OLIGOMERIC AND POLYMERIC BIBENZIMIDAZOLE BASED METAL
COMPLEXES AND CROSSLINKED POLYETHYLENIMINE
BASED FLAME RETARDANTS

by

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ABSTRACT

OLIGOMERIC AND POLYMERIC BIBENZIMIDAZOLE BASED METAL COMPLEXES AND CROSSLINKED POLYETHYLENIMINE BASED FLAME RETARDANTS

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In Part I, a simple and mild condensation route for the synthesis of novel bibenzimidazole oligomers and polymers is described using methyl 2,2,2-trichloroacetimidate as a key starting material. The dimer, trimer, tetramer, and polymers of bibenzimidazole were synthesized as a new series of potential conjugated chelating ligands for the metallopolymer studies. The polymers show the maximum absorption at around 400 nm. The optical band gap of the polymer is estimated to be 2.68 eV.
In Part II, a series of multinuclear Ru complexes containing di-, tetra-, and octa-Ru\textsuperscript{II} centers based on the oligomeric bibenzimidazoles were synthesized and characterized. The species with high nuclearity exhibit extended, one-dimensional structures. They show very intense ligand-centered (LC) absorptions ($\varepsilon$ up to $3.6 \times 10^5$ M$^{-1}$·cm$^{-1}$) and moderately intense metal-to-ligand charge transfer bands in the visible region ($\varepsilon$ up to $6.6 \times 10^4$ M$^{-1}$·cm$^{-1}$). The interactions between the Ru metal centers across the bidentate bibenzimidazole ligands, and along the oligomeric bibenzimidazole ligands are relatively weak, which is not expected.

In Part III, the homochiral multinuclear Ru complexes of the oligomeric bibenzimidazoles were synthesized stereospecifically using $\Lambda$-[Ru(bpy)$_2$(py)$_2$][(-)-O,O'-dibenzoyl-L-tartrate]$\cdot$12H$_2$O as the enantiomerically pure chiral building block. The complexation of bibenzimidazole and the chiral building block proceeds with the complete retention of configuration. The tetra-Ru complex has an estimate size of 2.1 × 1.1 × 1.0 nm$^3$. They were characterized by means of circular dichroism, NMR spectroscopy, and mass spectrometry.

In Part IV, a new intumescent flame retardant system for use in olefinic polymers was discovered by crosslinking polyethylenimine ("Lupasol") with pyromellitic dianhydride, and then further treating with phosphoric acid to make the phosphate salts. The LOI of the phosphate salts can be greater than 70.0, and the char yield at 800 °C reaches 37.6%, which indicates that they could be non-halogenated, environmentally friendly, low smoke level, and cost effective intumescent flame retardants for polyolefins.
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LIST OF ABBREVIATIONS

BiBzImH$_2$: 2,2'-bibenzimidazole
Bpy: 2,2'-bipyridine
Bpm: 2,2'-bipyrimidine
DMAC: $N,N$-dimethylacetamide
DMF: $N,N$-dimethylformamide
DMSO: dimethylsulfoxide
NMP: 1-methyl-2-pyrrolidinone
R.T.: room temperature
CV: cyclic voltammogram
CD: circular dichroism
PART I

EFFICIENT SYNTHESIS AND CHARACTERIZATION OF NOVEL BIBENZIMIDAZOLE OLIGOMERS AND POLYMERS AS POTENTIAL CONJUGATED CHELATING LIGANDS
CHAPTER 1
INTRODUCTION

1.1 Metal Containing Conductive Polymers

Metal complexed conjugated polymers have attracted significant attention in recent years.\textsuperscript{1-4} The incorporation of transition metals has the potential to greatly expand the function and ultimate applications of conducting polymer systems. More specifically, there is a steady and growing effort to incorporate redox-active metal centers into conducting polymer structures to create highly efficient redox modulated conductivity for sensory (i.e., anions and small molecules), catalytic, photochemical, and photoelectronic applications. In conducting metallopolymers, an understanding of the interactive roles that the metal centers and the organic polymer backbone play is in its early stages.

A variety of $\pi$ conjugated heteroaromatic polymers which serve as electrically conducting, rigid chelating ligands have been prepared and their metal complexes have been investigated.\textsuperscript{5-11} Yamamoto and co-workers have reported that complexes of RuCl$_3$ with polypyridine and polybipyridine (1) (Chart 1.1) exhibit notable photocatalytic cleavage of water to H$_2$.\textsuperscript{8} Swager and co-workers have developed a series of polymetallorotaxanes for sensory\textsuperscript{9} and molecular electronic applications.\textsuperscript{10}
1.2 Mechanisms of Conductivity in Metallopolymers

Electron transport in redox polymers has been shown to occur by at least three mechanisms — outer sphere, superexchange and mediated, as illustrated schematically in Figure 1.1. The outer sphere mechanism is distinguished by the lack of mixing the respective metal orbitals. In contrast, in unsaturated systems, and particularly in highly conjugated systems, the electron transport can also occur through the polymer backbone by mediated and/or superexchange mechanisms. These are distinguished by the availability of redox states of suitable energy on the polymer to mediate electron transport. If such states are available, the electrons can hop between a localized metal-based redox site, a polymer-based site, and a second metal site in two steps (mediated mechanism). If such states are not available, then electron transfer through the backbone must result from a mixing of appropriate orbitals of both metals with the HOMO and/or LUMO of the polymer backbone (superexchange). It is important to note that the rate of electron transfer by this mechanism is highly dependent on the nature of the bridging ligand and its orbital overlap with the two metal centers. \(^\text{11}\)
Figure 1.1 Mechanisms for Electron Transfer Between Metal Sites in a Metallopolymer

![Diagram of electron transfer mechanisms]

Chart 1.2

1.3 Examples of Metal Complexed Poly(benzimidazoles)

It has been demonstrated by Pickup and co-workers that the existence of superexchange interactions between metal centers coordinated to conjugated polymer backbones enhanced the rate of electron transport through the polymer in a series of Ru- and Os-complexed polybenzimidazoles based on benzimidazole-pyridine or benzimidazole-pyrazine as the repeat units. For example, Ru(bpy)$_2$ or Os(bpy)$_2$
complexed poly(6,6′-bibenzimidazole-2,2′-diyl)-2,5-pyridine (2) and Os(bpy)$_2$
complexed poly(6,6′-bibenzimidazole-2,2′-diyl)-2,5-pyrazine (3) (Chart 1.2).$^{7,11,12}$ It was predicted that higher rates of electron transport could be achieved by better matching of orbital energies between the metal based $d\pi$ orbitals and the polymer $\pi$ or $\pi^*$ orbitals.

1.4 Our Project: Synthesis of Poly(bibenzimidazoles) and Their Metal Complexes

To probe the orbital interactions between metals and conjugated polymers, poly(bibenzimidazoles) (4) with 2,2′-bibenzimidazole (5) as the repeat unit were chosen in our research as the $\pi$ conjugated backbones. It appears that polybenzimidazoles are attractive choices for a number of reasons.$^4$ They tend to be very robust and remain stable under considerable thermal and chemical stress.$^{13}$ The studies of binuclear benzimidazole complexes have shown that they possess significant electronic coupling between the two metals.$^{14-16}$ In addition, the removal of the imidazole proton allows pH control of the electron density on the conjugated ligands.$^{17-24}$

![Chart 1.3](image)

Polybenzimidazoles are generally synthesized via melt polymerization of aromatic bis(o-diamine)s with dicarboxylic acid derivatives.$^{25-27}$ Another common
method is solution polymerization performed in poly(phosphoric acid). However, the drawbacks with these protocols often include high temperatures, long reaction times and strongly acidic conditions. In addition, the structures and the molecular weights of the obtained polymers are difficult to determine. Our initial attempts for the synthesis of poly(bibenzimidazole) started with the condensation reaction between 3,3′-diaminobenzidine (6) and oxamide (7) or oxalic acid in polyphosphoric acid in the presence of phosphorus pentoxide, but both of the polymer products met with limited success when using them for further metal complexation.

In this regard, the synthesis and investigation of a discrete set of oligomers with precise lengths has been an exciting approach to provide specific information for interpreting structural and conformational properties of the corresponding polymers. This is because oligomers serve as excellent models for the solution, electronic, photonic, thermal, and morphological properties of their corresponding polymers. In addition, the metal complexes of the oligomers would also provide further information about the metallopolymers. However, the synthesis of well-defined bibenzimidazole oligomers has not been reported.

In chapter 2, a concise and mild route for the first synthesis of bibenzimidazole oligomers and polymers using methyl 2,2,2-trichloroacetimidate (8) as the key starting material will be described. From a retrosynthetic standpoint, a bibenzimidazole unit is constructed via a ring-closure reaction of o-phenylenediamine (9) with 2-trichloromethylbenzimidazole (10) or its derivative. This methodology does not involve
tedious precursor synthesis and metal-catalyzed aryl–aryl bond formation, which is commonly used for heterocyclic aromatic oligomer and polymer synthesis.\textsuperscript{32}
CHAPTER 2
RESULTS AND DISCUSSION

2.1 Synthesis of Bibenzimidazole Monomer

Initial attempts for the synthesis of 2,2′-bibenzimidazole monomer (5) followed the most commonly used method in the literature via a condensation reaction of o-phenylenediamine (9) and oxamide (7) in ethylene glycol at reflux, which was reported by Fieselmann et al. in 1978 (Scheme 2.1). However, the drawbacks of this approach are the high reaction temperature (around 196 °C), low product yield, and difficulties in the purification of the desired product due to the formation of an isomeric byproduct fluoflavin 11 (ca. 10%). Interestingly, the formation of 11 in this reaction was never reported in the literature. Due to the similar solubility to that of 2,2′-bibenzimidazole, fluoflavin 11 was very difficult to be separated from the monomer 5. Furthermore, this method cannot be extended to the synthesis of either bibenzimidazole oligomers or polymers due to the nature of the reaction and the formation of the mixed products.

Scheme 2.1 Formation of 2,2′-Bibenzimidazole 5 and Byproduct Fluoflavin 11
Therefore, an alternative and more efficient approach is required. In an older report, in 1967, Holan and coworkers published a series of papers describing their studies on the synthesis and reactions of 2-trichloromethylbenzimidazole (10).\textsuperscript{35-38} A mild and efficient synthesis of 2,2′-bibenzimidazole (5) was also reported by simply reacting \textit{o}-phenylenediamine (9) with methyl 2,2,2-trichloroacetimidate (8) in methanol at room temperature (Scheme 2.2). The pure product 5 was obtained in an excellent 90% yield after a simple filtration. The advantages of this method are obvious: the reaction occurred at the room temperature; the desired product precipitated out from the reaction mixture, which allowed easy separation and purification; no byproduct formed and recrystallization was not necessary. Surprisingly, despite the practical convenience, high yields, simple product purification and mild reaction conditions, this approach for the synthesis of bibenzimidazole has been largely overlooked in the literature.

\textbf{Scheme 2.2 Holan’s Synthesis of 2,2′-Bibenzimidazole}

\[
\begin{align*}
\text{2} & \quad \text{NH}_2 \\
\text{9} & \quad + \quad \text{NH} \\
\text{Cl}_3 \text{C} & \quad \text{OCH}_3 \\
\text{8} & \quad \xrightarrow{\text{Methanol}} \\
\text{90\%} & \quad \text{R. T.} \\
\text{5} & \quad \text{N} \\
\text{N} & \quad \text{N}
\end{align*}
\]

Intrigued by these advantages, we explored the synthesis of bibenzimidazole oligomers by utilizing similar methodology for the construction of the bibenzimidazole unit. The successful extension of this efficient method for the synthesis of bibenzimidazole oligomers (\(n = 2–4\), \(n\) is the number of the repeat unit in the oligomers)
and the applications for the synthesis of bibenzimidazole polymers are described in this chapter.

2.2 Synthesis of Bibenzimidazole Dimer

Following Holan’s procedures,\textsuperscript{35} the key intermediate 2-trichloromethylbenzimidazole (10) for the synthesis of the oligomers was prepared by reacting \textit{o}-phenylenediamine (9) with methyl 2,2,2-trichloroacetimidate (8) in acetic acid. The use of a weak acid, e.g., acetic acid, was the key to the successful suppression of the formation of bibenzimidazole (5) and isolation of the relatively stable trichloride 10. Holan and co-workers have demonstrated that 10 can react with a variety of \textit{o}-bifunctional nucleophiles 12 to generate heterocyclic ring systems 13 (Scheme 2.3).\textsuperscript{38}

![Scheme 2.3 Holan’s Synthesis and Reactions of Trichloride 10](image)

We have found that when 3,3'-diaminobenzidine (6) was employed as a bis-\textit{o}-bifunctional nucleophile and treated with two equivalents of trichloride 10 under similar reaction conditions at reflux, the desired bibenzimidazole dimer 14 was obtained in 70% yield (Scheme 2.4).
The X-ray structure determination reveals that it is a rigid coplanar structure and this will be discussed in detail (Figure 2.2).

Scheme 2.4 Synthesis of Bibenzimidazole Dimer 14

2.3 Synthesis of [(4-(2-(1H-Benzo[d]imidazol-2-yl)-1H-benzo[d]imidazol-5-yl) benzene-1,2-diamine)] (15)

The key nonsymmetric building block for the synthesis of bibenzimidazole trimer and the tetramer is the 4-bibenzimidazole substituted o-phenylenediamine derivative 15 (Scheme 2.5). It possesses one bibenzimidazole unit with an o-phenylenediamino functionality, which could further participate in a similar cyclization process with either imidade 8 or trichloride 10 as o-phenylenediamine (9) does (Schemes 2.2 and 2.3) to generate more bibenzimidazole units.

To synthesize the compound 15, the cyclization of 3,3′-diaminobenzidine 6 with trichloride 10 has to occur on one side of 3,3′-diaminobenzidine, which could be achieved by controlling the stoichiometry. Therefore, when the trichloride 10 was treated with an excess of 3,3′-diaminobenzidine in DMF at room temperature for several hours and then heated at 130 °C for 44 h, the desired amine 15 was obtained in 51% yield, along with 6% of the dimer 14. A third byproduct was also isolated in 30% yield (entry 1, Table 1), for which 1H NMR spectroscopy showed a singlet proton at
9.25 ppm. In accordance with the spectroscopy data, the structure of the byproduct was assigned as \(2-(1H\text{-}\text{benzo}[d]\text{imidazol-2-yl})-5-(1H\text{-}\text{benzo}[d]\text{imidazol-5-yl})-1H\text{-}\text{benzo}[d]\text{imidazole (16)}, \) presumably produced by the cyclization of the diamine 15 with DMF.

Subsequent control experiments provided supportive evidence for the formation of the byproduct 16. For example, when diamine 15 was heated in DMF in the presence or absence of Et\(_3\)N, 16 was formed exclusively in ca. 76% yield. It is interesting to note that the formation of benzimidazole derivative by the cyclization of aromatic diamine with DMF without an appropriate activating agent has not been reported in the literature.\(^{39}\)

Scheme 2.5 Synthesis of Diamino Compound 15

Table 2.1 Comparisons of the Reactions at Different Temperatures in Scheme 2.5

<table>
<thead>
<tr>
<th>entry</th>
<th>reaction conditions</th>
<th>diamine 15</th>
<th>dimer 14</th>
<th>byproduct 16</th>
</tr>
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<tr>
<td>1</td>
<td>RT 5 h, then 130 °C 44 h</td>
<td>51%</td>
<td>6%</td>
<td>30%</td>
</tr>
<tr>
<td>2</td>
<td>RT 5 h, then 75 °C 7–10 h</td>
<td>63%</td>
<td>10%</td>
<td>0%</td>
</tr>
</tbody>
</table>
To prevent the further cyclization of diamine 15 with DMF, the reaction of trichloride 10 with 3,3'-diaminobenzidine (6) was performed at a relatively low temperature: room temperature for several hours, then at 75–80 °C for 7–10 h. Under these conditions, the formation of the byproduct 16 was completely suppressed and the desired diamine 15 was obtained in a satisfactory 63% yield, along with a small amount of the dimer 14 (ca. 10%) (entry 2, Table 2.1), which was readily separated from 15 by fractional precipitation.

Scheme 2.6 Synthesis of Bibenzimidazole Trimer 17 and Tetramer 19
2.4 Synthesis of Bibenzimidazole Trimer and Tetramer

With 15 in hand, the synthesis of the trimer 17 was readily achieved by condensation of two equivalents of 15 with imidate 8 at room temperature in 72% yield, following the same strategy used for the synthesis of 2,2′-bibenzimidazole (5) from o-phenylenediamine (Scheme 2.6).

Another important symmetric difunctional building block for the synthesis of the tetramer, bis(trichloride) (18), was prepared using the same strategy as that used for 2-trichloromethylbenzimidazole (10). 3,3′-Diaminobenzidine (6) was treated with 2.2 equivalents of imidate 8 in acetic acid providing the desired bis(trichloride) 18, which precipitated out from the reaction medium and was isolated in an excellent 85% yield after a simple filtration.

With both diamine 15 and bis(trichloride) 18 accessible, the tetramer 19 was synthesized by condensation of two equivalents of 15 with one equivalent of 18 using the previous diamine-trichloride cyclization conditions (Scheme 2.6). The product 19 precipitated from the reaction medium and was isolated in 60% yield. A small amount of DMF cyclization byproduct 16 was also formed under the reaction conditions and was removed by trituration of the crude product in DMF under heating (around 130 °C).

The melting point of the monomer bibenzimidazole 5 was greater than 300 °C.34 The melting points of the oligomers (14, 17, 19) were not measured due to the high temperature. The thermal properties of polybenzimidazoles have been widely investigated.13 The polybenzimidazoles have \( T_g \)’s greater than 430 °C.13 The thermal properties are discussed in the following section.
The dimer, trimer and tetramer are all brownish yellow powders and are soluble in concentrated sulfuric acid and methanesulfonic acid. The dimer is soluble in DMAC, DMF, DMSO, CF₃COOH, and HCOOH. The trimer and tetramer are partially soluble in DMAC and HCOOH, and sparingly soluble in DMF, DMSO, NMP, and CF₃COOH.

### 2.5 Synthesis of Bibenzimidazole Polymers

Poly(bibenzimidazoles) (4) were synthesized by two methods (Scheme 2.7). One method is the polycondensation reaction between 3,3′-diaminobenzidine (6) and methyl 2,2,2-trichloroacetimidate (8) in different solvents. For the polymer 4a, the interfacial polycondensation of equal amounts of 3,3′-diaminobenzidine (6) and methyl 2,2,2-trichloroacetimidate (8) was carried out in a nonsolvent ethanol. The reaction was initiated at room temperature and then heated to reflux for 82 h to ensure that the cyclization went to completion. The brown polymer 4a was obtained by simple filtration in 70% yield. The number average molecular weight ($M_n$) was around 19000 based on the viscosity determination (discussed in the viscosity section).

The synthesis of polymer 4b was carried out in a homogeneous solution using DMF as the solvent in the presence of ethanol. The brown polymer 4b precipitated out from the solution in 60% yield with a number average molecular weight ($M_n$) around 15000.

The comparison of these two reaction conditions indicates that the interfacial polymerization gave a higher molecular weight polymer (4a) than the solution polymerization, which produces the polymer 4b. On the basis of Holan’s study of the
reaction between the diaminocompound and methyl 2,2,2-trichloroacetimidate (8), the reactions need to be initiated at room temperature for at least several hours and then heated to around 70 °C to ensure that the cyclization goes to completion. If the reaction is heated directly to 70 °C without being stirred at room temperature, it would not provide the polymer with the expected structure.

Scheme 2.7 Synthesis of Poly(bibenzimidazole)s 4a-d

4a: In ethanol, RT, then reflux. 4b: In DMF in the presence of ethanol, RT, then 75 °C. 4c: RT, then 75–80 °C. 4d: RT, then 75 °C, then 120–130 °C, and then 150 °C.

The other method of synthesizing poly(bibenzimidazole) (4c–d) is the polycondensation reaction between diaminobenzidine 6 and bis(trichloride) 18 in DMF under different conditions. The direct polycondensation of equal amounts of 3,3’-diaminobenzidine (6) and bis(trichloride) 18 was carried out in a homogeneous DMF solution in the presence of Et3N and ethanol. For the polymer 4c, the reaction was initiated at room temperature for 5 h, then heated to 75 °C, and kept at 75–80 °C for 72 h. The orange-colored polymer was obtained by addition of water to the reaction mixture and precipitate out in 83% yield.
For the polymer 4d, the reaction was initiated at room temperature for 5 h, then heated to 75 °C, then to 120–130 °C, and eventually to a maximum of 150 °C. The greenish yellow polymer 4d precipitated out from the reaction mixture and was isolated in 65% yield.

