCM morphology, Scheme 1.20 a). As the PDI was increased, a larger fraction of the polymer chains possessed longer PAA blocks, and the ability of the sample to form LCM's was decreased. In addition, the longer soluble blocks were more able to stabilize spherical micelles, and thus primarily spherical micelles were observed.<sup>118</sup>

In related work, polymers with higher PDI's could form vesicles, even though similar polymers with lower PDI's did not.<sup>117</sup> Vesicles formed because in
samples with a variety of PAA block lengths, the chains with the shorter soluble PAA blocks segregated to the inner surface of the vesicles and chains with longer PAA blocks segregated to the outsides (Scheme 1.20 b). In addition, as the PDI was increased, the average vesicle diameter decreased due to greater segregation of the long and short PAA blocks on the outer and inner surfaces of the vesicles, respectively. The increased PAA length on the outside caused an increase in the corona-corona chain repulsion which favors a smaller radius of curvature and hence smaller vesicles. The short PAA chains on the inside enabled this. When the PDI's of the polymer mixtures used in this study became much higher (~2), spherical micelles were also observed. At that point, the increased proportion of large soluble PAA blocks likely became dispersed among the longer ones to allow more spacing between them (Scheme 1.20 c).

Scheme 1.20. Schematics of morphologies obtained with polymers with increasing PDI. (a) large compound micelle; (b) vesicle with short PAA chains on , the inside and longer PAA chains outside; (c) micelle with shorter PAA chains dispersed among longer chains to help decrease steric repulsion.



#### 1.6.2. Self-assembly of different polymer architectures

While the vast majority of solution self-assembly studies have involved block copolymers composed of relatively small monomer units that are more or less equal in size, as in those described above, there are fewer studies on more "exotic" block copolymer architectures. Self-assembly studies on "rod-coil" block copolymers, which possess a rigid-rod-like block, have dramatically increased,<sup>119</sup> and there are also reports describing polymers possessing very bulky substituents.<sup>120</sup> However, the solution self-assembly of ROMP polymers<sup>121</sup> that contain double bonds along the backbone, or of metal-containing block copolymer systems (see section 1.6.3 below) in particular, has only been described in a limited number of reports. Self-assembly of metal-containing block copolymers could result in the formation of aggregates in which the metal units are concentrated within specific nanoscale domains. The metal complexes may have interesting properties such as electroactivity or luminescence. The other (non-metallic) block could be designed as to control the morphologies of the self-assembled aggregates, as well as to enable specific solubility properties, cross-linking ability, and molecular- or biorecognition recognition. Such functional structures could be useful in applications involving catalysis, sensing, and energy conversion.

#### 1.6.3. Self-assembly of metal-containing block copolymers

Possibly the most well known metal-containing block copolymers are the ferrocene-based systems that have been developed and thoroughly studied by the groups of Manners and Winnik. Living ring-opening polymerization of strained phosphorous-bridged<sup>122</sup> or silicon-bridged<sup>123</sup> ferrocenophanes has allowed for the generation of a variety of well-defined ferrocene-based block copolymers (Scheme 1.21a and b, respectively). The second and third blocks of these polymers have been varied to some extent,<sup>124</sup> but the majority of studies have

focused on copolymers containing poly(dimethylsiloxane) (PDMS) or poly(isoprene) (PI).<sup>125</sup>

Scheme 1.21. Block copolymers containing ferrocene: (a) Phosphorus-bridged, and (b) silicon-bridged.



One of the interesting features of these polymers is their propensity to form cylindrical structures and hollow nanotubes when the ratio of the soluble and insoluble blocks would normally dictate the formation of spherical micelles. This has been attributed to the crystallinity of the ferrocene-based core-forming block.<sup>126</sup> Because the core is semicrystalline, the length of the metal-containing block is very important.<sup>127</sup> For these polymers, the self-assembly also depends on the coronal block length, the temperature, and the solvents used for self-assembly.<sup>128</sup> Since the formation of a crystalline domain results in tight packing of coronal chains, there is a balance between 1) the interfacial energy between the core and solvent, 2) the packing of the semi-crystalline block within the core, and 3) the stretching within the corona due to the overlap of adjacent coils.<sup>124e,129</sup>

These polymers are redox active and have potential application in chargetransport materials and ferromagnetic ceramics.<sup>130</sup> They have also been shown to induce the formation of nanoparticles inside the tubules,<sup>131</sup> catalyze the growth of carbon nanotubes,<sup>132</sup> and tune the optical properties of colloidal photonic crystals.<sup>133</sup>

In addition to the reports regarding ferrocene-based polymers, limited studies describing the self-assembly of block copolymers containing other metals can be found. Examples include polymers that contain copper,<sup>134</sup> cobalt,<sup>135</sup> rhenium,<sup>136</sup> and palladium.<sup>137</sup>

## 1.7. Context and scope of the thesis

Polymers containing  $Ru(bpy)_3^{2+}$  have been studied in detail and incorporated into a variety of designs for detection, artificial photosynthesis and light-emitting applications. In these systems, the polymer chain serves several purposes it acts as a scaffold to arrange the metal complexes to help prevent uncontrolled and ill-defined aggregation over time, and it improves the processability and handling of the metal-containing materials. Designs for these applications still suffer some drawbacks. In systems designed to create separated positive and negative charges, such as photosynthesis mimics, where these opposite charges are to be shuttled away from each other to either participate in reactions or generate a current, rapid charge recombination can decrease the efficiency of the device. Another problem is that while non-covalently doping the  $Ru(bpy)_3^{2+}$  complex into polymer matrices can yield materials with enhanced absorption and emission properties, uncontrolled complex aggregation can cancel out any benefits gained from incorporating the complex. This is a problem for sensing and light emitting applications. In addition, the larger-scale arrangement of  $Ru(bpy)_{a}^{2+}$  complexes has not been achieved to any appreciable degree. The proline-based systems developed by Meyer (Section 1.4) have started to address this issue. Dendrimers have been constructed that incorporate many metal complexes into well-defined structures, but these generally involve demanding synthetic procedures, and there is an upper limit as to how many metal complexes can ultimately be included.

Of all the ruthenium containing polymers, block copolymers that contain a dense arrangement of  $Ru(bpy)_3^{2+}$  complexes remain a relatively unexplored class

of materials. Block copolymers, with their ability to self-assemble, may provide the opportunity to expand the potential properties and applications of  $Ru(bpy)_3^{2+}$  based polymers. Well-characterized systems that can self-assemble into welldefined larger-scale aggregates may provide a solution to some of the problems encountered with conventional polymer systems. Encapsulated molecules inside aggregates may be able to form longer-lived charge separated states with different molecules added to the outsides. Self-assembled block copolymers could also allow for interesting studies regarding the effects of concentrating the complex into well-defined morphologies, as compared to the uncontrolled aggregation that occurs when the metal complex is non-covalently doped into a material. Because of the consistency that is possible with the self-assembly of well-defined polymers, any effects of concentrating the complex could possibly be included in the calibration of sensing devices. Block copolymers also allow specific ordering of molecules in applications requiring precise arrangement of chromophores, such as light harvesting. While complex arrangement of species has been achieved using dendrimers or star-shaped polymers with ruthenium at the center, self-assembled block copolymers offer the possibility of ordering molecules in three dimensions on a much larger scale.

In this thesis, a new class of  $Ru(bpy)_3^{2+}$ -containing block copolymers are examined with the goal of establishing these systems as new materials that possess useful properties. These systems could conceivably open the door to new materials for use in light-harvesting, light-emitting, and sensing applications.

Chapter 2 of this thesis includes and expands on the content of a published manuscript, "Luminescent Vesicles, Tubules, Bowls, and Star Micelles from Ruthenium-Bipyridine Block Copolymers." Metera, K.L.; Sleiman, H.F. *Macromolecules*, 2007, 40, 3733. This Chapter describes an examination of the solution self-assembly of novel block copolymers that contain  $Ru(bpy)_3^{2+}$  concentrated in one block, and the generation of a number of reproducible morphologies.

Chapter 3 describes the luminescence properties of self-assembled  $Ru(bpy)_3^{2+}$  -containing block copolymers. The ability of these self-assembled structures to undergo electron transfer with an electron donor and an electron acceptor is also demonstrated using fluorescence quenching measurements.

In Chapter 4, a slightly different  $\operatorname{Ru}(\operatorname{bpy})_3^{2+}$  -containing polymer is described; this polymer self-assembles in water to give micelles with the metal complex in the core. Fluorescence spectroscopy is used to determine that energy transfer occurs between the metal complex and both an energy donor and an energy acceptor that are non-covalently encapsulated inside the micelle core.

Chapter 5 includes the content of a published manuscript, "Biotin-Terminated Ruthenium Bipyridine Ring-Opening Metathesis Polymerization Copolymers: Synthesis and Self-Assembly with Streptavidin." Chen, B.; Metera, K.; Sleiman, H. F. *Macromolecules*, **2005**, *38*, 1084, and describes the selfassembly of other  $\text{Ru}(\text{bpy})_3^{2+}$  polymers that also form micelles in water. These polymers have a biotin group attached to the end that extends into the corona, and the biotin-streptavidin interaction is used to bring self-assembled morphologies together. This demonstrates the potential of combining molecular recognition functionalities with such systems, and this might be relevant for detection assays.

Appendix A outlines some of the early work performed on block copolymers that contain hydrogen-bonding-based molecular recognition functionality. This work eventually led to the more detailed studies on the ruthenium-containing polymers that were described in the main chapters of the thesis.

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# Chapter 2: Self – Assembly of Ru(bpy)<sub>3</sub><sup>2+</sup> - Containing Block Copolymers

# Chapter 2: Self – Assembly of Ru(bpy)<sub>3</sub><sup>2+</sup>-Containing Block Copolymers

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#### 2.1. Introduction

Ruthenium bipyridine complexes have been intensely studied in the past three decades due to their interesting and useful photophysical and electrochemical properties. These complexes are relatively stable, absorb in the visible range, have a large Stokes shift and long luminescence lifetimes. They can also readily undergo electron and energy transfer reactions.<sup>1</sup> As a result of these properties, ruthenium bipyridine-based complexes have been incorporated into polymers for a number of important applications, such as light emitting devices, photovoltaic cells, photoconductors, sensors, and light harvesting devices.<sup>2</sup>

A particularly attractive class of materials are block copolymers containing ruthenium bipyridine units. Because of their ability to undergo self-assembly into micellar structures, they hold the potential to greatly enhance the range of applications of  $\operatorname{Ru(bpy)_3}^{2+}$  systems. The self-assembly of these block copolymers should result in the confinement of the metal complex within a nanoscale domain of well-defined aggregates. Morphologies such as star micelles or vesicles, for example, can be used to encapsulate reactive molecules for catalysis, segregate electron donors and acceptors to increase the efficiency of solar energy conversion, and to further tune the photophysical properties of the nanoconfined ruthenium centers. However, despite the intense interest in macromolecular systems containing this metal complex, there have been very few methods to

construct  $\operatorname{Ru(bpy)_3}^{2^+}$  polymers by living polymerization.<sup>3,2a</sup> Polymers incorporating ruthenium bipyridine units have most often been generated by attaching the complex to a preformed polymer backbone,<sup>4</sup> by non-living polymerization of a metal-containing monomer,<sup>5</sup> or by using the metal as a junction between different polymer chains in a coordination polymer.<sup>6</sup>

While self-assembly of block copolymers has been extensively investigated, there are far fewer reports on the formation of morphologies from polymers containing transition metals. Ferrocene-containing block copolymers have been investigated in elegant studies by the groups of Manners and Winnik,<sup>7</sup> and a few limited studies on the self-assembly of other block copolymers containing ferrocene,<sup>8</sup> rhenium,<sup>9</sup> cobalt,<sup>10</sup> and palladium<sup>11</sup> have also appeared.

We have previously reported the synthesis of ruthenium bipyridinecontaining polymers and block copolymers by ring-opening metathesis polymerization.<sup>3</sup> The living nature of this polymerization was established, thus providing ready access to polymers of narrow molecular weight distribution, and to the first block copolymers containing a dense arrangement of ruthenium bipyridine units in one of their blocks. Such polymers possess an unusual architecture, and may not self-assemble in solution as predicted based on more commonly investigated polymers. In this Chapter we describe a detailed study of the self-assembly in acetonitrile/toluene mixtures of a series of block copolymers, consisting of a ruthenium bipyridine-based block and a hydrophobic block. The block length, block ratio, polymer concentration and solvent composition were systematically varied in order to understand the effects of these parameters on the obtained morphology. We report the observation of a range of morphologies, including star micelles, nanobowls, tubules and vesicles. In all of these morphologies, the ruthenium complex is confined within the insoluble domain of the aggregate. The predictable formation of the desired morphology in solution is a crucial step in using such self-assembled polymer structures for applications such as catalysis, light-harvesting, and sensing.



### 2.2. Results and Discussion

Monomers  $1^{12}$  and  $2^3$  and ROMP catalyst  $3^{13}$  were synthesized according to previously published procedures (Scheme 2.1). Block copolymers 4a-i, containing a ruthenium bipyridine block and a hydrophobic block, were generated by sequential addition of monomers 1 and 2 to catalyst 3 in acetone-d<sub>6</sub>. In order to systematically study the effect of block copolymer composition on the selfassembly of these molecules, we created a number of such block copolymers 4a-i, where the ratios of the two blocks, as well as the overall polymer length were systematically varied. The polymers were characterized by <sup>1</sup>H NMR, UV/vis, fluorescence spectroscopy and differential scanning calorimetry (DSC).

Scheme 2.1. Synthesis of block copolymers containing  $Ru(bpy)_3^{2+}$  and polymers examined in this Chapter.



## 2.2.1. Self-assembly of polymers 4a and 4b

We first investigated the generation of simple spherical star micelles from our block copolymers 4. For this, we synthesized polymers 4a ( $Ru:C_4$  30:140)

and **4b** (Ru:C<sub>4</sub> 20:40), which possess significantly longer hydrophobic blocks (C<sub>4</sub>) than the metal-containing block (Ru). The two blocks are soluble in acetonitrile, and the hydrophobic block is soluble in toluene, while the ruthenium-containing block is insoluble in this solvent. Upon addition of toluene to an acetonitrile solution of this polymer, aggregation of the copolymer is expected to induce the formation of morphologies with the ruthenium block in their core, and the hydrophobic block as their corona. At high toluene contents, turbidity was observed. Samples were drop-cast onto carbon coated transmission electron microscopy (TEM) grids. The grids were not stained, since the ruthenium-containing blocks provide sufficient contrast for visualization of the polymer aggregates.



Figure 2.1. TEM images of a) polymer 4a (scale bar is 100 nm) and b) polymer 4b (200 nm) in 20% toluene in acetonitrile.

For polymers 4a-b (initial polymer concentration 5 mg/ml), TEM showed the formation of spherical aggregates at 20% toluene (Figure 2.1). In addition, as the toluene content of the solution was further increased, no change in morphology was observed for either polymer. Analysis of the TEM images revealed that the micelles formed by both polymer 4a (Fig. 2.1a) and 4b (Fig. 2.1b) were approximately 30-40 nm in diameter. This similarity in micellar size was unexpected, considering the large difference in overall length between polymers 4a (Ru:C<sub>4</sub> 30:140) and 4b (Ru:C<sub>4</sub> 20:40). However, the lengths of the ruthenium bipyridine-containing blocks in polymers 4a and 4b are estimated to be similar, approximately 16-17 nm and 11-12 nm, respectively. The observed 30-40 nm diameter is thus likely the result of preferential TEM visualization of the high electron density ruthenium-containing block, rather than the hydrophobic block on the unstained grids. Dynamic light scattering results were more representative of the actual size of these aggregates in solution, showing spherical aggregates for both polymers, with average diameters of about 130 nm for polymer 4a and 80 nm for polymer 4b.

#### 2.2.2. Self-assembly of polymers 4c-i in acetonitrile/toluene

Block copolymers containing a larger volume fraction of the insoluble block, compared to the soluble block, can fall in the "crew-cut" regime, and give rise to a range of morphologies, in addition to micelles.<sup>14</sup> We were interested in exploring the possibility of forming such crew-cut morphologies from copolymers 4. In the most commonly studied block copolymer systems (eg, polystyreneblock-polyacrylic acid), the two polymer blocks are usually linear and possess similar structures, and thus a significantly longer insoluble block is required to produce these morphologies.<sup>14</sup> In contrast, the ruthenium-containing, coreforming block in copolymers 4 possesses bulky and positively charged metal complexes with aromatic coordination spheres, attached to the polymer backbone by ethylene glycol-based linkers, and has a high glass transition temperature (Scheme 2.1., Tg = $210^{\circ}$ C for poly-Ru<sub>19</sub>). The hydrophobic, corona block possesses much smaller and more flexible butyl units. The polymers in this study also contain double bonds along the polymer backbone. Thus copolymers 4 are not necessarily expected to display parallel structure-morphology relationships to previously reported "crew-cut" polymers.

We first examined the self-assembly of copolymers 4c (Ru:C<sub>4</sub> 10:8) and 4d (Ru:C<sub>4</sub> 14:10), which possess a short backbone and similar block lengths, thus a significantly larger volume ratio of the ruthenium-containing block. Using an

initial polymer concentration of 25 mg/mL, polymer **4c** showed a range of interesting morphologies upon gradual and slow addition of toluene, such as interconnected bilayer structures (30% toluene, Figure 2.2a), coexistence of vesicles and interconnected bilayers (40% toluene, Figure 2.2b), vesicles and tubular structures (60% toluene, Figure 2.2c) and large spherical bilayers (80% toluene, Figure 2.2d). The aggregates of polymer **4d** changed even more significantly with toluene content. At initial polymer concentration of 20 mg/mL, the polymer aggregates evolved from predominately large compound micelles (LCM, 40% toluene, Figure 2.3a), to a coexistence of LCM's and vesicles (50% toluene, Figure 2.3b), to mainly vesicles with a large size distribution (60% toluene, Figure 2.3c), to small and uniformly sized vesicles at high toluene contents (80% toluene, Figure 2.3d). The wall thickness of these vesicles is also uniform at approximately 18 nm (TEM analysis), which is consistent with the length of two ruthenium-containing blocks.<sup>15</sup>



Figure 2.2. TEM images of polymer 4c as toluene content increases; a) 30% toluene (scale bar is 200 nm), b) 40% toluene (1  $\mu$ m), c) 60% toluene (500 nm), d) 80% toluene (1  $\mu$ m). Insets are magnified images.





Figure 2.3. TEM images of polymer 4d as toluene content increases; a) 40% toluene (scale bar is 1  $\mu$ m), b) 50% toluene (200 nm), c) 60% toluene (200 nm), d) 80% toluene (500 nm) (top inset:magnification), e) bowl structures from polymer 4d (500 nm).

Thus, copolymers **4c** and **4d** show a preference for bilayer morphologies, including luminescent vesicles, tubules, and interconnected bilayers. The formation of stable bilayer morphologies over a range of solvent compositions has been previously reported to occur as a result of the rigidity and stiffness of one of the copolymer blocks.<sup>16</sup> Because of this rigidity, the entropic cost of aggregation is small, thus the minimization of the interfacial energy dominates the energetics of aggregation, and bilayer structures present smaller interfacial areas than cylinders or spheres.<sup>16</sup> In copolymers **4c-d**, the formation of stable bilayer structures is likely the result of the significant rigidity and high volume ratio of the ruthenium bipyridine-containing block and the presence of the double bonds in the polymer backbone.

Upon more rapid addition of toluene to acetonitrile solutions of polymer 4d, large compound micelles and, more interestingly, bowl-like structures were obtained (40-50% toluene, Figure 2.3e), instead of the previously observed bilayer structures. The sizes of these morphologies were large and polydisperse (200-500 nm, up to 1 µm). While large compound micelles are relatively common morphologies.<sup>17a</sup> the observation of nanobowl structures from block copolymers has only previously appeared in two recent reports.<sup>17</sup> These intriguing "container" structures are thought to arise in the process of formation of large compound micelles. As the selective solvent (toluene) is added, acetonitrile is drawn out from the spherical aggregates, thus increasing the viscosity and resulting in the formation of a hard 'skin' around the sphere, which prevents homogeneous shrinkage. Instead, 'polymer-poor' spaces (bubbles) can form, and many of these can coalesce to form a large 'bubble', resulting in a nanobowl morphology.<sup>17</sup> For this to occur, the polymer viscosity should be high enough to cause formation of a 'skin', but also low enough to allow coalescence of the bubbles. The ruthenium-containing block most likely endows copolymer 4d with a high enough viscosity, and the overall short length of both polymer blocks likely places its viscosity within the range required for the generation of bowl morphologies. It is of note that the formation of these nanobowls has been observed reproducibly, using different samples of 4d and a range of solvent compositions.

Despite the intriguing potential applications of kinetically obtained morphologies such as nanobowls, we were interested in the generation of ruthenium bipyridine-containing vesicles over a wide range of solvent compositions and conditions, and in a method less dependent on the rate of toluene addition. There are exceptionally few accounts of metal-containing polymer vesicles in the literature,<sup>18</sup> and none to our knowledge of polymer vesicles with the ruthenium-bipyridine complex as an integral part of the vesicle wall. These structures could allow stable and facile encapsulation of agents for photoinduced electron transfer with the ruthenium complex concentrated in the

vesicle wall, or the segregation of a donor (eg, inside the vesicle) and acceptor (eg, outside the vesicle) using ruthenium bipyridine as a photomediator. This has exciting potential in applications including sensing, catalysis and photosynthetic mimicry.

We thus synthesized copolymer 4e, which possesses a much larger ratio of the insoluble ruthenium-based block (Ru:C<sub>4</sub> 67:11), and is expected to fall more strongly within the "crew-cut" regime. To our knowledge, copolymer 4epossesses the highest number of ruthenium bipyridine units on a polymer chain reported to date. However, this copolymer (20 mg/mL) only gave rise to the coexistence of large compound micelles with smaller crew-cut micelles, regardless of the toluene content and the rate of toluene addition (Figure 2.4). The lack of morphological evolution in this copolymer is likely due to the bulkiness of the long ruthenium-containing block and its high glass transition temperature. Initially formed large compound micelle morphologies might therefore become kinetically trapped ("frozen") in solution, and hence these aggregates cannot evolve by the rearrangement of polymer chains as a means of minimizing the energy of the system.



Figure 2.4. TEM image of polymer 4e in 60% toluene (scale bar is 500 nm).

We also synthesized copolymer 4f, which has the block ratio of Ru:C<sub>4</sub> 19:12. Like polymer 4e, this polymer also has a Ru block length that is long compared to a short C<sub>4</sub> block. With this polymer, we find that predominantly large compound micelles are formed when the initial polymer concentration is

20 mg/ml (Figure 2.5). These results are in accordance with the results of polymer 4e. We believe that for this polymer as well, the  $C_4$  block is too short to sufficiently solubilize the large Ru block, and that morphologies, once formed, become trapped as polymer chains cannot rearrange as toluene is added to the solution.



Figure 2.5. TEM of polymer 4f in 50% toluene (scale bar is 500 nm)

Considering the results obtained with copolymers 4c-f, we reasoned that kinetically trapped morphologies could possibly be prevented by generating a copolymer with (i) an insoluble metal block that is short enough to allow for rearrangement of polymer chains in solution, and (ii) a hydrophobic block that is long enough to solubilize the polymer over a wider range of morphologies than polymers 4c-d, (iii) but short enough to still place the polymer within the "crewcut" regime in our solvent system. We therefore synthesized polymer 4g (Ru: $C_4$ 20:20), containing a block ratio of 1:1 similar to 4c-d, but longer than these polymers. Self-assembly of copolymer 4g in acetonitrile (20 mg/ml polymer)/ toluene solutions of increasing toluene content gave tubule structures (20% and 35% toluene, Figure 2.6a and 2.6b, respectively) which evolved to large spherical bilayers (40% toluene, Figure 2.6c), to smaller and more uniformly sized vesicles at higher toluene contents (70% toluene, Figure 2.6d). The wall thickness of these vesicles is approximately 28 nm, and the estimated backbone length of one ruthenium block is approximately 11 nm. These morphologies and their evolution were obtained reliably and reproducibly, and thus kinetically trapped structures were prevented with this polymer.



**Figure 2.6.** TEM images of polymer **4g** as toluene content increases; a) 20% toluene (scale bar is 200 nm), b) 35% toluene (1000 nm), c) 40% toluene (500 nm), d) 70% toluene (500 nm), e) polymer **4g** frozen in 70% benzene in acetone (200 nm). Insets are magnified images.

As mentioned earlier, our TEM imaging method involves evaporation of an acetonitrile/toluene solution of the micellar aggregates of copolymers 4 on a TEM grid. One concern may be that this method gives rise to structures which are the result of preferential evaporation of one of the two solvents on the grid, and may thus be different from the true solution morphologies. In order to address this, we prepared TEM samples of 4g by freeze-drying acetone/benzene solutions of this copolymer, rather than direct room temperature evaporation. This method is likely to result in TEM images which better reflect the solution morphologies. As shown in Figure 2.6e, vesicles were also obtained by this preparation from copolymer 4g. Thus, the preference of copolymer 4g for vesicle formation is not a result of kinetically trapped structures because of solvent evaporation, but is most likely due the presence of these structures on the phase diagram of this copolymer at a range of solvent compositions.



Polymer **4h** is very similar to polymer **4g**, having a block ratio of  $\operatorname{Ru}:C_4$ 17:18. This polymer, when dissolved at an initial polymer concentration of 20 mg/ml, also formed bilayer morphologies, primarily vesicles at higher toluene contents (Figure 2.7).



Figure 2.7. TEM of 4h in (a) 30% toluene (scale bar is 200 nm) and (b) 70% toluene (500 nm).

An interesting case is found with the polymer 4i ( $Ru:C_4$  10:18). For this polymer, the metal-based block is relatively shorter than the soluble C<sub>4</sub> block, which may place it in the realm of the star micelle-forming polymers. On the other hand, the overall polymer length is rather short and approximately similar to the ratio of polymer 4d (Ru(14)-C<sub>4</sub>(10)), which fell into the crew-cut regime and formed bilayer morphologies. At initial polymer concentrations of 20 mg/ml in acetonitrile, predominantly large bilayer structures were observed at lower toluene contents, which evolved to vesicles as toluene was added (Figure 2.8). That there is an evolution of morphology for this polymer is interesting because the insoluble metal-containing block is shorter than the soluble C4 block, and as mentioned above, may be expected to result in the formation of star micelles. The evolution of the morphology of this polymer to vesicles may be explained by its short overall polymer length and the comparatively large bulk of the rutheniumcontaining block. The overbearing bulk of the metal-based block may allow it to influence the self-assembly process more strongly than what its comparative length alone may suggest. This would likely be aided by the generally short polymer length, which may allow the individual polymer chains to rearrange as the toluene content increases. Thus, even though the soluble block is technically longer than the core-forming block, the polymer generally self-assembles in acetonitrile/toluene solutions as a crew-cut polymer.



Figure 2.8. TEM image of polymer 4i in (a) 35% toluene (scale bar is 500 nm) and (b) 80% toluene (200 nm).

#### 2.2.3. Self-assembly of polymers 4c-i at lower initial polymer concentrations

Finally, we examined the self-assembly of copolymers 4c-i at lower initial polymer concentrations (5 mg/mL). For all polymers, the morphologies observed by TEM did not change significantly as a function of the toluene content in acetonitrile. Polymers 4c and 4d appeared to form partially hollow structures (Figures 2.9a and b, respectively), and predominantly micelles and large compound micelles were obtained for 4e and 4f (Figure 2.9c and d, respectively). Notably, polymer 4g, which formed vesicles at high polymer concentrations, also formed vesicles at low concentrations (Figure 2.9e). Polymer 4h formed vesicles and large compound vesicles (Figure 2.9f), and 4i formed a mixture of morphologies including vesicles and large bilayer structures (Figure 2.9g). The lack of morphology evolution, or the apparent kinetic "freezing" of the initially formed aggregates at higher dilution is possibly a result of the low chain mobility of the ruthenium block in these dilute solutions, where the ratio of toluene to this insoluble block is high.





Figure 2.9. TEM images of polymers a) 4c (scale bar is 500 nm), b) 4d (200 nm), c) 4e (200 nm), d) 4f (500 nm), e) 4g (200 nm), f) 4h (200 nm), g) 4i (200 nm) with initial polymer concentration of 5 mg/mL in acetonitrile. Insets are magnified images.

# 2.2.4. Additional experiments: self-assembly in acetonitrile/water and acetonitrile/methanol solutions

In addition to studying the self-assembly of these polymers in acetonitrile/toluene solutions, we also performed preliminary experiments using other solvents. In these experiments, we dissolved the polymer in acetonitrile to solubilize both blocks, as before, but added either water or methanol instead of toluene. This was done in an attempt to invert our self-assembled structures and position the  $Ru(bpy)_3^{2+}$ -containing block on the outside (corona) rather than hide it inside the core.

One of the polymers we tried this approach with was polymer 4d (Ru:C<sub>4</sub> 14:10). In this case, with a shorter insoluble C<sub>4</sub> block and a longer soluble Ru block the polymer may form star micelles with a  $Ru(bpy)_3^{2+}$ -containing corona. For this polymer, self-assembly was done with initial polymer concentrations of 20 mg/ml and 4.5 mg/ml in acetonitrile, similar to the conditions used in the studies described above. Methanol was then added, and on the TEM grids primarily micelles and LCM's were observed (Figure 2.10).



**Figure 2.10**. TEM images of polymer **4d** at initial polymer concentration of 20 mg/ml in (a) 20% methanol (scale bar is 500 nm) and (b) 60% methanol in acetonitrile (200 nm) and at initial polymer concentration of 5 mg/ml in (c) 10% methanol (200 nm).

In other experiments we added water to acetonitrile solutions of polymer 4b (Ru:C<sub>4</sub> 20:40). We hoped that in a solvent mixture in which the longer C4 block formed the core that this polymer would form crew-cut morphologies that evolved with increasing water content. By TEM analysis, however, mainly only LCM's were observed, regardless of the water content or whether the initial polymer concentration was 20 mg/ml or 4.5 mg/ml in acetonitrile (Figure 2.11).


**Figure 2.11**. TEM images of polymer **4b** at an initial polymer concentration of 20mg/ml in (a) 20% water (scale bar is 200 nm), (b) 80% water (500 nm) in acetonitrile, and at an initial polymer concentration of 4.5 mg/ml in (c) 10% water (200 nm) and (d) 70% water (200 nm).

The final polymer with which we tried this method of self-assembly was polymer **4a** (Ru:C<sub>4</sub> 30:140). This polymer, in a solvent system in which the C<sub>4</sub> block was insoluble and the Ru block soluble, should definitely form crew-cut aggregates. When we added water to acetonitrile solutions (20 mg/ml or 4.5 mg/ml polymer), the samples became cloudy by 20% water, and predominantly only LCM's were observed on the TEM grids (Figure 2.12). When methanol was added instead of water, the samples did not become cloudy until the solvent content was approximately 40% methanol. As an initial polymer concentration of 20 mg/ml, a mixture of micelles and LCM's were observed on all grids, regardless of the methanol content. Mostly LCM's were observed when the initial polymer concentration was 4.5 mg/ml (Figure 2.13).



**Figure 2.12**. TEM images of polymer **4a** at initial polymer concentration of 15 mg/ml in (a) 10% water (scale bar is 200 nm) and (b) 50% water (200 nm) in acetonitrile, and **4a** at initial polymer concentration of 4.5 mg/ml in (c) 10% water (200 nm) in acetonitrile.



**Figure 2.13**. TEM images of polymer **4a** at an initial polymer concentration of 20 mg/ml in (a) 40% methanol (scale bar is 500 nm) and (b) 80% methanol (500 nm) in acetonitrile, and **4a** at an initial polymer concentration of 4.5 mg/ml in (c) 30% methanol (200 nm) in acetonitrile.

For polymers 4a and 4b, we had hoped that by inverting the aggregates, and turning the long C<sub>4</sub> block into the core-forming block, we would form a new series of interesting morphologies that evolved with changing solvent content and contained  $\text{Ru}(\text{bpy})_3^{2+}$  as their corona. The most likely cause of our inability to observe anything other than LCM's for these polymers is the limited solubility of the  $\text{Ru}(\text{bpy})_3^{2+}$  -containing block in methanol and in water, thus leading to kinetically frozen large compound micelle morphologies at the time scale of the experiments.

### 2.3. Conclusions

We have conducted a detailed study of the self-assembly of ruthenium bipyridine-containing block copolymers, generated by living ring-opening metathesis polymerization. Preliminary studies were done in acetonitrile/water and acetonitrile/methanol solutions, but more thorough studies were conducted in acetonitrile/toluene mixtures. Manipulation of the block ratios, polymer length and solvent conditions has allowed the reproducible generation of a number of morphologies containing Ru(bpy)<sub>3</sub><sup>2+</sup> units in their micellar core/vesicle wall, such as vesicles, star micelles, large compound micelles, tubules and bowls. These structures, and vesicles in particular, hold exciting potential for the encapsulation and segregation of reactive components, and for applications in artificial photosynthesis and catalysis.

#### **2.4. Experimental Procedures**

**Materials.** Reagents were purchased from Aldrich and used as received; naphthoquinone was recrystallized from ethanol. Deuterated solvents were purchased from Cambridge Isotope Laboratories.

**Instrumentation.** <sup>1</sup>H NMR spectra were recorded on a Varian M400 instrument. Transmission electron microscopy (TEM) images were recorded on a JEOL 2000FX electron microscope operating at 80 kV. 400 mesh carbon coated grids were purchased from Electron Microscopy Sciences. Dynamic light scattering (DLS) measurements were performed on a Brookhaven Instruments Corporation system equipped with a BI-200SM goniometer, a BI-9000AT digital correlator and a Compass 315-150 CW laser light source from Coherent Inc. operating at 532 nm (150 mW). Vials were purchased from Canadawide Scientific and samples were filtered through 0.45 µm PTFE syringe filters from Chromatographic Specialties Inc. Differential Scanning Calorimetry (DSC) measurements were performed on a TA Instruments model DSC Q1000 instrument calibrated with an indium sample. Polymer samples were heated from

0-250°C at a rate of 15°C/min under continuous flow of nitrogen of 50 mL/min. Glass transition temperatures were recorded during the second heating scan.

Synthesis of Copolymers 4.<sup>3</sup> Monomer  $1^{12}$  and catalyst  $3^{13}$  were mixed in d<sub>6</sub>acetone, in a sealable NMR tube within a glove box, and the polymerization was monitored by <sup>1</sup>H NMR (monomer olefin peaks). When the polymerization was complete, a subsample was removed for quenching, and the ruthenium monomer  $2^3$  was added to the polymerization reaction. The reaction was again monitored by <sup>1</sup>H NMR and upon completion (2-3 hours), the polymerization was quenched with ethyl vinyl ether. The degree of polymerization was determined by NMR: the ratio of the methyl peak of monomer 1 to the terminal phenyl peaks (7.2-7.5 ppm) in the quenched subsample gave the average number of units of monomer 1 per chain, while comparison of the methyl peak of monomer 1 with the bipyridine peaks of the ruthenium-containing block then gave the number of metal units (it is important to note here that we had previously shown that this polymerization under the above conditions is living).<sup>3</sup>

**Self-assembly.** Polymers **4** were dissolved in acetonitrile at the desired initial concentration, and toluene was added dropwise with approximately 5 seconds in between drops. At desired intervals a sample of the solution was dropcast directly onto a TEM grid. Excess solution was wicked away and the grid left to air dry in a fume-hood. For freezing experiments, polymers were dissolved in acetone, and benzene was added dropwise. Two subsamples were removed; one control sample for room temperature deposition onto a grid, and the second for deposition onto a grid frozen by placement onto a metal block cooled in liquid nitrogen. The frozen bubble and grid were placed into a vacuum chamber and lyophilized. No TEM sample grids were stained because the ruthenium blocks provide sufficient contrast for visualization.

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Chapter 3: Luminescence and Electron Transfer in Self-Assembled Ru(bpy)<sub>3</sub><sup>2+</sup> Block Copolymers

# Chapter 3: Luminescence and Electron Transfer in Self-Assembled Ru(bpy)<sub>3</sub><sup>2+</sup> Block Copolymers

### **3.1 Introduction**

Ruthenium bipyridine complexes have been the focus of intense research over the past few decades.<sup>1-5</sup> This is due to their unique photophysical and electrochemical properties, including chemical and photochemical stability, ready tunability of excited state properties, long luminescence lifetimes, absorption in the visible range and large Stokes shift. For example, as a result of its long lifetime, the  $Ru(bpy)_3^{2+}$  excited state is capable of participating in a variety of reactions, including energy and electron transfer. It is largely due to these interesting photophysical properties that polymers containing ruthenium bipyridine complexes have been examined for use in applications including artificial light-harvesting, light emitting devices, photoconductors and catalysis.<sup>1</sup>

A variety of synthetic approaches to generating  $Ru(bpy)_3^{2+}$  -containing polymers have been reported. These have resulted in a number of polymer architectures, including random copolymers,<sup>2</sup> homopolymers,<sup>3</sup> or structures that contain the metal as a junction between polymer chains or as the center of a starshaped polymer.<sup>4</sup> Given the excitement that these ruthenium-containing polymers have generated due to their variety of potential uses, there have been surprisingly few reports regarding  $Ru(bpy)_3^{2+}$ -containing block copolymers.<sup>5</sup> Well-defined metal-containing block copolymers, with pre-determined block lengths and metal content, as well as the ability to self-assemble, may provide an interesting route to controlling the placement of metal complexes in the design of functional devices. Assembly of these block copolymers should result in confinement of the metal units within a nanoscale domain of a well-defined aggregate, and both blocks of a diblock copolymer can be adjusted for a number of desired properties of the final product. The metal-containing block is not only a scaffold to hold the complexes in a defined arrangement, but its block length and backbone properties would also affect the self-assembly. The second block can be adjusted for control over the solubility and molecular- or biorecognition, in addition to contributing to the selfassembly. Such metal-containing nanoscale packets may therefore be useful in a variety of applications, including catalysis, chemical and biochemical sensors, encapsulation of reactive agents, and artificial light harvesting systems.

Our laboratory has reported the synthesis of well-defined rutheniumcontaining block copolymers by living ring-opening metathesis polymerization (ROMP).<sup>5</sup> We also recently described the solution self-assembly in acetonitrile/toluene mixtures of a series of  $Ru(bpy)_3^{2+}$  block copolymers (Chapter 2).<sup>5c</sup> Polymer morphologies including star micelles, bowls, tubules and vesicles were reproducibly obtained, each of these containing confined  $Ru(bpy)_3^{2+}$ complexes within the micellar core or vesicle wall. Among these, star micelles and vesicles can be useful to design working models for solar energy conversion. Through encapsulation of small molecules, they can potentially spatially segregate electron donors and acceptors on the inside and outside of the  $Ru(bpy)_3^{2+}$  micellar aggregate, and thus reduce charge recombination for efficient light harvesting. In addition, when labeled with a biological recognition unit, micelles containing multiple  $Ru(bpy)_3^{2+}$  chromophores can be useful in biodetection applications because of the potential for signal amplification and reversible self-assembly.<sup>5b</sup>

Of particular importance to the use of these structures in functional devices is (i) the effect that self-assembly-induced confinement of the metal units may have on their photophysical properties, and (ii) the extent to which these  $Ru(bpy)_3^{2+}$  units, which are confined in the micellar core or vesicle wall, can communicate with molecules (eg, electron donors and acceptors) on the exterior of these morphologies. Although extensive photophysical studies of  $Ru(bpy)_3^{2+}$ polymers have been described,<sup>1</sup> there are, to our knowledge, no reports on the luminescence properties of self-assembled  $Ru(bpy)_3^{2+}$  block copolymers. This Chapter describes a systematic investigation of the luminescence behaviour of

 $Ru(bpy)_3^{2^+}$ -diblock copolymers, both as open chains and as self-assembled micelles or vesicles, where the metal-containing block composes the micelle core or vesicle wall. We also explore the ability of the excited state of  $Ru(bpy)_3^{2^+}$  within the micelle core or vesicle wall to undergo electron transfer reactions with two different small molecules on the outside of the structures. These are fundamental studies on a relatively new class of  $Ru(bpy)_3^{2^+}$ -containing structures. The effect of self-assembly on the photophysical properties of block copolymers will determine the potential usefulness of self-assembled systems in applications including light harvesting, catalysis and sensing.

### 3.2 Results and Discussion

Our studies here focus on three systems (Scheme 3.1). Polymers 2 and 3 each contain two blocks: a block containing n-butyl chains in the repeat units (the "C<sub>4</sub>" block), which is soluble in both acetonitrile and toluene, and the metalcontaining "Ru" block, which is soluble in acetonitrile but is insoluble in toluene and thus would form the core of an aggregate as toluene is added. The two polymers have comparable Ru block lengths, but polymer 2 has a proportionately long C<sub>4</sub> solubilizing block, while in polymer 3 the C<sub>4</sub> block is shorter. Due to the block ratios of the polymers, polymer 2 forms star micelles as toluene is added to acetonitrile solutions, and polymer 3 forms vesicles (Figure 3.1 and Chapter 2).<sup>5c</sup> The third system we examine is the ruthenium-based monomer 1. The structures of 1, 2, and 3 as well as the morphologies obtained from polymers 2 and 3 are shown in Scheme 3.1 and Figure 3.1.

Scheme 3.1.  $Ru(bpy)_3^{2^+}$ -containing monomer and polymers





Figure 3.1. TEM images of (a) polymer 2 (scale bar is 100 nm) and (b) polymer 3 (200 nm) self-assembled in 70% toluene.

# 3.2.1. Luminescence Studies

The luminescence behavior of  $Ru(bpy)_3^{2+}$ -based complexes is known to be affected by several factors, including the solvent content and the rigidity of the environment. In acetonitrile, polymers 2 and 3 are unassociated chains and provide the opportunity to study the effect of incorporating the metal centers into

a densely loaded polymer chain. In 70% toluene, polymers 2 and 3 are selfassembled structures, and allow for the examination of the effect of self-assembly and confinement of the Ru centers into the core of these morphologies. Monomer 1 provides a model compound to evaluate the effect of incorporation of  $Ru(bpy)_3^{2+}$  units into a polymer, and as it cannot self-assemble as toluene is added, it also acts as a control for the effect of solvent on the photophysical properties of the Ru complex. The absorbance and emission properties of the monomer and polymers are shown in Table 3.1 and discussed in the next sections.

Table	3.1.	Absorbance	and	luminescence	properties	of	$Ru(bpy)_3^{2+}$ -based
monon	ner and	d diblock cope	olyme	ers:			

		Absorbance	Emission			
Sample	Solvent	$\lambda \max(\varepsilon)$	$\lambda$ max	Φ	Lifetime (ns) <sup>a</sup>	
1	MeCN	455 (13878)	628	0.069	1293	
1	70% toluene	456 (14665)	623	0.091	1248	
2	MeCN	455 (17011)	630	0.065	1212 (67%);	
					288 (32%)	
2	70% toluene	459 (16886)	629	0.073	1172 (74%);	
					304 (26%)	
3	MeCN	451 (10835)	629	0.056	1177 (75%);	
					284 (25%)	
3	70% toluene	451 (10283)	629	0.053	1010 (47%);	
					315 (53%)	

<sup>a</sup> Lifetimes for the polymers were determined using a biexponential model.

### 3.2.1.1. Properties of 1, 2 and 3 in Acetonitrile

In acetonitrile there is no self-assembly, and the polymers are unassociated chains. In this solvent, comparisons between the monomer and the polymers indicate the effect of concentrating the metal complex within one block of a diblock copolymer. The absorbance spectra in the range of approximately 400-500 nm are very similar for monomer 1 and polymers 2 and 3, with no obvious changes in the band shape or absorbance maximum of the metal-to-ligand charge transfer (MLCT) absorption (Figure 3.2). As well, the steady state emission wavelengths and band shapes are similar for the three samples, indicating that the Ru(bpy)<sub>3</sub><sup>2+</sup> units on the polymer chains essentially behave as individual chromophores.<sup>6</sup> Monomer 1 has a quantum yield of 0.069, comparable to the reference compound Ru(bpy)<sub>3</sub><sup>2+</sup> ( $\Phi = 0.062^7$ ). Polymers 2 and 3 both have similar quantum yields within error (~10%) in acetonitrile, suggesting that incorporation into the polymer results in near complete retention of the Ru(bpy)<sub>3</sub><sup>2+</sup> luminescence intensity.



Figure 3.2. Normalized absorbance (a) and emission (b) of 1 (black points), 2 (grey line), and 3 (black line) in acetonitrile. In (b), the emission of polymers 2 and 3 closely overlap.

The most significant difference between the monomer and polymer samples in acetonitrile is found upon examination of the lifetimes of the three samples (Table 3.1, Fig 3.3). The decay of the monomer is mono-exponential, but the polymers do not exhibit mono-exponential decay. The decays of the polymers were much better fit with a bi-exponential model. These fits indicate that in acetonitrile there is a majority of a long-lived component with a similar lifetime to the monomer, as well as a new shorter-lived species.



Figure 3.3. Luminescence decay of (a) monomer 1 and (b) polymers 2 (grey line) and 3 (black line) in acetonitrile.

In other reports in the literature, bi-exponential fits have been applied to the luminescence decays of ruthenium-based polymers,<sup>8</sup> and similar results have been obtained (i.e., a majority of a long-lived species and a smaller proportion of a shorter-lived component). However, this does not necessarily imply that there are two distinct species within the polymer samples, but rather that there may be at least two different photoprocesses occurring on different time scales.<sup>6,9</sup>

For certain types  $Ru(bpy)_3^{2+}$  containing polymers, a number of factors have been demonstrated to contribute to non-exponential decay. Within a single polymer chain, there can be multiple photons absorbed, resulting in multiple excited complexes,<sup>10</sup> and this may have two effects. First, triplet-triplet

annihilation between two excited state  $Ru(bpy)_3^{2+}$  units along the same chain may occur.<sup>6</sup> For example, it has been observed that triplet-triplet annihilation causes an increase in the proportion of the shorter-lived species when the concentration of  $Ru(bpy)_3^{2+}$  complexes encapsulated in SDS micelles is increased.<sup>11</sup> The second effect arises from the sensitivity of the metal complex to its environment. When a complex is excited, it forms a charge-separated MLCT state and the solvent molecules in the vicinity rearrange, creating a local polarized field. If a second complex is excited within that polarized field, its MLCT excited state is stabilized by that environment. Based on the energy gap law, this is expected to increase the rate of non-radiative decay and shorten the emission lifetime.<sup>3b,8a</sup> These "multiphoton effects" have been shown to contribute to non-exponential decay in previous studies of Ru(bpy)<sub>3</sub><sup>2+</sup>-polymers.<sup>1h,3b,8a</sup> Energy migration has also been observed for Ru-containing polymers, where the \*Ru excited state migrates along the chain by a random walk mechanism, at a rate much faster than the lifetime of the excited state.<sup>9</sup> Although in our system the probability of having more than one excited complex per polymer chain may be low,<sup>12</sup> all of these phenomena, combined with the generally non-homogeneous environment of the ruthenium complexes along the polymer chains, may contribute to the nonexponential decay of the polymer in acetonitrile.

Based on the results listed above (Table 3.1), incorporation of  $\text{Ru(bpy)}_3^{2+}$  complexes into one block of a diblock copolymer in acetonitrile does not adversely affect the quantum yield of the complex. In addition, the non-exponential decay of the polymer samples is consistent with energy migration and possibly also multiphoton effects, operating in these polymers.

## 3.2.1.2. Properties of 1, 2, and 3 in 70% Toluene

When toluene is added slowly to a final content of 70%, the polymers selfassemble into either micelles (polymer 2) or vesicles (polymer 3) (Fig 3.1). The monomer cannot self-assemble, and acts as a control for the effect of toluene addition on the luminescence properties of  $\operatorname{Ru}(bpy)_3^{2+}$ .

The monomer, upon toluene addition, shows essentially no change in absorbance maximum and only a very small (5 nm) blue-shift in its emission maximum. This is consistent with a slight destabilization of the MLCT excited state due to the presence of the nonpolar solvent toluene. The quantum yield of the monomer also increases from 0.069 to 0.091. The lifetime of the monomer does not significantly change upon toluene addition.



Figure 3.4. Normalized absorbance (a) and emission (b) of 1 (black points), 2 (grey line), and 3 (black line) in 70% toluene. In (b), the emission of polymers 2 and 3 closely overlap.

The absorbance and emission wavelengths and band shapes of polymers 2 and 3 do not change upon addition of toluene and formation of aggregates, and they are similar to monomer 1 in 70% toluene (Figure 3.4). In contrast to the monomer, the quantum yields of the polymers are not significantly increased, and the emission wavelength is unchanged when toluene is added. The fact that the polymers do not exhibit an increase in quantum yield or undergo a blue-shifted emission likely indicates that they are not exposed to the toluene solution. Selfassembly is, in fact, a result of the incompatibility of one block of block copolymers with the solvent environment, and the  $Ru(bpy)_3^{2+}$  block is incompatible with toluene. The monomer decay is monoexponential in 70% toluene, but as in acetonitrile, the decays of both polymers in 70% toluene are fit much better by a biexponential model than a monoexponential one (Table 3.1). Surprisingly, when star micelles are formed from polymer 2, there is not really a significant change in the proportions of the long- and short-lived species compared to the unassociated polymer chains. In contrast, when vesicles are formed by polymer 3, the proportion of the short-lived component increases significantly. This may be due to an increase in the local concentration of ruthenium excited states, both within the same chain and between different chains, leading to enhanced interactions (multiphoton effects) within the vesicle system compared to the unassociated chains of polymer 3.