Polymer 4c has a higher molecular weight ($M_n = 9600$) than does polymer 4d ($M_n = 6400$). Keeping the reaction temperature at 75 °C leads to the formation of the higher molecular weight polymer 4c. For the polymer 4d, the temperature was eventually increased to 150 °C, which might lead to the cyclization of the diamino groups with DMF and therefore terminate the chain growth.

Polymers 4a, b are partially soluble in concentrated sulfuric acid, methanesulfonylic acid, and HCOOH; but are not soluble in CF$_3$COOH, DMAC, DMF, DMSO, and NMP. Polymer 4c is soluble in all the above solvents. Polymer 4d is soluble in concentrated sulfuric acid and methanesulfonylic acid; partially soluble in HCOOH and CF$_3$COOH; not soluble in DMAC, DMF, DMSO, and NMP. The solubility of polymer 4c is different from those of polymers 4a, b and d, probably because the reaction temperature of 75 °C is not high enough for the complete cyclization in the polymer chains.

### 2.6 NMR Studies of Bibenzimidazole Oligomers

$^1$H NMR spectra of the oligomers (5, 14, 17, and 19) are shown in Figure 2.1. In order to clarify the NMR spectra by removing the tautomer effect, CF$_3$COOD was used as the solvent as well as forming the trifluoroacetate salts of the oligomers. The
crystal structure of the dimer 14 shows that the rings are coplanar and the molecule is centrosymmetric. In the aromatic region of the $^1$H NMR spectrum, the dimer shows five groups of peaks ($H_1$, $H_2$, $H_3$, $H_{4/4'}$ and $H_{5/5'}$). The singlet ($H_1$) is at 8.43 ppm; there are two double doublets at 8.28 and 8.26 ppm, which represent the protons $H_2$ and $H_3$ in the repeat unit; there are two double doublets at 8.12 and 7.93 ppm, which represent the protons $H_{4/4'}$ and $H_{5/5'}$ on both sides of the end groups. The NMR spectrum of trimer 17 and dimer 14 are very similar, which indicates that the trimer might have the coplanar structure. But the spectrum of the tetramer 19 is a little different from those of the dimer and the trimer. There are three singlets representing $H_1$, $H_{1'}$, and $H_{1''}$ respectively, instead of one singlet in the dimer and trimer; $H_{2/2'/2''}$ and $H_{3/3'/3''}$ show multiplets instead of the two double doublets in the dimer and the trimer. This indicates that $H_1$, $H_{1'}$, $H_{1''}$ are different, as well as $H_2$, $H_{2'}$, $H_{2''}$ and $H_3$, $H_{3'}$, $H_{3''}$. The tetramer may not have the coplanar structure that the dimer does. This noncentrosymmetric nature may lead to the nonequivalence of the protons in the repeat units.
Figure 2.1 $^1$H NMR Spectra of Bibenzimidazole Oligomers in CF$_3$COOD. The CF$_3$COO$^-$ counter ions were omitted from the structures for clarity; “d” indicates that the NMR of the tetramer was in CF$_3$COOD/D$_2$O to improve the solubility.
Figure 2.2 Crystal Structure and Packing Pattern of 
[Bis(bibenzimidazole)]$_2$(CF$_3$COOH)$_{12}$
(a): Coplanar structure. (b): Zigzag pattern and alternating stacking column

2.7 X-ray Structure of Bibenzimidazole Dimer

Yellow block single crystals of the CF$_3$COOH salt of the dimer 14 were grown by slow evaporation of a CF$_3$COOH solution at room temperature [monoclinic space group $P2_1/C$ (Figure 2.2)]. The X-ray crystal structure analysis reveals the almost coplanar structure of the dimer. One dimer of bibenzimidazole was protonated with four CF$_3$COOH molecules, and the rest of the CF$_3$COOH molecules are in the lattice to support the crystals by intermolecular H-bonding interactions. The protonated
bis(bibenzimidazole) formed a zigzag pattern with alternating stacking columns. The structure indicates an efficient \( \pi \)-stacking in the solid state with an intermolecular spacing of 7.90 Å.

| Table 2.2 Photophysical Properties of Bibenzimidazole Oligomers and Polymers |
|----------------------------------|--------|--------|--------|--------|--------|--------|
| compound                        | MW     | \( \lambda_{\text{max}}^{\text{abs}} \) (nm) | \( \varepsilon \times 10^4 \) (M \( \text{cm}^{-1} \)) | \( E_g \) (eV) | \( \lambda_{\text{max}}^{\text{em}} \) (nm) | stokes shift (nm) |
| monomer 5                       | 234.28 | 340    | 4.22   | -      | 414    | 74     |
| dimer 14                        | 466.54 | 373    | 9.21   | 2.89   | 495    | 122    |
| trimer 17                       | 698.74 | 382    | 14.82  | 2.81   | 495    | 113    |
| tetramer 19                     | 930.98 | 389    | 20.72  | 2.78   | 490    | 101    |
| polymer 4a                      | 19000  | 400    | -      | 2.68   | 498    | 98     |
| polymer 4b                      | 15000  | 400    | -      | 2.65   | 495    | 95     |
| polymer 4c                      | 9600   | 388    | -      | 2.70   | 505    | 117    |
| polymer 4d                      | 6400   | 397    | -      | 2.75   | 495    | 98     |

2.8 UV–vis Properties of Bibenzimidazole Oligomers and Polymers

The UV–vis properties of the oligomers and the polymers were investigated in the protonated forms in methanesulfonic acid (Figures 2.3–2.6, Table 2.2). The bibenzimidazole monomer 5 has a maximum absorption at 340 nm, which represents the \( \pi–\pi^* \) transition. The X-ray crystal analysis of the dimer 14 shows the coplanar structure. Its \( \lambda_{\text{max}} \) (\( \pi–\pi^* \) transition) is at 373 nm, which indicates the extension of the conjugation. The \( \lambda_{\text{max}} \) of the trimer 17 is at 382 nm, which indicates further extension of
conjugation, but not as much as from the monomer to the dimer. The tetramer 19 only red-shifted 7 nm to 389 nm compared to that of the trimer, which indicates the large chain length extension does not produce the expected further decrease of the HOMO–LUMO gap. This phenomenon indicates that the structure of the tetramer might not be coplanar.

Figure 2.3 UV–vis Spectra of Bibenzimidazole Oligomers in Methanesulfonic Acid (10⁻⁶ M)

Figure 2.4 shows the linear relationship between the extinction coefficient and the number of the repeat unit in the oligomers. The solid line, a, is the experimental data; the dotted line, b, is the theoretical data assuming that there is no interaction between the repeat units. The slope of the solid line a (5.51 × 10⁴) is larger than that of the dotted line b (4.22 × 10⁴), which indicates that there are some interactions between the repeat units due to the π orbital overlap. The extinction coefficients ε (M⁻¹·cm⁻¹) per repeat unit were found to be 4.22 × 10⁴ in the monomer, 4.61 × 10⁴ in the dimer, 4.94 ×
10^4 in the trimer, and 5.18 \times 10^4 in the tetramer. This suggests that in the tetramer, one repeat unit absorbs 1.2 times more light than one repeat unit in the monomer. The extinction coefficients of the trimer and the tetramer are larger than 140000 M^{-1}.cm^{-1}, which is unusually large for the short chain oligomers.

![Figure 2.4 Extinction Coefficient vs the Number of Repeat Unit in Bibenzimidazole Oligomers](image)

(a, Solid line): Experimental value; (b, dotted line): Theoretical values, assuming the repeat units are isolated with no interactions.

The \( \lambda_{\text{max}} \) values of the polymers 4(a–d) are at 388–400 nm, which are very similar to that of the tetramer (Figures 2.5 and 2.6). From the onset of the absorptions, the band gap of polymer 4a in methanesulfonic acid is estimated at 2.68 eV. An optical saturation or near saturation occurred at around 400 nm. 4a shows a narrow absorption band centering at 400 nm, while 4b shows a broad absorption band centering at around 350 nm with a shoulder at 400 nm. This indicates that the interfacial polycondensation reaction in ethanol gives polymer 4a with a uniform molecular weight distribution,
while the solution polymerization in DMF gives polymer 4b with a broad molecular weight distribution.

![Graph](image1)

**Figure 2.5** UV–vis Spectra of Poly(bibenzimidazole)s 4a,b in Methanesulfonic Acid (10⁻⁶ M)

![Graph](image2)

**Figure 2.6** UV–vis Spectra of Poly(bibenzimidazole)s 4c,d in Methanesulfonic Acid (10⁻⁶ M)
2.9 Photoluminescence Properties of Bibenzimidazole Oligomers and Polymers

The photoluminescence spectra of the oligomers and the polymers in the diluted solution of methanesulfonic acid are shown in Figures 2.7–2.9. All the oligomers and the polymers have similar emission bands with the maxima at 490–505 nm. These results indicate that there is little effect of the chain length on the solution luminescence of the protonated oligomers and the polymers. Large excitation and emission energy differences were observed for the oligomers and polymers in the solution. From the dimer to the polymer, the Stokes shifts between the excitation and emission decreased from 122 to 95 nm (Table 2.2).

![Photoluminescence Spectra of Bibenzimidazole Oligomers in Methanesulfonic Acid Based on the Same Molar Concentration (5.7 × 10⁻⁸ mol/L)](image)

(The excitation wavelength was 340 nm for the monomer 5, 373 nm for the dimer 14, 382 nm for the trimer 17, 389 nm for the tetramer 19.)
Figure 2.8 Photoluminescent Intensity at $\lambda_{\text{max}}^{\text{em}}$ vs the Number of Repeat Unit in Bibenzimidazole Oligomers
(a, Solid line): Experimental value; (b, dotted line): Theoretical values, assuming the repeat units are isolated with no interactions.

Figure 2.9 Photoluminescence Spectra of Poly(bibenzimidazole)s 4a–d in Methanesulfonic Acid (The excitation wavelength was 400 nm for the polymer 4a,b, 388 nm for the polymer 4c, 397 nm for the polymer 4d.)

Figure 2.8 shows the linear relationship between photoluminescent intensity at $\lambda_{\text{max}}^{\text{em}}$ and the number of the repeat units in the oligomers. The solid line, a, is the
experimental value; the dotted line, b, is the theoretical value assuming that there is no interaction between the repeat units. The slope of the solid line a (5.84) is larger than that of the dotted line b (4.60), which indicates that there are some interactions between the repeat units due to the $\pi$ orbital overlap. This suggests that in the tetramer, one repeat unit emits 1.27 times more light than one repeat unit in the monomer, which is consistent with the UV–vis properties shown in Figure 2.4, that in the tetramer, one repeat unit absorbs 1.2 times more light than one repeat unit in the monomer.

### 2.10 Viscosity and Molecular Weight of Poly(bibenzimidazole)s 4a–d

The viscosities of the poly(bibenzimidazole) (4a–d) were determined in methanesulfonic acid at 30.00 °C (Figure 2.10, Table 2.3). (The plots of 4b–d are similar to the plot of 4a shown in Figure 2.10). The inherent viscosity $\eta_{inh}$ is 0.705 and 0.553 dL/g at a concentration of 0.400 g/dL for 4a and 4b, respectively. The intrinsic viscosity $[\eta]$ of 4a is 0.720 dL/g, and $[\eta]$ of 4b is 0.521 dL/g obtained by extrapolating to zero concentration. The number average molecular weight ($M_n$) of 4a can be roughly estimated to be around 19000, and the $M_n$ of 4b is around 15000 based on the molecular weight-inherent viscosity relationship established for poly[2,2′-(m-phenylene)-5,5′-bibenzimidazole]. The inherent viscosity $\eta_{inh}$ is 0.425 and 0.287 dL/g at a concentration of 0.400 g/dL for 4c and 4d, respectively. The intrinsic viscosity $[\eta]$ of 4c is 0.387 dL/g, and $[\eta]$ of 4d is 0.344 dL/g obtained by extrapolating to zero
concentration. The number average molecular weight ($M_n$) of 4c can be roughly estimated to be around 9600, and the $M_n$ of 4d is around 6400.

![Figure 2.10 Plots of Inherent Viscosity $\eta_{inh}$ and Reduced Specific Viscosity $\eta_{sp}/c$ vs Concentration of Poly(bibenzimidazole) (4a) at 30.00 °C in Methanesulfonic Acid. Solid line: $\eta_{red} = \eta_{sp}/c$. Dotted line: $\eta_{inh} = (\ln \eta)/c$](image)

Table 2.3 Viscosities of Poly(bibenzimidazole)s 4a–d in Methanesulfonic Acid

<table>
<thead>
<tr>
<th>entry</th>
<th>$\eta_{inh}$ (dL/g) at 0.400 g/dL</th>
<th>$[\eta]$ (dL/g)</th>
<th>$M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>polymer 4a</td>
<td>0.705</td>
<td>0.720</td>
<td>19000</td>
</tr>
<tr>
<td>polymer 4b</td>
<td>0.553</td>
<td>0.521</td>
<td>15000</td>
</tr>
<tr>
<td>polymer 4c</td>
<td>0.425</td>
<td>0.387</td>
<td>9600</td>
</tr>
<tr>
<td>polymer 4d</td>
<td>0.287</td>
<td>0.344</td>
<td>6400</td>
</tr>
</tbody>
</table>
2.11 Infrared Analysis of Poly(bibenzimidazole)s 4a–d

The infrared spectra of a variety of polybenzimidazoles have been discussed previously.\textsuperscript{28,42,43} The characteristic infrared peaks of the benzimidazoles are observed in the bibenzimidazole oligomers (5, 14, 17, 19) and polymer series (4a–d). In the spectral region between 3500 and 2500 cm\(^{-1}\), a very broad peak was observed. A relatively sharp peak at 3403 cm\(^{-1}\) was attributed to the stretching absorption of isolated, non-hydrogen bonded N-H groups. The very broad, asymmetric absorption, approximately centered at 3145 cm\(^{-1}\), was assigned to hydrogen bonded N–H groups. The low intensity peak at 3053 cm\(^{-1}\) was attributed to the stretching modes of the aromatic C–H groups.

The region at 1660–1480 cm\(^{-1}\) is very characteristic of benzimidazoles. The C=\(\text{C}/\text{C}=\text{N}\) stretching vibrations (1622 cm\(^{-1}\)) are observed in this region, as well as ring modes which are characteristic of the conjugation between the benzene and the imidazole rings (1585 cm\(^{-1}\)). Strong absorptions due to in-plane ring modes are found at 1422 and 1397 cm\(^{-1}\). An imidazole ring-breathing mode gives rise to a peak at 1280 cm\(^{-1}\). The in-plane C–H bending bands, characteristic of substituted benzimidazoles, are found at 1230–1090 cm\(^{-1}\). For the benzene C–H out-of-plane bending modes, typically the tri-substituted benzene ring modes are observed in the range 950–675 cm\(^{-1}\), especially at 947 and 802 cm\(^{-1}\).

Polymers 4c,d made by the reaction of 3,3′-diaminobenzidine (6) and bis-trichloride 18 show the characteristic IR peaks described above. In addition, they show
weak absorption at around 1670 cm\(^{-1}\), which might be due to the formation of the amide functionality in the polymer chain or at the end groups by hydrolysis in the presence of base and ethanol.\(^{35}\)

### Table 2.4 Thermostability of Bibenzimidazole Oligomers and Polymers under N\(_2\)

<table>
<thead>
<tr>
<th>entry</th>
<th>onset decomposition temp ((T_d, ^\circ C))</th>
<th>residue at 800 (^\circ C) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimer 14</td>
<td>516</td>
<td>17.44</td>
</tr>
<tr>
<td>trimer 17</td>
<td>561</td>
<td>52.78</td>
</tr>
<tr>
<td>tetramer 19</td>
<td>572</td>
<td>59.30</td>
</tr>
<tr>
<td>polymer 4a</td>
<td>656</td>
<td>47.39</td>
</tr>
<tr>
<td>polymer 4b</td>
<td>646</td>
<td>50.80</td>
</tr>
<tr>
<td>polymer 4c</td>
<td>639</td>
<td>54.90</td>
</tr>
<tr>
<td>polymer 4d</td>
<td>662</td>
<td>68.98</td>
</tr>
</tbody>
</table>

#### 2.12 Thermostability of Bibenzimidazole Oligomers and Polymers

The oligomers and the polymers are thermally stable (Table 2.4). The TGA graph of the dimer 14, trimer 17, tetramer 19, and polymer 4a under N\(_2\) are shown in Figures 2.11 and 2.12. The onset decomposition temperatures \((T_d)\) from the trimer to the polymers are all higher than 500 \(^\circ C\). With the extension of the chain length, the \(T_d\) increases. The smooth curve in Figure 2.12 indicates a uniform polymer structure.
Figure 2.11 TGA Curves of Bibenzimidazole Dimer, Trimer and Tetramer under N$_2$ at a Heating Rate of 10 °C / min
Dashed dotted line: tetramer 19.

Figure 2.12 TGA Curves of Poly(bibenzimidazole) 4a under N$_2$ at a Heating Rate of 10 °C / min
2.13 Conclusions

The oligomers of bibenzimidazole (dimer, trimer and tetramer) were first synthesized using a concise and efficient synthetic strategy. This methodology is very practical overall, requires few synthetic steps, and is suitable for the synthesis of the bibenzimidazole polymers. The X-ray structure of the dimer shows that it is coplanar and centrosymmetric. This series of oligomers provides useful information for the analysis of the poly(2,2′-bibenzimidazole)s. The UV–vis spectra show that the chain extension results in a decrease of the HOMO–LUMO gap, and the maximum absorption saturates at around 400 nm. The optical band gap of the polymer is estimated to be 2.68 eV.

The synthesis and properties of the metal complexes of the oligomers will be discussed in Part II and Part III.
CHAPTER 3
EXPERIMENTAL DETAILS

3.1 General

3.1.1 Reagents and Materials

All reagents were used without further purification. 1,2-Phenylenediamine (98%), 3,3′-diaminobenzidine (99%), methyl 2,2,2-trichloroacetimidate (98%), and methanesulfonic acid (99.5%) were purchased from Aldrich. Ethanol and DMF (EMD) were used as received without further purification.

3.1.2 Measurements

$^1$H NMR (500 MHz) and $^{13}$C NMR (125 MHz) spectra were obtained on a JEOL Eclipse+ 500 MHz spectrometer. Chemical shifts (δ values) were given in parts per million with tetramethylsilane as an internal standard. UV–vis spectra were measured using a Varian Cary 500 UV–vis–NIR spectrophotometer. The photoluminescence (PL) emission spectra were obtained with a Jobin–Yvon Horiba Spex Fluoromax–3 Fluorimeter. Elemental analysis was performed by Quantitative Technologies Inc. (QTI) (Whitehouse, NJ). Mass analysis was performed by Scripps Research Institute (La Jolla, CA). ESI-MS spectra were obtained on a Waters–Micromass LCT. X-ray crystal structure of the dimer (14) was solved by Dr.
Douglas Ogrin at the Texas Center for Crystallography at Rice University and Dr. Simon Bott at University of Houston. FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer with KBr pellets. Intrinsic viscosity $\eta$ of the polybibenzimidazoles was determined at 30.00 ± 0.05 °C in methanesulfonic acid using a Cannon–Ubbelohde dilution viscometer (Size 150).²⁸,⁴⁴

3.2 Synthesis

2-Trichloromethylbenzimidazole (10). This is a known compound,³⁵ but NMR data was not reported. To a cooled suspension of the o-phenylenediamine (9) (5.41 g, 0.05 mol) and glacial acetic acid (100 mL), methyl 2,2,2-trichloroacetimidate (8) (8.82 g, 6.19 mL, 0.05 mol) was added slowly. When the resultant exothermic reaction subsided, the reaction mixture was kept at the room temperature for 10 h. A white powdered 2-trichloromethylbenzimidazole (10) precipitated and was collected by filtration, washed with a small amount of water, and vacuum-dried at 50 °C for 15 h. Yield: 85%. $^1$H NMR (500 MHz, CF$_3$COOD): 7.94 (dd, $J = 6.6, 3.3$ Hz, 2H), 7.85 (dd, $J$ = 6.6, 3.3 Hz, 2H); $^{13}$C NMR (125 MHz, CF$_3$COOD): $\delta = 149.6, 132.4, 131.8, 116.7, 83.6$. ESI-MS ($m$/z): 234 [M − H]$^+$. FTIR (KBr pellet, cm$^{-1}$): 3500–2500 broad (3061, 2983, 2908, 2829, 2724, 2658, 2603, 2478), 1620, 1590, 1448, 1428, 1309, 1278, 1228, 1043, 892, 816, 741, 683, 501.