The differences in the proportions of the long- and short-lived components of the decays of self-assembled polymers **2** and **3** may be related to structural differences between the star micelles and the vesicles. There are three important differences between these two aggregates. The first is the chain stretching and alignment within the micelle core and the vesicle wall. The vesicle wall thickness is ~27 nm, while the Ru(bpy)<sub>3</sub><sup>2+</sup> core in the micelles is far greater, ~50 nm, for the same Ru block length. The second is the length of the soluble C<sub>4</sub> block that shields the metal complex from the solvent. The micelle core is surrounded by a corona with long chains of the C<sub>4</sub> block, while this block is much shorter for the vesicles. The third is the proportion of ruthenium centers at the core-corona interface, which is significantly higher for the vesicles, with their

inner and outer surfaces, than for the star micelles, and these may experience a different environment than complexes residing in the center. Any or all of these factors may result in different energy migration and multiphoton effects for these structures, and thus the observed differences in the proportions of the faster- and slower- decaying components.

Based on the above findings, we conclude that (i) incorporation of  $Ru(bpy)_3^{2+}$  complexes into densely loaded block copolymers, or into the core domain of self-assembled micellar aggregates does not result in quenching of their luminescence, (ii) however, energy migration and possibly interactions among excited complexes occur, resulting in the appearance of a short-lived component and non-exponential decay, (iii) self-assembly of  $Ru(bpy)_3^{2+}$  into the core of star micelles or the wall of vesicles shields these units from the toluene solvent, as evidenced by the lack of increase in quantum yields or change in emission wavelength for these units, and (iv) self-assembly and confinement of the metal units in a vesicle wall significantly affects excited state interactions, while star micelles largely retain the photophysical features of the unassembled polymers.

### 3.2.2. Luminescence Quenching by Electron Transfer

Energy migration among the confined  $Ru(bpy)_3^{2+}$  chromophores in the micellar core implies that this excited state energy can potentially be harvested by molecules on the exterior of these aggregates. For this reason, we wanted to assess the ability of these confined ruthenium complexes to undergo excited state reactions. Within a self-assembled structure, the ruthenium comprises the core domain, and it is thus hidden from the outside solvent and environment to some degree. It is also surrounded by the corona, the "C<sub>4</sub>" block, which could also potentially limit the ability of the metal units to interact with the outside environment. An examination of the ability of the sequestered  $Ru(bpy)_3^{2+}$  complexes to participate in electron transfer reactions with molecules outside the structure is relevant in determining how useful self-assembled aggregates might

be in a number of applications, including sensing, photocatalysis and light harvesting.

Table 3.2 shows the results of quenching monomer 1 and polymers 2 and 3 with naphthoquinone (NQ, an electron acceptor) and phenothiazine (PTZ, an electron donor). In the case of the self-assembled polymers in 70% toluene, the quencher was added after self-assembly was induced.

	<u></u>	Naphtho	quinone (NQ)	Phenothiazine (PTZ)	
Sample	Solvent	K <sub>sv</sub>	$k_q (x \ 10^9 \ s^{-1})$	K <sub>SV</sub>	$k_q (x \ 10^9 \ s^{-1})$
1	MeCN	7176	5.55	7707	5.96
	70% toluene	3942	3.16	7110	5.70
2	MeCN	9875	8.83	6710	6.00
	70% toluene	6162	5.60	3188	2.90
3	MeCN	8950	8.06	4929	4.44
	70% toluene	8479	10.2	925	1.12

Table 3.2. Quenching data for 1, 2, and 3 by naphthoquinone and phenothiazine.

The quenching rate constant  $(k_q)$  values for polymers 2 and 3 were calculated using the average lifetimes of the unquenched samples and the Stern-Volmer constant  $(K_{SV})$  from steady-state quenching experiments  $(k_q=K_{SV}/\tau)$ . Average lifetimes were calculated using the equation  $(A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$ .<sup>13</sup> Each value reported is the average of several experiments. Literature value<sup>14</sup> of PTZ quenching is  $5.5 \times 10^9 \text{ s}^{-1}$ . Literature value<sup>15</sup> of NQ quenching is  $8.0 \times 10^9 \text{ s}^{-1}$ .



### 3.2.2.1. Quenching by Napthoquinone

Naphthoquinone quenches the  $Ru(bpy)_3^{2+}$  excited state by oxidative electron transfer.

\*
$$\operatorname{Ru}(\operatorname{bpy})_{3}^{2^{+}}$$
 + NQ  $\longrightarrow$   $\operatorname{Ru}(\operatorname{bpy})_{3}^{3^{+}}$  + NQ<sup>-</sup>

Comparison of the results in acetonitrile allows examination of the effects of incorporating the metal complex into the block copolymer on the accessibility of the metal complex to small molecules. The Stern-Volmer plots ( $I_0/I$  vs [NQ]) for all samples were linear in acetonitrile (Fig 3.5). When the luminescence decays of polymer 2 in acetonitrile in the presence of increasing amounts of NQ quencher are compared (Figure 3.6), there is no decrease in initial intensity, suggesting that static quenching is not a major mechanism acting on these samples. Examination of the values of  $k_a$ , the quenching rate constant, for the monomer and polymers in acetonitrile reveals that the quenching rate is slightly higher for the polymers than for the monomer, although all are close to the diffusion-control limit. The increase in  $k_q$  for the polymers might be a result of a number of factors. There can be differences in diffusion kinetics between the polymers and the monomer, as well as energy migration effects. For the monomer system, quencher molecules must collide with individual excited  $Ru(bpy)_3^{2+}$  complexes for quenching to occur. For the polymers, a quencher molecule may only need to collide with any part of an open polymer chain, and energy migration or hopping (see above) will ensure that an excited ruthenium unit on the polymer chain is in close enough proximity to be quenched. As well, depending on the rate of backelectron transfer and the number of excited ruthenium complexes per polymer, NQ may be able to quench multiple excited states per polymer chain.<sup>16</sup> Thus, while slower diffusion kinetics in the polymer systems may result in fewer collisions between NQ molecules and individual  $Ru(bpy)_3^{3+}$  units, energy migration in the polymer may increase the effectiveness of the quenching process, and ensure that the overall rate of quenching is high.





Figure 3.5. Stern-Volmer plots for NQ quenching of (a) 1, (b) 2, and (c) 3 in acetonitrile (diamonds) and 70% toluene (squares). For all samples, the [Ru] is  $4 \times 10^{-6}$  M.



**Figure 3.6.** Luminescence decay traces for polymer 2 as NQ is added in acetonitrile (a) and 70% toluene (b). In each graph, the equivalents of NQ (per Ru complex) added is, from the top curve to the bottom curve, 0 eq, 10 eq, 50 eq, and 100 eq.

In a second set of experiments, toluene was added, and polymer chains selfassembled into micelles or vesicles before the quencher was added to these preformed aggregates. Several factors are expected to affect the electron transfer

quenching rates in this case. First, the presence of the non-polar solvent should cause a decrease in the quenching rate.<sup>16</sup> Second, the  $Ru(bpy)_3^{2+}$  moieties units within the self-assembled structures are expected to be less accessible to external quencher molecules than in open chains. Finally, there can be heterogeneities in the extent of interaction with external molecules within a micellar core. Units that reside on the core-corona interface may interact with the quencher molecules to a higher extent than complexes that are deeply buried in the core.

The ruthenium-based monomer cannot self-assemble and acts as a control for the effects of toluene in the system. The Stern-Volmer plot for the monomer quenching by NQ in 70% toluene is shown in Figure 3.5a, and the data is given in Table 3.2. As expected,<sup>16</sup> the rate of electron transfer quenching of the monomer in 70% toluene is slower than in pure acetonitrile (57% of its value in acetonitrile).

Interestingly, a similar decrease in quenching rate was also observed for polymer 2 (63% of its value in acetonitrile). In all cases, the quenching constants are still high, on the order of  $10^9$  s<sup>-1</sup>. The result for polymer 2 is surprising, as it suggests that micellization does not significantly hinder the ability of the  $Ru(bpv)_{2}^{2+}$  to interact with molecules outside the micelle. The observed efficient quenching may be due to rapid energy migration<sup>1a,1f</sup> between the complexes within the micelle core (see above). Previous work on unassembled polymers containing  $Ru(bpy)_3^{2+}$  has demonstrated that quenching of the  $Ru(bpy)_3^{2+}$  excited state can occur following a delay attributed to prior rapid energy migration between ruthenium complexes.<sup>1f</sup> In addition, Ru(bpy)<sub>3</sub><sup>2+</sup> complexes incorporated into the walls of small molecule vesicles have been shown to engage in electron transfer reactions.<sup>18</sup> As well, in thin films composed of polymer-appended  $Ru(bpy)_3^{2+}$  complexes, energy migration resulted in  $Ru(bpy)_3^{2+}$  quenching by ferrocene in a second film layer.<sup>1a</sup> With the thin films, quenching efficiency increased with increasing concentration of  $Ru(bpy)_3^{2+}$  in the film layers, and therefore ruthenium complexes that were not directly in the vicinity of an active interface could participate in light harvesting. The same appears to apply here; even from within a micelle core, ruthenium complexes may be able to undergo excited state quenching with external molecules, through fast energy migration to complexes at the core-corona interface. The Stern-Volmer plot for the quenching of polymer 2 in 70% toluene is given in Fig 3.5b. It is linear, indicating that the emitting species are more or less equally quenched by naphthoquinone.

When NQ is added to preformed vesicles (polymer 3) the quenching rate constant, kq, slightly *increases* as compared to open polymer 3 chains (Table 3.2). This implies that, once again, the formation of vesicles does not hinder the ability of the ruthenium excited states within the vesicle wall to be quenched by outside molecules. In this self-assembled system, the core-corona interface may be even more accessible to the quencher molecules than for star micelles from polymer 2, as the shielding corona block is considerably shorter for this polymer, and this may explain the higher observed quenching constant for the vesicles than for the micelles.<sup>19</sup>

### **3.2.2.2.** Quenching by Phenothiazine

After determining that oxidative electron transfer quenching of the  $Ru(bpy)_3^{2+}$  complexes was maintained in the self-assembled polymers through energy migration among the metal complexes, we conducted similar experiments with an electron donor, phenothiazine (PTZ).

\* $Ru(bpy)_3^{2+}$  + PTZ  $\rightarrow$   $Ru(bpy)_3^{+}$  + PTZ'+

It was observed in another report<sup>20</sup> that for a  $Ru(bpy)_3^{2+}$ -based monomer, reductive electron transfer quenching with PTZ was decreased by increased alkyl substitution on the metal complex, while oxidative quenching (with methyl viologen) was less affected. This indicates that PTZ quenching may be more sensitive to steric access to the metal center than quenching by NQ. It is thus important to determine if energy migration among the metal complexes could also result in reductive electron transfer quenching of the Ru(bpy)<sub>3</sub><sup>2+</sup> luminescence. The results of quenching the three samples are shown in Table 3.2 and Figure 3.7.

In general, the rates of PTZ quenching are lower than for NQ quenching. The results obtained for monomer quenching are similar to literature references.<sup>14</sup>



Figure 3.7. Stern-Volmer plots for quenching of monomer 1 (a) and polymers 2 (b) and 3 (c) with PTZ, in acetonitrile (diamonds) and 70% toluene (squares).

When toluene is added, the rates of electron transfer quenching with PTZ are decreased for all 3 samples compared to their acetonitrile solutions. However, for self-assembled polymers 2 and 3, this decrease compared to acetonitrile solutions is more pronounced than for monomer 1. For the micelles of polymer 2, the quenching rate constant decreases by a factor of 2, and for vesicles, the quenching rate constant is decreased by a factor of approximately 4 compared to the unassociated polymers in acetonitrile. These reduced quenching rates are possibly due to the greater sensitivity of PTZ quenching to hindered access to the Ru(bpy)<sub>3</sub><sup>2+</sup> core caused by the corona block.<sup>20</sup> However, again, quenching rate constants in all cases are still on the order of  $10^9$  s<sup>-1</sup>, even for the vesicle system. Thus, rapid energy hopping likely occurs here as well, to allow the efficient quenching of emission of complexes within the micelle core and vesicle wall by external PTZ molecules, as observed for NQ quenching.

It of note that, based on our observations for both NQ and PTZ quenching, the small molecule quenchers do not likely penetrate into the inside of the micelle core or the vesicle wall, and therefore do not come in direct physical contact with the metal complexes buried inside these domains. The glass transition temperature of the metal-containing block is high ( $T_g = 210^{\circ}C$  for poly-Ru<sub>19</sub>),<sup>5c</sup> and thus diffusion through the insoluble core should be slow on the time scale of our measurements (emission is measured within minutes of quencher addition). In addition, diffusion into the core or wall on such a short time scale would not be expected to be completely uniform throughout the insoluble domain, and thus non-linear Stern-Volmer plots might be expected, rather than the observed linear ones that indicate that all emitting species are equally quenched. Finally, there is no decrease in the initial intensity of the luminescence decay trace as quencher is added to preformed micelles of polymer **2**, thus ruling out static quenching by NQ or PTZ molecules which have penetrated into the micellar core.

Within the micellar aggregates the ruthenium complexes are concentrated in a small, well-defined domain, and thus one question may be the extent to which inner filter effects play a role in the luminescence of these micellar systems. While the ruthenium concentration used in these studies was  $4 \times 10^{-6}$  M,

corresponding to absorbances of less than 0.1, the local effective concentration of ruthenium complexes inside the micelle cores or vesicle walls would be higher. We considered the possibility that only those complexes near the core surface were being excited by the incident light, while excitation of complexes deeper within the core was significantly reduced due to inner filter effects. In this case, the quenching data could arise exclusively from direct interaction of the complexes near the core surface with quencher molecules. We believe that such inner filter effects are not significant in our self-assembled systems for several reasons. First, for samples of the same ruthenium concentration, the steady state luminescence intensities are very similar for unassembled polymer chains in acetonitrile and for self-assembled polymers in 70% toluene. This would not be expected if inner filter effects were reducing the emission of the complexes in the innermost regions of the core. In addition, although there are some differences between quenching of the unassembled polymer chains and the self-assembled structures (see above), for samples of the same ruthenium concentration, the peak intensities in acetonitrile and in 70% toluene remain relatively comparable as quencher is added. If quencher molecules were only acting on the fraction of ruthenium complexes near the micelle surface, the luminescence peak intensities of the micelle samples would not be expected to decrease in a similar manner as the open polymer chains, where quenchers have equal access to all ruthenium molecules. Thus, inner filter effects do not operate to a significant extent in these systems and cannot account for the observed quenching data.

The important observation is that although electron transfer quenching is slightly affected by the presence of toluene and the formation of self-assembled aggregates, all of the observed quenching rates approach the diffusion control limit. This means that the  $Ru(bpy)_3^{2+}$  complexes that are sequestered inside a micelle core or vesicle wall are capable of undergoing efficient excited state electron transfer with molecules on the outside of the structure. This is likely a result of rapid hopping of the excitation to the core surface where it can be harvested by external molecules. Thus, these self-assembled systems can be useful in a range of applications including sensing and light harvesting.

### 3.2.3. Additional Experiments

The experiments conducted above in acetonitrile and acetonitrile/toluene solutions were aimed at demonstrating that the ruthenium complexes in the micelle cores or vesicle walls of self-assembled structures were able to participate in electron transfer reactions with small molecules added to the *outside* of the self-assembled structure. A particularly useful property of these morphologies is that they may encapsulate materials. If electron transfer reactions between small molecules *inside* the structures and the Ru(bpy)<sub>3</sub><sup>2+</sup> complexes that make up the core domains could occur, it might be possible to design a system in which charge separation between molecules on the inside and molecules on the outside could be facilitated by the Ru(bpy)<sub>3</sub><sup>2+</sup> complexes in the core/wall.

Scheme 3.2. Polymer forming micelles in water for encapsulation of NQ and PTZ.



In preliminary experiments towards this, we wanted to encapsulate NQ and PTZ inside self-assembled aggregates. These quenchers, however, are soluble in toluene and are therefore not likely to be encapsulated inside the core domains of

the polymers studied above. For proof-of-concept experiments, then, we used a different polymer system (see Chapter 4). This particular polymer, polymer 4, shown in Scheme 3.2, possesses a  $\text{Ru}(\text{bpy})_3^{2+}$ -containing block and a C<sub>4</sub> block, similar to that discussed above, but also includes a block based on poly(ethylene glycol), or "PEG". The "PEG" block is water soluble, while the C<sub>4</sub> and Ru blocks are not; therefore, when water is added to acetonitrile solutions of this polymer, micelles form with the C<sub>4</sub> and Ru blocks in the core, and the PEG units forming the corona. Since neither NQ nor PTZ are soluble in water, they are preferentially partitioned inside the micelle core.

NQ and PTZ were each dissolved in acetonitrile. The quencher solutions were then used to dissolve samples of polymer 4. After stirring for several minutes, water was slowly added to the polymer/quencher solution to induce micelle formation. When the water content reached 80%, the sample (~1 ml total volume) was dialyzed against deionized water for at least 24 hours to remove the acetonitrile and to remove any sparingly soluble, unencapsulated quencher. After dialysis, the sample containing PTZ was cloudy, indicating that there was some PTZ that was not encapsulated and was not removed by dialysis. The NQ- and PTZ-loaded samples were therefore centrifuged, and the clear orange solution obtained was used for absorbance and luminescence measurements. As a control, a polymer sample was prepared using the same procedure but no quencher was added to it. TEM was used to confirm that micelles were retained after encapsulation, dialysis, and centrifugation.

We tried to estimate the amount of quencher encapsulated inside the micelles. The amount of NQ or PTZ added to the polymer was approximately 22 equivalents of quencher to  $Ru(bpy)_3^{2+}$ . Analysis of the tiny pellet remaining after centrifugation of the PTZ-loaded micelles indicated that approximately 21 equivalents of PTZ to  $Ru(bpy)_3^{2+}$  were encapsulated. No pellet formed when the NQ loaded micelles were centrifuged, and so we estimate that close to the 22 equivalents added must have been encapsulated.

To determine if the luminescence of the metal complex was quenched by the electron acceptor or the electron donor inside the micelles, the absorbance and luminescence of a series of samples was measured. The graph in Figure 3.8 shows representative data for the steady-state emission of  $\text{Ru}(\text{bpy})_3^{2+}$  vs the absorbance of the MLCT band of the ruthenium complex (neither quencher absorbs in this region). This allows comparison of micelles that contain either NQ, PTZ, or no quencher. It is clear from the graph that for a particular ruthenium absorbance (and concentration) the emission is much attenuated when either quencher is trapped inside the micelles in close proximity to the metal complex.



Figure 3.8. Emission (peak area) vs absorbance of micelles containing no quencher (diamonds), micelles with NQ encapsulated (squares) and micelles with PTZ encapsulated (triangles).

These preliminary experiments demonstrate that electron transfer can also occur between small molecules inside the self-assembled aggregates and metalbased micelle cores. While this may not be a completely surprising result, it establishes the potential of  $Ru(bpy)_3^{2+}$ -based block copolymers to facilitate a long-lived charge separated state between molecules on the inside and on the outside of self-assembled polymer morphologies.

### 3.3. Conclusions

Our results indicate that self-assembly of  $Ru(bpy)_3^{2+}$ -containing block copolymers confines the metal complexes within well-defined core domains without significantly decreasing their quantum yield. The luminescence decays of the polymer samples, however, are not mono-exponential like the monomer, but become non-exponential. This is interpreted as the result of excited state interactions and energy migration between the ruthenium complexes, as well as the non-homogeneous environment along the polymer backbone. Perhaps most interesting is that the complexes, even when sequestered within a micelle core or vesicle wall, can participate in excited state oxidative and reductive electron transfer with external molecules, to similar extents as the open polymers. This is most likely due to energy migration processes that can result in rapid hopping of the excitation from the complexes buried within the core to the core surface, where it can be harvested by external donors and acceptors. In preliminary experiments we also established the ability of the metal complex inside a micelle core to participate in electron transfer reactions with small molecules *inside* a micelle. The ability of self-assembled  $Ru(bpy)_3^{2+}$ -containing block copolymers to undergo excited state interactions with molecules inside and outside the selfassembled structure significantly increases their potential utility in photocatalysis, light-harvesting and sensing applications.

### **3.4. Experimental Procedures**

**Materials**: Reagents and solvents were purchased from Sigma-Aldrich. Naphthoquinone was recrystallized from ethanol. Phenothiazine was purchased as an analytical standard and used as received. The ruthenium (bipyridine) monomer and polymers were synthesized as described earlier.<sup>5a</sup>

General methods: Solvents were distilled and freshly degassed by bubbling with argon for at least 40 min. Solutions were prepared in vials that were septum-sealed and had been evacuated and refilled with argon (at least 3 cycles).

Measurements were done in fluorescence cuvettes that contained septa-sealable caps and that were also evacuated and refilled with argon. All transfers of solvents and solutions were carried out using gas-tight syringes flushed with argon. For samples in water, the water was air-equilibrated.

Absorbance measurements were done using a Cary 5000 UV-Vis-NIR Spectrophotometer. Fluorescence measurements, steady-state and lifetime, were performed on a PTI instrument. For steady state measurements, samples were excited at 450 nm. The lifetime measurements (single photon counting) utilized a nitrogen laser with a dye optimized at 481 nm, with monitoring at 625 nm. The laser energy was ~50  $\mu$ J. Lifetimes were determined using the PTI software.

**Self-Assembly**: A typical self-assembly experiment in acetonitrile and toluene was carried out as follows: A sample was weighed into a vial equipped with a stir bar, sealed with a septum, and evacuated then flushed with high purity argon (at least 3 cycles). It was then dissolved in degassed acetonitrile transferred by syringe. Ruthenium polymer samples were dissolved to make a polymer concentration of 5 mg/ml. Monomer samples were dissolved so that the initial ruthenium concentration was comparable to that in the polymers. In some cases toluene was then slowly added drop-wise through a syringe to a final content of 70% to induce self-assembly in the polymer samples, or to adjust the solvent content for the monomer samples. For the water-based experiments, water was added slowly to acetonitrile solutions of polymer or polymer/quencher.

**Fluorescence Studies**: For fluorescence measurements, the initial polymer or monomer sample was diluted to a  $Ru(bpy)_3^{2+}$  concentration of 4 x 10<sup>-6</sup> M by transferring an aliquot via argon-flushed syringe directly to a fluorescence cuvette containing solvent appropriate for dilution (ie, samples prepared in pure acetonitrile were diluted in acetonitrile, while samples prepared in 70:30 toluene: acetonitrile were diluted in 70:30 toluene: acetonitrile). For the polymer samples, dynamic light scattering confirmed that dilution to fluorescence concentrations did not cause dissociation of the self-assembled aggregates.

Steady state measurements were done with slit widths of 3 nm. Emission intensity was integrated between 525 - 850 nm.<sup>19</sup> Lifetime measurements were

done using the same concentrations as for steady-state measurements. Three averages were used for each measurement, and lifetimes were determined using the software of the instrument. No attenuation of the initial intensity was observed over the course of the three averages, indicating that for these experiments there were no harmful effects of the continuous flashing of the sample. All lifetime measurements reported are the average of several separate measurements.

Quantum yields were determined using two standards:  $Ru(bpy)_3^{2+}$ , chloride salt in water, or PF<sub>6</sub> salt in acetonitrile, and the references were cross-checked. The reference values were 0.042 or 0.062, respectively. Each sample or standard was prepared in 4-5 concentrations, all on the order of  $10^{-6}$  M in  $Ru(bpy)_3^{2+}$ , that gave absorbance values of less than 0.1. The luminescence of each sample was also recorded. The emission intensity (area) was plotted against the absorbance value to give linear traces. Using the slopes of the straight lines of the samples and the reference, the quantum yields were obtained using the equation: QY = QY(ref) x[slope/slope(ref)] x [n<sup>2</sup>/n(ref)<sup>2</sup>], where (ref) is the reference sample, QY is quantum yield, and n is refractive index. Each value reported is the average of several trials. The values of  $\varepsilon$ , the molar extinction coefficient were also obtained during these experiments.

For the quenching experiments, aliquots of NQ or PTZ were added directly to the cuvette. Stern-Volmer plots were constructed using steady-state data.