2,2′-Bibenzimidazole (5). (i) Following Holan’s method:³⁵ o-Phenylenediamine (9) (5.52 g, 0.05 mol) and methyl 2,2,2-trichloroacetimidate (8) (4.40 g, 3.10 mL, 0.025
mol) were kept stirring in methanol (50 mL) at room temperature for 24 h. After the aqueous quenching, the yellow-colored precipitate was filtered, rinsed with water, and vacuum-dried to afford the pure 2,2′-bibenzimidazole (10.5 g, 90%). It melts generally above 360 °C. \(^1\)H NMR (500 MHz, CF\(_3\)COOD): 8.10 (dd, \(J = 6.3, 3.3 \text{ Hz}, 4\)H), 7.92 (dd, \(J = 6.3, 3.3 \text{ Hz}, 4\)H). \(^{13}\)C NMR (125 MHz, CF\(_3\)COOD): \(\delta = 133.9, 133.8, 132.4, 117.0\). FTIR (KBr pellet, cm\(^{-1}\)): 3500–2500 broad (3029, 2949, 2870, 2798, 2750, 2673, 2585), 1616, 1586, 1500, 1397, 1343, 1271, 1235, 1183, 1143, 949, 742.

(ii) Following Fieselmann’s method:\(^{33}\) o-Phenylenediamine (9) (22 g, 0.20 mol) and oxamide (7) (8.81 g, 0.10 mol) were mixed in 20 mL of ethylene glycol, and refluxed with stirring for 24 h. After the solution was cooled, it was added to 400 mL of refluxing water and was filtered while hot to give 13 g. of water-insoluble yellow product. The crude product contained around 10 : 1 molar ratio of 2,2′-bibenzimidazole 5 and its isomer fluoflavin 11 on the basis of NMR spectrum of the crude. The crude mixture was heated in di(ethylene glycol) methyl ether at 140 °C, then filter while hot. The collected solid contained mainly fluoflavin 11 (still contaminated with 12% of 2,2′-bibenzimidazole). The filtrate was set to recrystallize to provide the yellow powder which was mainly 2,2′-bibenzimidazole 5 (mixed with 2.7% of fluoflavin 11). Fluoflavin 11 is soluble in concentrated H\(_3\)PO\(_4\). The pure 11 was obtained by the addition of water into the concentrated H\(_3\)PO\(_4\) solution to precipitate, and then neutralized with 5% NaOH solution. The NMR data of 11 is consistent with that of the literature reported.\(^{34}\) \(^1\)H NMR (500 MHz, CF\(_3\)COOD): 7.45 (dd, \(J = 6.1, 3.1 \text{ Hz}, 4\)H),
7.37 (dd, $J = 6.1$, 3.1 Hz, 4H). $^{13}$C NMR (125 MHz, CF$_3$COOD): $\delta = 144.0$, 131.7, 127.1, 120.1.

**Bis(2,2'-bibenzimidazole)-1.5H$_2$O (14).** To a suspension of 3,3'-diaminobenzidine (6) (1.24 g, 5.8 mmol) and 2-trichloromethylbenzimidazole (10) (3.00 g, 12.7 mmol) in absolute ethanol (50 mL), triethylamine (5.86 g, 58 mmol) was added dropwise. The suspension was stirred at room temperature for 12 h and then refluxed under nitrogen for 36 h. The precipitated bis(2,2'-bibenzimidazole) ([bis(BiBzImH$_2$)]) was collected by filtration and washed with hot glacial acetic acid. Then it was stirred in diluted ammonium hydroxide solution to neutralize the acid residue. The final product was a yellow powder. Yield: 70%. DMF can also be the solvent to replace ethanol. If DMF was used as the solvent, then 10 equiv of absolute ethanol was needed to facilitate the reaction. The reaction in DMF was stirred at room temperature under nitrogen for 5–10 h, and then heated at 75–80 °C for 24 h. The produced dimer was soluble in DMF and was precipitated by adding water dropwise to the DMF solution. The final product was collected by filtration. $^1$H NMR (500 MHz, CF$_3$COOD): $\delta = 8.43$ (s, 2H), 8.29 (d, $J = 8.8$ Hz, 2H), 8.26 (d, $J = 8.8$ Hz, 2H), 8.12 (dd, $J = 6.6$, 3.3 Hz, 4H), 7.94 (dd, $J = 6.6$, 3.3 Hz, 4H). $^{13}$C NMR (125 MHz, CF$_3$COOD): $\delta = 144.0$, 135.3, 134.8, 134.3, 134.1, 133.7, 132.5, 132.3, 118.2, 117.0, 116.1. $^{13}$C NMR (125 MHz, D$_2$SO$_4$) (for comparison with the spectra of trimer, tetramer and polymers): $\delta = 143.1$, 133.0, 132.6, 132.5, 132.3, 132.2, 130.5, 117.5, 116.4, 116.3, 115.3, 115.2. ESI-MS ($m/z$): 467.2 [M + H]$^+$. FTIR (KBr pellet, cm$^{-1}$): 3500–2500
broad (3350, 3203, 3052), 1650, 1619, 1586, 1560, 1520, 1447, 1315, 1276, 809, 740.

Anal. Calcd for C\textsubscript{28}H\textsubscript{18}N\textsubscript{8}\cdot1.5\textsubscript{2}O: C, 68.14; H, 4.29; N, 22.71. Found: C, 67.60; H, 3.79; N, 22.27.

\[(4-(2-(1\textsubscript{H}-Benzo[d]imidazol-2-yl)-1\textsubscript{H}-benzo[d]imidazol-5-yl)benzene-1,2-
diamine)\] (15). 3,3'-Diaminobenzidine (6) (4.00 g, 19 mmol) was dissolved in 200 mL of DMF. 2-Trichloromethylbenzimidazole (10) (2.00 g, 8.6 mmol) was dissolved in 45 mL of DMF and added dropwise to the above solution, followed by addition of absolute ethanol (2.5 mL). Triethylamine (6 mL) was added dropwise to the above solution. The solution was stirred at room temperature for 5 h and heated at 75–80 °C under nitrogen for 7–10 h. The reaction mixture was cooled and filtered to remove the small amount of dark brown impurity. To the filtrate, 150 mL of water was added to precipitate the solid, which was bis(2,2'-bibenzimidazole) ([bis(BiBzImH2)]) (14) (0.40 g, 0.857 mmol, yield 20%). Then to the filtrate of the above solution after 14 was removed by filtration, around 600 mL of water was added to precipitate the compound 15 (1.86 g, 5.46 mmol, yield 63%). In total, 7.17 mmol of 2-trichloromethylbenzimidazole (10) was consumed to form compounds 14 and 15. The overall yield was 83% based on the consumed 2-trichloromethylbenzimidazole. Product 15 was further purified as follows: 100 mg of crude sample was dissolved in 15 mL of DMF, then 30 mL of water was added dropwise to precipitate the desired product. The collected solid was washed with 300 mL of water (3×) to remove DMF and dried in a vacuum oven for 20 h at 60 °C to afford the final pure product 15 as a yellow powder. \(^{1}\text{H} \text{NMR} (500 \text{ MHz, CF}_3\text{COOD})\): \(\delta\)
= 8.33 (s, 1H), 8.26 (d, J = 1.7 Hz, 1H), 8.24 (d, J = 8.8 Hz, 1H), 8.12 (dd, J = 8.8, 1.7 Hz, 1H), 8.09 (dd, J = 6.6, 3.3 Hz, 2H), 8.09 (d, J = 8.3 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.92 (dd, J = 6.6, 3.3 Hz, 2H). $^{13}$C NMR (125 MHz, CF$_3$COOD): $\delta$ = 145.6, 142.0, 135.6, 134.9, 134.6, 134.0, 133.7, 132.9, 132.5, 131.4, 129.6, 127.9, 126.8, 126.0, 118.3, 117.0, 115.7. ESI-MS (m/z): 341 [M + H]$^+$. FTIR (KBr pellet, cm$^{-1}$): 3500–2500 broad (3345, 3177, 3058, 2970), 1621, 1587, 1524, 1424, 1399, 1337, 1274, 805, 766, 748, 738. Anal. Calcd for C$_{20}$H$_{16}$N$_6$·H$_2$O: C, 67.02; H, 5.06; N, 23.45. Found: C, 67.65; H, 4.75; N, 23.89.

2-(1H-benzo[d]imidazol-2-yl)-5-(1H-benzo[d]imidazol-5-yl)-1H-benzo[d]imidazole (16). The following is the procedure for the formation of the compound 16 as a byproduct. 3,3'-Diaminobenzidine (6) (4.00 g, 19 mmol) was dissolved in 150 mL of DMF. 2-Trichloromethylbenzimidazole (10) (1.76 g, 7.50 mmol) was dissolved in 20 mL of DMF and added dropwise to the above solution, followed by the addition of absolute ethanol (3 mL, around 6.8 equiv). Triethylamine (7 mL, around 6.7 equiv) was added dropwise to the above solution. The solution was stirred at room temperature for 6 h and heated at 130 °C under nitrogen for 44 h. The reaction mixture was cooled and filtered to remove the small amount of dark brown impurities. To the filtrate, 200 mL of water was added to precipitate the solid, which was the bis(2,2'-bibenzimidazole) (14) (0.300 g, 0.643 mmol). Then, to the filtrate of the above solution after 14 was removed by filtration, around 200 mL of water was added dropwise to precipitate the compound 16 (1.17 g, 3.34 mmol). Then, to the
filtrate of the above solution after 16 was removed by filtration, around 200 mL of water was added dropwise to precipitate the compound 15 (1.85 g, 5.43 mmol). In total, 6.73 mmol of 2-trichloromethylbenzimidazole (10) was consumed to form compounds 14, 15 and 16. The overall yield was 89% based on the consumed 2-trichloromethylbenzimidazole (10). Product 16 was further purified by dissolving 100 mg of the crude sample in 15 mL of DMF. Then 20 mL of water was added dropwise to precipitate the desired product. The product was washed with 300 mL of water (3×) to remove DMF and dried in a vacuum oven at 70 °C for 20 h. The final product 16 was a beige-colored powder. $^1$H NMR (500 MHz, CF$_3$COOD): $\delta$ = 9.25 (s, 1H), 8.35 (s, 1H), 8.25 (d, $J$ = 8.6 Hz, 1H), 8.24 (s, 1H), 8.20 (d, $J$ = 8.6 Hz, 1H), 8.11 (dd, $J$ = 6.1, 3.1 Hz, 2H), 8.10 (d, $J$ not determined due to the overlap, 2H), 7.93 (dd, $J$ = 6.1, 3.1 Hz, 2H). $^{13}$C NMR (125 MHz, CF$_3$COOD): $\delta$ = 144.7, 142.0, 141.4, 141.3, 135.0, 134.7, 134.0, 133.9, 133.7, 132.7, 132.5, 132.4, 132.3, 132.2, 130.1, 117.3, 117.0, 115.8. ESI-MS (m/z): 351 [M + H]$^+$ FTIR (KBr pellet, cm$^{-1}$): 3500–2500 broad (3048, 2968, 2887, 2794), 1398, 1377, 1344, 1282, 948, 812, 738. Anal. Calcd for C$_{21}$H$_{14}$N$_6$: C, 71.99; H, 4.03; N, 23.99. Found: C, 71.38; H, 4.08; N, 23.60.

**Tris(2,2′-bibenzimidazole) (17).** Compound 15 (0.20 g, 0.588 mmol) was suspended in 20 mL of absolute ethanol and stirred at room temperature for 1 h. Methyl 2,2,2-trichloroacetimidate (8) (0.060 g, 0.294 mmol, 0.04 mL) was added by syringe dropwise. The above suspension was stirred at room temperature for 23 h and filtered to collect the solid. The crude product was purified by heating in 50 mL of ethylene glycol
at 145 °C for 24 h to remove the soluble impurity. After the suspension was cooled to room temperature, the brownish yellow trimer was collected by filtration, washed with water, and dried under vacuum at 60 °C for 40 h. Yield: 72%. 

$^1$H NMR (500 MHz, CF$_3$COOD): \( \delta = 8.43 \) (s, 4H), \( 8.29 \) (dd, \( J = 8.8 \) Hz, 3.3 Hz, 4H), \( 8.26 \) (dd, \( J = 8.8 \) Hz, 3.3 Hz, 4H), \( 8.11 \) (dd, \( J = 6.6 \) Hz, 3.3 Hz, 4H), 7.93 (dd, \( J = 6.6 \) Hz, 3.3 Hz, 4H). 

$^{13}$C NMR (125 MHz, D$_2$SO$_4$; 17 dissolves well in D$_2$SO$_4$, but does not dissolve well in CF$_3$COOD, so the $^{13}$C NMR spectrum was taken in D$_2$SO$_4$): \( \delta = 143.2, 143.0, 133.1, 133.0, 132.5, 132.4, 132.3, 132.2, 131.8, 130.6, 117.4, 116.3, 115.3 \). 

ESI-MS (\( m/z \)): 699 \([M + H]^+\) (CF$_3$COOH as the solvent for ESI). 

FTIR (KBr pellet, cm$^{-1}$): 3500–2500 broad (3402, 3057, 2965, 2858, 2774), 1622, 1585, 1422, 1396, 1372, 1335, 1280, 947, 810, 783, 745. 

Anal. Calcd for C$_{42}$H$_{26}$N$_{12}$·2H$_2$O: C, 68.65; H, 4.12; N, 22.88. Found: C, 68.85; H, 3.88; N, 21.91.

**Bis(2-trichloromethylbenzimidazole) (18).** To a solution of 3,3′-diaminobenzidine (6) (2.14 g, 0.01 mol) in glacial acetic acid (50 mL), methyl 2,2,2-trichloroacetimidate (8) (4.41 g, 3.10 mL, 0.025 mol) was added dropwise. The reaction mixture was kept at the room temperature for around 15 h. The precipitated pale yellow product bis(trichloride) 18 was collected by filtration and washed with a small amount of water. Yield: 85%. 

$^1$H NMR (500 MHz, DMSO-\(d_6\)): \( 7.93 \) (s, 2H), \( 7.78 \) (d, \( J = 8.7 \) Hz, 2H), \( 7.71 \) (d, \( J = 8.7 \) Hz, 2H). 

$^{13}$C NMR (125 MHz, DMSO-\(d_6\)): \( \delta = 151.2, 138.8, 137.8, 136.9, 123.7, 116.9, 114.2, 88.7 \). 

$^{13}$C NMR (125 MHz, CF$_3$COOD): \( \delta = 150.8, 143.5, 133.3, 132.5, 131.6, 117.8, 116.1, 83.5 \). 

ESI-MS (\( m/z \)): 431 [M – Cl + H]$^+$.

FTIR
(KBr pellet, cm$^{-1}$): 3500–2500 broad (3427, 3075, 2916, 2823), 1626, 1584, 1419, 1293, 1206, 1028, 876, 815, 776, 679, 514. Anal. Calcd for C$_{16}$H$_8$Cl$_6$N$_4$: C, 40.98; H, 1.72; N, 11.95. Found: C, 40.62; H, 1.62; N, 11.82.

**Tetra(2,2'-bibenzimidazole)-2.5H$_2$O (19).** To a suspension of compound 15 (0.700 g, 2.05 mmol) in 40 mL of DMF, bis(trichloride) 18 (0.385 g, 0.82 mmol) and absolute ethanol (0.50 mL) were added, followed by the dropwise addition of triethylamine (0.83 g, 8.20 mmol, 1.15 mL). The suspension was stirred at room temperature for 10 h and then heated at 75 °C under nitrogen for 34 h. The precipitated yellow tetra(2,2'-bibenzimidazole) ([tetra(BiBzImH$_2$)]) (19) was collected by filtration and washed with water. Then it was heated in 90 mL of ethylene glycol or DMF at around 130 °C for 24 h to remove the soluble impurities. After the suspension was cooled to room temperature, the product was collected by filtration and washed with 300 mL of water ($3 \times$). The final product was a brownish yellow powder after vacuum-drying at 70 °C for 40 h. Yield: 60%. The NMR solvent was a combination of CF$_3$COOD/D$_2$O, since [tetra(BiBzImH$_2$)] does not dissolve well in CF$_3$COOD. $^1$H NMR (500 MHz, CF$_3$COOD/D$_2$O): δ = 8.47 (s, 2H), 8.45 (s, 2H), 8.44 (s, 2H), 8.25 (multiplet, 12H), 8.11 (dd, $J = 6.6$, 3.3 Hz, 4H), 7.91 (dd, $J = 6.6$, 3.3 Hz, 4H). $^{13}$C NMR (125 MHz, CF$_3$COOD/D$_2$O) (some peaks are overlapped and show multiplets, and some peaks are overlapped with CF$_3$COOD between δ 120–113 ppm): δ = 143.6, 135.2, 135.0, 134.9, 134.4, 134.3, 133.9, 133.7, 132.1, 131.8, 116.8. $^{13}$C NMR (125 MHz, D$_2$SO$_4$, the tetramer dissolves well in D$_2$SO$_4$, but does not dissolve well in
CF$_3$COOD, so $^{13}$C NMR spectrum was taken in D$_2$SO$_4$ for comparison): $\delta = 143.3$, 143.2, 133.2, 133.1, 132.7, 132.6, 132.5, 132.4, 132.0, 130.6, 117.6, 116.5, 116.4, 115.5, 115.3. ESI-MS ($m/z$): 931 [M + H]$^+$ (CF$_3$COOH as solvent for ESI). FTIR (KBr pellet, cm$^{-1}$): 3500–2500 broad (3411, 3058, 2970, 2863, 2779), 1622, 1585, 1422, 1396, 1372, 1335, 1280, 947, 814, 783, 749. Anal. Calcd for C$_{56}$H$_{34}$N$_{16}$·2.5H$_2$O: C, 68.91; H, 4.03; N, 22.96. Found: C, 69.09; H, 3.69; N, 22.81.

**Poly(2,2′-bibenzimidazole) (4a).** 3,3′-Diaminobenzidine (6) was purified following the known procedures by making the tetrahydrochloride salt of it and regenerating it into the pure 3,3′-diaminobenzidine by using 5% NaOH solution.$^{27}$ The slightly pink of 3,3′-diaminobenzidine (6) (500 mg, 2.33 mmol) was suspended in 50 mL of absolute ethanol and the solution was degassed under nitrogen for 10 min. Methyl 2,2,2-trichloroacetimidate (8) (411 mg, 0.288 mL, 2.33 mmol) was added dropwise. The reaction suspension was stirred at room temperature for 26 h and then refluxed for 82 h. After the suspension was cooled to room temperature, the precipitated orange brown polymer was collected by filtration. Then it was stirred in 300 mL of deionized water (3×) for around 15 h each time to remove solvent ethanol. The final orange brown polymer was collected by filtration and dried under vacuum at 70 °C for 80 h. Yield: 70%. It is partially soluble in concentrated sulfuric acid, methanesulfonic acid, and HCOOH and not soluble in CF$_3$COOH, DMAC, DMF, DMSO, and NMP. The NMR spectra were taken in D$_2$SO$_4$, due to the low solubility in CF$_3$COOD. $^1$H NMR (500 MHz, D$_2$SO$_4$): $\delta = 8.48$ (s), 7.92 (s, br), 7.85–7.70 (multiplet), 7.58 (weak...
multiplet). $^{13}$C NMR (125 MHz, D$_2$SO$_4$), signals were relatively weak compared to those of the $^{13}$C NMR of polymer 4d, due to the lower solubility of 4a: $\delta =$ 143.3 (br), 133.1, 132.5 (br), 131.8, 131.4, 131.0, 117.5 (br), 115.3 (br). FTIR (KBr pellet, cm$^{-1}$): 3500–2500 (broad), 1624, 1585, 1420, 1394, 1275, 947, 804. Anal. Calcd for (C$_{14}$H$_8$N$_4$H$_2$O)$_n$: C, 67.19; H, 4.03; N, 22.39. Found: C, 66.53; H, 3.73; N, 21.95.