### 3.5. References and notes

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# Chapter 4: Energy Transfer with Self-Assembled Ru(bpy)<sub>3</sub><sup>2+</sup>-Containing Block Copolymers

# Chapter 4: Energy Transfer with Self-Assembled Ru(bpy)<sub>3</sub><sup>2+</sup>-Containing Block Copolymers

### 4.1. Introduction

Energy transfer is a key process in designs for artificial photosynthesis<sup>1</sup> and for sensing assays.<sup>2</sup> In artificial photosynthesis schemes, an antenna array can use energy transfer from strongly absorbing dyes to sensitize a central chromophore, resulting in more efficient excitation of the central chromophore. As well, energy transfer from fluorescent polymers to  $Ru(bpy)_3^{2+}$  complexes has been used to increase the efficiency of light-emitting devices.<sup>3</sup> In biodetection assays, energy transfer between a dye with a high quantum yield but short lifetime and a long lived metal complex can result in a tandem system possessing both a high quantum yield and longer effective lifetime.<sup>4</sup>

Energy transfer with  $\text{Ru(bpy)}_3^{2^+}$  complexes has been intensely studied.  $\text{Ru(bpy)}_3^{2^+}$  absorbs in the visible region and has a long-lived excited state. It is capable of acting as the donor in triplet-triplet energy transfer to both organic molecules<sup>5</sup> and metal complexes such as  $Os(bpy)_3^{2^+,6}$  It can also act as an acceptor in energy transfer with singlet excited species.<sup>7</sup>

Energy transfer involving  $Ru(bpy)_3^{2+}$ -based *polymer* systems has been increasingly studied for light harvesting and detection applications. Star shaped polymers<sup>7a,b</sup> that possess both  $Ru(bpy)_3^{2+}$  complexes and organic dyes have been studied as antenna systems for artificial photosynthesis. As well, there are examples of linear polymers that contain  $Ru(bpy)_3^{2+}$  complexes appended to the same polymer backbones as either organic dyes or other metal complexes.<sup>6,7c</sup> In these polymers, the organic chromophores absorb light and sensitize  $Ru(bpy)_3^{2+}$  complexes that are at the centre of the star or along the polymer chain through energy transfer.

When the Ru(by)<sub>3</sub><sup>2+</sup> complexes are appended to the same polymer backbone as the energy donor or acceptors, sometimes complicated synthetic procedures are required to attach all the different species to the pre-formed polymers, or to prepare the various species for polymerization. This approach also suffers the disadvantage that a new polymer system must be synthesized for each energy donor or acceptor to be tested, and thus optimization of the system can be time-consuming and synthetically demanding. Using self-assembled polymer systems, however, could potentially decrease some of these complications. For different applications, the same polymer could be used to encapsulate different small molecules, thus requiring only one polymer synthesis and only a simple self-assembly procedure for any new energy donor or acceptor. As well, self-assembly can be reversible, which might have practical applications, particularly for biodetection assays or when recovery of the polymer or small molecule is desirable after an experiment.

Our lab has previously described ring opening metathesis polymerization to generate well-defined block copolymers that contain multiple  $Ru(bpy)_3^{2+}$ complexes concentrated into one block.<sup>8</sup> One system we reported<sup>8b</sup> incorporated a  $Ru(bpy)_3^{2+}$  -based block with a molecular recognition element and these polymers, upon self-assembly, formed micelles that contained biotin groups around their peripheries (see Chapter 5). These micelles aggregated in the presence of the protein streptavidin, demonstrating that such self-assembled structures could recognize biomolecules, and thus have potential in biodetection assays. Later work has focused on the further development of  $Ru(bpy)_3^{2+}$ -based micelle systems for biodetection applications.<sup>9</sup> While  $Ru(bpy)_3^{2+}$  complexes absorb in the visible range and have long lifetimes, they have relatively low quantum yields compared to organic dyes. One way to potentially make them brighter is by energy transfer, either by sensitization of the metal complex by an organic dye,  $7^{\circ}$  or by energy transfer from Ru(bpy)<sub>3</sub><sup>2+</sup> to an organic dye with a high quantum yield, resulting in an increase of both the effective quantum yield of the  $Ru(bpy)_{3}^{2+}$  unit and the effective lifetime of the organic dye.<sup>4</sup>

We also previously examined the ability of the  $Ru(bpy)_3^{2+}$  complex within self-assembled systems to participate in electron transfer reactions. The metal complex could interact with both an electron donor and an electron acceptor that were on the outside or the inside of the self-assembled structures, facilitated by energy migration among the metal complexes. Therefore, such self-assembled systems might be able to function in designs for artificial photosynthesis.

To further explore the potential usefulness of self-assembled  $Ru(bpy)_3^{2+}$  containing polymers in applications like sensing or light harvesting, it is pertinent to examine the ability of these polymers to engage in energy transfer reactions. In this Chapter, we examine the ability of self-assembled polymer structures to undergo energy transfer with an  $Os(bpy)_3^{2+}$ -based complex and a coumarin molecule.

#### 4.2. Results and Discussion

## 4.2.1. Polymer self-assembly

The  $Ru(bpy)_3^{2+}$  polymers and  $Ru(bpy)_3^{2+}$  - based monomer used in this study are shown in Scheme 4.1. Polymer 1 contains three blocks. The poly(ethylene glycol) block is water soluble, while the metal-containing "Ru" block and the "C<sub>4</sub>" block, so named because of the butyl chain, are not. Polymer 2 contains only PEG and Ru blocks.

Scheme 4.1. Polymers used in this study, schematics of the micelles that they form, and the ruthenium containing monomer.



The polymers were dissolved in acetonitrile, in which all blocks are soluble, and self-assembly was induced by the slow addition of water (Scheme 4.1). This results in the formation of micelles which possess a PEG corona and  $\text{Ru}(\text{bpy})_3^{2+}$  inside the cores. For polymer 1, the C<sub>4</sub> block is also part of the core.<sup>10</sup> Figure 4.1 shows a TEM image of the micelles formed.



Figure 4.1. TEM image of micelles formed upon water addition to polymer 1.

#### 4.2.2. Encapsulation Methods

In these studies, the small molecules, Coumarin 2 (C2) and an  $Os(bpy)_3^{2+}$  based molecule, used to study energy transfer with  $Ru(bpy)_3^{2+}$  are not very soluble in water. Therefore, they should be preferentially partitioned inside the micelle core, rather than in the surrounding aqueous solution (Scheme 4.2). Several methods were used to try to maximize the amount of material encapsulated inside the micelles.

In Method 1, the small molecule (either Coumarin 2 or  $Os(bpy)_3^{2+}$  monomer 4) was dissolved in acetonitrile, and that acetonitrile solution was used to dissolve the polymer. After stirring for several minutes, water was then slowly added to induce self-assembly. The final water content was at least 80%. The small molecules, being insoluble in water, should then be partitioned inside the micelle cores in close proximity to the ruthenium complexes. Samples were then dialyzed against deionized water to remove acetonitrile from the micelle cores and unencapsulated material from the sample, and then centrifuged to remove any precipitated, unencapsulated material.

In the second method, a film was formed by dissolving the small molecule in a solvent in which it is readily soluble ( $CH_2Cl_2$  for Coumarin, acetonitrile for monomer 4), and letting the solvent evaporate to leave a film of the molecule in a vial. Micelles were separately pre-formed by adding water to an acetonitrile solution. At a water content of 90%, the micelles were then added to the vial containing the coumarin or Os(bpy) film. The mixture was stirred over several days to allow the small molecule to diffuse into the micelle. The sample was then dialyzed and centrifuged to remove acetonitrile and unencapsulated material.

In the third method, a film of the small molecule was formed as before, and again the polymer was separately self-assembled into micelles, with a final water content of 95%. The aqueous micelle solution was added to the small molecule film and stirring continued for several days. This time, instead of dialysis, each sample was centrifuged briefly to remove undissolved, unencapsulated material, and the supernatant was transferred into a Microcon filtration set-up. The filter had a molecular weight cut-off (MWCO) of 10,000, so small molecules and solvent could pass through upon centrifugation, while self-assembled polymers were retained. The samples were centrifuged (filtered), and deionized water was added to the retained polymer, and the samples were centrifuged again. This wash step was repeated several times. By this method, any unencapsulated-but-dissolved material was filtered out, and the retained solution should eventually contain only self-assembled polymer (+ encapsulated small molecules) in water.

For each method, a control containing only self-assembled polymer was processed in the same manner as the samples containing polymer + small molecule.

Scheme 4.2. Encapsulation of small molecules inside micelle core (polymer 2 shown).



\*Coumarin +  $\operatorname{Ru}(\operatorname{bpy})_3^{2+} \longrightarrow \operatorname{Coumarin} + \operatorname{Ru}(\operatorname{bpy})_3^{2+}$ (results in enhanced  $\operatorname{Ru}(\operatorname{bpy})_3^{2+}$  emission)

\*Ru(bpy)<sub>3</sub><sup>2+</sup> + Os(bpy)<sub>3</sub><sup>2+</sup>  $\longrightarrow$  Ru(bpy)<sub>3</sub><sup>2+</sup> + \*Os(bpy)<sub>3</sub><sup>2+</sup> (results in quenching of Ru(bpy)<sub>3</sub><sup>2+</sup> emission)

### 4.2.3. Coumarin dyes

The emission of some coumarin molecules overlaps significantly with the absorption of  $\text{Ru}(\text{bpy})_3^{2+}$ , and thus they can potentially transfer energy to the metal complex. Some coumarin molecules initially tested include Coumarin 2, Coumarin 343, Coumarin 102 and Coumarin 110. Early experiments were performed with all of these coumarin dyes, but since the most thorough studies were conducted with Coumarin 2, that is the dye that will be discussed in the following section. Coumarin 2 absorbs at 356 nm and emits at 421 nm.



Coumarin 2

In initial tests, Coumarin 2 was added to the  $Ru(bpy)_3^{2+}$  based monomer 3 in acetonitrile solutions, where both the coumarin and the metal complex were freely diffusing. Figure 4.2a shows the emission of the  $Ru(bpy)_3^{2+}$  complexes, with up to 10 equivalents of coumarin to monomer 3, upon excitation of the coumarin at 356 nm. These results indicate that the emission of the metal complex at 630 nm is not enhanced significantly due to energy transfer from Coumarin 2. At higher coumarin concentrations, the coumarin emission decreased, probably due to self-quenching since there was still no observed increase in ruthenium emission.

The excitation spectrum of a monomer 3/coumarin mixture is shown in Figure 4.2b. In water, the coumarin emission is centered at around 450 nm when excited at 356 nm. The excitation spectrum of the mixture, when monitored at the  $Ru(bpy)_3^{2+}$  emission at 630 nm, does not indicate that there is a significant contribution to the emission of the ruthenium complex from the coumarin. Förster energy transfer between freely diffusing monomeric coumarin and  $Ru(bpy)_3^{2+}$  complexes has been reported in the literature.<sup>7d</sup> However, in that case the concentration of metal complex was as high as  $1 \times 10^{-2}$  M, and inner filter effects complicated the analysis, whereas the metal concentration used in this study is  $4 \times 10^{-6}$  M.



Figure 4.2. (a) Luminescence of Ru monomer 3 with coumarin added. Excitation wavelength of the samples was 356 nm. The arrows indicate the number of equivalents of Coumarin 2 to monomer 3. (b) Normalized excitation spectrum, monitored at 630 nm, of monomer 3 with (solid grey line) and without (dotted black line) coumarin added.

Based on these results, it appears that energy transfer would not efficiently occur between freely diffusing metal complexes and coumarin molecules under our experimental conditions. We reasoned that energy transfer might be more efficient if the coumarin molecules were encapsulated inside the micelles in close proximity to the ruthenium complexes. Such a method would not necessitate such high concentrations of dye molecules, eliminating complications like inner filter effects.

We first investigated the use of method 1 to encapsulate coumarin inside the block copolymers 1 and 2. In this method, the coumarin and polymer were stirred together in acetonitrile before water was slowly added to induce micellization. The absorbance spectra of polymer 1 and polymer 2 are shown in Figure 4.3a and b, respectively. The absorbance of the coumarin should be noticeable at around 360 nm, and there is at best only a small increase in absorbance in that area for the coumarin-containing systems. Based on these results, it appears that coumarin was not successfully encapsulated inside the micelles to any significant degree.

For polymer 1, compared to micelles with no coumarin added, there was no increase in the luminescence of the  $Ru(bpy)_3^{2+}$  complexes when the samples were excited at 356 nm, and no clear evidence of energy transfer from the Coumarin 2 to the metal complex. When polymer 1 self-assembles into micelles, both the Ru and C<sub>4</sub> blocks comprise the core. We cannot be certain if the C<sub>4</sub> and Ru blocks form separate regions within the micelle core, as depicted in Scheme 4.1, or if they form a more continuous core domain. If the former is true, then it is possible that any small organic dye molecules that are encapsulated are preferentially partitioned within the C<sub>4</sub> domain and are not in close enough contact with the ruthenium complexes for energy transfer to occur.

For this reason, we thought that if we had only encapsulated a very small amount of coumarin, we might have a greater probability of observing energy transfer with polymer 2. In this case, there is no C<sub>4</sub> block, and thus no C<sub>4</sub>-rich domain inside the micelle core can exist for the coumarin molecules to reside in (Scheme 4.1). For the samples shown in Figure 4.3b, the ratio of Coumarin 2 :  $Ru(bpy)_3^{2+}$  in the initial solution was approximately 17:1, and the absorbances of the dialyzed samples are normalized to the  $Ru(bpy)_3^{2+}$  MLCT absorbance at 458 nm. Figure 4.4a shows the related emission of polymer 2 when excited at the

coumarin excitation wavelength of 356 nm, and Figure 4.4b shows the excitation spectra of polymer 2, monitored at the  $Ru(bpy)_3^{2+}$  emission wavelength of 630 nm. Comparison of the emission and excitation spectrum of the sample with and without coumarin added indicates that energy transfer does not occur to any appreciable degree.



Figure 4.3. Absorbance of micelles of (a) polymer 1 and (b) polymer 2 in water with (solid grey line) and without (black dotted line) Coumarin 2.





Method 1 was not very effective at encapsulating Coumarin 2. The main problem was likely that Coumarin 2 is only somewhat soluble in acetonitrile, and therefore it is difficult to add more than about 15-20 equivalents of coumarin to ruthenium, especially given the small volumes used for these experiments. Methods 2 and 3, which involved adding preformed micelles to a film of coumarin, allowed a greater excess of coumarin to be added to the samples to try to maximize the amount that ends up inside the micelles. When method 2 was used with polymer **2** and coumarin, the results were very similar to those obtained using the first method. In method 2, after the micelles were stirred with the coumarin film, the whole sample was dialyzed. It took several weeks to remove all the unencapsulated material in this way. Based on the results, we conclude that not very much material was encapsulated by this method, even though large excesses of coumarin can be added. The majority of the coumarin remained undissolved and unencapsulated. During the long dialysis step, as unencapsulated coumarin left the dialysis bag, it is possible that a gradient formed between the inside and outside of the micelles, and any coumarin initially inside the micelles diffused out.

For these reasons, method 3 was then used to try to encapsulate coumarin inside micelles of polymer 2. In this method, preformed micelles in 95% water were added to a film of coumarin inside a vial. After several days of stirring, the sample was briefly centrifuged to remove undissolved material, and then the solution was filtered through a Microcon filter (MWCO 10000) by centrifugal force. This washed out solvent and small molecules but retained larger molecules like the polymer micelles (and thus any material encapsulated inside them). The retained polymer solution was washed with water to remove any coumarin in the surrounding solution that was not encapsulated. The advantage of this procedure over dialysis is that coumarin can be removed from the surrounding aqueous solution much faster, hopefully minimizing the potential for leaching of coumarin from inside the micelles (by minimizing the time in which coumarin could leach out).



Figure 4.5. (a) Absorbance, (b) emission ( $\lambda_{ex}$ =356 nm), and (c) excitation ( $\lambda_{em}$ =630 nm) of polymer 2 with (grey line) and without (black dotted line) Coumarin 2 added.



Figure 4.5 shows the absorbance, emission and excitation spectra of the polymer sample, with and without coumarin added. Based on the absorbance spectrum, it is clear that there is coumarin present. In this case, an excess of approximately 55 equivalents of coumarin to  $Ru(bpy)_3^{2+}$  were added to the vial for mixing with the polymer micelles. However, comparison of the coumarin/polymer absorbances with a calibration curve of the absorbance of coumarin in water (acquired separately) established that approximately 5 equivalents of coumarin were in the micelle solutions. The majority did not dissolve and was removed during the first initial centrifugation. The filtrate from the Microcon filtration was also measured for evidence of coumarin and  $Ru(bpy)_3^{2^+}$ . There was not enough coumarin present to give a noticeable absorbance peak at 356 nm, but there was enough in the solution to saturate the detector on the fluorimeter. In addition, there was no  $Ru(bpy)_3^{2+}$  absorbance and only very minimal emission from the filtrate, indicating that the polymer micelles were indeed successfully retained by the filter, while unencapsulated coumarin dissolved in the water was successfully removed from the micelle solution.

When the micelle/coumarin mixture was excited at the coumarin absorption wavelength of 356 nm, there was no enhancement of the  $Ru(bpy)_3^{2+}$  emission (Figure 4.5b). In addition, the excitation spectrum of the sample, when monitored at the  $Ru(bpy)_3^{2+}$  emission at 630 nm, did not indicate a sizable contribution from the coumarin (Figure 4.5c). In a control experiment, the excitation spectrum of coumarin alone was monitored under the same conditions, and there was a very small contribution to emission at 630 nm, similar to what is found in the micelle/coumarin sample. It is apparent that even when coumarin is present in the sample in a slight excess, possibly encapsulated inside the micelles, energy transfer does not occur to any appreciable degree.

According to some relevant literature examples,<sup>7c,d,8a</sup> if energy transfer was occuring in our system, we should have been able to detect it. Primarily, we should have observed a decrease in the steady-state emission of the Coumarin 2 and a contribution from coumarin to the  $Ru(bpy)_3^{2+}$  emission in the excitation spectrum. Other important observations from the literature have been that the C2-

to-  $\text{Ru}(\text{bpy})_3^{2^+}$  energy transfer is primarily via the Förster mechanism, with a Förster distance of approximately 4 nm. In addition, there is also a report of a linear polymer to which  $\text{Ru}(\text{bpy})_3^{2^+}$  complexes and Coumarin 2 are attached, and in that case excitement of the coumarin at 350 nm resulted in greater  $\text{Ru}(\text{bpy})_3^{2^+}$  emission than if the metal complex was excited directly at 465 nm.<sup>7c</sup>

Comparison of these literature examples with our results suggests that energy transfer is not occurring in our system. In the literature examples, the emission of the donor molecule (coumarin) is substantially decreased in the presence of the acceptor  $(Ru(bpy)_3^{2+})$ , while our measurements always show very strong emission from the coumarin species. We also examined the emission of Coumarin 2 in aqueous solution in the absence of  $Ru(bpy)_3^{2+}$ , and used absorbance spectra to match coumarin-only samples with coumarin/ $Ru(bpy)_3^{2+}$ micelle systems. No significant difference in the coumarin emission profile was observed, indicating that the coumarin emission from our (hopefully) encapsulated material was not affected by the presence of the metal complexes. This was the case even though the C2: $Ru(bpy)_3^{2+}$  ratio estimated to be inside the micelles was greater than in some of the literature examples.

It is possible that more coumarin inside the micelles would allow energy transfer to be observed. One concern was that the bulk of the metal complexes would cause crowding in the micelle core, and would ultimately limit the number of coumarin molecules that could fit inside. However, there are many reports that describe the encapsulation of large molecules (such as porphyrin-, cholesterol-, or natural product-based molecules or large fluorophores) inside micelles smaller than ours.<sup>11</sup> Therefore, the bulk of the core-forming block is probably not a substantial barrier to the encapsulation of a small molecule like Coumarin 2.

For all of our efforts to encapsulate Coumarin 2 inside the cores of micelles that contain  $Ru(bpy)_3^{2+}$ , it appears that we were not successful. Convincing evidence of energy transfer, such as a decrease in coumarin emission at 450 nm when it is "inside" the cores near the ruthenium or a contribution to the  $Ru(bpy)_3^{2+}$  emission from the coumarin dye at 350 nm, was not obtained. Yet coumarin must be present in the system, since it emits very strongly. The most

likely explanation is that the Coumarin 2 is not actually encapsulated to any significant degree, but is instead existing in the surrounding aqueous solvent or even within the micellar PEG corona. The encapsulation of coumarin is probably not limited by spatial restrictions within the micelle, but more likely by the solubility of coumarin in acetonitrile solutions. Coumarin 2 is slightly soluble in acetonitrile, but is also very slightly soluble in water as well. Therefore it is not likely to be preferentially partitioned inside the micelle core to a degree significant enough to result in energy transfer. If Coumarin 2 resides within the PEG corona or in the surrounding aqueous solvent it would likely be too far away for energy transfer to the ruthenium-containing core to occur.

Since the most probable reason for our inability to observe energy transfer was the lack of preferential partitioning inside the micelle core, we devised a new strategy. By modifying the Coumarin 2 molecule, we hoped to increase its solubility in acetonitrile (and thus its compatibility with the micelle core) and decrease its solubility in water. We therefore synthesized a benzyl derivative of Coumarin 2 (Scheme 4.3).<sup>12</sup> This derivatized coumarin (benzyl-coumarin) was much more soluble in acetonitrile, and much less soluble in water, than Coumarin 2.

#### Scheme 4.3. Synthesis of benzyl-coumarin



To encapsulate benzyl-coumarin inside our micelles, we dissolved it in acetonitrile, and used that benzyl-coumarin/acetonitrile solution to dissolve polymer 2. After the mixture was stirred for several minutes, water was slowly added, and the solution was dialyzed against deionized water (method 1).

Figure 4.6a shows the absorbance of the micelles of polymer 2 (with benzylcoumarin encapsulated) and benzyl-coumarin alone (in acetonitrile). The samples have the same benzyl-coumarin absorbance. Figure 4.6b shows the fluorescence of the same samples when excited at the benzyl-coumarin absorbance of 345 nm. In Figure 4.6b, the emission peak at 440 nm is due to the benzyl-coumarin; when the coumarin is inside the micelles, the coumarin emission is greatly decreased.



Figure 4.6. (a) Absorbance and (b) emission ( $\lambda_{ex}$ =345 nm) of benzyl-coumarin (solid grey line) and polymer 2 with benzyl-coumarin encapsulated (black dotted line).

A comparison of the micelles of polymer 2 with and without benzylcoumarin encapsulated is shown in Figure 4.7. The absorbance spectra (Figure 4.7a) of the two samples show that they have the same  $Ru(bpy)_3^{2+}$  absorbance (and concentration). When the samples are excited at the  $Ru(bpy)_3^{2+}$  MLCT absorbance of 450 nm, the emission is unaffected by the presence of the coumarin. A control test confirmed that excitation of the benzyl-coumarin at 450 nm results in no emission in the region of 500-850 nm. When the "empty"  $Ru(bpy)_3^{2+}$ -containing micelles are excited at 345 nm, there is a small emission peak observed at 630 nm, even when there is no coumarin present. When benzylcoumarin is encapsulated, however, the emission of  $Ru(bpy)_3^{2+}$  at 630 nm is enhanced (Figure 4.7b). Another relevant observation is that the excitation spectrum of the micelles that contain benzyl-coumarin shows a definite contribution at approximately 350 nm that is not present when the micelles do not contain benzyl-coumarin (Figure 4.7c).

Based on the results described in Figures 4.6 and 4.7, the modified coumarin has an increased ability to be encapsulated inside the micelles and energy transfer was finally observed. The decrease in benzyl-coumarin emission at 440 nm when it is inside the micelles (Figure 4.6b) is most likely due to energy transfer. It could be suggested that the decrease in emission is actually due to self-quenching as a result of the coumarin molecules being in close proximity in high concentration inside the micelle core. However, the enhancement of the Ru(bpy)<sub>3</sub><sup>2+</sup> emission at 630 nm when the benzyl-coumarin is excited at 345 nm, and the contribution at ~350 nm in the excitation spectrum to the emission at 630 nm (Figures 4.7b and 4.7c) are strong evidence that energy transfer occurred from the benzyl-coumarin to the Ru(bpy)<sub>3</sub><sup>2+</sup> within the micelle cores.



Figure 4.7. (a) Absorbance, (b) emission ( $\lambda_{ex}$ =345 nm), and (c) excitation (monitor at 630 nm) of polymer 2 with (black dotted line) and without (grey solid line) benzyl-coumarin encapsulated.

In the experiment described in Figures 4.6 and 4.7, almost 60 equivalents of benzyl-coumarin to  $Ru(bpy)_3^{2+}$  were added to the polymer before self-assembly was induced by water addition. Notably, the benzyl-coumarin is a thick, viscous substance, and unencapsulated material separates from solution when water is added. When the sample was centrifuged, the supernatant became much lighter in colour than a sample with just micelles alone (no benzyl-coumarin). This indicates that a portion of the polymer micelles that had coumarin inside them were removed from solution as well (it was the supernatant that was used for absorbance and fluorescence measurements). This could be due to the polymer micelles "sticking" to the unencapsulated benzyl-coumarin that was centrifuged out. The dialysis and centrifugation steps make it difficult to use these samples to accurately determine the equivalents of benzyl-coumarin inside the micelles because the concentrations of the components are not known with certainty. However, considering the amount of material that separated from solution (benzyl-coumarin + micelles), it is considerably less than 60 equivalents.

To try to better estimate the amount of benzyl-coumarin inside the micelles, the absorbance spectra of known concentrations of benzyl-coumarin (in acetonitrile)<sup>13</sup> and polymer 2 micelles (in water) were compared to the absorbance spectra of the loaded micelles. Using this approximation, the micelles contained *at most* 5 equivalents of benzyl-coumarin per Ru(bpy)<sub>3</sub><sup>2+</sup>.

A control experiment was also performed in which benzyl-coumarin was added to  $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$  monomer **3** in degassed acetonitrile. In this case, no enhancement of the  $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$  emission at 630 nm can be detected because it is completely masked by the strong benzyl-coumarin emission ( $\lambda_{\max} = 450$  nm). The excitation spectrum, however, showed a very minimal contribution to the  $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$  emission from the benzyl-coumarin when 7.5 equivalents of benzyl-coumarin:  $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$  were added, and 22.5 equivalents of benzyl-coumarin were required to get approximately the same degree of contribution observed in the polymer system (Figure 4.8). This is further evidence that although almost 60 equivalents of benzyl-coumarin per  $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$  were added to the polymer, as described above, considerably less than that were encapsulated.

For the freely diffusing monomer 3 + benzyl-coumarin system, a benzylcoumarin:Ru(bpy)<sub>3</sub><sup>2+</sup> ratio of 22.5:1 resulted in the same contribution to Ru(bpy)<sub>3</sub><sup>2+</sup> emission as did a ~5:1 ratio when the coumarin was encapsulated inside the micelles. This discrepancy is likely explained by an enhancment of the energy transfer for the micelle system as a result of the coumarin being trapped in much closer proximity to the Ru(bpy)<sub>3</sub><sup>2+</sup> complexes within the micelle cores.



Figure 4.8. Excitation spectrum (monitored at 626 nm) of ruthenium monomer 3, in degassed acetonitrile, with different amounts of benzyl-coumarin added. The arrows indicate the number of equivalents of benzyl-coumarin to  $\text{Ru(bpy)}_3^{2^+}$  added.

In another experiment, we attempted to increase the loading of the micelles with almost 180 equivalents of benzyl-coumarin to  $\text{Ru}(\text{bpy})_3^{2^+}$ . In this case, the benzyl-coumarin precipitated out of solution at a low water content (~20% water) and formed such a thick, gooey substance that a stir bar could not spin in the vial. The solution was quite a pale yellow; the majority of the ruthenium-containing polymer precipitated out as well, likely a result of being stuck to the viscous benzyl-coumarin.

One possible future modification of this experiment to try to increase the benzyl-coumarin encapsulated may be to use a different solvent system. The acetonitrile in this system dissolves both the polymer and the benzyl-coumarin, while the purpose of the water is to induce self-assembly of the polymer and to cause the benzyl-coumarin to partition inside the micelles to hide from the water. Replacing water with a solvent that is *slightly* more compatible with benzyl-coumarin may delay the onset of its precipitation and increase the chance for it to partition into the micelle core. This new solvent would also have to be incompatible with the Ru(bpy)<sub>3</sub><sup>2+</sup> block but good for the PEG-block and result in the formation of similar micelles. The solvents used can greatly affect the morphologies formed from self-assembled polymers, but a suitable solvent system may exist that can result in similar micelles as the system examined here.

# 4.2.4. $Os(bpy)_3^{2+}$

Since use of benzyl-coumarin established that  $Ru(bpy)_3^{2+}$  complexes that were part of micelle cores could indeed act as energy acceptors, the next step was to determine their potential to act as energy donors. In systems containing  $Ru(bpy)_3^{2+}$  and  $Os(bpy)_3^{2+}$  complexes,  $Os(bpy)_3^{2+}$  is the energy acceptor and quenches the emission of  $Ru(bpy)_3^{2+}$ . For our experiments, we used an  $Os(bpy)_3^{2+}$ -based ROMP monomer 4.



As for the coumarin compounds, we performed initial tests with freely diffusing ruthenium (3) and osmium (4) complexes in degassed acetonitrile solutions.



**Figure 4.9**. Emission of  $\text{Ru(bpy)}_3^{2^+}$  momomer **3** and  $\text{Os(bpy)}_3^{2^+}$  monomer **4**, upon excitation at 450 nm. The curves, in descending order from the top, represent 0, 0.7, 2.1, 5.5, and 10.9 equivalents of  $\text{Os(bpy)}_3^{2^+}$  to Ru monomer **3**.

From Figure 4.9 it is clear that the addition of  $Os(bpy)_3^{2+}$  monomer 4 to the ruthenium complex results in a quenching of the  $Ru(bpy)_3^{2+}$  emission. At much higher  $Os(bpy)_3^{2+}$  concentrations than used here, it is even possible to detect the  $Os(bpy)_3^{2+}$  emission at around 720 nm.<sup>14</sup>

We also measured the lifetime of the ruthenium complex as the amount of osmium was increased (Figure 4.10). The lifetime in each case was mono-exponential, and the lifetime of the ruthenium complex decreased somewhat (from 1240 ns to 961 ns) during these additions of  $Os(bpy)_3^{2+}$ .



**Figure 4.10**. Lifetime decay of ruthenium monomer **3**, monitored at 630 nm. The first three curves closely overlap and represent 0, 0.7 and 2.1 equivalents of  $Os(bpy)_3^{2^+}$  to  $Ru(bpy)_3^{2^+}$ . The lower two curves are 5.5 equivalents (grey) and 10.9 equivalents (black). The inset shows the log(I) vs time plots and the linear fits to the decay.

Interestingly, as the amount of  $Os(bpy)_3^{2^+}$ -based complex 4 is increased, the initial intensity of the lifetime decay trace starts to decrease (Figure 4.10), suggesting that static quenching begins to occur. This would be unexpected for these two freely diffusing complexes at the concentrations used for this study ( $\mu$ M for Ru,  $\leq 40 \mu$ M for Os), particularly since they are both positively charged, and thus should electrostatically repel each other, and Ru(bpy)\_3<sup>2+</sup> is relatively photochemically stable, and so the intensity should not decrease as a result of photodecomposition.<sup>15</sup>

One possible explanation for the apparent static quenching that occurs with increased concentration of the osmium complex 4 may be related to the inner filter effect. Indeed, the absorbance of these samples, 3 alone and 3 in the presence of increased amounts of 4 were measured (Figure 4.11), and for the higher amounts of  $Os(bpy)_3^{2+}$  complex added, the absorbance at around 450 nm increased greatly. For other experiments in which many more equivalents of the osmium complex were added, the sample solution was much darker in colour than

for this example and the initial intensity of the lifetime decay trace was significantly reduced. For these samples, then, adding more than a few equivalents of  $Os(bpy)_3^{2+}$  to the monomer **3** is not useful because inner filter effects (due to the very dark-coloured Os(bpy) species) begin to affect the analysis.



Figure 4.11. Absorbance of ruthenium monomer 3 with and without added osmium complex 4. The solid black line with the lowest absorbance is 3 alone, and the increasing absorbances are for 0.7, 2.1, 5.5 and 10.9 equivalents of  $Os(bpy)_3^{2+}$  to  $Ru(bpy)_3^{2+}$ . The inset shows the magnified MLCT absorbance region.

We were able to observe a decrease in the lifetime of the ruthenium complex (1240 ns to 961 ns) and this is an indication that energy transfer did occur between the  $Ru(bpy)_3^{2+}$ -based monomer 3 and the osmium complex 4.

We hoped that by encapsulating the osmium complex inside the  $Ru(bpy)_3^{2^+}$ containing micelles that we would be able to see more efficient energy transfer. Similar to the coumarin sample, we again started our analysis using method 1 to encapsulate the osmium inside polymer 1 (C4<sub>10</sub>-Ru<sub>20</sub>-PEG<sub>5</sub>). In this technique, the osmium is dissolved in acetonitrile, and the osmium/acetonitrile solution is used to dissolve the ruthenium-based polymer. The sample is stirred for a few minutes before water is added to induce self-assembly and hopefully trap the osmium complex inside the micelles that form. The sample is then dialyzed to remove acetonitrile and unencapsulated osmium complexes. Figure 4.12 shows the significant quenching of the emission of the ruthenium complexes in polymer 1. For this example, 12 equivalents of osmium complex 4 to ruthenium moieties were added, and in reality, it is likely that slightly less than that was actually encapsulated. This is compared to 10.9 equivalents for the freely diffusing monomers described above. In this case, the Ru(bpy)<sub>3</sub><sup>2+</sup> emission is decreased more significantly than for the monomers, even though the equivalents of osmium are comparable. The increased quenching efficiency is likely due to the decreased separation between the ruthenium and osmium complexes inside the micelle core, similar to what we observed for the benzyl-coumarin/Ru(bpy)<sub>3</sub><sup>2+</sup> combination.



Figure 4.12. Luminescence of polymer 1 with (grey line) and without (dotted black line)  $Os(bpy)_3^{2+}$  added.

While it was possible to quench the emission of polymer 1 using method 1, we wanted to also test the quenching of polymer 2 ( $Ru_{20}$ -PEG<sub>5</sub>), which does not

possess the C<sub>4</sub> block. Figure 4.13 shows the luminescence spectrum (normalized to the absorbance at 459 nm) of polymer **2** with and without monomer **4** added. In this case, only about 8 equivalents of osmium were added, and significant quenching was achieved. It is also important to note that for these samples, the absorbance at 450 nm, due to both the  $Ru(bpy)_3^{2+}$  and  $Os(bpy)_3^{2+}$  complexes was less than 0.1, and therefore inner filter effects are not likely responsible for the observed quenching.



Figure 4.13. Luminescence of polymer 2 with (grey line) and without (dotted black line) osmium complex 4.

**Table 4.1.** Lifetime measurements of ruthenium complexes in polymer 2 using a biexponential model (monitored at 630 nm). The error in the proportions of the long- and short-lived components is estimated to be 10% for the empty micelles and approximately 40% for the micelles with encapsulated complex 4.

Sample	τ <sub>1</sub> (%)	τ <sub>2</sub> (%)
Micelles of polymer 2 only	799 ± 29 (48)	254 ± 32 (52)
Micelles of polymer 2 with 4 inside	708 ± 190 (35)	265 ± 92 (65)



The lifetime decay of polymer 2 was also examined (Table 4.1) in the presence and absence of osmium monomer 4. The decay of the polymer samples was fit much better by a biexponential model than a single exponential, as has been previously observed for ruthenium-containing polymers examined by our lab and others.<sup>16</sup> There appears to be no significant change in the lifetime or proportions of either the long-lived or short-lived components. One possible reason for this may be that somewhat less than the 8 equivalents of Os:Ru were actually encapsulated. In fact, when the sample solution was centrifuged after dialysis, a dark pellet was obtained. We did see quenching of the steady-state emission, and so therefore another feasible explanation is that when the osmium complex is encapsulated inside the micelles, static quenching occurs since the osmium and ruthenium complexes are in close proximity. This could account for the combination of decreased steady-state emission and the unchanged lifetime.

Method 3 was then used to try to increase the amount of monomer 4 encapsulated inside micelles of polymer 2. In this procedure, pre-assembled micelles are added to a film of complex 4, and the mixture is stirred for several days. The sample is then centrifuged briefly to remove undissolved material, and then washed in a Microcon filter with water to remove dissolved, unencapsulated osmium monomer. The osmium monomer  $4:\operatorname{Ru}(\operatorname{bpy})_3^{2+}$  ratio inside the micelle solution was estimated to be, at most, 4-5:1, based on analysis of the amount of material that was removed during the initial centrifugation and that remained part of the original film.



Figure 4.14. (a) Absorbance, (b) steady-state luminescence, and (c) lifetime decay of polymer 2 (monitored at 630 nm) in the absence (black dotted line) and presence (grey line) of osmium monomer 4.

Figure 4.14 shows the spectra obtained from polymer 2 with and without the  $Os(bpy)_3^{2+}$  complex incorporated. In this case, the ruthenium complex emission is reduced to almost 1/3 of the emission obtained when no osmium is present. Also, the lifetime decays do not indicate that static quenching is a predominant mechanism, and a decrease in the lifetime of the ruthenium moieties is observed (Table 4.2).

 Table 4.2. Lifetime measurements (biexponential model) of polymer 2 with and

 without osmium 4 encapsulated (using method 3).

Sample	τ <sub>1</sub> (%)	τ <sub>2</sub> (%)
Micelles of polymer 2 only	792 ± 29 (46)	289 ± 26 (54)
Micelles of polymer 2 with 4 inside	575 ± 20 (35)	265 ± 15 (65)

It seems that methods 1 and 3 are probably equally effective at encapsulating osmium complex 4 inside the micelles of polymer 2. This could be due to the similarity in solubility properties of the osmium monomer and  $Ru(bpy)_3^{2+}$  complex; they are both PF<sub>6</sub> salts and are readily soluble in acetonitrile but precipitate in aqueous media. For both methods, any Os(bpy)<sub>3</sub><sup>2+</sup> not encapsulated precipitated out of solution.

 $Ru(bpy)_3^{2+}$  to  $Os(bpy)_3^{2+}$  energy transfer is triplet-triplet energy transfer, and is formally forbidden by a dipole-dipole (Coulombic or Förster) mechanism. This is because Förster energy transfer is partially dependent on the molar extinction coefficient of the acceptor, which is generally very low for a ground state-to-triplet excited state transition.<sup>17</sup> The rate of energy transfer is also dependent on the rate of radiative decay of the donor, which for  $Ru(bpy)_3^{2+}$  is not exceedingly high (~10<sup>5</sup> s<sup>-1</sup>). However, in the  $Ru(bpy)_3^{2+}$ -to-Os(bpy)<sub>3</sub><sup>2+</sup> case, several factors exist to facilitate energy transfer. First, spin-orbit coupling with the heavy metal centers of the complexes imparts singlet character to the metal
complexes and helps to decrease the "forbidden-ness" of the transition, and thus helps to allow energy transfer to occur. In addition, the ruthenium bipyridyl complex has a long excited state lifetime, helping to increase the chance that a ruthenium complex will encounter a quencher while it is in the excited state. The Förster distance for  $Ru(bpy)_3^{2+}$  to  $Os(bpy)_3^{2+}$  energy transfer is reported to be ~26-35 Å.<sup>18</sup>

#### 4.3. Conclusions

In these experiments we demonstrated that the ruthenium complexes that comprised the cores of self-assembled block copolymers could participate in energy transfer reactions. Energy transfer reactions are key steps in the sensitization of chromophores in designs for artificial photosynthesis mimics, and can also be important for light-emitting devices and for sensor applications. We have previously demonstrated the ability of self-assembled ruthenium-based block copolymers to engage in electron transfer with molecules both inside and outside self-assembled micelles (Chapter 3). The ability of ruthenium polypyridyl complexes in self-assembled polymer systems to engage in energy transfer could only expand the potential usefulness of these systems.

To bring the energy donor and acceptor in close proximity to the  $Ru(bpy)_3^{2+}$  groups inside the micelle cores, we preferred to non-covalently encapsulate the small molecules rather than covalently append them to the polymer chain. We used a number of different methods to try to encapsulate small molecules (an energy donor and an acceptor) inside the micelles. For the Coumarin 2 species, however, none of the methods used were particularly successful, and we eventually derivatized Coumarin 2 to improve its solubility in acetonitrile and its compatibility with the ruthenium-containing micelle core. As a result of the improved partitioning of the modified coumarin inside the micelle cores, energy transfer from the excited benzyl-coumarin to the Ru(bpy)<sub>3</sub><sup>2+</sup> was detected. We were also able to observe significant quenching of the ruthenium emission upon

encapsulation of an osmium-based complex. Importantly, encapsulation increased the efficiency of the energy transfer, compared to freely diffusing metal complexes.

Our results indicate that the  $Ru(bpy)_3^{2+}$  complexes inside micelle cores can undergo energy transfer with other species, both energy donors and acceptors. This, coupled with their ability to participate in electron transfer reactions, could have implications for applications such as energy harvesting and sensors.

#### 4.4. Experimental Procedures

**Materials:** The coumarins were purchased from Sigma-Aldrich and Acros Chemicals. Solvents and reagents were purchases from Sigma-Aldrich. The  $Ru(bpy)_3^{2+}$  and  $Os(bpy)_3^{2+}$ -containing monomers and the polymers were synthesized by N.B. Sankaran following procedures described elsewhere.<sup>8a</sup>

**Instrumentation:** Absorbance measurements were done on a Cary 5000 UV-Vis-NIR Spectrophotometer. Steady-state fluorescence measurements were done on a PTI instrument equipped with a xenon lamp. Lifetime measurements were done using a PTI instrument (single photon counting) equipped with a nitrogen/dye laser system optimized at 481 nm. Lifetimes were determined using the system software.

Synthesis of benzyl-coumarin: (7-(benzyl-ethyl-amino)-4,6-dimethyl-2Hchromen-2-one). Kindly synthesized by Violeta Toader. Coumarin 2 (0.082 g, 0.377 mmol), potassium carbonate (270 mg, 1.95 mmol), and 18-crown-6 (21.6 mg, 0.082 mmol) were placed in a dry flask that was then evacuated and refilled with argon 3 times. Dry THF (6 ml), and then benzyl bromide (196 mg, 1.148 mmol) were added via a syringe. The reaction was stirred at reflux for 3 days. After the reaction cooled, ethyl acetate was added to the mixture. The aqueous layer was extracted with ethyl acetate and  $CH_2Cl_2$ . The combined organic layers (including the initial ethyl acetate layer) were washed once with water and once with brine, dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The



sample ( $R_f$ =0.85) was purified on a silica gel column with hexane:ethyl acetate 3:2. <sup>1</sup>H NMR  $\delta$  (CDCl<sub>3</sub>): 7.36(s, 1H), 7.30-7.26(m), 6.92(s, 1H), 6.13(s, 1H), 4.20(s, 2H), 3.06(q, 2H), 2.41(s, 3H), 2.38(s, 3H), 1.06(t, 3H). <sup>13</sup>C NMR  $\delta$ (CDCl<sub>3</sub>): 161.9, 154.0, 152.8, 152.6, 138.3, 129.6, 128.6, 128.3, 127.3, 126.7, 114.9, 112.7, 109.4, 56.8, 46.5, 18.9, 18.8, 12.1.

**Fluorescence measurements:** Experiments in acetonitrile (for Ru monomer 3) were done in degassed solutions in sealed cuvettes filled with argon, and energy transfer agents were added using argon-flushed syringes. Experiments in water (self-assembled polymers) were done in air-equilibrated deionized water. For the polymers, the Ru(bpy)<sub>3</sub><sup>2+</sup> concentrations could not be determined based on the initial starting sample (due to the dialysis and centrifugation steps), but samples were compared based on the absorbance of the MLCT band at 450 nm.

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# Chapter 5: Biotin-Terminated Ruthenium Bipyridine ROMP Copolymers: Synthesis and Self-Assembly with Streptavidin

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#### 5.1. Introduction

Ruthenium bipyridine-containing polymers have recently been the subject of increasing interest due to their numerous potential applications as photoconductive materials, photocatalysts, solar energy conversion materials, as well as sensors and supramolecular building blocks.<sup>1-10</sup> One interesting and underexplored application for this class of polymers is in the luminescence detection and labeling of biological molecules.<sup>11</sup> Ruthenium bipyridine complexes present a number of distinct advantages as chromophores for biological assays, including long excited state lifetimes, chemical inertness and photostability, tunability of their photophysical characteristics, relative insensitivity of these photophysical properties to environmental changes, and large Stokes shifts.<sup>12</sup> Their incorporation in a polymeric backbone or dendrimer can provide a facile method to amplify a luminescence signal triggered by the recognition of a biological molecule.<sup>13</sup> In order to achieve an even greater degree of luminescence amplification, we have been interested in the construction of diblock copolymers containing ruthenium(II) bipyridine chromophores. Self-assembly of these copolymers is expected to yield luminescent nanoscale micellar aggregates, containing a large number of Ru(II) chromophores. When labeled with molecular recognition units, these micelles can

act as a strong luminescence marker for specific biological molecules.

We have recently reported the synthesis of Ru(II) bipyridine-containing homopolymers and diblock copolymers using the ring-opening metathesis polymerization (ROMP).<sup>14</sup> In order to access block copolymers suitable for biomolecule detection, we needed to devise a method to end-functionalize these ROMP polymers with a molecular recognition unit. While the end-termination of ROMP polymers generated using the Schrock molybdenum-based catalyst is relatively straightforward.<sup>15</sup> fewer reports have described this process for the more functional-group tolerant ruthenium-based catalysts. The group of Grubbs has reported the creation of telechelic ROMP polymers with functional groups at both ends, by carrying out the ROMP reaction in the presence of disubstituted olefins.<sup>16</sup> Kiessling et al have also generated end-functionalized neoglycopolymers by quenching the active ROMP polymer chain with functionalized enol ethers.<sup>17</sup> In this Chapter we report a facile method to create ROMP diblock copolymers containing Ru(II) bipyridine units, and end-functionalized with a biotin molecule. Self-assembly of these copolymers yields luminescent micellar aggregates with biotin at their periphery. DLS and TEM studies reveal their ready association and crosslinking with the tetravalent protein streptavidin.

#### 5.2. Results and Discussion

#### 5.2.1. Synthesis of chain-transfer agent 4

To generate biologically compatible ROMP polymers, we chose to attach the molecule biotin, which has found widespread applications in bioassays,<sup>18</sup> to the end of our polymers. Biotin is known to bind to the proteins avidin or streptavidin with very high affinities ( $K_d \sim 10^{-15}$  M). In addition, (strept)avidin can bind up to four biotin units, thus allowing it to act as a linker between two (or more) biotinylated

molecules. We have recently shown that biotinylated ruthenium(II) bipyridine units can be used as effective luminescence markers for the protein avidin.<sup>19</sup> In order to create ROMP polymers that are end-functionalized with biotin, we used enol ether **4** (Scheme 5.1) to quench the active ROMP polymer chain. This molecule was accessed by a facile and relatively high-yield four step synthesis, starting from the commercially available 6-bromo-hexanol (Scheme 5.1). PCC oxidation of this compound yielded aldehyde **1** (80%),<sup>20</sup> which was subjected to a Wittig reaction with PPh<sub>3</sub>=CHOCH<sub>3</sub> to give enol ether **2** (56% crude product). Heating **2** with a large excess of piperazine and potassium carbonate in acetonitrile gave amino compound **3** (95%). Biotinylated molecule **4** was then obtained by coupling **3** with the N-hydroxysuccimide ester<sup>21</sup> of biotin (83%). All compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and HR-ESI-MS. The <sup>1</sup>H NMR

#### Scheme 5.1 Synthesis of biotinylated chain-transfer agent 4



a) PCC,  $CH_2Cl_2$ , r.t., 1 h, 80%; b) PPh<sub>3</sub>CH<sub>2</sub>OCH<sub>3</sub>Cl, KOt-Bu, THF, r.t. 56% (2 steps); c) Piperazine,  $K_2CO_3$ ,  $CH_3CN$ , reflux, 12 h, 95%; d) Et<sub>3</sub>N,  $CHCl_3$ /iso-propanol, r.t, 1 h, 83%.

#### 5.2.2. End-termination of ROMP polymers with biotin

In order to assess the ROMP quenching efficiency with chain-transfer agent 4, we

first carried out the polymerization reaction of N-butyl oxanorbornene imide 5 with the first generation Grubbs catalyst (PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>Ru=CHPh 6 (monomer: initiator 20:1). After monomer conversion (<sup>1</sup>H NMR), a solution of chain transfer agent 4 in acetone (30 equiv) was added to half of the reaction mixture at room temperature. <sup>1</sup>H NMR showed the complete disappearance of the alkylidene signal corresponding to the propagating polymer chain at 18.85 ppm after 3 hours, and the appearance of a new signal at 14.46 ppm, which we have assigned as the carbene proton of the Fisher-type complex  $9^{22}$  (Scheme 5.2). Biotinylated polymer 10 was then isolated and purified from the excess chain transfer agent 4 by repeated precipitation from ether. The second half of this reaction was quenched with excess ethyl vinyl ether, and polymer 8 was purified by repeated precipitation from hexane (Scheme 5.2). Comparison of the  ${}^{1}$ H NMR spectra of polymers 8 and 10 revealed that the end-termination of 10 with biotin was successful (Figure 5.1). The  ${}^{1}$ H NMR spectra clearly show the feature signals of the biotin moiety at 2.7 (d) and 2.9 ppm (dd) (SC $H_2$ ). Integration of the phenyl peaks of 10 at 7.2-7.5 ppm versus the characteristic biotin peaks at 2.9 ppm and 2.7 ppm, showed a ratio of 5:1:1. This corresponds to termination efficiency above 95% for this ROMP reaction.

Scheme 5.2. Synthesis of homopolymers 8 and 10



a)  $d_6$ -Acetone, r.t. 20 min; b) ethyl vinyl ether, 20 min; c) 4,  $d_6$ -Acetone, 3 h.



Figure 5.1. <sup>1</sup>H NMR spectra of homopolymers 8 and 10 in CD<sub>2</sub>Cl<sub>2</sub>.