**Poly(2,2′-bibenzimidazole) (4b).** The slightly pink, purified 3,3′-diaminobenzidine (6) (700 mg, 3.27 mmol) was dissolved in 50 mL of DMF and the solution was degassed under nitrogen for 15 min. Methyl 2,2,2-trichloroacetimidate (8) (576 mg, 0.404 mL, 3.27 mmol) was added dropwise, followed by the addition of absolute ethanol (1.9 mL, 33 mmol). The deep orange brown reaction solution was stirred at room temperature for 54 h and then heated at 60–70 °C for 40 h. After the mixture was cooled to room temperature, the precipitated orange brown polymer was collected by filtration. Then it was stirred in 300 mL of deionized water (3×) for around 1 day each time to remove solvent DMF. The final orange brown polymer was collected by filtration, and dried under vacuum at 70 °C for 80 h. Yield: 60%. It is partially soluble in concentrated sulfuric acid, methanesulfonic acid, and HCOOH and not soluble in CF$_3$COOH, DMAC, DMF, DMSO and NMP. The NMR spectra were taken in D$_2$SO$_4$, due to the low solubility in CF$_3$COOD. $^1$H NMR (500 MHz, D$_2$SO$_4$): $\delta =$ 8.46 (s), 7.92–7.57 (multiplet, br). $^{13}$C NMR (125 MHz, D$_2$SO$_4$): not obtained due to the low solubility. FTIR (KBr pellet, cm$^{-1}$): 3500–2500 (broad), 1624, 1585, 1420,
Poly(2,2′-bibenzimidazole) (4c). The slightly pink, purified 3,3′-diaminobenzidine (6) (365.5 mg, 1.706 mmol) was dissolved in 50 mL of DMF and the solution was degassed under nitrogen for 15 min, followed by the addition of absolute ethanol (2 mL, 34 mmol). Bis(trichloride) (18) (800.0 mg, 1.706 mmol) was added in one portion. Then triethylamine (4.75 mL, 34 mmol) was added dropwise to the above solution over 10 min. (After around 4 equiv of triethylamine was added, the reaction mixture became gel-like and difficult to stir, with the formation of precipitate.) The color of the mixture was brownish orange. The reaction mixture was stirred at room temperature for 8 h, then heated at 70–75 °C. The precipitate was almost completely dissolved after 8 h at 75 °C. The mixture was kept at 70–75 °C for totally 72 h and then cooled down. The orange polymer was precipitated out from the reaction mixture by the addition of deionized water, and collected by filtration. Then it was stirred in 300 mL of deionized water (3×) for around 1 day each time to remove DMF. The final orange powdered polymer was collected by filtration and dried under vacuum at 70 °C for 80 h. Yield 83%. It is soluble in concentrated sulfuric acid, methanesulfonic acid, HCOOH, CF₃COOH, DMAC, DMF, DMSO, and NMP. ¹H NMR (500 MHz, D₂SO₄): δ = 8.49 (s), 7.93–7.50 (multiplet, br). ¹³C NMR (125 MHz, D₂SO₄): δ = 143.2, 140.2 (br, weak), 133.1, 132.6 (br), 132.4, 131.9, 131.4, 127.8, 117.6, 116.6, 115.3. FTIR (KBr pellet, cm⁻¹): 3500–2500 broad (3060), 1624, 1585, 1420, 1379, 1334, 1283, 946, 803.

**Poly(2,2′-bibenzimidazole) (4d).** The slightly pink, purified 3,3′-diaminobenzidine (6) (365.5 mg, 1.706 mmol) was dissolved in 50 mL of DMF and the solution was degassed under nitrogen for 15 min, followed by the addition of absolute ethanol (2 mL, 34 mmol). Bis(trichloride) (18) (800.0 mg, 1.706 mmol) was added in one portion. Then triethylamine (4.75 mL, 34 mmol) was added dropwise to the above solution over 10 min. (After around 4 equiv of triethylamine was added, the reaction mixture became gel-like and difficult to stir, with the formation of precipitate. The color of the mixture was brownish orange.) The reaction mixture was stirred at room temperature for 7 h and then heat at 75–80 °C, the precipitate was almost completely dissolved after 8 h at 78 °C. The reaction was maintained at 75–80 °C for 20 h, then heated at 120–130 °C. After around 20 h, a gray yellow precipitate formed. The mixture was heated at 120–130 °C for an additional 20 h, then heated at 145–50 °C for 46 h. After the mixture was cooled to room temperature, the precipitated greenish yellow polymer was obtained by filtration. Then it was stirred in 300 mL of water (3×) for around 1 day each time to remove DMF. The final yellow powdered polymer was collected by filtration and dried under vacuum at 70 °C for 80 h in 65% yield. It is soluble in concentrated sulfuric acid and methanesulfonic acid; partially soluble in CF₃COOH, and HCOOH and not soluble in DMAC, DMF, DMSO, and NMP. The NMR solvent was D₂SO₄, due to the low solubility in CF₃COOD. $^1$H NMR (500 MHz,
D\textsubscript{2}SO\textsubscript{4}): \(\delta = 8.48\) (s), 7.93 (s, br), 7.85–7.70 (multiplet), 7.58 (weak multiplet). \(^{13}\)C NMR (125 MHz, D\textsubscript{2}SO\textsubscript{4}): \(\delta = 143.2\) (br), 140.3 (br, weak), 133.1, 132.6 (br), 132.4, 131.9, 131.4, 131.0, 129.3, 117.6, 116.7, 115.3, 114.8. FTIR (KBr pellet, cm\(^{-1}\)): 3500–2500 broad (3060), 1624, 1585, 1420, 1379, 1334, 1283, 946, 803. Anal. Calcd for (C\(_{14}\)H\(_{8}\)N\(_{4}\)\centerdot H\(_2\)O): C, 67.19; H, 4.03; N, 22.39. Found: C, 67.87; H, 3.54; N, 22.70.

The procedures for the initial attempts on the synthesis of poly(2,2\textsuperscript{'}-bibenzimidazole)s using the condensation reactions between 3,3\textsuperscript{'}-diaminobenzidine (6) and oxamide (7) or oxalic acid in polyphosphoric acid in the presence of phosphorus pentoxide are listed below for comparison. Both of the polymer products met with limited success when using them for further metal complexation. The possible reasons are: 1) The polymer 4e is not soluble in the high boiling point solvents, rendering the difficulty in the metal complexation. This is probably due to the high molecular weight. The molecular weight was not determined due to the low solubility. 2) The polymerization reaction between 3,3\textsuperscript{'}-diaminobenzidine (6) and oxalic acid provided a low molecular weight compound 4f and the starting material 3,3\textsuperscript{'}-diaminobenzidine (6). The polymer was not formed due to the decomposition of oxalic acid.

**Poly(2,2\textsuperscript{'}-bibenzimidazole) (4e).** The slightly pink, purified 3,3\textsuperscript{'}-diaminobenzidine (6) (3.00 g, 14.0 mmol), polyphosphoric acid (PPA) (83.3%, 29.56 g), oxamide (7) (1.23 g, 14.0 mmol) and P\(_2\)O\(_5\) (4.80 g, 34 mmol) were added into a 3-
neck round bottom flask. The mixture was thoroughly degassed by repeated evacuations and flushes with N₂ for 1 h. Under a positive N₂ pressure, a mechanic stirrer was set up. The mixture was heated to 50 °C and kept at this temperature for 5 h. Then it was heated to 120 °C slowly in 2 h. The mixture turned dark brown. It was kept at this temperature for 12 h. The reaction temperature was increased to 220 °C slowly in 4 h and held at this temperature for 68 h. The mixture turned to very viscous dope, with orange red color, and eventually very deep red color. The polymerization dope in PPA was cooled, and precipitated in water. PPA was extracted with deionized water for 1 day, and then the mixture was filtered to collect the solid. The deep red crude polymer was treated with 1 liter of aqueous solution of 0.30 M NH₄OH (2x) for 2 days. The polymer turned black. Then the polymer was washed with a large amount of water to ensure that it was free of any residual acid PPA. The solid was dried under vacuum at 60 °C for 48 h to give a black solid in a yield of 100%. ¹H NMR (500 MHz, in D₂SO₄, very deep red solution): a broad peak in the region of δ = 6.5–8.0, centering at δ = 7.0. FTIR (KBr pellet, cm⁻¹): 3500–2500 broad (3325, 3198, 3042), 1608, 1581, 1443, 1397, 1271, 1115, 869, 806. Anal. Calcd for (C₁₄H₈N₄⋅H₂O)ₙ: C, 67.18; H, 4.03; N, 22.39. Found: C, 68.65; H, 3.33; N, 22.81. UV–vis (in methanesulfonic acid): λ_max at 535 nm, with a shoulder at 496 nm; in the UV region: 274 nm.

**Poly(2,2'-bibenzimidazole) (4f).** The slightly pink, purified 3,3'-diaminobenzidine (6) (8.00 g, 37.3 mmol), and polyphosphoric acid (PPA) (83.3%, 55.79 g) were added to a three-neck round bottom flask, and thoroughly degassed by
repeated evacuations and flushes with N\textsubscript{2} for 1 h. Under a positive N\textsubscript{2} pressure, a mechanic stirrer was set up, and oxalic acid (3.36 g, 37.3 mmol) was added. Then the mixture was slowly heated to 114 °C and kept at this temperature for 3 h. The light gray-brown mixture foamed up, probably due to the decomposition of oxalic acid. Then it was cooled down to 95 °C, and P\textsubscript{2}O\textsubscript{5} (23 g, 162 mmol) was added under a positive N\textsubscript{2} pressure to compensate the water released from the condensation reaction. Then the mixture was heated to 124 °C, and kept at this temperature for 12 h; then heated to 144 °C, and held at this temperature for 11 h. The reaction temperature was eventually raised to 200 °C and was allowed to proceed at this temperature for 49 h. The mixture turned to very viscous dope, with bright orange red color. The polymerization dope in PPA was cooled, and precipitated in water. PPA was extracted with water for 3 days, and then the mixture was filtered to collect the solid. The bright orange red polymer was treated with 1 liter of aqueous solution of 0.30 M NH\textsubscript{4}OH (2x) for 2 days. The polymer turned greenish black color. Then the polymer was washed with a large amount of water to ensure that it was free of any residual acid PPA. The polymer was dried under vacuum at 60 °C for 40 h to give a greenish black solid in 25% yield. \textsuperscript{1}H NMR (500 MHz, in D\textsubscript{2}SO\textsubscript{4}, dark brown solution): δ = 7.00–7.60 (sharp multiplet). FTIR (KBr pellet, cm\textsuperscript{-1}): 3500–2500 broad (3342), 1615, 1584, 1475, 1397, 1281, 1123, 806, 747. Anal. Calcd for (C\textsubscript{14}H\textsubscript{8}N\textsubscript{4}·2.5H\textsubscript{2}O)\textsubscript{n}: C, 60.63; H, 4.73; N, 20.21. Found: C, 60.88; H, 4.60; N, 19.85. UV–vis (in methanesulfonic acid): λ\textsubscript{max} at 461 nm, with two shoulders at 430 and 495 nm; in the UV region: 270 nm.
The NMR data of 3,3'-diaminobenzidine (6) in D$_2$SO$_4$ is listed here for comparison. $^1$H NMR (500 MHz, in D$_2$SO$_4$): $\delta = 7.53$ (d, $J = 8.3$ Hz, 2H), 7.48 (s, 2H), 7.43 (d, $J = 8.3$ Hz, 2H). FTIR (KBr pellet, cm$^{-1}$): 3388, 3357, 3302, 3182, 1634, 1575, 1499, 1410, 1276, 1251, 1164, 1088, 939, 876, 823, 762, 719.
PART II

MULTINUCLEAR RU COMPLEXES OF BIBENZIMIDAZOLE OLIGOMERS
CHAPTER 4
INTRODUCTION

Polynuclear metal complexes based on ruthenium(II) and/or osmium(II) polypyridine building blocks constitute a class of compounds which has attracted the attention of many researchers in the last decade and continue to be subject to an ever increasing research effort. Primarily this is because the building blocks exhibit an unusual combination of properties rarely found simultaneously in other compounds.

Ru(II) and Os(II) form low-spin octahedral complexes with strong-field ligands such as bipyridine and phenanthroline. The stability of these complexes is presumably enhanced by the symmetrical $t_{2g}^6$ configuration. The relevant properties of Ru(II) polypyridine complexes are: (i) good stability of the ground as well as the excited and redox states; (ii) absorption in the visible region, due to intense spin-allowed metal-to-ligand charge transfer (MLCT) bands; (iii) relatively long-lived (typically in the microsecond time range) and luminescent excited states; (iv) reversible metal-centered oxidation and ligand-centered reduction processes at accessible potentials; (v) tunability of all the properties. This unique combination of photophysical and redox properties has allowed Ru(II) polypyridine complexes to be perfect candidates for the synthesis of new redox active metallopolymers.
In this part, the synthesis and characterization of the multinuclear Ru complexes based on the oligomeric bibenzimidazoles using \([\text{Ru(bpy)}_2]^{2+}\) as the building block are discussed. The following molecular orbital approximation is discussed first to understand the properties of the Ru complexes.

### 4.1 Localized Molecular Orbital Approximation

The spectroscopic, redox, and kinetic properties of transition metal complexes are usually discussed with the assumption that the ground state, the excited states, and the redox species can be described in a sufficiently approximate way by localized molecular orbital configurations.\(^{45,47,49-55}\) To better understand this point, it is convenient to make reference to schematic molecular orbital (MO) diagrams shown in Figure 4.1, which represents the case of an octahedral complex. In this very simplified diagram, each MO is labeled as metal (M) or ligand (L) according to its predominant localization. Thus, for example, the low-energy \(\sigma\)-bonding MO's, which result from the combination of metal and ligand orbitals of appropriate symmetry, are labeled L since they receive the greatest contribution from the ligand orbitals. In the ground electronic configuration of transition metal complexes in their usual oxidation states, the \(\sigma_L\) and \(\pi_L\) orbitals are completely filled, the \(\pi_M\) orbitals are either partially or completely filled, and the higher orbitals are usually empty. Light absorption and redox processes change the orbital population, and each excited or redox state is assumed to be described by a single MO configuration.
4.2 Classification of the Excited States in Mononuclear Ru Complexes

The assignment of the various bands which appear in the absorption spectra of transition metal complexes is often a very difficult problem because the absorption spectra reflect the complexity of the electronic structure of these molecules. By using a diagram shown in Figure 4.1, it is possible to make a classification of the various electronic transitions according to the localization of the MO's involved. Specifically, we may identify three fundamental types of electronic transitions: \(45,47,53-55\)

(i) Transitions between MO's predominantly localized on the central metal, usually called metal-centered (MC), ligand-field, or \(d-d\) transitions. For example, promotion of an electron from \(t_{2g}\) to \(e_g\) orbitals gives rise to a weak (Laporte forbidden)
absorption band ($\varepsilon = \text{ca. } 100 \text{ M}^{-1}\cdot\text{cm}^{-1}$); (ii) transitions between MO's predominantly localized on the ligands, usually called *ligand-centered* (LC) or intraligand transitions. For example, the transitions within the ligand $\pi$-bonding orbital to the $\pi^*$-antibonding orbital, labeled $\pi \rightarrow \pi^*$ transitions, usually lie at high energies and are substantially ligand in character; (iii) transitions between MO's of different localization, which cause the displacement of the electronic charge from the ligands to the metal or *vice versa*. These transitions are called *charge-transfer* (CT) transitions and, more specifically, can be distinguished into *ligand-to-metal charge-transfer* (LMCT) and *metal-to-ligand charge-transfer* (MLCT) transitions. For example, excitation of a metal $t_{2g}$ electron to $\pi^*$-antibonding orbital on the ligand gives rise to $d \rightarrow \pi^*$ states. These transitions have significant absorptions in the visible region ($\varepsilon = \text{ca. } 20,000\text{–}25,000 \text{ M}^{-1}\cdot\text{cm}^{-1}$).\textsuperscript{53}

Less frequently encountered types of transitions (not shown in Figure 4.1) are those from a metal-centered orbital to a solvent orbital (*charge-transfer to solvent, CTTS*), or between two orbitals predominantly localized on different ligands of the same metal center (*ligand-to-ligand charge-transfer, LLCT*).

It should also be noticed that the energy ordering of the various orbitals may be different from that shown in Figure 4.1. For example, in the case of $[\text{Ru(bpy)}_3]^{2+}$ the $\pi^*_{\text{L}}$ orbital is thought to be lower in energy than the $\sigma^*_{\text{M}}$ orbital.

### 4.3 Redox Behavior of Mononuclear Ru Complexes

In the localized MO approximation, oxidation and reduction processes are viewed as metal or ligand centered.\textsuperscript{51,56,57} The highest energy occupied molecular orbital
(HOMO) is most usually metal centered, whereas the lowest unoccupied molecular orbital (LUMO) is either metal or ligand centered, depending on the relative energy ordering. When the ligand field is sufficiently strong and/or the ligands can be easily reduced, reduction takes place on the ligand. When the ligand field is weak and/or the ligands cannot be easily reduced, the lowest empty orbital can be metal centered.

Typical examples of well-behaved compounds are the Ru$^{II}$-polypyridine complexes. Their oxidation is metal centered and leads to Ru(III) compounds (low-spin $\pi_M(t_{2g})^5$ configuration) which are inert to ligand substitution:

$$[\text{Ru}^{III}(L)_3]^{3+} + e^- \rightarrow [\text{Ru}^{III}(L)_3]^{2+}$$  \hspace{1cm} (eq. 4.1)

Reduction of the Ru$^{II}$-polypyridine complexes takes place on a $\pi^*$ orbital of the polypyridine ligands. Therefore the reduced form, keeping the low-spin $\pi_M(t_{2g})^6$ configuration, is usually inert and the reduction process is reversible:

$$[\text{Ru}^{II}(L)_3]^{2+} + e^- \rightarrow [\text{Ru}^{II}(L)_2(L^-)]^+$$  \hspace{1cm} (eq. 4.2)

The added electron is localized on a single ligand.$^{51,58,59}$ Several reduction steps can often be observed in the accessible potential range. For example, in DMF at $-54^\circ$C, up to six CV waves can be observed for [Ru(bpy)$_3$]$^{2+}$ in the potential range between $-1.33$ and $-2.85$ V (vs SCE), which are assigned to successive first and second reduction of the three bpy ligands yielding a complex that can be formulated as $[\text{Ru}^{2+}(bpy^{2-})_3]^{4-}$.$^{60}$

In Chapter 5, the synthesis and characterization of the multinuclear Ru complexes based on the oligomeric bibenzimidazoles will be discussed.
CHAPTER 5
RESULTS AND DISCUSSION

5.1 Bibenzimidazole-Based Ru Complexes [Ru(bpy)₂(BiBzImH₂)](PF₆)₂ (20), [Ru(bpy)₂(BiBzIm)] (21) and [Ru(bpy)₂(BiBzIm)Ru(bpy)₂](PF₆)₂ (22)

5.1.1 Synthesis of [Ru(bpy)₂(BiBzImH₂)](PF₆)₂ (20), [Ru(bpy)₂(BiBzIm)] (21) and [Ru(bpy)₂(BiBzIm)Ru(bpy)₂](PF₆)₂ (22)

Synthesis of the Ru complexes based on 2,2'-bibenzimidazole (5) are summarized in Scheme 5.1 following the reported procedures.¹⁶,²⁰ The reaction of Ru(bpy)₂Cl₂ with 2,2'-bibenzimidazole (5) in ethanol/water (1:1 v/v) gave the desired mix-ligand complex [Ru(bpy)₂(BiBzImH₂)](PF₆)₂ (20). The acidity of the bibenzimidazole ligand increases upon the coordination with the ruthenium ion. This is consistent with the ease of deprotonation of the coordinating ligand. The pKₐ values of [Ru(bpy)₂(BiBzImH₂)]²⁺ in 50% acetonitrile/water mixture have been reported.¹⁷,²⁰ The pKₐ₁ and pKₐ₂ are 5.74 ± 0.05 and 10.51 ± 0.05 at 25 °C, respectively (equation 5.1).

\[
\begin{align*}
[Ru(bpy)₂(BiBzImH₂)]^{2+} & \overset{pKₐ₁}{\underset{H^+}{\rightleftharpoons}} [Ru(bpy)₂(BiBzImH)]^+ \\
[Ru(bpy)₂(BiBzImH)]^+ & \overset{pKₐ₂}{\underset{H^+}{\rightleftharpoons}} [Ru(bpy)₂(BiBzIm)] \\
\text{(eq. 5.1)}
\end{align*}
\]
Deprotonation of the complex 20 in methanol with sodium methoxide gave rise to a purple suspension. The purple solid was isolated as the neutral complex [Ru(bpy)$_2$(BiBzIm)] (21).

The fully deprotonated complex 21 may further act as a bidentate ligand. It was complexed with another equivalent of Ru(bpy)$_2$Cl$_2$ to give binuclear ruthenium complex [Ru(bpy)$_2$(BiBzIm)Ru(bpy)$_2$](PF$_6$)$_2$ (22).

Scheme 5.1 Synthesis of Ru Complexes 20–22
5.1.2 UV−vis Properties of [Ru(bpy)$_2$(BiBzImH$_2$)]($PF_6$)$_2$ (20) and [Ru(bpy)$_2$(BiBzIm)] (21)

The UV−vis spectral comparisons are illustrated in Figure 5.1, and the accumulated data are summarized in Table 5.1. The optical transitions have been separated into those related to metal-to-ligand charge transfer (MLCT) transitions ($d\pi−\pi^*$) and those characteristic to intraligand $\pi−\pi^*$ transitions. For the mix-ligand complex 20, it is difficult to make assignments related to the specific ligand involved in the transition. The optical transitions are often the overlapping bands and difficult to deconvolute into their components. The low-energy maxima at 463 nm is more likely related to $d\pi−\pi^*$ (bpy) due to the fact that coordinated bpy rather than the coordinated BiBzImH$_2$ is reduced electrochemically. The transitions located at 328 and 347 nm are assigned as $\pi−\pi^*$ (BiBzImH$_2$) and the 290-nm band is assigned as $\pi−\pi^*$ (bpy). The far−UV bands appear to be related to transitions involving both ligands. Compared with the MLCT of [Ru(bpy)$_3$]$^{2+}$ at 452 nm, the MLCT transition energies of [Ru(bpy)$_2$L]$^{2+}$ decrease in the order of L = bpy > BiBzImH$_2$, which is consistent with the $\pi$-donor ability of the imidazole ligands. A stronger $\pi$-donor bibenzimidazole ligand increases the electron density on the metal, which results in the decrease of the MLCT band energies.
Figure 5.1 UV−vis Spectra of [Ru(bpy)$_2$(BiBzImH$_2$)](PF$_6$)$_2$ (20), [Ru(bpy)$_2$(BiBzIm)] (21) and [Ru(bpy)$_2$(BiBzIm)Ru(bpy)$_2$](PF$_6$)$_2$ (22) in CH$_3$CN

Figure 5.2 UV−vis Spectra of Stepwise Deprotonation of [Ru(bpy)$_2$(BiBzImH$_2$)](PF$_6$)$_2$ (20) in CH$_3$CN by Adding NaOCH$_3$/CH$_3$OH Solution

The stepwise deprotonation of [Ru(bpy)$_2$(BiBzImH$_2$)](PF$_6$)$_2$ (20) at various pH’s has been reported previously.$^{20}$ In our study, the complex 20 was deprotonated by the stoichiometric titration with NaOCH$_3$ as shown in Figure 5.2. After the addition of 0.5 and 1 equivalents of NaOCH$_3$, the MLCT transition red shifted to 500 nm and 506
nm, respectively. Two equivalents of NaOCH$_3$ make the MLCT transition red shifted to 512 nm, with the peak at 543 nm growing up. In total, four equivalents of NaOCH$_3$ was added to ensure the fully deprotonation of the complex. The results indicate that the dication of 20 in solution undergoes two successive deprotonations to exist as an equilibrium mixture with the monocation (20a) and neutral species (21) as shown in Scheme 5.2. Upon the fully deprotonation, the lowest energy MLCT of the complex [Ru(bpy)$_2$(BiBzIm)] (21) red shifted to 543 nm, with the lower intensity.

![Scheme 5.2 Stepwise Deprotonation of Ru Complex 20](image-url)
Table 5.1 UV–vis Absorption Spectral Data for Ru Complexes (20–26) Based on Bibenzimidazole Oligomers in CH$_3$CN at 298 K ($\lambda$, nm ($\epsilon$, M$^{-1}$·cm$^{-1}$))

<table>
<thead>
<tr>
<th>Ru Complex</th>
<th>$\pi - \pi^*$ (bpy)</th>
<th>$\pi - \pi^*$ (BiBzImH$_2$)</th>
<th>$d\pi - \pi^*$ (bpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)$_2$(BiBzImH$_2$)]$^{2+}$ (20)$^{a,b}$</td>
<td>240 (39375)</td>
<td>290 (63125)</td>
<td>328 (37500)</td>
</tr>
<tr>
<td>[Ru(bpy)$_2$(BiBzIm)] (21)$^a$</td>
<td>243 (55125)</td>
<td>295 (54688)</td>
<td>333 (30425)</td>
</tr>
<tr>
<td>[(Ru(bpy)$_2$(BiBzIm)]$^{2+}$ (22)$^b$</td>
<td>245 (74700)</td>
<td>294 (89700)</td>
<td>318 (24280)</td>
</tr>
<tr>
<td>[(Ru(bpy)$_2$(bis-BiBzImH$_2$)]$^{3+}$ (23)</td>
<td>244 (66649)</td>
<td>290 (108108)</td>
<td>353 (sh)</td>
</tr>
<tr>
<td>[(Ru(bpy)$_2$(bis-BiBzIm)] (24)</td>
<td>246 (80950)</td>
<td>295 (101397)</td>
<td>350 (57095)</td>
</tr>
<tr>
<td>[(Ru(bpy)$_2$(bis-BiBzIm)]$^{4+}$ (25)</td>
<td>244 (138956)</td>
<td>293 (202045)</td>
<td>363 (71184)</td>
</tr>
<tr>
<td>[(Ru(bpy)$_2$(tetra-BiBzIm)]$^{5+}$ (26)</td>
<td>245 (230670)</td>
<td>293 (357460)</td>
<td>368 (141650)</td>
</tr>
</tbody>
</table>

$^a$Reference 20. $^b$References 15 and 61.

5.1.3 UV–vis Properties of [(Ru(bpy)$_2$(BiBzIm)](PF$_6$)$_2$ (22)

Spectral changes related to BiBzIm$^{2-}$-based bis-Ru complex [(Ru(bpy)$_2$(BiBzIm)]$^{2+}$ (22) are illustrated in Figure 5.1. The following features are noted:61 (1) The $\pi - \pi^*$ (BiBzImH$_2$) transitions found in the [Ru(bpy)$_2$(BiBzImH$_2$)]$^{2+}$ complex (20) are lost. (2) The intensity of the low-energy transition (506 nm) appears to
be related to the number of Ru(bpy)$_2^{2+}$ units, suggesting that this transition arises from these components and, on the basis of the discussion above, can be assigned as d$\pi$−$\pi^*$ (bpy). (3) The spectral activity in the 350 nm region consists of the overlapping metal-to-ligand charge transfer (MLCT) bands. (4) The absorption maximum at 294 nm has its primary origin $\pi$−$\pi^*$ (bpy) transitions. As of the stoichiometry of the complexes, the monometallic complex has two bipyridine ligands, the bimetallic complex has four. The relative intensity of the complex 22 is two times larger than that of the complex 21. (5) The far UV transitions increase in a systematic manner as the number of heterocyclic ligands increases, and most likely are overlapping $\pi$−$\pi^*$ transitions associated with both bpy and BiBzImH$_2$ ligands.

5.1.4 Electrochemical Studies of [Ru(bpy)$_2$(BiBzImH$_2$)]Cl$_2$ (20) and [Ru(bpy)$_2$(BiBzIm)] (21)

5.1.4.1 Oxidation of [Ru(bpy)$_2$(BiBzImH$_2$)]Cl$_2$ (20) and [Ru(bpy)$_2$(BiBzIm)] (21)$^{17}$

In accordance with Haga’s report,$^{17}$ the cyclic voltammogram (CV) of the mono-ruthenium complex 20 shows one reversible oxidation couple and one irreversible oxidation wave at more positive potentials at pH 7.1 (Figure 5.3). For the Ru(II)/Ru(III) couple, the potentials are pH independent in the pH < 0.6 and > 10.4 regions. At these two regions, the major Ru(II) species are [Ru(bpy)$_2$(BiBzImH$_2$)]$^{2+}$ (20) and [Ru(bpy)$_2$(BiBzIm)] (21) respectively. The electrode processes are defined as$^{17}$. 
[Ru\(^{II}\)(bpy)\(_2\)(BiBzImH\(_2\))]\(^{2+}\)  

[Ru\(^{III}\)(bpy)\(_2\)(BiBzImH\(_2\))]\(^{3+}\) + e\(^-\) (pH < 0.6)  \hspace{1cm} (eq. 5.2)

[Ru\(^{II}\)(bpy)\(_2\)(BiBzIm)]\(^+\)  

[Ru\(^{III}\)(bpy)\(_2\)(BiBzIm)]\(^+\) + e\(^-\) (pH > 10.4)  \hspace{1cm} (eq. 5.3)

Over the range 0.6 < pH < 5 and 7 < pH < 10, plots of \(E_{1/2}\) vs pH are linear with slopes of 53 mV, which are consistent with one-electron, one-proton processes as follows:\(^\text{17}\)

[Ru\(^{II}\)(bpy)\(_2\)(BiBzImH\(_2\))]\(^{2+}\)  

[Ru\(^{III}\)(bpy)\(_2\)(BiBzImH)]\(^2+\) + H\(^+\) + e\(^-\) (0.6 < pH < 5)  \hspace{1cm} (eq. 5.4)

[Ru\(^{II}\)(bpy)\(_2\)(BiBzImH)]\(^+\)  

[Ru\(^{III}\)(bpy)\(_2\)(BiBzIm)]\(^+\) + H\(^+\) + e\(^-\) (7 < pH <10)  \hspace{1cm} (eq. 5.5)

Figure 5.3 Cyclic Voltammogram of [Ru(bpy)\(_2\)(BiBzImH\(_2\))]Cl\(_2\) (20) in 0.10 M Bu\(_4\)NPF\(_6\)/CH\(_3\)CN Solution at a Scan Rate of 50 mv/s
The concentration of the Ru complex is around 2.11\times10^{-4} M.
Deprotonation of \([\text{Ru(bpy)}_2(\text{BiBzImH}_2)]\text{Cl}_2\) (20) to give \([\text{Ru(bpy)}_2(\text{BiBzIm})] \) (21) shifts the \(\text{Ru}^{3+/2+}\) potential from 1.12 to 0.43 V vs SSCE. This effect is electrostatic in nature, leaving a net \(-2\) charge on each \(\text{BiBzIm}\) ligand, which suggests the stronger \(\pi\) donation of the deprotonated \(\text{BiBzIm}\) to metal stabilizes the higher oxidation states. The \(d\pi\) orbitals respond to this perturbation by increasing their energy.

5.1.4.2 Reduction of \([\text{Ru(bpy)}_2(\text{BiBzImH}_2)]\text{Cl}_2\) (20)

By analogy to \([\text{Ru(bpy)}_3]^{2+}\), the reductions can be assigned to the reduction of the coordinated bipyridine ligands.\(^{62}\) The two reductions of \([\text{Ru}^{II}(\text{bpy})_2(\text{BiBzImH}_2)]^{2+}\) (20) are illustrated in equations 5.6 and 5.7:

\[
\begin{align*}
[\text{Ru}^{II}(\text{bpy})_2(\text{BiBzImH}_2)]^{2+} + e^- & \rightarrow [\text{Ru}^{II}(\text{bpy})(\text{bpy}^-)(\text{BiBzImH}_2)]^+ \quad \text{(eq. 5.6)} \\
[\text{Ru}^{II}(\text{bpy})(\text{bpy}^-)(\text{BiBzImH}_2)]^+ + e^- & \rightarrow [\text{Ru}^{II}(\text{bpy}^-)(\text{bpy}^-)(\text{BiBzImH}_2)] \quad \text{(eq. 5.7)}
\end{align*}
\]

5.1.5 Electrochemical Properties of \([[(\text{Ru(bpy)}_2)_2(\text{BiBzIm})](\text{PF}_6)_2]\) (22)

5.1.5.1 Oxidation of \([[(\text{Ru(bpy)}_2)_2(\text{BiBzIm})](\text{PF}_6)_2]\) (22)

For the bisnuclear Ru complex \([(\text{Ru(bpy)}_2)_2(\text{BiBzIm})]^{2+}\) (22), two successive electrode oxidation couples are observed at +0.75 V and +1.04 V (Figure 5.4). The electrode processes are shown in equations 5.8 and 5.9. The separations in peak potentials, \((\Delta E_p = E_{pa} - E_{pc})\), are about 60 mV, and the ratios of oxidation to reduction peak height are 1.0 ± 0.1, which indicates that the electrode oxidation processes are quasireversible. When the oxidation potentials of the binuclear complex is compared with that of mononuclear one, it is found that the first oxidation potential of binuclear
complex is 0.3 V lower than that of the mononuclear complex \([\text{Ru}(\text{bpy})_2(\text{BiBzImH}_2)]^{2+}\) (20). This suggests that the BiBzIm bridging ligand in binuclear complex has an electron-donor property.

\[
\begin{align*}
[\text{Ru}^{II}(\text{bpy})_2(\text{BiBzIm})\text{Ru}^{II}(\text{bpy})_2]^{2+} & \rightarrow [\text{Ru}^{II}(\text{bpy})_2(\text{BiBzIm})\text{Ru}^{II}(\text{bpy})_2]^{3+} + e^- \quad (\text{eq. 5.8}) \\
[\text{Ru}^{II}(\text{bpy})_2(\text{BiBzIm})\text{Ru}^{III}(\text{bpy})_2]^{3+} & \rightarrow [\text{Ru}^{III}(\text{bpy})_2(\text{BiBzIm})\text{Ru}^{III}(\text{bpy})_2]^{4+} + e^- \quad (\text{eq. 5.9})
\end{align*}
\]

It has been shown that when the Ru(II/III) oxidation potential is regarded as a function of the metal ion in the second Ru(bpy)_2 site, the oxidation potential depends only on the charge of the second metal ion; i.e., the observed Ru(II/III) oxidation potentials are +0.78 and +1.0 V vs SCE for +2 and +3 charged second metal ions, respectively.\(^{15}\) These results suggest that the electronic delocalization through BiBzIm is relatively small and the electrostatic interaction becomes an important factor for determining the oxidation potential in the present system.\(^{14,15,61}\)

![Figure 5.4 Cyclic Voltammogram of \([\text{Ru}(\text{bpy})_2(\text{BiBzIm})](\text{PF}_6)_2\) (22) in 0.10 M Bu_4NPF_6/CH_3CN Solution at a Scan Rate of 50 mv/s. The concentration of the Ru complex is around 2.11×10^{-4} M.](image)
5.1.5.2 Reduction of [(Ru(bpy)$_2$)(BiBzIm)](PF$_6$)$_2$ (22)

Two chemically reversible reduction waves at –1.54 and –1.82 V are observed for the bis-ruthenium complex 22. They are both resolved into two closely spaced one-electron reduction processes with similar half-wave potentials rather than a single two-electron process: the peak-to-peak separation of both processes in cyclic voltammogram is around 100 mV, which is considerably larger than the theoretically predicted value of 28 mV for a reversible two-electron-reduction process. It has been reported that they are ligand-based.$^{14}$ Since the BiBzIm ligand acts as a π donor, the π* orbitals associated with BiBzIm are at much higher energies than those of bpy. Therefore, bpy can be regarded as the electroactive ligand. Furthermore, the monomeric complex, [Ru(bpy)$_2$(BiBzImH)$_2$]$^{2+}$, has been reported to exhibit two bpy ligand-based processes at –1.60 and –1.90 V.$^{61}$ Thus, it can be concluded that four one-electron reduction processes based on the bpy ligand are observed in the dinuclear complex.$^{14}$

The existence of four substituted bpy ligands in the present symmetrical dinuclear complex are expected to show a maximum of eight reduction steps. However, only four reduction processes are observed within the accessible potential range. Since two Ru(bpy)$_2$ moieties are separated by a BiBzIm bridge, the interactions of the bpy ligand between the different moieties are relatively small. Thus, the first electron added to the dinuclear complex are predicted to be localized in a bpy ligand on one Ru(bpy)$_2$ moiety (equation 5.10). Further electrons may be accepted by the other bpy ligands on each Ru(bpy)$_2$ moiety at a more negative potential. Thus, the reduction processes can be summarized by equations 5.10–5.13. The separation of the reduction potential between
the first and second processes (equations 5.10 and 5.11) is smaller than that between the third and fourth ones (equations 5.12 and 5.13), which can be attributed to the electronic repulsion energy as pointed out by Vlcek, et al.\textsuperscript{57}

\[
[Ru(bpy)\textsubscript{2}(BiBzIm)Ru(bpy)\textsubscript{2}]^{2+} + e^- \rightarrow [Ru(bpy)\textsubscript{2}(BiBzIm)Ru(bpy)(bpy')]^+ \quad \text{(eq. 5.10)}
\]

\[
[Ru(bpy)\textsubscript{2}(BiBzIm)Ru(bpy)(bpy')]^+ + e^- \rightarrow [Ru(bpy)(bpy')(BiBzIm)Ru(bpy)(bpy')] \quad \text{(eq. 5.11)}
\]

\[
[Ru(bpy')(BiBzIm)Ru(bpy)(bpy')] + e^- \rightarrow [Ru(bpy')(BiBzIm)Ru(bpy')\textsubscript{2}]^+ \quad \text{(eq. 5.12)}
\]

\[
[Ru(bpy')(BiBzIm)Ru(bpy')\textsubscript{2}]^- + e^- \rightarrow [Ru(bpy')\textsubscript{2}(BiBzIm)Ru(bpy')\textsubscript{2}]^{2-} \quad \text{(eq. 5.13)}
\]

### Table 5.2 Cyclic Voltammogram Data for Ru Complexes (20–26)

<table>
<thead>
<tr>
<th>complex</th>
<th>oxidation</th>
<th>reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(E_{1/2}(1)), (V) (E_{1/2}(2)), (V) (E'<em>{1/2}(1)), (V) (E'</em>{1/2}(2)), (V)</td>
<td></td>
</tr>
<tr>
<td>([Ru(bpy)\textsubscript{2}(BiBzImH\textsubscript{2})]^{2+}\textsuperscript{a,b} (20))</td>
<td>1.12 (70)</td>
<td>-1.60 (80)</td>
</tr>
<tr>
<td>([Ru(bpy)\textsubscript{2}(BiBzIm)]^\textsubscript{b} (21))</td>
<td>0.43 (68)</td>
<td>-1.58 (60)</td>
</tr>
<tr>
<td>([Ru(bpy)(BiBzIm)]^{2+}\textsuperscript{b,c} (22))</td>
<td>0.76 (60)</td>
<td>1.04 (64)</td>
</tr>
<tr>
<td>([Ru(bpy)\textsubscript{2}(bis-BiBzImH\textsubscript{2})]^{4+} (23))</td>
<td>1.09 (94)</td>
<td>-1.41 (140)</td>
</tr>
<tr>
<td>([Ru(bpy)\textsubscript{2}(bis-BiBzIm)] (24))</td>
<td>0.39 (72)</td>
<td>-1.64 (70)</td>
</tr>
<tr>
<td>([Ru(bpy)\textsubscript{2}(bis-BiBzIm)]^{4+} (25))</td>
<td>0.75 (81)</td>
<td>1.04 (72)</td>
</tr>
<tr>
<td>([Ru(bpy)\textsubscript{2}(tetra-BiBzIm)]^{8+} (26))</td>
<td>0.71 (78)</td>
<td>1.00 (69)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Solutions were 0.1 M TBNPF\textsubscript{6} in acetonitrile. The potentials \(E_{1/2}\) were calculated from the equation \((E_{pa} + E_{pc}) / 2\) where \(E_{pa}\) and \(E_{pc}\) are anodic and cathodic peak potentials respectively. The values in parentheses are peak-to-peak separations, \(\Delta E_p = E_{pa} - E_{pc}\).