We have previously reported the synthesis of diblock copolymer 14 (Scheme 5.3), containing a hydrophobic block, as well as a block of Ru(II) bipyridine units.<sup>14</sup> With an efficient method to end-functionalize ROMP polymers in hand, we proceeded to attach a terminal biotin moiety to the Ru(II)-containing diblock copolymers. Thus, monomer 5, with an n-butyl chain (C4 monomer), was reacted with catalyst 6 (pre-dissolved in a minimum amount of  $CD_2Cl_2$ ) in d<sub>6</sub>-acetone at room temperature. After complete consumption of 5 (monitored by <sup>1</sup>H NMR), an average degree of polymerization of ~10 for poly (5) was deduced (<sup>1</sup>H NMR integration of the methyl group in the repeat unit of 5 (0.95 ppm) to the terminal phenyl group (7.2-7.5 ppm)). Ru(II) bipyridine monomer 11 was then added to the reaction mixture. <sup>1</sup>H NMR showed complete conversion of the monomer after 2h at room temperature, and the ratio of poly(5) to poly(11) in block copolymer 12 was calculated as ~1:1 (<sup>1</sup>H NMR integration of the peak at 0.95 ppm for the methyl

group of poly(5) vs. the peak at 8.06 ppm for to the hydrogens ortho to the bipyridine nitrogens of poly(11)). The reaction mixture was divided into two portions. To the first portion was added biotin quenching agent 4 (30 equiv), and the mixture was stirred for 3h at room temperature. Again, complete disappearance of the alkylidene proton of the active ROMP chain at 18.85 ppm, as well as appearance of a new carbene signal at 14.47 ppm, corresponding to the Fischer-type complex 9 were observed by  $^{1}$ H NMR. The resulting copolymer 13 was purified by repeated precipitations from ether. The second portion was quenched by ethyl vinyl ether, and a similar alkylidene proton shift from 18.85 ppm to 14.46 ppm was also observed. This polymer, copolymer 14, was purified by repeated precipitations from ether. Comparison of the <sup>1</sup>H NMR spectra of copolymers 13 and 14 again showed successful end-functionalization with biotin. The <sup>1</sup>H NMR integration ratio for the biotin peaks (2.9 and 2.7 ppm, biotin SCH<sub>2</sub>) to the poly(5) block (0.95 ppm,  $-CH_3$ ) was found to be ~2:30, again indicating an excellent end-functionalization efficiency (~95%) for the chain-transfer agent 4. Thus, the above one-pot synthesis resulted in the efficient formation of a ROMP diblock copolymer, containing luminescent and redox-active Ru(II) bipyridine units, and end-terminated with the protein binding molecule biotin. Using the same method, we also synthesized longer diblock copolymers 15 and 16, with a ratio of poly(5):poly(11) (C4:Ru) of 45:45, and we carried out the end-functionalization of copolymer 15 with biotin as above (Scheme 5.3).





a)  $d_6$ -acetone/CD<sub>2</sub>Cl<sub>2</sub>, 20 min, r.t.; b) monomer 11,  $d_6$ -acetone, 2 h, r.t.; c) compound 4 (30 equiv.),  $d_6$ -acetone, r.t., 3 h; d) ethyl vinyl ether, r.t. 20 min.

#### 5.2.3. Micelle formation

The self-assembly of diblock copolymer **15** was examined in an acetonitrile/water solvent mixture. In this copolymer, the hydrophobic block poly(**5**) is soluble in acetonitrile, and completely insoluble in water, while the Ru(II)-containing block poly(**11**) is soluble in acetonitrile and somewhat soluble in water. Thus, the self-assembly of copolymer **15** in acetonitrile/water is expected to be driven by the incompatibility of poly(**5**) with water, and yield micellar aggregates with poly(**5**) in

the core, and poly(11) as the corona. Because it is attached to the end of the poly(11) block, the biotin functionality in these polymers would then reside at the periphery of these micelles (Scheme 5.4). Copolymer 15 was first dissolved in acetonitrile, and water was added dropwise under vigorous stirring, until the solution became turbid, indicating the onset of aggregation. In order to ensure the stability of the obtained morphology, a large excess of water was then added, and the solution was dialyzed against water to remove acetonitrile. With excess water, the decreased solubility of the poly(5) block is expected to result in decreased chain mobility, and structural rearrangement of the morphology is expected to be slow (the micelles are "frozen").

The morphology of the copolymer micelles was examined by transmission electron microscopy (TEM). A drop of dilute micellar solution was deposited on a carbon-coated TEM grid, and water was evaporated overnight at room temperature. Figures 5.2a, c, and d show representative transmission electron micrographs of the micellar aggregates of biotin-labeled copolymer **15** in pure water. Due to the presence of a large number of ruthenium centers in their corona, the copolymer affords sufficient electronic contrast for direct observation of the micelles without any further staining. Small spherical star micelles, with an average diameter of 41 nm (standard deviation of 11 nm) constitute the majority of these aggregates. Similar TEM results were obtained from the self-assembly of copolymer **16**, which contains the same composition of poly(**5**) and poly(**11**), but does not possess a biotin end-group (Fig. 5.2g and h).





**Figure 5.2.** Left column images (a, c, e): TEM of micelle solutions of copolymer **15** in water before addition of streptavidin (different magnification). Right column images (b, d, f): TEM of micellar solutions of **15** in water after addition of streptavidin; g and h: TEM of micelle solutions of copolymer **16** in aqueous solution before addition of streptavidin; i and j: TEM of micellar copolymer **16** in aqueous solution after addition of streptavidin.

The aqueous micellar solution of 15 was also studied by DLS (Figures 5.3a and b), and showed a monomodal distribution of aggregates. A population with hydrodynamic  $D_h$  of 42 nm and narrow size distribution was attributed to star-like micelles from copolymer 15, consistent with the TEM results. The hydrodynamic

sizes and relative proportions of these micellar aggregates remained constant over extended periods of time, in agreement with slow rearrangement dynamics of these aggregates in water. Previous work has shown that DLS histograms where the scattering intensity is plotted as a function of size tend to overestimate the number of larger aggregates (which scatter more light than smaller aggregates, and thus dominate the DLS signal).<sup>23</sup> When number percentages instead of scattering intensity were plotted as a function of size, the proportion of the larger size aggregate was found to be low, consistent with the TEM results. Similar DLS results were obtained for micellar solutions of copolymer **16** (Figures 5.3c and d).



Figure 5.3. Intensity percentage (a) and number percentage (b) of micellar solutions of biotin-labeled copolymer 15. Intensity percentage (c) and number percentage (d) of micellar solutions of copolymer 16.

Emission spectra for copolymer 15 in water (where micelle formation is expected) and acetonitrile (where 15 is not aggregated) were obtained upon excitation at 455 nm (298 K), and the emission spectra are shown in Figure 5.4. All samples were purged with argon for 30 min prior to use. The emission peak of copolymer 15 in acetonitrile is centered at 627 nm and shifts to 641 nm in pure water, likely due to the stabilization of the MLCT state in polar solvents. The luminescence intensity is partially retained upon micelle formation in water, compared to acetonitrile. The observed reduction in intensity is consistent with the decrease in quantum yield of Ru(bpy)<sub>3</sub><sup>2+</sup> with increasing solvent polarity.<sup>24</sup>



Figure 5.4. Emission spectra of copolymer 15 in acetonitrile and water.

#### 5.2.4. Self-assembly of copolymer 15 micelles with Streptavidin

With the preparation and characterization of biotinylated Ru(II) micelles, we examined their association with streptavidin. This protein possesses four biotin binding sites, thus it is expected to crosslink, and initiate the aggregation of these biotin-labeled micelles (Scheme 5.4).

Scheme 5.4. Cross-linking of biotin-labelled micelles with streptavidin.



A solution of the micellar aggregates of copolymer 15 (1.5 mL, 0.25 mg/mL) was incubated with 260  $\mu$ L streptavidin (1.0  $\mu$ M in phosphate buffer) for 3 h. The ratio of biotin to streptavidin was estimated to be  $\sim 20:1$ . Thus, we also carried out transmission electron microscopy studies on the micellar solution of copolymer 15 with streptavidin (Figures 5.2b, d and f). These show the predominance of larger, irregular aggregates, with a size range from 100 to 1000 nm, consistent with crosslinking of the star micelles of copolymer 15. This is consistent with streptavidin-induced aggregation of the individual micelles into larger particles. A small proportion of individual, non-aggregated micelles were also observed in these TEM samples. In a control experiment, streptavidin was added to micellar solutions of the non-biotinylated copolymer 16. In contrast to copolymer 15, TEM images (Figures 5.2i and j) showed no aggregation of the individual micelles upon streptavidin addition. Thus, the observed aggregation of the micelles from 15 is most likely the result of binding of streptavidin to the biotin at the periphery of these micelles, and crosslinking of these micelles by the protein (Scheme 5.4). This demonstrates the accessibility of these biotin units, and suggests the usefulness of these micelles as strong luminescence markers for biomolecules. In addition, there has been increasing interest in creating nanostructures (e.g., metal and

semiconductor nanoparticles) which can undergo further self-assembly into networks, in order to build functional devices incorporating these structures.<sup>25,26</sup> Our streptavidin-induced crosslinking approach represents a new method to potentially mediate the association of *polymeric micellar aggregates* into higher-order networks.

#### 5.3. Conclusions

We have shown the ready synthesis of ruthenium(II) bipyridine containing block copolymers, which are end-functionalized with the molecular recognition unit biotin. Self-assembly of these copolymers in acetonitrile/water yields luminescent star micelles with a hydrophobic core, a Ru(II)-containing corona, and biotin units at their periphery. Addition of streptavidin to these micelles induces their crosslinking into larger aggregates, through biotin-streptavidin binding. In addition to its usefulness as a method to organize polymeric nanostructures into networks, the end-conjugation of these ROMP polymers with biotin has created micellar aggregates containing a large number of luminescent Ru(II) centers, and surface accessible biotin units. We are currently exploring the potential of these micelles for the luminescence detection and signal amplification of biomolecules.

#### **5.4. Experimental Procedures**

**General Considerations.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian M300 spectrometer operated at 300.140 MHz. Chemical shifts are reported in ppm relative to the deuterated solvent resonance. Fluorescence experiments were carried out on a PTI (Photon Technology International) TimeMaster Model C-720F spectrofluorimeter. Compound 1 was synthesized according to the literature method.<sup>20</sup>

**Micelle Formation and Transmission Electron Microscopy.** Double distilled water was added dropwise into the block copolymer **15** or **16** solution in CH<sub>3</sub>CN (initial concentration is 5 mg/mL) with stirring to reach a final volume of 5 ml. The micelle solution was dialyzed against pure water several times over 36 h to remove CH<sub>3</sub>CN, and the final concentration was adjusted to 0.25 mg/mL. Samples were prepared by placing a drop of this solution onto transmission electron microscopy (TEM) copper grids (400 mesh, carbon-coated, purchased from Electron Microscopy Sciences), the excess of solution was blotted with a filter paper to form a thin aqueous film on the grids. The grids were air-dried for 12 h. The aggregates were then examined using a JEOL 2000FX electron microscope operated at 80 kV.

**Dynamic Light Scattering.** DLS measurements were performed with a Brookhaven Instruments Corporation system, equipped with a BI-200SM goniometer, a BI-900 AT digital correlator and a Compass 315-150 CW laser light source from Coherent Inc. operating at 532 nm (150 mW). DLS data reported are the average of 3 times measurements at 90°. The distribution histogram of  $D_h$  was calculated by the CONTIN routine.

Synthesis of 2 and 3 Potassium tert-butoxide (1 M in THF, 3.35 mL 3.35 mmol) was added to a suspension of (methoxymethyl)triphenylphosphonium chloride (1.15 g, 3.35 mmol) in dry THF at 0°C. The dark red solution was stirred at 0°C under N<sub>2</sub> for 5 min. Then the solution was transferred to a flask containing 0.6 g (3.35 mmol) 6-bromo-1-hexanal 1 in 10 ml THF. The orange color disappeared rapidly, and a grey precipitate formed. The reaction was quenched with saturated aqueous NaCl (20 mL) and extracted with  $CH_2Cl_2$  (3×15 mL). The combined organic solution was washed with water and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent, the crude product was obtained (56%) and used for next step without further purification. 0.86 g (10 mmol) piperazine and 0.4 g compound 2 were then dissolved in 10 mL dry CH<sub>3</sub>CN, and K<sub>2</sub>CO<sub>3</sub> (0.4 g) was added. After

refluxing overnight and cooling to room temperature, the mixture was filtered, and the solvent and excess piperazine were removed in vacuo. The pure product **3** was obtained by chromatography on alumina with CH<sub>2</sub>Cl<sub>2</sub>/methanol (100.5) <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  ppm: 1.32 (4H, m), 1.49 (2H, m), 1.93 (2H, q, J=6.9Hz), 2.30 (2H, t, J=7.8Hz), 2.42 (bs, 4H), 2.91 (4H, t, J=5.0Hz), 3.52 (2H, s, trans-OCH<sub>3</sub>), 3.57 (1H, s, cis-OCH<sub>3</sub>), 4.32 (0.33H, d×t, J=7.1×7.0Hz, cis-OCH=CH), 4.71 (0.66H, d×t, J=12.3×7.5Hz, trans-OCH=CH), 5.85 (0.33H, d×t, J=6.2×1.5Hz, cis-OCH=CH), 6.26 (0.66, d, J=11.1Hz, trans-OCH=CH); <sup>13</sup>CNMR (CDCl<sub>3</sub>),  $\delta$ ppm: 24.14, 26.83, 27.31, 27.58, 27.96, 30.08, 31.05, 46.26, 54.70, 56.21, 59.66, 103.23, 107.08, 146.21, 147.16

Synthesis of compound 4. Compound 3 (200 mg, 0.94 mmol) and biotinyl-N-hydroxylsuccinimide (350 mg, 1.0 mmol) were dissolved in CHCl<sub>3</sub>/ 2-propanol (2:1) 20 mL and triethylamine (200 µl) was added. Slight warming and ultrasonication dissolved this mixture into a clear solution. The mixture was stirred for 1 h at room temperature to complete the reaction. The solvents were removed under reduced pressure. Pure product (83%) was obtained by chromatography on alumina eluted with CH<sub>2</sub>Cl<sub>2</sub>/Methanol (98:2). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ ppm: 1.33 (4H, m), 1.49 (4H, m), 1.68 (4H, m), 1.93 (2H, m), 2.09 (1.2H, trans-OCH=CHCH<sub>2</sub>), 2.38 (8H,  $-CH_2N(CH_2-)_2$ ), 2.73 (1H, bd, J=10.8Hz, SCH<sub>2</sub>), 2.91 (1H, dd, J=12.9×4.8Hz, SCH<sub>2</sub>), 3.16 (1H, m, CHS), 3.20-3.60 (7H, m, cis- and trans-OCH<sub>3</sub>, -CON(CH<sub>2</sub>)<sub>2</sub>, 4.31 (1.33H, m, NCH and cis-OCH=CH), 4.5 (1H, m, NCH), 4.71 (0.66H, d×t, J=12.3×7.5Hz, trans-OCH=CH), 5.2 (1H, NH), 5.8 (1H, NH), 5.85  $(0.33H, d \times t, J=6.2 \times 1.5Hz, cis-OCH=CH)$ , 6.26 (0.66, d, J=11.1 Hz)trans-OCH=CH); <sup>13</sup>CNMR (CDCl<sub>3</sub>), δ ppm: 24.12, 25.44, 27.02, 27.20, 27.47, 27.96, 28.64, 28.69, 30.04, 31.01, 33.00, 40.91, 41.89, 45.97, 53.23, 53.84, 55.65, 56.23, 58.89, 60.44, 62.11, 103.17, 106.99, 146.27, 147.21, 163.53, 171.42

Synthesis of homopolymer 8 and 10. Monomer 5 (22.1 mg, 0.1 mmol) and

catalyst 7 (4.1 mg, 0.005 mmol) were dissolved in  $CD_2Cl_2$ , and transferred to an NMR tube under argon. The polymerization was monitored by <sup>1</sup>H NMR, and monomer consumption was observed after 20 min. The reaction mixture then was divided into two portions. One of these was quenched with ethyl vinyl ether (large excess) within 20 min and precipitated (3x) from hexanes to obtain **8**. Chain-transfer agent **4** (30 equiv.) was added to the other portion of the reaction. After 3 h, the end-biotinylated homopolymer **10** was obtained by precipitation (6x) from ether.

Homopolymer 8: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  ppm: 0.95 (60H, CH<sub>3</sub>), 1.32 (40H, CH<sub>2</sub>), 1.57 (40H, CH<sub>2</sub>), 3.34-3.48 (80H, NCH<sub>2</sub> and OCCHCHCO), 4.47 (30H, trans-CHO), 4.95 (10H, cis-CHO), 5.82 (10H, cis-CH=CH), 6.09 (30H, trans-CH=CH), 7.2-7.5 (5H, phenyl-H); <sup>13</sup>CNMR (CDCl<sub>3</sub>),  $\delta$  ppm:13.77, 20.38, 30.01, 38.92, 77.80, 81.25, 131.21, 132.23, 175.71

Homopolymer 10: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  ppm: 0.95 (60H, CH<sub>3</sub>), 1.32 (40H, CH<sub>2</sub>), 1.57 (40H, CH<sub>2</sub>), 2.08 (1H, OCH=CHCH<sub>2</sub>), 2.73 (1H, bd, J=12.9Hz, SCH<sub>2</sub>), 2.91 (1H, dd, J=12.9×4.8Hz, SCH<sub>2</sub>), 3.34-3.48 (84H), 4.47 (30H, trans-CHO), 4.95 (10H, cis-CHO), 5.82 (10H, cis-CH=CH), 6.09 (30H, trans-CH=CH), 7.2-7.5 (5H, phenyl-H); <sup>13</sup>CNMR (CD<sub>3</sub>Cl),  $\delta$  ppm:13.77, 20.38, 30.01, 38.94, 77.80, 81.30, 131.22, 132.23, 175.73

Synthesis of Copolymers 13, 14, 15, 16: Monomer 5 (2.0 mg, 0.009 mmol) was dissolved in 0.5 mL d<sub>6</sub>-acetone. The solution of monomer 5 was added to a catalyst 6 (0.0003 mmol) solution in 0.2 mL of  $CD_2Cl_2$ . The mixture was allowed to stir at room temperature. After the complete consumption of monomer 5 (monitored by <sup>1</sup>H NMR), monomer 11 (10.7 mg, 0.009 mmol) in 1 mL of d<sub>6</sub>-acetone was added to the remaining solution. After complete consumption of monomer 11 (monitored by <sup>1</sup>HNMR), the reaction mixture was divided into two portions. One of the portions was added to a d<sub>6</sub>-acetone solution of excess biotin-quencher 4 (30 eqv), and stirred

for 3 h. The copolymer 13 was obtained by precipitation from ether six times. The other half was quenched by addition of ethyl vinyl ether and precipitation from ether to obtain copolymer 14. Similar procedures were used to obtain 15 and 16. Copolymer 13: <sup>1</sup>H NMR (CD<sub>3</sub>CN), δ ppm: 0.94 (br, 3H), 1.31 (br, 2H), 1.54 (br, 2H), 2.53(br, 3H), 2.8-3.0(0.2H, biotin-SCH<sub>2</sub>), 3.1-3.2(0.4H), 3.2-3.6(br, 18H), 4.2-4.88(br, 4H), 5.5-6.1(br, 4H), 7.28(br, 1H), 7.40(br, 4H), 7.60(br, 1H), 7.66(br, 1H), 7.66(br, 1H), 7.66(br, 1H), 7.60(br, 1H), 7.66(br, 1H), 7.66(br, 1H), 7.60(br, 1H), 7.66(br, 1H), 7.66(br, 1H), 7.60(br, 1H), 7.66(br, 1H), 7.66(br, 1H), 7.66(br, 1H), 7.60(br, 1H), 7.60(br, 1H), 7.66(br, 1H), 7.60(br, 1H), 7.60(br, 1H), 7.60(br, 1H), 7.66(br, 1H), 7.60(br, 1H),

1H), 7.75(br, 4H), 7.86(br,1H), 8.06(br, 4H), 8.50(br, 4H), 8.60(br, 1H), 8.90(br, 1H).

Copolymer 14: <sup>1</sup>H NMR (CD<sub>3</sub>CN), δ ppm: 0.94 (br, 3H), 1.31 (br, 2H), 1.54 (br, 2H), 2.53(br, 3H), 3.2-3.6(br, 18H), 4.2-4.88(br, 4H), 5.5-6.1(br, 4H), 7.28(br, 1H), 7.40(br, 4H), 7.60(br, 1H), 7.66(br, 1H), 7.75(br, 4H), 7.86(br, 1H), 8.06(br, 4H), 8.50(br, 4H), 8.60(br, 1H), 8.90(br, 1H).

Copolymer **15**: <sup>1</sup>H NMR (CD<sub>3</sub>CN), δ ppm: 0.92 (br, 3H), 1.33 (br, 2H), 1.54 (br, 2H), 2.53(br, 3H), 3.2-3.6(br, 18H), 4.2-4.5(br, 2.6H), 4.88(br, 1.4H), 5.5-6.1(br, 4H), 7.28(br, 1H), 7.40(br, 4H), 7.60(br, 1H), 7.66(br, 1H), 7.75(br, 4H), 7.86(br, 1H), 8.06(br, 4H), 8.50(br, 5H), 8.90(br, 1H).

Copolymer **16:** <sup>1</sup>H NMR (CD<sub>3</sub>CN), δ ppm: 0.92 (br, 3H), 1.33 (br, 2H), 1.54 (br, 2H), 2.53(br, 3H), 3.2-3.6(br, 18H), 4.2-4.5(br, 2.6H), 4.88(br, 1.4H), 5.5-6.1(br, 4H), 7.28(br, 1H), 7.40(br, 4H), 7.60(br, 1H), 7.66(br, 1H), 7.75(br, 4H), 7.86(br,1H), 8.06(br, 4H), 8.50(br, 5H), 8.90(br, 1H).

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### Chapter 6: Conclusions, Contributions to Original Knowledge, and Suggestions for Future Work

### Chapter 6: Conclusions, Contributions to Original Knowledge, and Suggestions for Future Work

#### 6.1. Conclusions and contributions to original knowledge

This thesis has explored the self-assembly and luminescence properties of novel block copolymers that contain the metal complex ruthenium tris(bipyridine). While there are examples of polymers that contain this metal complex, thorough studies involving *block copolymers* containing Ru(bpv)<sub>3</sub><sup>2+</sup> had not been previously conducted. The interesting photophysical properties of the metal complex combined with the ability of block copolymers to self-assemble under controlled conditions has allowed for the creation of a new class of materials. Some advantages that self-assembled block copolymers have over more conventional  $Ru(bpy)_3^{2+}$  polymer architectures are i) the ability to concentrate the functional metal complex into nanoscale domains; ii) the potential to form a physical barrier on the nanoscale between reactive agents such as electron donors and acceptors; and iii) the feasibility of forming larger-scale organization of species by positioning along the core and corona regimes. Because of these features, specific to self-assembled polymer systems,  $Ru(bpy)_3^{2+}$ -based block copolymers have interesting potential in applications such as sensing and artificial photosynthesis, where long-lived charge separation and the organization of multiple components are advantageous. The incorporation of molecular recognition functionality into these systems can increase their potential to interact with other molecules, which could be useful for both higher-order organization or for detection schemes.

In this thesis, the solution self-assembly of these block copolymers was first examined. Then, two of these self-assembled structures were carried through for further analysis of the effects of self-assembly on the luminescence properties on the metal complex. The ability of the  $Ru(bpy)_3^{2+}$  within these polymers and self-

assembled structures to participate in electron and energy transfer reactions was also examined. Such  $Ru(bpy)_3^{2+}$ -based polymers were also incorporated into a design combining self-assembly, luminescence, and molecular recognition.

These polymers were synthesized using ring-opening metathesis polymerization, and the living nature of this method allowed for the generation of a series of well-defined block copolymers. The self-assembly of these block copolymers could therefore be examined as a function of block length, block ratio, and polymer length, as well as polymer concentration and solvent conditions. As toluene was added to acetonitrile solutions of these polymers, the metal-containing block formed the core domain of the self-assembled structures. Using transmission electron microscopy, a number of morphologies were reproducibly observed. These include star micelles, large compound micelles, tubules and vesicles, in which the  $Ru(bpy)_3^{2+}$  complex forms the micelle core and vesicle wall. Attempts were also made to induce the self-assembly of these polymers such that the metal-containing block formed the soluble corona blocks. These studies demonstrated the range of morphologies accessible for our  $Ru(bpy)_3^{2+}$ -based block copolymers, and by studying the forces contributing to the self-assembly, we learned to predict and control the self-assembled morphologies obtained.