\textsuperscript{b} Reference 20. \textsuperscript{c} Reference 15 and 61. \textsuperscript{d} This work.
Scheme 5.3 Synthesis of Ru Complexes 23–25

14 + Ru(bpy)₂Cl₂ → Ethylene Glycol
150 °C
Crude yield: 85%

NaOCH₃
CH₃OH

89%

Ru(bpy)₂Cl₂ → Crude yield: 85%
5.2 Bis(bibenzimidazole)-Based Ru Complexes [(Ru(bpy)$_2$)$_2$(bis(BiBzImH$_2$))]Cl$_4$ (23), [(Ru(bpy)$_2$)$_2$(bis(BiBzIm))] (24) and [(Ru(bpy)$_2$)$_4$(bis(BiBzIm))](PF$_6$)$_4$ (25)$^6$

5.2.1 Synthesis of [(Ru(bpy)$_2$)$_2$(bis(BiBzImH$_2$))]Cl$_4$ (23), [(Ru(bpy)$_2$)$_2$(bis(BiBzIm))] (24) and [(Ru(bpy)$_2$)$_4$(bis(BiBzIm))](PF$_6$)$_4$ (25)$^6$

The multinuclear Ru complexes 23–25 based on the dimer of bibenzimidazole [bis(bibenzimidazole)] (14) were prepared following the procedures of making the complexes 20–22. One equivalent of the bis(bibenzimidazole) (14) was complexed with two equivalents of Ru(bpy)$_2$Cl$_2$ to give the bis-Ru complex 23 (Scheme 5.3).

It should be noticed that after the complexation, the protons on the bis(BiBzImH$_2$) ligand (14) in the complex [(Ru(bpy)$_2$)$_2$(bis(BiBzImH$_2$))]$^{4+}$ (23) become acidic and tend to be partially deprotonated in the reaction media, providing a mixture of protonated and partially deprotonated species. The deprotonation also occurs during the purification of 23 with Al$_2$O$_3$ (neutral) column. In order to circumvent this problem, the crude complex 23 was completely deprotonated first by NaOCH$_3$ in CH$_3$OH at reflux to provide the neutral complex [(Ru(bpy)$_2$)$_2$(bis(BiBzIm))] (24), which could be easily purified due to the insolubility in acetone. Then 24 was protonated back by HCl to give the pure complex 23. The tetranuclear Ru complex 25 was synthesized by the complexation of the neutral complex 24 with two equivalents of Ru(bpy)$_2$Cl$_2$.

The formation of the tetra-Ru complex 25 was confirmed by MALDI-TOF analysis (Figure 5.5) and the satisfactory elemental analysis. The mass spectrum clearly shows the parent ion complex minus 1PF$_6^-$, 2PF$_6^-$, 3PF$_6^-$, and 4PF$_6^-$ fragments.
5.2.2 UV–vis Properties of [(Ru(bpy)$_2$)$_2$(bis(BiBzIm)$_2$)]Cl$_4$ (23), [(Ru(bpy)$_2$)$_2$(bis(BiBzIm))](PF$_6$)$_4$ (24) and [(Ru(bpy)$_2$)$_4$(bis(BiBzIm))](PF$_6$)$_4$ (25)

The spectroscopic properties of the complexes 23–25 are shown in Figure 5.6 and 5.7. For [(Ru(bpy)$_2$)$_2$(bis(BiBzImH$_2$))](PF$_6$)$_4$ (23), the extended conjugation of the bibenzimidazole ligand resulted in the appearance of a bis(BiBzImH$_2$) $\pi-\pi^*$ band at 367 nm. The lowest energy MLCT transition remains at 464 nm. Compared to the mononuclear complex [Ru(bpy)$_2$(BiBzImH$_2$)](PF$_6$)$_2$ (20), the lowest energy MLCT transition remains nearly constant, while the extinction coefficient doubles upon the
complexation of two Ru(bpy)$_2$ components. After the deprotonation, the lowest energy MLCT band of the neutral [(Ru(bpy)$_2$)$_2$(Bis(BiBzIm))] (24) red shifts to 543 nm. The lowest energy MLCT band is still the $d\pi-\pi^*$ (bpy) in nature. This is identical to the deprotonated mono-Ru complex 21.

Figure 5.6 UV–vis Spectra of [(Ru(bpy)$_2$)$_2$(bis(BiBzImH$_2$))]Cl$_4$ (23) and [Ru(bpy)$_2$(BiBzImH$_2$)]Cl$_2$ (20) in CH$_3$CN

Figure 5.7 UV–vis Spectra of [(Ru(bpy)$_2$)$_2$(bis(BiBzImH$_2$))]Cl$_4$ (23), [(Ru(bpy)$_2$)$_2$(bis(BiBzIm))] (24), and [(Ru(bpy)$_2$)$_4$(bis(BiBzIm))](PF$_6$)$_4$ (25) in CH$_3$CN
For the tetranuclear complex [(Ru(bpy)$_2$)$_4$(bis(BiBzIm))](PF$_6$)$_4$ (25), the band at 363 nm was broader than the 367-nm band of dinuclear complex 23. This region consists of bis(BiBzIm) based $\pi-\pi^*$ transition overlapped with the multiple MLCT bands. The broadening of the band is probably due to the presence of the multinuclear effect. The lowest energy MLCT absorption is at the same position as the MLCT of the dinuclear complex 22 (506 nm). The extension of the bridging ligand from the monomer (5) to the dimer of bibenzimidazole (14) does not change the position of the lowest energy MLCT transition, which is still $d\pi-\pi^*$ (bpy) in nature.

![Figure 5.8 UV-vis Spectra of Stepwise Deprotonation of [(Ru(bpy)$_2$)$_2$(bis(BiBzImH$_2$))](Cl)$_4$ (23) in CH$_3$CN by Adding NaOCH$_3$/CH$_3$OH Solution](image)

5.2.3 Proton-Induced Tuning of the Chemical Properties

The stepwise deprotonation of [(Ru(bpy)$_2$)$_2$(bis(BiBzImH$_2$))](Cl)$_4$ (23) in CH$_3$CN by NaOCH$_3$/CH$_3$OH is shown in Figure 5.8. There are four dissociable protons in this
complex. During the deprotonation process, the intensity at 440 nm and 464 nm decreases, and the lowest energy MLCT transition progressively shifts to the lower energy. After the addition of the 1st and the 2nd equivalents of NaOCH$_3$, the lowest energy MLCT transition red-shifts to 500 nm and 506 nm, respectively. The addition of the 3rd equivalent of NaOCH$_3$ makes the lowest energy MLCT transition red shifted to 512 nm, with the peak at 543 nm growing up. After the addition of the 4th equivalent of NaOCH$_3$, the peak at 543 nm grows up to be the major peak. In total, six equivalents of NaOCH$_3$ was added to ensure the fully deprotonation of the complex. This is similar to the stepwise deprotonation of the mono-Ru complex [Ru(bpy)$_2$(BiBzImH$_2$)][PF$_6$)$_2$ (20) shown in Figure 5.2. The isosbestic points are at 491 nm and 520 nm, which indicate that the dinuclear Ru complex 23 in solution undergoes two successive deprotonations to exist as an equilibrium mixture with the monocation and neutral species. This result also indicates that the interaction between the two Ru centers is weak, which is consistent with the electrochemistry results.

5.2.4 Electrochemical Properties of [((Ru(bpy)$_2$)$_2$(bis(BiBzImH$_2$)))Cl$_4$ (23), [(Ru(bpy)$_2$)$_2$(bis(BiBzIm))} (24) and [(Ru(bpy)$_2$)$_4$(bis(BiBzIm))] (PF$_6$)$_4$ (25)

5.2.4.1 Oxidation Processes

The cyclic voltammogram of the dinuclear Ru complex 23 (Figure 5.9) shows the oxidation potential at $+1.09$ V. No difference is observed in the oxidation between the dinuclear complex 23 and the mononuclear complex 20, which indicates that the electronic communication between the two Ru centers along the conjugated ligand bis(2,2'-bibenzimidazole) (14) is weak.
Figure 5.9 Cyclic Voltammogram of [(Ru(bpy)$_2$)$_2$(bis(BzImH$_2$))](PF$_6$)$_4$ (23) in 0.10 M Bu$_4$NPF$_6$/CH$_3$CN Solution at a Scan Rate of 50 mv/s
The concentration of the Ru complex is around 2.11×10$^{-4}$ M.

The cyclic voltammogram (CV) of the tetranuclear Ru complex (25) is shown in Figure 5.10. It exhibits two oxidation waves at +0.75 V and +1.04 V. They are close to the oxidation potentials +0.77 V and +1.06 V of the dinuclear complex 22. The
separations between the anodic and cathodic peak potentials $\Delta E_p$ are 81 mv and 72 mv, respectively; the ratios of the oxidation to the reduction peak heights are 1.0 V, which indicate that the oxidation processes are quasireversible. Four one-electron steps are involved in these two oxidation processes. The electronic interaction between the Ru metals along the conjugated bis(2,2′-bibenzimidazole) (14) is weak.

It has been shown that the first oxidation potential of the dinuclear Ru complex 22 was 0.3 V lower than those of the mononuclear complex 20, which indicates that the BiBzIm bridging ligand in the dinuclear complex 22 has an electron donor property. The oxidation potentials of the tetranuclear complex 25 has the same oxidation behavior as the dinuclear complex 22 does, which suggests that the dimer of BiBzIm (14) also has an electron donor property. The Ru-Ru electrostatic interactions across the bridging ligand bis(BiBzIm) is similar to the Ru-Ru interaction in the dinuclear complex 22.

5.2.4.2 Reduction Processes

The dinuclear complex 23 exhibits the reduction potentials at −1.41 V and −1.64 V. The tetranuclear complex 25 exhibits the reduction potentials at −1.47 V and −1.64 V. The sharp spikes might be due to the adsorption on the electrode. They may be the bpy ligand-based processes according to the previous results. The $\Delta E_p$ spacings (140 mV and 484 mV) and the increased currents suggest that more than one single electron transfer step occurs at each wave. This is reasonable given the presence of more than one Ru(bpy)$_2^{2+}$ unit.
5.3 Tetra(bibenzimidazole)-Based Octa-Ru Complex
\[ [(\text{Ru(bpy)}_2)_8(\text{tetra(BiBzIm)})](PF_6)_8 \] (26)

5.3.1 Synthesis of Octa-Ru Complex \[ [(\text{Ru(bpy)}_2)_8(\text{tetra(BiBzIm)})](PF_6)_8 \] (26)

The octa-Ru complex 26 was prepared in one pot as shown in Scheme 5.4. The tetramer of bibenzimidazole ligand 19 becomes acidic after being complexed with \text{Ru(bpy)}_2\text{Cl}_2, and tends to be partially deprotonated in the reaction media, providing a mixture of protonated and partially deprotonated species. To ensure that the tetramer bridging ligand is fully complexed with eight \text{Ru(bpy)}_2\text{Cl}_2, \text{NaOCH}_3 was added to fully
deprotonate the complex. Therefore, all the bidentate chelating sites on the tetramer bridging ligand were complexed with eight Ru metals.

The formation of the octa-Ru complex 26 was confirmed by the MALDI-TOF analysis (Figure 5.11). The spectra clearly shows the parent ion complex minus 1PF$_6^-$, 2PF$_6^-$, …, 7PF$_6^-$, and 8PF$_6^-$ fragments.

![MALDI-TOF Spectra](image)

Figure 5.11 MALDI-TOF Spectra of [(Ru(bpy)$_2$)$_8$(tetra(BiBzIm))](PF$_6$)$_8$ (26)


5.3.2 UV–vis Properties of Octa-Ru Complex [(Ru(bpy)$_2$)$_8$(tetra(BiBzIm))](PF$_6$)$_8$ (26)

For the octa-Ru complex 26, the UV–vis spectra (Figure 5.12) is very similar to the tetra-Ru complex 25. The extinction coefficient doubled compared to that of the tetra-Ru complex 25. The lowest energy MLCT transition remains at 506 nm ($\varepsilon = 65300$ M$^{-1}$·cm$^{-1}$), which is $d\pi–\pi^*$ (bpy) in nature. The $\pi^*$ of the bpy is lower than $\pi^*$ of the tetra-BiBzImH$_2$, therefore, the lowest energy MLCT transition is $d\pi–\pi^*$ (bpy). The progressive lowering of the $\pi^*$ orbitals of the bridging ligands from the dimer to the
tetramer of bibenzimidazole does not change the position of the lowest energy MLCT transition. This indicates that the extension of the conjugated chain length of the bridging ligands does not provide the pathway for the electronic communication between the metal centers.

![UV−vis Spectra of Bis-Ru Complex](image)

**Figure 5.12** UV−vis Spectra of Bis-Ru Complex [(Ru(bpy)$_2$(BiBzIm))(PF$_6$)$_2$ (22), Tetra-Ru Complex [(Ru(bpy)$_2$(bis(BiBzIm)))(PF$_6$)$_4$ (25), and Octa-Ru Complex [(Ru(bpy)$_2$(tetra(BiBzIm)))(PF$_6$)$_8$ (26) in CH$_3$CN

### 5.3.3 Electrochemical Properties of Octa-Ru Complex [(Ru(bpy)$_2$(tetra(BiBzIm)))(PF$_6$)$_8$ (26)]

The cyclic voltammogram (CV) of the octa-nuclear Ru complex (26) is shown in Figure 5.13. It exhibits two oxidation waves at +0.71 V and +1.00 V. They are close to the two oxidation potentials +0.77 V and +1.06 V of the dinuclear complex 22. The Ru complex 26 based on the tetramer of bibenzimidazoles 19 still undergoes the bpy-based reduction at −1.51 and −1.72 V. The Ru-Ru electrostatic interactions across the bridging ligand tetra(BiBzIm) is similar to the Ru-Ru interactions in the dinuclear and
tetranuclear complexes 22 and 25. However, interactions along the tetramer of bibenzimidazole ligand are relatively weak.

![Cyclic Voltammogram of Octa-Ru Complex](image)

**Figure 5.13 Cyclic Voltammogram of Octa-Ru Complex**

\( [(\text{Ru(bpy})_2\text{(tetra(BiBzIm))})(PF_6)_8 \text{ (26)} \text{ in 0.10 M Bu}_4\text{NPf}_6/\text{CH}_3\text{CN Solution}} \)

at a Scan Rate of 50 mv/s

The concentration of the Ru complex is around 2.11×10\(^{-4}\) M.

### 5.4 Conclusions

A series of multinuclear Ru complexes containing di-, tetra-, and octa-Ru\(^{II}\) centers based on the oligomeric bibenzimidazoles were synthesized and characterized. The species with high nuclearity exhibit extended one-dimensional structures. They show very intense ligand-centered (LC) absorptions (\(\varepsilon\) up to 3.6 × 10\(^5\) M\(^{-1}\).cm\(^{-1}\)) and moderately intense metal-to-ligand charge transfer bands in the visible region (\(\varepsilon\) up to 6.6 × 10\(^4\) M\(^{-1}\).cm\(^{-1}\)). The interactions between the Ru metal centers across the bidentate bibenzimidazole ligands, and along the oligomeric bibenzimidazole ligands are relatively weak, which is not expected.
CHAPTER 6
EXPERIMENTAL DETAILS

6.1 General

6.1.1 Reagents and Materials

All reagents were used without further purification. RuCl$_3$·$x$H$_2$O (99.9%) was purchased from Alfa. 2,2$'$-Bipyridine (99%+) and ammonium hexafluorophosphate (95+%) were purchased from Aldrich. Acetonitrile was distilled over CaH$_2$ before use. Nylon membranes filter paper (pore size: 0.2 µm or 0.45 µm) for the filtration of the Ru complexes was purchased from Cole-Parmer Instrument Co.

6.1.2 Measurements

$^1$H NMR (500 MHz) and $^{13}$C NMR (125 MHz) spectra were obtained on a JEOL Eclipse+ 500 MHz spectrometer. Chemical shifts (δ values) were given in parts per million with tetramethylsilane as an internal standard. UV–vis spectra were obtained using a Varian Cary 500 UV–vis–NIR spectrophotometer. Elemental analysis was performed by Quantitative Technologies Inc. (QTI) (Whitehouse, NJ). Mass analysis was performed by Scripps Research Institute (La Jolla, CA). ESI-MS spectra were obtained on a Waters–Micromass LCT mass spectrometer. MALDI-TOF spectra were obtained on Applied Biosystems Voyager–STR Mass spectrometer. Cyclic
Voltammogram experiments were performed at 20 °C using a PC-controlled potentiostat (CH Instruments, electroanalytical analyzer). The working electrode was a 1.5 mm glassy carbon electrode and the auxiliary electrode was a platinum wire. The reference electrode was a no leak Ag/AgCl reference electrode. They were purchased from Cypress Systems, Inc. (Lawrence, KS).

6.2 Synthesis

The synthesis of Ru(bpy)$_2$Cl$_2$·2H$_2$O, $^{64,65}$ [Ru(bpy)$_2$(BiBzImH$_2$)](PF$_6$)$_2$, [Ru(bpy)$_2$(BiBzIm)], and [(Ru(bpy)$_2$)$_2$(BiBzIm)](PF$_6$)$_2$ followed previously published procedures.$^{16,20}$

[(Ru(bpy)$_2$)$_2$(bis(BiBzImH$_2$))](PF$_6$)$_4$·H$_2$O (23). Bis(BiBzImH$_2$) (14) (0.30 g, 0.64 mmol) was suspended in 80 mL of ethylene glycol. The mixture was degassed for 30 min under nitrogen, then heated at 120 °C for 3 h to dissolve bis(BiBzImH$_2$). Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.74 g, 1.42 mmol) was added to the above suspension, and heated at 150 °C for 16 h under nitrogen. The resulting deep brownish red solution was cooled, diluted with water, and filtered to remove the insoluble part. Then a saturated aqueous solution of NH$_4$PF$_6$ was added dropwise to precipitate the crude complex. The crude complex was directly used in the next deprotonation step without further purification. The pure product was obtained by protonation of the pure deprotonated complex 24 using HCl (6M), then reprecipitation with NH$_4$PF$_6$. MALDI-TOF (m/z): 1291 [(M – 4HPF$_6$) + H]$^+$. Anal. Calcd for C$_{68}$H$_{50}$F$_{24}$N$_{16}$P$_4$Ru$_2$·2H$_2$O: C, 43.18; H, 2.77; N, 11.85. Found: C, 43.12; H, 2.70; N, 11.68.
[(Ru(bpy)$_2$)(bis(BiBzIm))] (24). The crude [(Ru(bpy)$_2$)$_2$-(bis(BiBzImH$_2$))](PF$_6$)$_4$ (23) (0.44 g, 0.23 mmol) was added to 50 mL of methanol and the suspension was degassed for 20 min under nitrogen. NaOCH$_3$ (0.20 g, 3.76 mmol) was added to the above mixture. The color of the solution turned from deep brownish red to purple. The solution was refluxed for 5 h under nitrogen and then cooled. The solvent was condensed to a half volume by rotary evaporation. The solid product was collected by filtration and purified by washing with acetone. Yield: 89%. Anal. Calcd for C$_{68}$H$_{46}$N$_{16}$Ru$_2$⋅8H$_2$O: C, 56.97; H, 4.36; N, 15.63. Found: C, 56.88; H, 3.67; N, 14.95.

[(Ru(bpy)$_2$)$_4$(bis(BiBzIm))](PF$_6$)$_4$·4H$_2$O (25). [(Ru(bpy)$_2$)$_2$(bis(BiBzIm))] (24) (0.15 g, 0.12 mmol) and Ru(bpy)$_2$Cl$_2$⋅2H$_2$O (0.13 g, 0.26 mmol) were suspended in 24 mL of ethanol/water (1:1 v/v). Then it was degassed for 30 min and then refluxed under nitrogen for 15 h. The resulting deep brownish red solution was cooled and filtered to remove the insoluble part it may have. Ethanol was removed by rotary evaporation. Then a saturated aqueous solution of NH$_4$PF$_6$ was added dropwise to precipitate the complex. Around 250 mg of the solid crude product was collected by filtration. Half of the crude product (125 mg) was dissolved in a minimum of acetonitrile, and chromatographed over a neutral alumina column (21 cm in length, 17 mm in diameter). The first deep red broad band was collected. The eluate was concentrated to around 25 mL by rotary evaporation, and then diethyl ether was added dropwise to precipitate the desired complex. Overall yield: 68%. MALDI-TOF (m/z): 2551 [M − 1PF$_6$]$^+$, 2406 [M
− 2PF$_6^+$, 2261 [M − 3PF$_6^+$], 2116 [M − 4PF$_6^+$]. Anal. Calcd for C$_{108}$H$_{78}$F$_{24}$N$_{24}$P$_4$Ru$_4$·4H$_2$O: C, 46.86; H, 3.13; N, 12.14. Found: C, 46.37; H, 2.70; N, 11.85.