The photophysical properties of the polymer-bound  $Ru(bpy)_3^{2+}$  complex were then examined. Two polymers, one that formed micelles and one that formed vesicles, were compared to the metal-containing monomer in both acetonitrile (unassembled polymer chains) and in 70% toluene/acetonitrile (micelles and vesicles). Comparison of the monomer and the polymers in acetonitrile indicated that incorporation of the metal complex into a block copolymer chain did not negatively affect its quantum yield. Analysis of the lifetime decay of these samples in acetonitrile showed that while the monomer decay was monoexponential, the decay of the polymers became better fit by a biexponential model, and is likely more realistically described as non-exponential. This was attributed to effects such as energy migration within the polymer chains,

with possible contributions from triplet-triplet annihilation and multiphoton effects. When toluene was added to these samples, comparison of the monomer and polymers indicated the effects of self-assembly on the luminescence properties of the  $Ru(bpy)_3^{2+}$ . While the quantum yield of the monomer increased due to the presence of non-polar toluene, the quantum yield of the  $Ru(bpy)_3^{2+}$ within the polymers was not significantly increased. This was attributed to the fact that self-assembly results in a shielding of the insoluble metal-based block. In this solvent mixture, the  $Ru(bpy)_3^{2+}$  within the micelles largely retained the photophysical properties of the polymer prior to self-assembly, while the formation of vesicles seems to have had a more noticeable effect on the metal complex emission. The increase in the amount of the short-lived component was attributed to possible structural differences between the micelles and vesicles. Based on these luminescence studies, we concluded that neither incorporation into block copolymers, nor self-assembly of these block copolymers into micelles or vesicles, caused a significant reduction in the luminescence of the  $Ru(bpv)_3^{2+}$ complex.

The ability of the metal complex inside the core domains of self-assembled structures to engage in electron transfer reactions was then explored. An electron donor or an electron acceptor was added to the block copolymers and the monomer in two sets of experiments. In one set, the quencher was added to the open polymer chains in acetonitrile, where comparison with the monomer again allowed the determination of the effects of polymerization on the accessibility of the complex to small molecules. For the electron acceptor, the quenching rate increased somewhat compared to the monomeric Ru(bpy)<sub>3</sub><sup>2+</sup>, likely due to energy migration along the polymer chains. In the second set of experiments, the quencher was added to pre-assembled structures in 70% toluene. Comparison with the monomer in the same solvent allowed for correction for the presence of non-polar toluene on the electron transfer reaction, while comparison with the unassembled polymer chains in acetonitrile allowed determination of the effects of self-assembly on the accessibility and reactivity of the metal complex from inside the aggregates. It was found that while the quenching rates did decrease

for the self-assembled structures, it was difficult to determine how much this decrease could be attributed to self-assembly and how much to the presence of non-polar solvent. Most importantly, the quenching rates were high, indicating that even from within the self-assembled structures, the metal complexes were still accessible and capable of participating in electron transfer reactions. This is likely facilitated by energy migration among the ruthenium units in polymers. Some experiments were also conducted in which the same electron transfer quenchers were encapsulated inside the micelles of different polymers, and it was determined that electron transfer quenching could occur with molecules on the insides of these structures, as well as the exteriors.

The ability of  $Ru(bpy)_3^{2^+}$ -based polymers to engage in energy transfer reactions was then examined. Different polymers from those previously studied were used; these could self-assemble when water was added to acetonitrile solutions. Attempts were made, using different methods, to encapsulate an energy acceptor,  $Os(bpy)_3^{2^+}$ , and an energy donor, coumarin 2.  $Os(bpy)_3^{2^+}$  could be encapsulated inside the micelles, but no methods were successful in encapsulating coumarin 2. Eventually, coumarin 2 was derivatized to decrease its water solubility and to increase its compatibility with the  $Ru(bpy)_3^{2^+}$ -based micelle cores. Absorbance and fluorescence (steady-state and lifetime) techniques were used to determine that energy transfer could indeed occur with the encapsulated small molecules. This means that energy transfer may be incorporated into systems involving self-assembled ruthenium-containing block copolymers, as either antenna components of light harvesting designs or as components in sensor arrays.

Towards the development of micellar systems for biodetection assays,  $Ru(bpy)_3^{2+}$ -containing polymers were synthesized that were terminated with the molecular recognition functionality biotin. These polymers could self-assemble in acetonitrile/water solutions into micelles that possessed the biotin moieties on their periphery. The addition of the protein streptavidin to these micelle solutions resulted in the aggregation of the micelles, attributed to the cross-linking of

several biotin groups from different micelles by the protein. The ability to incorporate molecular recognition moieties into self-assembled polymer systems could likely be useful in the development of detection systems. In addition, the ability to create higher-order arrangements of aggregates could potentially be useful for catalysis and light-harvesting applications.

#### **6.2.** Suggestions for future work

Future work regarding the self-assembly of these block copolymers could involve a number of different studies. For one, different solvents, instead of acetonitrile/toluene mixtures, may be found to yield predictable solution morphologies. This could allow the formation of different morphologies, or increase the range of conditions under which certain aggregates could be obtained. It could also allow for the eventual use of different electron transfer quenchers, or may improve the quenching rates we achieved here. For example, in our case, the presence of non-polar toluene contributed to a decrease in the quenching rate for the self-assembled systems, making it difficult to know with certainty how much self-assembly affected the rate. If a solvent system can be found that is less detrimental to electron transfer efficiency, a more accurate assessment of the effects of self-assembly might be obtained.

Other possible work involving the self-assembly of these polymers may be to explore their film-forming ability, or their self-assembly in the bulk phase. If reproducible films or bulk self-assembled morphologies can be obtained, this may increase the potential applications of these types of polymers, particularly in terms of incorporation into devices.

When we examined the ability of self-assembled polymers to participate in electron transfer quenching, we used star micelles and vesicles not only because they have well-defined core regimes, but also because they are capable of encapsulating small molecules. It should therefore be possible to have an electron donor on the inside of the vesicles or within the cores of the micelles and an
electron acceptor on the outside of the structure (or vice versa). This might decrease the rate of charge recombination that occurs in many other systems and allow for the creation of a long-lived charge separated state between a positively-charged donor and a negatively-charged acceptor, facilitated by the Ru(bpy)<sub>3</sub><sup>2+</sup> complex. For our polymers in acetonitrile/toluene mixtures, electron transfer could occur with small molecules outside the aggregates. Electron transfer from the inside was demonstrated using a different polymer system. The logical extension would be to develop a system in which one quencher could be encapsulated on the inside and a second quencher is added to the outside. Fast spectroscopic techniques might be required to detect the charged donor and acceptor species after irradiation of the Ru(bpy)<sub>3</sub><sup>2+</sup>, depending on how long-lived the charge-separated state was.

To determine if the  $Ru(bpy)_3^{2+}$  within our self-assembled polymers could participate in energy transfer reactions, we used small molecules: energy donors (coumarin molecules) and an acceptor  $(Os(bpy)_3^{2+})$ . A slight complication with our system was an apparent limit to the amount of benzyl-coumarin that could be encapsulated, due to its solubility properties in water. The use of a different solvent system, one that could also induce self-assembly and micelle formation while delaying somewhat the precipitation of benzyl-coumarin from the mixture, may allow more coumarin to be encapsulated. In addition, while the benzylcoumarin and  $Os(bpy)_3^{2+}$  compounds sufficed to demonstrate that energy transfer could occur, other agents could also be used. Future work in this area could continue to explore other energy transfer agents, particularly energy donors, to increase the sensitization of the Ru(bpy)\_3<sup>2+</sup> complex.

Even further extensions of this research could involve combining energy transfer and electron transfer within the same self-assembled system. A suitable energy donor that sensitizes the  $Ru(bpy)_3^{2+}$  may help to improve the efficiency of electron transfer reactions. Other extensions could involve the use of the living ROMP polymerization reaction to covalently attach electron or energy donors to the polymer backbone. Much of the work presented in this thesis demonstrated

that  $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$  could participate with electron and energy transfer agents that were non-covalently associated with the self-assembled structure, which may be advantageous for certain applications. The covalent attachment of these agents to the polymer backbone would very likely enhance electron- and energy transfer interactions, and may allow the spatial arrangement of species on a large scale (chromophores arranged within the core and corona domains of a 50 nm micelle vs a single star polymer or dendrimer).

In our studies involving  $Ru(bpy)_3^{2^+}$ -containing block copolymers, we used primarily fluorescence spectroscopy to examine the photophysical properties of the metal complex. To further explore the properties of these interesting new materials, a logical extension would be to conduct thorough electrochemical, studies. This would yield more detailed information on the potential of these systems to function in applications involving electron transfer reactions.

When polymer chains were terminated with the biotin moiety, it was demonstrated that molecular recognition could cause the formation of higher order aggregates of self-assembled structures. An important potential application of these polymers is in the design of sensors for biological components. The use of other molecular recognition groups could enhance the range of possible applications for self-assembled  $Ru(bpy)_3^{2+}$ -based polymers. For example. improvements of the systems initiated in Appendix 1, involving  $Ru(bpy)_3^{2+}$ -based polymers that also possessed hydrogen bonding blocks, could yield selfassembled polymers with hydrogen bonding groups at their peripheries. Such systems could conceivably be developed for DNA-based assays, or for the sensing of particular small molecules. The use of added molecules (such as streptavidin in the case of biotin-functionalized micelles) to promote the large-scale organization of functional units like  $Ru(bpv)_3^{2+}$  micelles could also be useful for catalysis applications, or even for light-harvesting applications where particular ordering of various components is very important.

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### Appendix A: Block copolymers with Hydrogen Bonding-Based Molecular Recognition Capability

### Appendix A: Block copolymers with Hydrogen Bonding-Based Molecular Recognition Capability

#### A.1. Introduction

Hydrogen bonding of small molecules with polymer chains<sup>1</sup> and of intraand intermolecular hydrogen bonding interactions among polymer chains,<sup>2</sup> has been detailed in many reports from the last several years. Hydrogen bonding involving polymer chains has been examined not only for the formation of new types of polymer architectures and higher-order self-assembled morphologies, but also for creating polymer systems that are capable of molecular recognition.<sup>3</sup> The selectivity possible with hydrogen bonding interactions means that such systems may be useful for mimicking and studying biological processes, as well as in drug delivery, biocatalysis and bio-detection applications.<sup>4</sup>

In the Sleiman lab, initial studies on block copolymers that possess hydrogen-bonding based molecular recognition capability were conducted with the goal of developing systems that could mimic the selectivity of DNA molecules or that could respond to environmental stimuli. Early successes were based on the generation of di- and triblock copolymers that contained hydrogen bonding units and could self-assemble in solution.<sup>5</sup> We then wanted to design polymers that, in response to an added stimulus (such as an added guest), would undergo an observable change in morphology. As such, we synthesized polymers that possessed complementary hydrogen bonding units, with the idea that hydrogen bonding interactions within the self-assembled polymer aggregates could be disrupted by added guest molecules and a change in morphology could be observed.

This report details research conducted regarding self-assembly studies of hydrogen bonding-based block copolymers, and attempts to elucidate the actual solution morphologies formed. This work was extended to include some

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experiments involving hydrogen bonding-based interactions with small molecules, and eventually involved polymers that also contained  $\text{Ru(bpy)}_3^{2^+}$ . Subsequent to the research described in this chapter, new polymers were constructed containing slightly different hydrogen bonding groups, and it was demonstrated that the self-assembled structures formed could be altered by the addition of small molecules that interact by hydrogen bonding.<sup>6</sup>

#### A.2. Results and Discussion

Our goal was to create self-assembled systems that would undergo a change in morphology in response to an added stimulus. Specifically, we tried to design a system in which hydrogen bonding interactions within self-assembled structures would be disrupted by added molecules (guests). The polymers synthesized in these studies have a structure like that depicted in Scheme A.1. These polymers possess a block containing a maleimide-like ("NH") block and a diamidopyridinebased ("DAP") block, separated by a spacer group containing n-butyl chains (the "C4" block). Both the NH and DAP units are capable of hydrogen bonding, and are complementary to each other. In self-assembled aggregates held together by hydrogen bonding, then, the DAP-NH interactions among polymer chains could potentially be disrupted by added molecules that were complementary to either NH or DAP. Scheme A.1. Block copolymers with hydrogen bonding-based molecular recognition moieties



The method used most commonly to induce self-assembly in these polymers was to dissolve the polymers directly in CH<sub>2</sub>Cl<sub>2</sub>, sometimes requiring heat and/or sonication, so that the DAP and NH blocks could interact with each other. In this solvent, however, the NH block is insoluble and the C4 and DAP blocks are soluble, and an added complication in our system is the insolubility of the NH block in CH<sub>2</sub>Cl<sub>2</sub>. There are thus two forces that may drive the self-assembly of these polymers. The first is microphase separation, in which the insolubility of the NH block may result in the NH block forming the core domain of a selfassembled morphology and the CH<sub>2</sub>Cl<sub>2</sub>-soluble DAP and C4 blocks forming the The result of this type of aggregation is depicted in Part (a) of Scheme corona. A.2. The second potential driving force is hydrogen bonding between the complementary NH and DAP units, which may result in a crosslinking of the polymer chains (Scheme A.2. b). In a third possible morphology for these polymers, somewhat intermediary between the two extremes, aggregates could form in which the NH and DAP blocks hydrogen bond together within a core domain of a morphology and the soluble C4 linker blocks loop out into the solvent (Scheme A.2. c).

**Scheme A.2.** Possible morphologies of NH-C4-DAP aggregates. "DAP" represents the DAP-based block, "NH" is the NH-based block, and the wavy line represents the C4 block that separates them in a polymer chain.



Unstructured, "crosslinked" morphologies due to hydrogen bonding. Dashed lines represent hydrogen bonding between the blocks.



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When CH<sub>2</sub>Cl<sub>2</sub> samples of our NH-C4-DAP triblock copolymers were dropcast onto TEM grids, we frequently observed no morphologies at all, and when structures were observed, there was generally a range of morphologies that were not reproducible and varied greatly even within the same TEM grid. Morphologies observed include lamellae and spheres (Fig A.1). Based on the irreproducibility of the morphologies we observed, and considering the occasional difficulties in solubilizing the polymers, we suspected that the random crosslinked structures were predominant. Additional support for this hypothesis was found in the GPC analysis of these polymers. When the first monomer polymerized was the NH monomer, the NH homopolymer and the NH-C4 diblock both had fairly narrow PDI's (<1.2). When the DAP block was added, the PDI became very broad and in the GPC trace there was sometimes a large tail on the high molecular weight side that could be indicative of aggregation among the polymer chains (Fig A.2). We therefore set out to try to determine if selfassembly was in fact driven by hydrogen bonding rather than by solvent-induced microphase separation. We used four different methods: IR, <sup>1</sup>H NMR, dynamic light scattering (DLS), and pyrene fluorescence.



Figure A.1. TEM images of triblock copolymer  $NH_{14}$ -C4<sub>117</sub>-DAP<sub>15</sub> in CHCl<sub>3</sub>. The scale bars in the left and right images are 500 nm and 200 nm respectively.



**Figure A.2.** GPC traces of a (a) diblock copolymer without complementary blocks and (b) triblock copolymer with complementary NH and DAP blocks.

## A.2.1. Determination of polymer morphology (detection of hydrogen bonding) by IR spectroscopy

In the first approach to determine the morphologies of the self-assembled polymers, we used IR to look for signs of hydrogen bonding. Polymer and monomer samples were dissolved in either CHCl<sub>3</sub> (self-assembly) or DMSO (no

self-assembly) (sample concentrations were close to 10 mg/ml) and placed between KBr plates. The N-H stretching bands were not readily detectable for our samples; instead, we compared the peaks in the C=O region for the monomers and the polymers in both CHCl<sub>3</sub> and DMSO, hoping to see a shift to lower wavenumbers for the polymers as a result of interchain hydrogen bonding. The peaks from the C=O stretching region (1600-1750 cm<sup>-1</sup>) region are shown in Table A.1.

 Table A.1. IR peaks (C=O stretching) for monomers and polymers.

Sample	CHCl <sub>3</sub>	DMSO
NH monomer	1701 <sup>a</sup>	1767, 1716
DAP monomer	1773 <sup>b</sup> , 1702, 1698, 1587	1769, 1698, 1585
NH monomer +		
DAP monomer	1700, 1587	
(1:1, heated)		
DAP <sub>10</sub> homopolymer	1776 <sup><i>b</i></sup> , 1701, 1586	1774, 1701, 1585
NH10-C450-DAP10	1776 <sup>b</sup> , 1707	1774, 1701°
NH <sub>10</sub> -C4 <sub>20</sub> -DAP <sub>1</sub>	1776 <sup><i>b</i></sup> , 1705	1774, 1719, 1701

<sup>*a*</sup> The NH monomer was not very soluble in CHCl<sub>3</sub> and the resulting IR is noisy; <sup>*b*</sup> small peak;

<sup>c</sup> with a shoulder to the higher cm<sup>-1</sup> side

In DMSO, there is no self-assembly and the solvent hydrogen bonds with the NH and DAP blocks, so no significant differences between the monomer and the polymers is expected. In CHCl<sub>3</sub>, there should be no hydrogen bonding in the monomer samples, but it could occur in the polymers. There is essentially no difference between the individual monomers and the polymers when the spectra in CHCl<sub>3</sub> are compared. The polymers that contain both NH and DAP motifs do not show significant shifts in the C=O region as a result of interchain hydrogen bonding (that could not be present in the monomer samples). This could be an indication that the NH - and DAP blocks were not hydrogen bonding with each other, and that possibly microphase separation was the force behind self-assembly for this system. However, we also mixed the NH and DAP monomers in a 1:1 ratio and heated the samples in CHCl<sub>3</sub>. Shifts in the <sup>1</sup>H NMR spectra (see below) indicate that hydrogen bonding likely occurred, but no significant shifts were observed by IR (see the third row entry in Table A.1).

One possibility is that the monomer samples were measured at a sufficiently high concentration that dimerization occurred within the samples in CHCl<sub>3</sub>. In that case, it might be difficult to distinguish the hydrogen bonding interactions within the monomer samples and the intermolecular hydrogen bonding interactions in the polymers. Considering that the dimerization association constants for DAP-DAP and NH-NH interactions are low ( $<10 \text{ M}^{-1}$ ),<sup>7</sup> this does not seem very likely.

While IR could have been valuable in detecting the presence of hydrogen bonding interactions, it appears that it was not very useful for our polymer systems. Any future attempts to use IR to detect hydrogen bonding between selfcomplementary blocks of similar block copolymers may involve 1) varying the concentrations of both the monomer and polymer samples to try to rule out monomer dimerization or to more readily detect peak shifts in the polymers; or 2) using different IR techniques. In experiments performed later in our lab by Yoshihiro Ishihara,<sup>8</sup> IR was again attempted. Samples of triblock copolymers containing DAP, C4, and a thymine-based block (complementary to DAP) were analyzed at concentrations of up to 5 mg/ml in CHCl<sub>3</sub>. The samples were prepared the same way as described above (KBr disks) but no spectra were obtained and it was concluded that 1-5 mg/ml was too dilute. If using diluted samples may not work, using more concentrated samples may still be an option.

### A.2.2. Determination of polymer morphology (detection of hydrogen bonding) using <sup>1</sup>H NMR.

The second strategy we tried was to use <sup>1</sup>H NMR to look for peak shifts caused by hydrogen bonding within the polymers. We also hoped that this might yield information about whether the DAP block was exposed on the periphery of the aggregates, as depicted in Scheme A.2.a, and therefore more accessible to hydrogen bonding with small molecules than the NH block.

Qualitative preliminary tests were conducted by mixing the NH and DAP monomers. Figure A.3 shows the <sup>1</sup>H NMR of each monomer, and an equimolar mixture of the two monomers, all in CDCl<sub>3</sub>. The shifting of the peaks corresponding to the N-H protons on both the NH and DAP monomers indicates that hydrogen bonding occurs when the two monomeric species are mixed in solution.

Attempts to perform the same experiments with homopolymers  $NH_{10}$  and  $DAP_{10}$  were not successful because while the DAP homopolymer was soluble, the NH polymer was not. Heating and sonicating the NH polymer in the presence of the DAP polymer would still not result in the dissolution of the NH polymer, and no shift in the N-H peaks for the DAP polymer was measured.



**Figure A.3.** <sup>1</sup>H NMR (CDCl<sub>3</sub>) of NH- and DAP monomers individually and after mixing together with heating.

After measuring the monomer- and homopolymer control samples, we recorded the  ${}^{1}$ H NMR of a NH<sub>4</sub>-C4<sub>31</sub>-DAP<sub>7</sub> triblock in CDCl<sub>3</sub> (Figure A.4). In this case, the sample showed no peaks above 8.0 ppm. The lack of an observable N-H

peak for the NH monomer could indicate that our polymer self-assembled with the NH units inside the core and the DAP units forming the corona with no hydrogen bonding between the two blocks, as in Scheme A.1.a. We did observe characteristic DAP peaks (Figure A.4), which may lend further support for selfassembly according to Scheme A.1.a. However, it is also possible that the selfassembled structure was more like the cross-linked morphology such as Scheme A.1.b or the flower-like aggregate like that in Scheme A.1.c, with the NH and DAP units both in the aggregate core. The characteristic DAP peaks that we did observe are small, and so it may be possible that some DAP units are hidden (or partially hidden) on the inside of an aggregate with the NH block.



**Figure A.4.** <sup>1</sup>H NMR of NH<sub>4</sub>-C4<sub>31</sub>-DAP<sub>7</sub> triblock in CDCl<sub>3</sub>. The labeled peaks correspond to the N-H groups on the DAP block.

This technique was used in later work in our  $lab^6$  on similar hydrogen bonding based block copolymers of the composition  $DAP_{20}$ -C4<sub>40</sub>-Thymine<sub>20</sub> (thymine is complementary to DAP). It was found that the <sup>1</sup>H NMR of a related  $C4_{40}$ -Thymine<sub>20</sub> diblock copolymer showed peaks for the thymine component at 10.0 ppm (NH), 7.05 ppm (CH) and 1.89 (CH<sub>3</sub>) that disappeared in the triblock copolymer. This was attributed to the block copolymer self-assembling as depicted in Scheme A.2.c. This later work also determined that the strength of the DAP-Thy interactions in the core was dependent on the length of the DAP- and thymine blocks.

<sup>1</sup>H NMR certainly demonstrated potential for helping to discern the solution morphologies of our polymer systems. In our case, however, our results were somewhat inconclusive. Some evidence, such as the lack of signals corresponding to the NH monomer, suggested that the polymer aggregated as in Scheme A.2.a. Other observations, such as the very small DAP peaks, especially in light of the later studies with DAP-C4-Thymine polymers, mean that hydrogen bonding interactions cannot be ruled out.

In future experiments, one way to further examine the morphology of these self-assembled polymers by NMR may be to measure the shifts in peaks as a function of added guest. If DAP-NH interactions were occurring within the selfassembled polymers, the addition of a guest selective for either of these units should result in changes in the peaks for both the NH and DAP moieties.

### A.2.3. Determination of polymer morphology (interaction with small molecules) using dynamic light scattering (DLS).

We had little success using TEM imaging to observe our morphologies, so we tried to use dynamic light scattering (DLS) to determine if adding small molecules could affect the morphology of the polymer in solution. Succinimide, maleimide, and the NH monomer are complementary to the DAP moieties on the polymers, and the DAP monomer can hydrogen bond with the polymer NH groups. N-methyl maleimide is a control molecule and cannot hydrogen bond (Scheme A.3). If the DAP block of the polymer chains were exposed on the periphery of an aggregate (Scheme A.2.a), adding a small complementary molecule should not result a very large change in polymer size or morphology, if hydrogen bonding occurs between a polymer aggregate and the small molecule guest, it may just result in a "coating" of the aggregate. If adding the DAP monomer (complementary to NH) results in no observed morphology change for the polymers, it could also indicate that the NH units were hidden and inaccessible inside a micelle-like core and that self-assembly was driven by solvophobic interactions. If, on the other hand, a significant morphology change is induced by any of the added molecules, it may imply that the polymers were self-assembling into a structure more like that in Scheme A.2.b (cross-linking) or c (flower) above. In this scenario, the polymer morphology is dependent upon hydrogen bonding between the NH and DAP blocks, and these moieties should be more or less equally accessible to any added small molecule.

Scheme A.3. Molecules added to self-assembled NH-C4-DAP polymers.





√–H

Succinimide



NH monomer

CH<sub>3</sub>

DAP monomer

N-methyl maleimide

These experiments were conducted by refluxing the polymer sample in  $CHCl_3$  in the presence of a guest and allowing the sample to cool to room temperature. As a control, a sample of the polymer was refluxed alone. Samples were filtered through  $0.2\mu m$  filters into rinsed DLS vials, and multiple measurements were recorded at 3 different angles (45, 90 and 135 degrees). The preliminary results obtained (the averages of each angle) are shown in Table A.2. The values presented are the hydrodynamic radii of the aggregates in solution as determined using CONTIN fitting.

Angle		NH <sub>10</sub> -C4 <sub>50</sub> -DAP <sub>10</sub>					
	No guest	Succinimide	NH monomer	DAP monomer			
45	52.44	32.22	95.78	122.97			
90	33.56	21.14	110.02	123.31			
135	44.15	16.39	33.32	93.89			

**Table A.2.** DLS data for polymers after addition of small molecules.

Angle	NH <sub>10</sub> -C4 <sub>20</sub> -DAP <sub>1</sub>				
	No guest	N-methyl maleimide	Maleimide		
45	34	29	54		
90	34	18	81		
135	22	21			

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For these DLS experiments, if the size of the aggregates varies greatly among the different angles used, it could be an indication that the morphologies are not spherical. No attempts were made to extract more detailed information from the data. The numbers presented in Table A.2 are the average values, taken from several measurements; however, most samples had broad distributions (sometimes aggregates ranging in sizes spanning 50 nm would be predominant in the sample), making it difficult to truly determine the effect of adding small molecule guests to modify the polymer morphologies (Figure A.5). While some of the data appears to indicate that small molecules could affect the aggregate morphologies, it is difficult to conclude this definitively due to the large error of many of the measurements.