[(Ru(bpy)$_2$)$_8$(tetra(BiBzIm))](PF$_6$)$_8$ (26). Tetra(bibenzimidazole) (19) (0.050 g, 0.0537 mmol) was suspended in 25 mL of ethylene glycol. The mixture was degassed for 30 min under nitrogen, then heated at 160 °C for 8 h to partially dissolve the tetra(BiBzImH$_2$) ligand. Then the temperature was decreased to 110–120 °C, and Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.234 g, 0.451 mmol, 8.4 equiv) was added to the above mixture. The mixture was heated at 150 °C for 2 h, then NaOCH$_3$ (0.058 g, 1.074 mmol, 20 equiv) was added to facilitate the deprotonation of all the tetramer ligand. The reaction was kept at 150 °C for 15 h. The resulting deep red-brown solution was cooled, diluted with water, and filtered to remove the insoluble part. Then a saturated aqueous solution of NH$_4$PF$_6$ was added dropwise to the filtrated to precipitate the complex. The crude solid was collected by filtration. It was dissolved in a minimum of acetonitrile, and chromatographed over a neutral alumina column (21 cm in length, 17 mm in diameter). First, acetonitrile was used as the eluent. The first bright orange band was the excess [Ru(bpy)$_3$]$^{2+}$. Then a saturated acetonitrile solution of NH$_4$PF$_6$ was used to elute the deep-red broad band from the top of the column. The eluate was concentrated to around 25 mL by rotary evaporation and then ether was added dropwise to precipitate the desired complex. The product was vacuum-dried at 60 °C for 15 h. Yield: 52%.
PART III

STEREOSPECIFIC SYNTHESIS OF MULTINUCLEAR RU COMPLEXES
7.1 Stereochemical Issues of Polynuclear Ru Complexes

Polymetallic assemblies which contains d$_6$ transition metal centers (e.g. Ru$^{II}$, Os$^{II}$), particularly coordinated to polypyridyl ligands, have been of great interest because of their favorable photophysical and redox characteristics. Controlling the stereochemistry at the component octahedral metal centers should be of considerable importance as the spatial relationship of the components influences the nature of intramolecular electron and energy transfer processes within the assemblies. The polynuclear metal complexes without the stereocontrol of each octahedral center have generally been isomeric mixtures, and characterization using NMR technique has been extremely difficult, because the NMR spectra of the oligomeric assemblies are different for each stereoisomer (other than enantiomers) and thus complicated. In addition, crystals appropriate for X-ray structural studies of such assemblies, which could usually provide valuable information of the metal complexes, are very difficult to obtain. This is particularly true when bidentate ligands are involved. Since these bidentate ligands are important as they extend the three-dimensionality of resultant polynuclear species, the stereospecific synthesis of the metal complexes is required.
Our research is focused on the investigation of the photochemical and electrochemical properties of the polynuclear metal complexes based on the conjugated oligomeric bibenzimidazoles. The stereospecific synthesis of multinuclear ruthenium complexes using an enantiomERICally pure chiral building block $\Lambda$-[Ru(bpy)$_2$(py)$_2$][(-)O$_2$O'-dibenzoyl-L-tartrate] (27a) is described in this Part.

7.2 Stereoisomers of Octahedral Multinuclear Complexes

7.2.1 Enantiomers of Tris-bidentate Mononuclear Ru Complexes

The $D_3$ symmetric tris-bidentate octahedral complex such as [Ru(BiBzImH$_2$)$_3$]$^{2+}$, as shown in Figure 7.1, has a helical structure in which the three bibenzimidazole ligands lie along the threads of a screw. It has no symmetry plane because its two halves are not mirror images, but it does have a threefold symmetry axis, which passes through the Ru(II) ion and is nearly perpendicular to the plane of the figure. Like a hand, it is chiral and can exist in two nonidentical mirror-image forms—a “right-handed” enantiomer (designated as $\Delta$) in which the three bibenzimidazole ligands screw would advance into the page as you rotate it to the right (clockwise) about the threefold axis, and a “left-handed” enantiomer (designated as $\Lambda$) in which the bibenzimidazole ligands screw would advance into the page as you rotate it to the left (counterclockwise) about the threefold axis. The direction of the spiral is indicated in Figure 7.1 by the red arrows.

The enantiomers have identical properties except for their reactions with other chiral substances and their effect on plane-polarized light. They are labeled (+) or (−),
depending on the direction of rotation of the plane of polarization. A 50:50 mixture of the (+) and (−) isomers, called a racemic mixture, produces no net optical rotation because the rotations produced by the individual enantiomers exactly cancel.

Chart 7.1

Figure 7.1 Enantiomers of $D_3$ Symmetric [Ru(Bibenzimidazole)$_3$]$^{2+}$

7.2.2 Stereoisomers of Dinuclear Ru Complexes

Ligand-bridged dinuclear Ru species represent the simplest examples of the multinuclear assemblies (Figure 7.2). The individual metal centers are tris(bidentate) in
nature, each may inherently possess right- or left-handed chirality (Δ and Λ respectively). In principle, a dinuclear species may therefore exist in two diastereoisomeric forms—ΔΔ/ΛΛ (a pair of enantiomers) or ΔΛ/ΛΔ (meso) where the bridge is relatively rigid. The stereoisomerism has a profound effect on shape and on the electronic interactions within the molecule.  

![Figure 7.2 Stereoisomeric Forms of [(Ru(pp)_2)_2(µ-BL)]^{n+}

![bpm (2,2'-bipyrididine)]
![2,5-dpp [2,5-bis(2-pyridyl)pyrazine]]
![4,6-dppm [4,6-bis(2-pyridyl)pyrimidine]]

Chart 7.2

The most fundamental example of the dinuclear species is [(Ru(pp)_2)_2(µ-BL)]^{n+} [where pp is a symmetrical bidentate ligand (C_{2v} point group symmetry) such as bpy, and BL is a symmetrical (C_{2v}) bridging ligand such as 2,2'-bipyrimidine (bpm) (Chart 7.2). In this case there are two diastereoisomers [meso (point group symmetry C_{2h}) and...


racemic (point group symmetry $D_2$)], with the latter comprising two enantiomeric forms ($\Delta\Delta/\Lambda\Lambda$) (Figure 7.2).

Polynuclear and multifunctional species that are built from racemic unit yield up to $2^N$ isomers (where $N$ is the number of chiral units involved), depending on the overall symmetry of the species, if a racemic starting material is used. If artificial, self-assembling structures are envisaged with a large number of centers, the number of isomers may therefore soon become very large.$^{67}$

7.3 Stereospecific Synthesis of Multinuclear Ru Complexes

There are limited examples of complexes in the above categories where individual stereoisomers have actually been separated. Hua and von Zelewnsky established the convenient resolution of rac-$[\text{Ru(phen)}_2(\text{py})_2]^{2+}$ and rac-$[\text{Ru(bpy)}_2(\text{py})_2]^{2+}$ by conventional diastereoisomer formation using the chiral arsenyl-$(+)$-tartrate and $O,O'$-dibenzoyltartrate anions, respectively.$^{67-71}$ This resolution method yields excellent chiral building blocks since the $\Delta$- or $\Lambda$-[Ru(phen)$_2$(py)$_2$]$^{2+}$ or [Ru(bpy)$_2$(py)$_2$]$^{2+}$ undergo stereoretentive substitution of the two monodentate pyridine ligands. These chiral precursors were used to synthesize the dinuclear species[$(\text{Ru(pp)}_2)(\mu-$BL$)]^{4+}$ [pp = bpy or phen; BL = bridging ligands 2,2’-bipyrimidine (bpm), 2,5-bis(2-pyridyl)pyrazine (2,5-dpp), or 4,6-bis(2-pyridyl)pyrimidine (4,6-dppm)] with predetermined stereochemistry (i.e. $\Delta\Delta/\Lambda\Lambda$ or $\Delta\Lambda$). The methodology has also been used for analogous dinuclear complexes involving the bridging ligands 2,3-
bis(2-pyridyl)-pyrazine (2,3-dpp) and its fused analogue pyrazino[2,3-f]-[4,7]phenanthroline (ppz).\textsuperscript{72}

Keene and coworkers established the use of chiral \([\text{Ru}(\text{pp})_2(\text{CO})_2]^{2+}\) as a precursor for the synthesis of individual stereoisomers of the dinuclear complex \([\text{Ru}(\text{phen})_2(\text{Ru}(\text{Me}_4\text{bpy})_2)(\mu\text{-bpm})]^4+\),\textsuperscript{73} and the use of cation exchange chromatographic methods to separate the diastereoisomers of the dinuclear species.\textsuperscript{74,75} von Zelewsky and co-workers have reported the use of ligands (“chiragens”) which impose a particular stereochemistry on the monomer precursors (“stereospecificity”).\textsuperscript{76,77} A number of studies have been reported utilizing condensation reactions of chiral monomers containing the 1,10-phenanthroline-5,6-dione ligand, e.g. \([\text{Ru}(\text{phen})_2(\text{1,10-phenanthroline-5,6-dione})]^{2+}\),\textsuperscript{78} as the precursor to form bridged complexes of predetermined stereochemistry.\textsuperscript{79-81} Tor and coworkers have reported the use of the Hua and von Zelewsky precursor \(\Delta/\Lambda-[\text{Ru}(\text{phen})_2(\text{py})_2]^{2+}\) to produce the \(\Lambda\Lambda\Lambda\) and \(\Delta\Lambda\Delta\) diastereoisomers of alkyne-bridged trinuclear species.\textsuperscript{82}

Given the high thermal stereochemical stability of the chiral building blocks developed by Hua and von Zelewsky, we applied this method for the synthesis of the homochiral multinuclear complexes of oligomeric bibenzimidazoles, using \(\Lambda-[\text{Ru}(\text{bpy})_2(\text{py})_2][(-)\text{O},\text{O}'\text{-dibenzoyl-L-tartrate}]\) (27a) as the enantiomerically pure chiral building block.
Diastereomeric pure multinuclear complexes are usually characterized by the techniques such as NMR spectrometry, circular dichroism (CD) and mass spectrometry.
CHAPTER 8
RESULTS AND DISCUSSION

8.1 Enantiomerically Pure Chiral Building Block Λ-[Ru(bpy)$_2$(py)$_2$][(-)-O,O'-dibenzoyl-L-tartrate]·12H$_2$O (27a)

The resolution of rac-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ (27) was achieved by the diastereoisomer formation with the chiral disodium [(-)-O,O'-dibenzoyl-L-tartrate] (28). This resolution method yields excellent enantiomerically pure chiral building block Λ-[Ru(bpy)$_2$(py)$_2$][(-)-O,O'-dibenzoyl-L-tartrate]·12H$_2$O (27a). The two pyridine ligands in Λ-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ can be easily substituted by other bidentate ligands under the complete retention of configuration.

8.1.1 Preparation of Chiral Building Block

The complex cis-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ (27) (py = pyridine) was prepared from Ru(bpy)$_2$Cl$_2$·2H$_2$O with pyridine (29) as described previously. The resolution of cis-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ (py = pyridine) was achieved by the addition of an aqueous solution of disodium [(−)-O,O'-dibenzoyl-L-tartrate] (28) to an aqueous solution of cis-[Ru(bpy)$_2$(py)$_2$]Cl$_2$. Red crystals of Λ-[Ru(bpy)$_2$(py)$_2$][(-)-O,O'-dibenzoyl-L-tartrate]·12H$_2$O (27a) were obtained by the fractional recrystallization. 67,69,72
Scheme 8.1 Preparation of the Ru Chiral Building Block

Reflux

Water

Disodium [(-)-O,O'-dibenzoyl-L-tartrate]

Ru(bpy)₂Cl₂

Less Soluble in Water, Red Crystals

More Soluble in Water, Remains in Solution

Figure 8.1 Circular Dichroism Spectra of Λ-[Ru(bpy)₂(py)₂]Cl₂ (27c) in Acetonitrile

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8.1.2 Absolute Configuration of the Chiral Building Block

Assignment of the absolute configuration of the chiral building block Λ-[Ru(bpy)$_2$(py)$_2$][(-)-O,O'-dibenzoyl-L-tartrate]-12H$_2$O (27a) and of the corresponding substituted products can be made by applying exciton theory,\textsuperscript{84-86} i.e., in the regions of the long-axis-polarized transitions around 294 nm of the ligand bpy, the circular dichroism will appear strongly positive at lower energies and strongly negative at higher energies if the molecule has the absolute configuration related to (-)-[Fe(phen)$_3$]$^{2+}$ (Λ form). The circular dichroism (CD) spectra of the enantiomerically pure complexes exhibit typical excitonic interactions of the π−π* transitions\textsuperscript{86} and the expected Cotton effects of the metal-to-ligand charge transfer bands in the visible region. Λ-[Ru(bpy)$_2$(py)$_2$][(-)-O,O'-dibenzoyl-L-tartrate]-12H$_2$O (27a) was converted to the chloride salt Λ-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ (27c), of which the CD spectra is shown in Figure 8.1. It is consistent with the Λ configuration.

8.1.3 Optical Purity of the Chiral Building Block

The determination of optical purity of the chiral building block is of basic importance. The retention or partial loss of optical purity in the course of a reaction often gives valuable information. Accurate knowledge of the optical purity is especially important in the area of polynuclear metal complex synthesis. Due to the multiplication effect, a relatively small amount of the other enantiomer will yield significant amount of isomerically mixed products, even if the reactions proceed with complete retention of configuration. For example, in the case of a dinuclear species, an 80%/20% mixture of a
chiral building block leads to 64% of the desired enantiomer, plus 4% of the other enantiomer, and 32% of the meso form. Since we were interested in the use of the chiral building block for the synthesis of polynuclear ruthenium complexes, where the two pyridine ligands in general are replaced by the bidentate bibenzimidazole ligands, the determination of the optical purity of the obtained chiral building block is critical before it is used in the subsequent complexation.

A lower limit of the optical purity of the building blocks was determined by forming the diastereomers of \([\text{Ru(bpy)}_2 (R,R\text{-dach})]^{2+}\) (30) through a substitution reaction with an optically active bidentate ligand \((1R,2R)-(-)-1,2\text{-diaminocyclohexane}\) (31, \(R,R\text{-dach}\)) (Scheme 8.2). The obtained diastereoisomers give different \(^1\text{H NMR}\) chemical shifts (Figure 8.2). Spectrum (a) shows the \(^1\text{H NMR}\) (aromatic region) of \([\text{Ru(bpy)}_2 (R,R\text{-dach})]^{2+}\) (30) prepared from the racemic \(\text{cis-}[\text{Ru(bpy)}_2 (\text{py})_2]^{2+}\) (27), clearly giving the signals of two diastereoisomers \(\Lambda-[\text{Ru(bpy)}_2 (R,R\text{-dach})]^{2+}\) (\(\Lambda/RR\)) and \(\Delta-[\text{Ru(bpy)}_2 (R,R\text{-dach})]^{2+}\) (\(\Delta/RR\)) in a 1:1 molar ratio. Since each diastereoisomer possesses a \(C_2\) axis, the corresponding bpy protons in the complex are equivalent, giving a total of only eight nonequivalent protons. Spectrum (b) shows the \(^1\text{H NMR}\) of \(\Lambda-[\text{Ru(bpy)}_2 (R,R\text{-dach})]^{2+}\) (\(\Lambda/RR\)) prepared from \(\Lambda-[\text{Ru(bpy)}_2 (\text{py})_2]^{2+}\) (27a), clearly indicating the purity of the optically active chiral building block with the \(\Lambda/RR > 98\%\) de.
Scheme 8.2 Synthesis of \([\text{Ru(bpy)}_2(R,R\text{-dach})]^{2+}\) and \(\Lambda-\text{[Ru(bpy)}_2(R,R\text{-dach})]^{2+}\)

\[
\text{Scheme 8.2 Synthesis of } [\text{Ru(bpy)}_2(R,R\text{-dach})]^{2+} \text{ and } \Lambda-\text{[Ru(bpy)}_2(R,R\text{-dach})]^{2+}.
\]

\[
\text{Scheme 8.2 Synthesis of } [\text{Ru(bpy)}_2(R,R\text{-dach})]^{2+} \text{ and } \Lambda-\text{[Ru(bpy)}_2(R,R\text{-dach})]^{2+}.
\]

(a) \(30\) \\
\(\Lambda/RR, \Delta/RR\)

\[
(a) \ 30
\]
\(\Lambda/RR, \Delta/RR\)

(b) \(30a\) \\
\(\Lambda/RR\)

\[
(b) \ 30a
\]
\(\Lambda/RR\)

Figure 8.2 \(^1\)H NMR Spectra (500 MHz) of (a) \([\text{Ru(bpy)}_2(R,R\text{-dach})](\text{PF}_6)_2\) \((30)\) and (b) \(\Lambda-\text{[Ru(bpy)}_2(R,R\text{-dach})](\text{PF}_6)_2\) \((30a)\) in Acetonitrile-\(d_3\)
8.2 Synthesis of DiastereomERICALLY Pure Ru Complexes Based on 2,2’-Bibenzimidazole

Mono- and di-nuclear Ru complexes represent the simplest examples of the polynuclear assemblies. The studies with the stereoselective synthesis of individual enantiomeric or diastereoisomeric forms, or the separation of these individual stereoisomeric forms from a mixture would provide useful information for the characterization of the higher nuclearity. Our study to probe the stereochemical control in the polynuclear assemblies of the oligomeric bibenzimidazoles started with the synthesis of the enantiomerically pure (ep) monomer \( \Lambda -20 \) (Figure 8.3).

![Figure 8.3 Enantiomers of [Ru(bpy)₂(BiBzImH₂)](PF₆)₂ (20)](image)

8.2.1 Synthesis of \( \Lambda -[Ru(bpy)₂(BiBzImH₂)](PF₆)₂ (A-20) \), \( \Lambda -[Ru(bpy)₂(BiBzIm)] (A-21) \) and \( \Lambda \Lambda -[Ru(bpy)₂(BiBzIm)Ru(bpy)₂](PF₆)₂ (A22) \)

\( \Lambda -[Ru(bpy)₂(py)₂][(-)-O,O’-dibenzoyl-L-tartrate]⋅12H₂O (27a) \) was reacted with an excess of 2,2’-bibenzimidazole (5) in ethylene glycol at 120 °C. Interestingly, two complexes were obtained, which were proven to be the mono-deprotonated complex \( \Lambda -\).
and the bis-Ru complex $\Lambda\Lambda$-22 (2.2 : 1), through the NMR spectroscopy and the further control experiment (Scheme 8.3 and Figure 8.4).

Scheme 8.3 Synthesis of $\Lambda$-[Ru(bpy)$_2$(BiBzImH$_2$)](PF$_6$)$_2$ ($\Lambda$-20)

$\Lambda$-20

[Chemical Structure Image]

$\Lambda$-20

[Chemical Structure Image]

2.2 : 1

[Chemical Structure Image]
Figure 8.4 $^1$H NMR Spectra of the Chiral Ru Complexes in Scheme 8.3
1) Crude Reaction Mixture of $\Lambda$-20a and $\Lambda\Lambda$-22 (2.2 : 1). 2) $\Lambda$-21, $H_1'$, $H_2'$, $H_3'$, $H_4'$ are upfield compared to $H_1$, $H_2$, $H_3$, $H_4$. 3) $\Lambda\Lambda$-22. $H_{ab'}$, $H_{bb'}$ remained unchanged after the base treatment. 4) $\Lambda$-20, $H_1''$, $H_2''$, $H_3''$, $H_4''$ are downfield compared to $H_1'$, $H_2'$, $H_3'$, $H_4'$. 100
The formation of Λ-20a is due to the deprotonation of Λ-20 by pyridine released from the chiral building block 27a. As being discussed in Chapter 5, the acidity of the bibenzimidazole ligand increases upon the coordination with the ruthenium ion, rendering the easy deprotonation of the complex Λ-20. The pKₐ values of [Ru(bpy)₂(BiBzImH₂)]²⁺ in 50% acetonitrile/water mixture have been reported: pKₐ₁ and pKₐ₂ are 5.74 ± 0.05 and 10.51 ± 0.05 at 25 °C, respectively.¹⁷,²⁰ The pKa of pyridinium ion is 5.25, which means that pyridine is basic enough to deprotonate the formed model complex Λ-20, rendering the formation of Λ-20a and the bis-Ru complex ΛΛ-22.