**Figure A.5**. Sample DLS results. These results are from a mixture of  $NH_{10}$ -C4<sub>50</sub>-DAP<sub>10</sub> + the NH monomer.

Later work published from our group,<sup>6</sup> again involving DAP-C4-Thymine polymers, describes similar experiments using small molecules to break up self-

assembled structures. These studies demonstrated that the addition of small molecule guests to self-assembled polymers could result in the complete destruction of the self-assembled structures, but that this was dependent on the lengths of the hydrogen bonding -containing blocks. If the DAP- and thyminebased blocks were short (5 units each), then small molecules could disrupt the polymer morphologies, but if the blocks were longer (20 units each), then no small guests could disrupt the DAP-thymine interactions. To compare with our NH-C4-DAP polymers shown in Table A.2, the NH block is of intermediate size (10 units) and the DAP block is either small (1 unit) or also of intermediate size (10 units). In our case, adding small molecule guests did not, for any sample, result in the complete disruption of the polymer aggregates. In the case of the smaller polymer ( $NH_{10}$ -C4<sub>20</sub>-DAP<sub>1</sub>), the small DAP block would suggest that small molecules should break up the morphologies. However, in this case no significant changes in aggregate size were observed upon addition of maleimide. For the longer polymer (NH<sub>10</sub>-C4<sub>50</sub>-DAP<sub>10</sub>) more dramatic changes were measured for the addition of small molecules. A possible explanation for this strange result might be that for the polymer with the larger DAP block ( $NH_{10}$ -C4<sub>50</sub>-DAP<sub>10</sub>), hydrogen bonding interactions among the polymer chains are more significant, and thus more affected by the addition of small guests. For the shorter polymer (NH<sub>10</sub>-C4<sub>20</sub>-DAP<sub>1</sub>), hydrogen bonding interactions may be less important and microphase separation could contribute to the self-assembly. These results are somewhat unexpected considering the observations regarding the DAP-C4-Thymine polymers, but the large distributions of sizes measured for these polymers may help to explain the discrepancy.

#### A.2.4. Determination of polymer morphology using pyrene fluorescence.

Our fourth and final approach to try to ascertain the structure of our solution morphologies involved derivatizing the polymers with pyrene. We devised a strategy to append approximately one pyrene moiety to the end of the polymer using a pyrene-based ROMP monomer.<sup>9</sup> Pyrene has several features that make it useful for our study.<sup>10</sup> First, at lower concentrations, pyrene exists as a monomer, but at higher concentrations, pyrene excimers form whose emission can be distinguished from the monomeric form. The monomer: excimer ratio can therefore be used as an indicator of the local pyrene concentration. Second, the ratio of two particular emission bands, I<sub>1</sub> and I<sub>3</sub>, changes with the solvent polarity and can be used to gauge the polarity of the pyrene surroundings.

We synthesized two types of pyrene-labeled polymers. In the first set of polymers, the DAP end was labeled with pyrene; in the second set, the NH end was labeled (Scheme A.4). We reasoned that adding one pyrene unit to the end of a polymer would not greatly affect its self-assembly. In our strategy, the DAP-labeled polymer would be self-assembled, and the pyrene fluorescence measured. This would be compared to the fluorescence of the self-assembled NH-labeled polymer.

Scheme A.4. DAP-end labeled and NH-end labeled block copolymers



DAP-end labeled polymer

NH-end labeled polymer

If the polymer self-assembly was predominantly driven by solvent-induced phase separation, as depicted in Scheme A.2.a above, then the fluorescence of the polymer labeled at the DAP end might be notably different from the NH-labeled polymer. The portion of excimer should be higher in the polymer labeled at the NH end, since the NH block would comprise the core of any aggregate formed, and thus pyrene units would also be concentrated into the core. In contrast, the polymer labeled at the DAP end would have a lower portion of excimer, since pyrene units would be distributed around the aggregate corona surface. Also, with phase separation-based self-assembly, the  $I_1/I_3$  ratio may be different for the two polymers, since the polarity of the environment inside and outside of an aggregate surface may be different.

If, on the other hand, the polymer self-assembly was driven primarily by hydrogen bonding (second and third parts of Scheme A.2), the pyrene fluorescence of the polymer labeled at the NH end would not be significantly different from that of the polymer labeled at the DAP end. Since NH blocks and DAP blocks would be hydrogen bonded to each other, they would exist in similar environments, and thus the pyrene moieties would be in similar environments whether they were appended to the NH end or to the DAP end of a polymer chain. The polymers should also have similar monomer: excimer ratios, regardless of which end possessed the pyrene group.

A number of pyrene-labeled polymers were synthesized using the first generation Grubbs catalyst. The polymers, with block lengths determined by NMR, are shown in Table A.3, as are the polydispersity index (PDI) values for each polymer as measured by GPC. For each polymer, the pyrene unit was added last. Therefore, for polymers labeled with pyrene at the DAP end, the first block polymerized was the NH block; for those labeled at the NH end, the first block polymerized was the DAP block.

Polymer	PDI			
	Block 1	Diblock	Triblock	Tetrablock
NH14-C4113-DAP16-py1	1.14	1,1	1.5 <sup><i>a</i></sup>	1.5 b
NH14-C4117-DAP15-py1	1.12	1.07	1.11	1.15
NH <sub>16</sub> -C4 <sub>62</sub> -DAP <sub>8</sub> -py <sub>1</sub>	1.13	1.14	1.88 <sup>b</sup>	1.93 <sup>b</sup>
NH <sub>12</sub> -C4 <sub>42</sub> -DAP <sub>7</sub> -py <sub>1</sub>	1.12	1.13	1.33	1.2
DAP <sub>7</sub> -C4 <sub>31</sub> -NH <sub>4</sub> -py <sub>1</sub>	1.29	1.3	1.17	1.41
DAP <sub>13</sub> -C4 <sub>45</sub> -NH <sub>9</sub> -py <sub>1</sub>	1.3	1.56	1.48	1.71

Table A.3. Pyrene-labeled polymers and their PDI's as determined by GPC.

<sup>*a*</sup> Shoulder; <sup>*b*</sup> shoulder and tail.

While some results are listed here, in many cases, it proved difficult to attach the pyrene to a polymer. Since it was possible to generate a homopolymer of the pyrene-based monomer, the problem was most likely not the pyrene monomer itself, but a problem with the crossover from the DAP or NH monomer on the triblock copolymer to the pyrene monomer.



**Figure A.6.** Fluorescence of pyrene in NH-labeled polymer DAP<sub>7</sub>-C4<sub>31</sub>-NH<sub>4</sub>-py in DMSO (no self-assembly, black dotted line) and in CHCl<sub>3</sub> (self-assembly, grey solid line).



**Figure A.7.** Fluorescence of pyrene in DAP-labeled polymer  $NH_{12}$ -C4<sub>42</sub>-DAP<sub>7</sub>py in DMSO (no self-assembly, black dotted line) and in CHCl<sub>3</sub> (self-assembly, grey solid line).

Figures A.6 and A.7 show initial tests of a polymer labeled at the NH-end and at the DAP-end with pyrene, respectively. In DMSO, there is no selfassembly. The spectra of each polymer, normalized to the I<sub>3</sub> peak at 395 nm, of each sample in CHCl<sub>3</sub> and in DMSO show that the excimer peak ( $\lambda < 450$  nm) was somewhat increased due to self-assembly in CHCl<sub>3</sub>. The next step was then to compare the CHCl<sub>3</sub> spectra of polymers labeled at the NH-end and at the DAP end, to see if there was any difference in the amount of excimer emission.



Figure A.8. Fluorescence of pyrene in polymers  $NH_{12}$ -C4<sub>42</sub>-DAP<sub>7</sub>-py (DAP-labeled, grey solid line) and DAP<sub>7</sub>-C4<sub>31</sub>-NH<sub>4</sub>-py (NH-labeled, black dotted line) in CHCl<sub>3</sub>.

The fluorescence spectra of a DAP-labeled and an NH-labeled polymer in CHCl<sub>3</sub>, again normalized to the I<sub>3</sub> peak, are compared in Figure A.8. The I<sub>1</sub>/I<sub>3</sub> ratio was similar for the two polymers, which suggests that the pyrene was in the same environment whether it was attached to the NH-end or the DAP end of a polymer. Unexpectedly, with these examples the pyrene emission at wavelengths greater than 450nm (excimer) was actually greater for the DAP-labeled polymer

than for the NH-labeled polymer. If the polymers self-assembled due to solvophobic interactions (Scheme A.2.a), the NH-block should be on the inside, and thus pyrene moieties attached to the NH ends should also be concentrated inside the aggregate. When the polymer was labeled at the DAP end, those pyrene moieties would be arranged around the periphery of the aggregate, and thus should show a somewhat lower excimer emission when compared to the NH-labeled polymer. If the polymer was aggregating due to the formation of hydrogen bonds between the NH- and DAP blocks, then the excimer emission should be fairly similar, regardless of which end of the polymer was tagged with a pyrene molecule. Regardless of how these polymers self-assembled, the polymer with pyrene at the DAP-end should not show a higher excimer emission than the corresponding NH-labeled polymer.

One possible explanation for this result may be that the number of pyrene monomers attached to the end of the polymer chain may not have been all that well-controlled. While the amount of pyrene added was calculated to be one pyrene per polymer chain, it is possible that some chains contained 2 or even more pyrene moieties. This may be especially true when the pyrene was attached to the DAP-end of the polymer. While monitoring the polymerization by  ${}^{1}H$ NMR did indicate the disappearance of the pyrene monomer, if there were problems with the cross-over from the DAP units on the polymer chain to the pyrene monomer, some polymer chains may have ended up with multiple pyrene groups, while other chains would have none. Another explanation also relates to difficulties in the polymerization reactions, but in this scenario the DAP monomer is the problem, rather than the pyrene monomer. The PDI's of these polymers often became higher (>1.3) upon addition of the DAP monomer. This could be due to interactions between the DAP- and NH blocks, but it could also be due to uncontrolled polymerization of the DAP units as a result of either incomplete cross-over from the C4 block or simply problems with polymerizing the DAP monomer. Problems during the polymerization of the DAP monomer would be carried through to yield tetrablock copolymers that were not very well-defined.



For DAP-labeled polymers, problems with either the DAP block or the pyrene block could result in the addition of more than one pyrene to the end of some polymer chains. Figure A.9 shows the fluorescence spectra of the NH- and DAPlabeled polymers in DMSO, in which there is no self-assembly. Indeed, the excimer peak is slightly higher for the polymer labeled at the DAP-end of the chain, and this could indicate that there are multiple pyrene units polymerized together along the polymer chain.



**Figure A.9**. Fluorescence of pyrene in polymers  $NH_{12}$ -C4<sub>42</sub>-DAP<sub>7</sub>-py (DAP-labeled, grey solid line) and DAP<sub>7</sub>-C4<sub>31</sub>-NH<sub>4</sub>-py (NH-labeled, black dotted line) in DMSO.

Although using pyrene fluorescence to determine the morphology of our polymer aggregates was a very interesting approach, based on results like those presented in Figure A.8 it was concluded that problems with the polymerization reactions rendered this method unsuccessful. In future work regarding these polymers, the most likely solution to some of the problems regarding the polymerization would be to try using the third generation Grubbs catalyst rather than the first generation. The third generation catalyst may be more effective than the first generation, as it is at least as active but slightly more tolerant of air and water and other impurities, and could potentially be more effective at the crossover from the DAP block to the pyrene monomer. The synthesis of a wider range of well-defined pyrene-labeled polymers would allow a more complete study on the fluorescence properties of these systems.

This project started with the generation of triblock copolymers that contained both NH and DAP moieties; these groups are complementary to each other as hydrogen bonding motifs. Several approaches were used to try to determine if self-assembly was driven by solvent-polymer interactions or by hydrogen bonding interactions. The individual monomers and some triblock copolymers were analyzed by IR in both CHCl<sub>3</sub> and DMSO, but no significant changes were noted in the C=O stretching. <sup>1</sup>H NMR was also used, and while peak shifts of the N-H peaks could be detected for mixtures of the monomers, no Other experiments signs of shifted peaks were detected for the polymers. involved mixing polymers with small molecules that had hydrogen bonding motifs that were complementary to either the NH or the DAP blocks of the polymers, and measuring any changes in solution morphology by DLS. These experiments indicated that small molecules could cause a change in the morphology of the polymer aggregates, regardless of whether they were complementary to the NH or the DAP block. Many of the samples had a fairly broad distribution, however, and so drawing accurate conclusions based on the results was difficult. Finally, we attempted to attach a pyrene monomer to the ends of the polymer chains in the hopes that we could use pyrene fluorescence to determine the morphologies of the self-assembled aggregates. Unfortunately, although this method was really interesting, problems related to the polymerization reactions rendered the results somewhat inconclusive.

A number of difficulties were encountered during this project. These include not only the inconclusive or contradictory data presented above but more

general problems related to the polymerizations and lack of useable TEM images. Eventually, block copolymers containing the metal complex  $Ru(bpy)_3^{2+}$  and either the DAP monomer or a thymine-based monomer were generated with the idea that the combination of  $Ru(bpy)_3^{2+}$  luminescence and molecular recognition could lead to the development of biodetection system. It was also hoped that the high electron density of the metal complex would facilitate TEM imaging. Some preliminary self-assembly studies were also conducted with these block copolymers that contained both the  $Ru(bpy)_3^{2+}$  complex and hydrogen bonding motifs.

# A.2.5. Self-assembly of polymers containing $Ru(bpy)_3^{2+}$ complexes and hydrogen bonding units

The first polymer we synthesized had the approximate ratio of  $Ru_{18}$ -C4<sub>20</sub>-DAP<sub>3</sub> (Scheme A.5). The ratio is only approximate because the ruthenium-based monomer was polymerized first, and masked the signals from the phenyl group at the end of the polymer chain that are used to determine the degree of polymerization. Self-assembly of these polymers was done by dissolving the polymer in acetonitrile and then adding toluene. The ruthenium-containing block was insoluble in toluene and thus any aggregates that formed would have  $Ru(bpy)_3^{2+}$  in the core domain and the C4 and DAP blocks in the corona. The DAP blocks would hopefully be on the periphery of the aggregate. Figure A.10 shows the micelles that formed when toluene was added to the polymer solutions. The morphology did not change significantly as toluene was added. Compared to the polymers described above that contained complementary hydrogen bonding motifs, these polymers could only self-assembly based on microphase separation. Scheme A.5. Ru-C4-DAP polymer and Ru-C4-Thymine polymer, and the hydrogen-bonding interaction between DAP and thymine.







Figure A.10. TEM images of  $Ru_{18}$ -C4<sub>20</sub>-DAP<sub>3</sub> in (a) 40% toluene (scale bar is 200 nm), (b) 85% toluene (500 nm) in acetonitrile.



This experiment established that these polymers could self-assemble, and that we could finally use TEM to observe the morphologies formed. Since we now had polymer aggregates that were more well-defined and reproducible than what we had been able to achieve thus far, we wanted to see if we could utilize hydrogen-bonding interactions between different self-assembled polymers. Our plan was to self-assemble a polymer that possessed DAP groups along the periphery of the aggregate, and add that solution to a different polymer, separately self-assembled, that contained exposed thymine units. The complementarity between DAP and thymine might serve to bring the aggregates together.

The DAP groups were soluble in the toluene solution, but a homo(thymine)<sub>10</sub> polymer was not. Therefore, we reasoned that the thyminecontaining polymer should contain a large soluble C4 block as a spacer between the thymine and the  $Ru(bpy)_3^{2+}$  complex to better solubilize the thymine block. Such a polymer would hopefully form "star" micelles in acetonitrile/toluene solutions. The polymer we synthesized had the approximate ratio of  $Ru_5$ -C4<sub>21</sub>-Thy<sub>1</sub>, and formed a mixture of micelles and large compound micelles in acetonitrile/toluene solutions (Figure A.11).



Figure A.11. TEM image of  $Ru_5$ -C4<sub>21</sub>-Thy<sub>1</sub> polymer in 20% toluene in acetonitrile (scale bar is 500 nm).

Since the DAP block was soluble in toluene, we opted to label a "crew-cut" polymer with DAP, because a crew-cut polymer would have a shorter soluble corona block. We had hoped that a crew-cut polymer would have a different morphology than a "star" micelle, and we would be able to use TEM to detect any hydrogen bonding-induced aggregation between different polymers. We synthesized a DAP-containing polymer had a relative block ratio of Ru<sub>4</sub>-C4<sub>2</sub>-DAP<sub>1</sub>, but was probably closer to Ru<sub>12</sub>-C4<sub>6</sub>-DAP<sub>3</sub>, based on the monomer ratio used. This polymer, upon self-assembly, formed a mixture of large compound micelles and vesicles (Figure A.12).



Figure A.12. TEM image of  $Ru_{12}$ -C4<sub>6</sub>-DAP<sub>3</sub>, 90% toluene in acetonitrile (initial polymer concentration is 20 mg/ml).

We now had two polymers that self-assembled into different morphologies: a DAP-labeled polymer that could form LCM's and vesicles, and a thyminelabeled polymer that formed micelles and LCM's. With their complementary hydrogen bonding motifs, we hoped that mixing the two pre-assembled polymers would result in the formation of higher-order assemblies. For this experiment, we first induced self-assembly in each of these polymers and then added the two solutions together. TEM images taken either from the initial mixture or the sample after heating were essentially the same (Figure A.13). Micelles, vesicles and LCM's were all present, but there was no evidence that the individual polymer morphologies were becoming connected by hydrogen bonds.



Figure A.13. TEM image of a mixture of DAP-labeled vesicles/LCM's and thymine-labeled micelles/LCM's.

The most likely reason for the lack of noticeable interaction between the DAP-labelled vesicles and the thymine-labeled micelles and large compound micelles may be that the block lengths of the hydrogen bonding units were too short and were not sufficiently exposed along the periphery of the self-assembled aggregates. For both polymers the block lengths of the DAP or thymine units were short and, particularly thymine, which is not very soluble in toluene, may have been shielded by the coiling of the C4 corona chains. This problem may be solved by creating polymers with longer molecular-recognition blocks or with more rigid corona blocks that could help to force the molecular-recognition functionalities to the periphery. These solutions would require a balance between the solubility of the hydrogen bonding block with the solvent and its ability to hydrogen bond with other molecules.

#### A.3. Conclusions

We synthesized a number of block copolymers that contained complementary hydrogen bonding motifs. Since we had no success with TEM imaging of aggregates formed from these polymers, we tried a number of approaches to determine if hydrogen bonding or solvent-induced microphase separation was the main driving forces for self-assembly. IR, <sup>1</sup>H NMR, DLS and pyrene fluorescence were all attempted, but gave either inconclusive or contradictory results. Eventually we used polymers that contained a metal complex, Ru(bpy)<sub>3</sub><sup>2+</sup>, and were able to obtain better TEM images and observe consistent morphologies. Preliminary experiments to try to utilize hydrogen bonding to bring together different polymer aggregates were not successful, likely due to insufficient exposure of the molecular-recognition moieties on the periphery of the aggregates.

Although the hydrogen bonding based project was eventually discontinued in favour of more detailed studies involving  $Ru(bpy)_3^{2+}$  -containing block copolymers, a few suggestions are presented here for furthering studies on the hydrogen bonding block copolymers.

#### A.4. Experimental Procedures

Synthesis of NH monomer: Maleimide (5.2 g, 53 mmol) and furan (8.5 g, 125 mmol) were placed in a sealable bomb reactor with approx 50 ml ether. The mixture was freeze-pump thawed to degas the ether. The reaction vessel was then heated to 90°C overnight. After cooling to room temperature, the white product that precipitated out was filtered and washed with cold ether. 83% yield. <sup>1</sup>H NMR  $\delta(d_6$ -DMSO): 11.40 (s, 1H), 6.52 (s, 2H), 5.10 (s, 2H), 2.83 (s, 2H).

Synthesis of C4 monomer: The NH monomer (0.5 g, 3 mmol), 1-bromobutane (1 g, 7.5 mmol) and  $K_2CO_3$  (2.2 g, 16 mmol) were combined with 40 ml DMF in an oven-dried round bottom flask with a Schlenk adaptor. The reaction was flushed

with nitrogen and heated to 50°C for about 1.5 hours, then at room temp overnight. The crude product was combined with water and extracted with ethyl acetate. The ethyl acetate layer was concentrated, applied to a silica gel column and purified with 95:5 CH<sub>2</sub>Cl<sub>2</sub>:methanol. <sup>1</sup>H NMR  $\delta$ (CDCl<sub>3</sub>): 6.51 (s, 2H), 5.26 (s, 2H), 3.47 (t, 2H), 2.83 (s, 2H), 1.52 (m, 2H), 1.30 (m, 2H), 0.92 (t, 3H).

#### Synthesis of DAP monomer:

Synthesis of 2-acetamido-6-aminopyridine:



Diaminopyridine (DAP, 6.5 g, 60 mmol) was ground to a fine grey powder and dried under vacuum overnight. Dried DMAP (dimethyl amino pyridine, 36 mg, 0.3 mmol), acetic anhydride (6.1 g, 60 mmol) and distilled triethylamine (4.9 g, 49 mmol) was added to the DAP with approx 120 ml CH<sub>2</sub>Cl<sub>2</sub>. The reaction was refluxed for 48 hours. After cooling to room temperature, the mixture was washed with brine, and the organic layer was dried with MgSO<sub>4</sub> and evaporated to yield an orange powder in 29% yield. One spot on TLC (4% MeOH in CH<sub>2</sub>Cl<sub>2</sub>).

#### Synthesis of 2-acetylamino-6-[6-bromohexanoylamino]-pyridine:



The product from the previous reaction (1.0 g, 7 mmol) was dried with DMAP (91 mg, 0.7 mmol). Distilled  $CH_2Cl_2$  (50 ml) and triethylamine (1.2 g, 12 mmol)

were then added. 6-bromohexanoyl chloride (2.4 g, 11 mmol) was added last. The reaction was refluxed overnight. After cooling to room temperature, the mixture was washed with 5% NaHCO<sub>3</sub> and then with distilled water. The organic layer was dried and evaporated to yield a thick orange liquid from which crystals formed. <sup>1</sup>H NMR  $\delta$ (d<sub>6</sub>-DMSO): 10.04 (s, 1H), 9.99 (s, 1H), 7.68 (s, 3H), 3.62 (m, 1H), 3.52 (m, 1H), 2.39 (m, 2H), 2.08 (s, 3H), 1.85 (m, 1H), 1.70 (m, 1H), 1.58 (m, 2H), 1.39 (m, 2H).

Synthesis of DAP monomer:



The product from the previous reaction (1.5 g, 5 mmol) was added to the NH monomer (0.8 g, 5 mmol) and K<sub>2</sub>CO<sub>3</sub> (3.7 g, 27 mmol) in 60 ml DMF. The reaction was heated for 1.5 hours at 50°C under nitrogen, then stirred at room temperature overnight. It was then mixed with approx 60 ml water and extracted with ethyl acetate. The organic layer was concentrated and applied to a silica gel column and eluted with ethyl acetate. The final white powder was obtained in 48% yield. <sup>1</sup>H NMR  $\delta$ (d<sub>6</sub>-DMSO): 9.98 (s, 1H), 9.91 (s, 1H), 7.67 (s, 3H), 6.53 (s, 2H), 5.10 (s, 2H), 3.31 (m, 2H), 2.90 (m, 2H), 2.35 (m, 2H), 2.09 (s, 3H), 1.55 (m, 2H), 1.46 (m, 2H), 1.23 (m, 2H).

**Synthesis of polymers:** A typical polymer synthesis is as follows: all monomers and the Grubbs first or third generation catalyst were dissolved separately in Schlenk tubes using distilled and degassed solvents, either THF of CH<sub>2</sub>Cl<sub>2</sub>. The monomer was transferred to the catalyst via a canula. Small subsamples could be

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removed for NMR testing.<sup>5</sup> The polymerization of the NH monomer was generally complete in 15 minutes. A subsample (half) was removed and quenched with ethyl vinyl ether, and the C4 monomer was transferred into the main reaction. When the reaction was complete by NMR, half was removed and quenched, and the DAP monomer was added. When the reaction was complete (NMR), it was quenched with ethyl vinyl ether. Quenched samples were precipitated in either methanol or hexanes, and the block ratios of the final polymer were determined by NMR integrations.

**Self-assembly**: Experiments were done by either dissolving the polymer directly in  $CH_2Cl_2$  (usually needed sonication) or by dissolving the polymer in THF, then adding water until the solution was cloudy). TEM samples were prepared by drop-casting solutions onto TEM grids.

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