The mixture of the mono-deprotonated Λ-20a and the bis-Ru complex ΛΛ-22 was separated by the treatment with NaOCH₃. Λ-20a was fully deprotonated to give the complex Λ-21, which was not soluble in acetone. The bis-Ru complex ΛΛ-22 was stable, remaining unchanged under the basic condition, and its PF₆⁻ salt was soluble in acetone. Therefore, Λ-21 was easily separated from ΛΛ-22 by filtration. Then the pure deprotonated Λ-21 was protonated by HCl to give the pure protonated model compound Λ-20. The structures of the products were proven by the NMR study (Figure 8.4). The protons H₁/H₁'/H₁″ and Hₐ/Hₐ′ are on the bibenzimidazole ligand, which are in the shielding zone of the benzene ring of the bpy, therefore they are strongly shielded (δ = 5–6 ppm). The structure of the bis-Ru complex ΛΛ-22 was further confirmed by the experiment shown in the Scheme 8.4: the same bis-Ru complex was obtained by the
reaction of Λ-21 with one equivalent of the chiral building block Λ-[Ru(bpy)2(py)2][(-)-O,O’-dibenzoyl-L-tartrate]-12H2O (27a) (Scheme 8.4).

Scheme 8.4 Synthesis of ΛΛ-[Ru(bpy)2(BiBzIm)Ru(bpy)2](PF6)2 (ΛΛ-22)

Scheme 8.5 Synthesis of Racemic [Ru(bpy)2(BiBzImH2)](PF6)2 (20)

The single crystals of ΛΛ-[Ru(bpy)2(BiBzIm)Ru(bpy)2]Cl2 (ΛΛ-22) were grown by the ether diffusion to the methanol solution of the complex ΛΛ-22. The crystals are of poor quality, crumbling easily and being extremely prone to solvent evaporation.
Although the refined structure was not completely solved, the preliminary X-ray crystal analysis showed the connectivity of the complex.

Compared with the stereospecific synthesis, the synthesis of the racemic mono-Ru complex 20 by complexing bibenzimidazole (5) with racemic Ru(bpy)$_2$Cl$_2$ gave the desired complex 20 without deprotonation, along with a small amount of the dinuclear complex 22 in a ratio of 19 : 1 (Scheme 8.5).

8.2.2 Absolute Configuration of Λ-[Ru(bpy)$_2$(BiBzImH$_2$)](PF$_6$)$_2$ (Λ-20), Λ-[Ru(bpy)$_2$(BiBzIm)] (Λ-21) and ΔΔ-[Ru(bpy)$_2$(BiBzIm)Ru(bpy)$_2$]Cl$_2$ (ΔΔ-22)

The circular dichroism (CD) spectra of Λ-[Ru(bpy)$_2$(BiBzImH$_2$)](PF$_6$)$_2$ (Λ-20), Λ-[Ru(bpy)$_2$(BiBzIm)] (Λ-21) and ΔΔ-[Ru(bpy)$_2$(BiBzIm)Ru(bpy)$_2$]Cl$_2$ (ΔΔ-22) are shown in Figure 8.5 and 8.6. The Cotton effects are observed, which are in agreement with the expected Λ absolute configurations, i.e., under the long-axis-polarized band around 294 nm, the circular dichroism is at low energies strongly positive, at higher energies negative, and positive at the lowest energy MLCT transition. Therefore the substitution of the pyridine ligands proceeds with the retention of configuration.
Figure 8.5 Circular Dichroism Spectra of \( \Lambda-[\text{Ru(bpy)}_2(\text{BiBzImH}_2)](\text{PF}_6)_2 \) (\( \Lambda-20 \)) and \( \Lambda-[\text{Ru(bpy)}_2(\text{BiBzIm})] \) (\( \Lambda-21 \)) in Acetonitrile

Figure 8.6 Circular Dichroism Spectra of \( \Lambda\Lambda-[\text{Ru(bpy)}_2(\text{BiBzIm})_2\text{Ru(bpy)}_2]\text{Cl}_2 \) (\( \Lambda\Lambda-22 \)) in Acetonitrile
8.2.3 Optical Purity of $\Lambda\Lambda$-[Ru(bpy)$_2$(BiBzIm)Ru(bpy)$_2$](PF$_6$)$_2$ ($\Lambda\Lambda$-22)

$^1$H NMR spectra of [Ru(bpy)$_2$(BiBzIm)Ru(bpy)$_2$](PF$_6$)$_2$ (22) prepared from the racemic Ru(bpy)$_2$Cl$_2$, and $\Lambda\Lambda$-22 prepared from the chiral building block $\Lambda$-[Ru(bpy)$_2$(py)$_2$][(-)-$O,O'$-dibenzoyl-L-tartrate]-12H$_2$O (27a) are shown in Figure 8.7. With the use of the racemic Ru(bpy)$_2$Cl$_2$, the diastereoisomers ($\Delta\Delta/\Lambda\Lambda$ and $\Delta\Lambda$) were obtained (spectrum 1 in Figure 8.7). The relative abundance of the meso form and the enantiomeric pair is around 55 : 45, which is close to the statistical 50 : 50 value. The
$D_2$ symmetry of $\Lambda\Lambda$-[Ru(bpy)$_2$(BiBzIm)Ru(bpy)$_2$](PF$_6$)$_2$ ($\Lambda\Lambda$-22) requires the equivalence of the four bpy ligands. A total of 10 magnetically nonequivalent protons is therefore observed (spectrum 2 in Figure 8.7). $H_{a/a'}$ and $H_{b/b'}$ are the protons on the bibenzimidazole bridging ligand. $H_{a/a'}$ lie in the shielding zone of the adjacent bpy rings ($\delta = 5.5$ ppm). The rest of eight protons (c–j) are on the bpy ligand. The $^{13}$C NMR spectra of $\Lambda\Lambda$-[Ru(bpy)$_2$(BiBzIm)Ru(bpy)$_2$](PF$_6$)$_2$ gives 14 lines (10 lines from ligand bpy and 4 lines from BiBzIm). There is no sign of the formation of the other diastereoisomers compared with the spectrum 1 in Figure 8.7.

The use of a chiral building block almost entirely avoids the formation of the different isomers, with the $\Lambda\Lambda > 98\%$ de, which means that the complexation of the bibenzimidazole and the chiral building block is under the complete retention of configuration, without racemization under the reaction condition. In the following complexations of the bibenzimidazole oligomers with the chiral building block under the similar reaction conditions, it is reasonable to believe that reactions will still proceed with the complete retention of configuration.

### 8.3 Synthesis and Properties of $\Lambda\Lambda$-[(Ru(bpy)$_2$)$_2$(bis(BiBzImH$_2$))](PF$_6$)$_4$ ($\Lambda\Lambda$-23)

As shown in Figure 8.8, there are two diastereoisomers in the bis-Ru complex $\Lambda\Lambda$-[(Ru(bpy)$_2$)$_2$(bis(BiBzImH$_2$))](PF$_6$)$_4$ ($\Lambda\Lambda$-23): $\Lambda\Lambda/\Delta\Delta$ (racemic, a pair of enantiomers) and $\Delta\Lambda$ (meso). Due to the $C_5$ symmetry of the dimer of bibenzimidazole (14), there is the possibility of forming the four regioisomers (Figure 8.9). This leads to
the complexity of the NMR spectra, rendering the difficulties in the purification and characterization.

Figure 8.8 Diastereoisomers of [(Ru(bpy)$_2$)(bis(BiBzImH$_2$))](PF$_6$)$_4$ (23)
Two diastereoisomers: rac (ΑΑ, ΔΔ) and meso (ΔΛ)
Figure 8.9 Regioisomers of \(\Lambda\Lambda-[(\text{Ru(bpy})_2]{(\text{biBzImH}_2)}]}{(\text{PF}_6)_4}\) (\(\Lambda\Lambda-23\))

("Tran" means the two \(\text{Ru(bpy})_2\) are on the opposite side of \(\text{C}^-\text{C}\) bond.

"Cis" means the two \(\text{Ru(bpy})_2\) are on the same side of \(\text{C}^-\text{C}\) bond.

"Para" means the Ru is connected to the nitrogen atom para to the \(\text{C}^-\text{C}\) bond.

"Meta" means the Ru is connected to the nitrogen atom meta to the \(\text{C}^-\text{C}\) bond.)

\(\text{C}^-\text{C}\) bond: the \(\text{C}^-\text{C}\) bond between the two bibenzimidazole units.
Scheme 8.6 Synthesis of ΛΛ-[((Ru(bpy))₂₂(bis(BiBzImH₂)))(PF₆)₄ (ΛΛ-23)

The stereospecific synthesis of the homochiral [((Ru(bpy))₂₂(bis(BiBzImH₂)))(PF₆)₄ (ΛΛ-23) was attempted by the complexation of the dimer of bibenzimidazole (14) with the chiral building block (27a) following the same method...
for the synthesis of Λ-20. However, the reaction provided a mixture with a very low yield of the possible product ΛΛ-23 or its partially deprotonated form ΛΛ-23a (~30%). The possible reason for the formation of the complicated products is that the deprotonation by the pyridine released from the chiral building block during the reaction, and the over-complexation on both sides of the dimer of bibenzimidazole (14) to form the tris-Ru (Λ₃-Ru₃-32) or the tetra-Ru (Λ₄-Ru₄-25) complexes. No more studies were carried out to investigate the synthesis and structure of the stereoisomers of ΛΛ-23 due to the above complexities.

8.4 Synthesis and Properties of Λ₄-[(Ru(bpy)₂)₄(bis(BiBzIm))](PF₆)₄ (Λ₄-Ru₄-25)

To solve the above regioisomer and over-complexation issues, an easy way is to synthesize the homochiral tetra-Ru complex Λ₄-Ru₄-25. All the four bidentate sites of the dimer ligand 14 will be complexed by the Ru chiral building block 27a, which excludes the formation of the regioisomers. Therefore, the homochiral tetra-Ru complex would be the major product in the reaction shown in Scheme 8.7, which simplifies the isolation and crystallization processes.

An excess of the chiral building block (i.e. 4.4 equiv) was added to ensure the fully complexation of the dimer 14. The formation of the tetra-Ru complex Λ₄-Ru₄-25 was confirmed by MALDI-TOF analysis (Figure 8.10) and the satisfactory elemental analysis. The mass spectrum clearly shows the parent ion complex minus 1PF₆⁻, 2PF₆⁻, 3PF₆⁻, and 4PF₆⁻ fragments.
Scheme 8.7 Synthesis of \( \Lambda_4^-[\{\text{Ru(bpy)}_2\}_4\{\text{bis}(\text{BiBzIm})\}]\text{(PF}_6\text{)}_4 \) (\( \Lambda_4\text{-Ru}_4\text{-}25 \))

\[
\Lambda^-[\text{Ru(bpy)}_2\text{(py)}_2]((-)-O,O’) \text{ dibenzoyl-L-tartrate}
\]
(4.4 equiv)

27a + 14

Ethylene Glycol

120 °C, 8 h
(73%)

The single crystals of the \( \text{PF}_6^- \) salt of \( \Lambda_4\text{-Ru}_4\text{-}25 \) were grown from the acetone/water mixture by the slow evaporation. The crystals are of poor quality, crumbling easily and being extremely prone to solvent evaporation. The refined structure was not completely solved. The preliminary X-ray crystal structure showed the connectivity of the complexes in Figure 8.11. The structure showed that the bridging ligand is close to be planar after being complexed with four \( \Lambda^-[\text{Ru(bpy)}_2]^{2+} \). The molecule has an estimate size of \( 2.1 \times 1.1 \times 1.0 \text{ nm}^3 \).
Figure 8.10 MALDI-TOF Spectra of \( \Lambda_4 \)-[(Ru(bpy)\(_2\))\(_4\)(bis(BiBzIm))]PF\(_6\)\(_4\) (\( \Lambda_4\)-Ru\(_4\)-25)

2550 \([M - 1PF_6]^+\), 2410 \([M - 2PF_6]^+\),
2262 \([M - 3PF_6]^+\), 2116 \([M - 4PF_6]^+\).
Figure 8.11 X-ray Crystal Structure of $\Lambda_4$-[(Ru(bpy)$_2$)$_4$(bis(BiBzIm))](PF$_6$)$_4$
($\Lambda_4$-Ru$_4$-25) (Incomplete refinement)
(a): A size of $2.1 \times 1.1 \times 1.0$ nm$^3$
(b): The bridging ligand is close to be planar
The CD spectra of \( \Lambda_4\)-Ru\( _4 \)-25 is shown in the Figure 8.12. The Cotton effects are observed, indicating the absolute configurations corresponding to the \( \Lambda \) configuration, i.e., under the long-axis-polarized band around 294 nm, the circular dichroism appears strongly positive at low energies, strongly negative at higher energies, and positive at the lowest energy MLCT absorption.

**8.5 Synthesis and Properties of \( \Lambda_8\)-Ru\( _8 \)-26**

The same strategy was applied for the synthesis of the homochiral octa-Ru complex \( \Lambda_8\)-Ru\( _8 \)-26 of the tetramer of the bibenzimidazole (19) (Scheme 8.8). An excess of the chiral building block (27a) (8.4 equiv) and 20 equiv of NaOCH\(_3\) were added to ensure the fully deprotonation and complexation of the tetramer ligand 19. The formation of the octa-Ru complex \( \Lambda_8\)-Ru\( _8 \)-26 was confirmed by the MALDI-TOF
analysis (Figure 8.13). The spectra clearly shows the parent ion complex minus $1\text{PF}_6^-$, $2\text{PF}_6^-$, …, $7\text{PF}_6^-$, and $8\text{PF}_6^-$ fragments.

Scheme 8.8 Synthesis of $\Lambda_8$-[(Ru(bpy)$_2$)$_8$(tetra(BiBzIm))](PF$_6$)$_8$ ($\Lambda_8$-Ru$_8$-26)
The CD spectra of $\Lambda_8$-Ru$_8$-26 is shown in the Figure 8.14. The Cotton effects are observed, indicating the absolute configurations corresponding to the $\Lambda$ configuration, i.e., under the long-axis-polarized band around 290 nm, the circular dichroism appear strongly positive at low energies, strongly negative at higher energies, and positive at the lowest energy MLCT absorption.
Figure 8.14 Circular Dichroism Spectra of $\Lambda_8$-[(Ru(bpy)$_2$)$_8$(tetra(BiBzIm))](PF$_6$)$_8$ ($\Lambda_8$-Ru$_8$-26) in Acetonitrile

For the UV–vis and the electrochemical properties of the above homochiral Ru complexes, refer to the corresponding nonchiral complexes in Chapter 5.

8.6 Conclusions

The homochiral multinuclear Ru complexes of the oligomeric bibenzimidazoles were synthesized stereospecifically using $\Lambda$-[Ru(bpy)$_2$(py)$_2$][(-)-$O,O'$-dibenzoyl-L-tartrate]·12H$_2$O as the enantiomerically pure chiral building block. The complexation of bibenzimidazole and the chiral building block proceeds with the complete retention of configuration. The tetra-Ru complex has an estimate size of $2.1 \times 1.1 \times 1.0$ nm$^3$. 
CHAPTER 9
EXPERIMENTAL DETAILS

9.1 General

9.1.1 Reagents and Materials

All reagents were used without further purification. 2,2′-Bipyridine (99%), ammonium hexafluorophosphate (95+%%) and RuCl₃ (98%) were purchased from Alfa. Dibenzoyl-L-tartaric acid (98%) and tetrabutylammonium chloride (98%) were purchased from Aldrich. Acetonitrile was distilled over CaH₂ before use. Nylon membranes filter paper (pore size: 0.2 µm or 0.45 µm) for the filtration of the Ru complexes was purchased from Cole-Parmer Instrument Co.

9.1.2 Measurements

NMR spectra were obtained on a JEOL Eclipse+ 500 MHz spectrometer. UV–vis spectra were measured using a Varian Cary 500 UV–vis–NIR spectrophotometer. Elemental analysis was performed by Quantitative Technologies Inc. (QTI) (Whitehouse, NJ). Mass analysis was performed by Scripps Research Institute (La Jolla, CA). MALDI-TOF spectra were obtained on Applied Biosystems Voyager STR mass spectrometer. Cyclic Voltammogram experiments were performed at 20 °C using a PC-controlled potentiostat (CH Instruments, electroanalytical
The working electrode was a 1.5 mm glassy carbon electrode and the auxiliary electrode was a platinum wire. The reference electrode was a no leak Ag/AgCl reference electrode. They were purchased from Cypress Systems, Inc. (Lawrence, KS). Circular Dichroism spectra were recorded on a JASCO J–710 spectropolarimeter.

9.2 Synthesis

[Ru(bpy)$_2$(py)$_2$]Cl$_2$ (27). This material was prepared using a modification of a previously reported procedure.$^{72,83}$ A round bottom flask was charged with pyridine (23 mL), water (46 mL) and Ru(bpy)$_2$Cl$_2$ (2.00 g, 3.84 mmol). The reaction mixture was stirred while heating at reflux for 4 h, filtered while hot, and the solvent was evaporated under reduced pressure by the use of an oil pump. The deep red residue was dissolved in methanol (46 mL) and sufficient diethyl ether (around 170 mL) was added dropwise to result in the formation of a red precipitate. The mixture was allowed to stand at room temperature for 1 h, after which the precipitate was collected by suction filtration and the solids were washed with diethyl ether (2×50 mL). The recovered solid (2.30 g, yield: 93%) was identical in its properties to those previously reported for rac-[Ru(bpy)$_2$(py)$_2$]Cl$_2$. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta = 9.02$ (d, $J = 5.4$ Hz, 1H), 8.72 (d, $J = 8.1$ Hz, 1H), 8.64 (d, $J = 8.1$ Hz, 1H), 8.39 (d, $J = 5.4$, 2H), 8.25 (dd, $J = 8.1$ Hz, 8.1 Hz, 1H), 8.02 (dd, $J = 8.1$ Hz, 8.1 Hz, 1H), 7.94 (dd, $J = 6.7$, $J = 6.7$, 2H), 7.92 (d, $J = 6.1$, 1H), 7.89 (dd, $J = 6.7$ Hz, 6.7 Hz, 1H), 7.49 (dd, $J = 6.7$ Hz, 6.7 Hz, 1H), 7.40 (dd, $J = 6.7$ Hz, 6.7 Hz, 2H).
Resolution of [Ru(bpy)$_2$(py)$_2$]$^{2+}$ (27):$^{67,69,72}$

Disodium (−)-$O,O'$-dibenzoyl-L-tartrate solution (0.5 M) (28): This solution was prepared using a modification of a previously reported procedure.$^{72}$ NaOH (14.0 g.) was dissolved in 50 mL of deionized water to make a NaOH solution (concentration = 7 mol/L). (−)-$O,O'$-dibenzoyl-L-tartaric acid (4.6 g, 12.2 mmol) was dissolved in 20 mL of H$_2$O to make a suspension. 4.3 mL of the above NaOH solution (concentration = 7 mol/L, 30.1 mmol, 2.47 equiv) was added dropwise to the above (−)-$O,O'$-dibenzoyl-L-tartaric acid solution. Keep stirring at room temperature for 2 h until the pH = 9.1. (pH around 9.1 is important for the formation of the red crystals described below.)

Λ-[Ru(bpy)$_2$(py)$_2$][(-)-$O,O'$-dibenzoyl-L-tartrate] (27a). An aqueous solution of disodium (−)-$O,O'$-dibenzoyl-L-tartrate (28) (12 mL, 0.5 M, 6 mmol, 3.35 equiv) was added dropwise to a solution of rac-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ (27) (1.15 g, 1.79 mmol) in 22 mL of water. The mixture was stirred for 10 min. In a dark room, the solvent was allowed to evaporate naturally. The red crystals formed the next day. After 8–10 days, the red crystals of Λ-[Ru(bpy)$_2$(py)$_2$][(-)-$O,O'$-dibenzoyl-L-tartrate]-12H$_2$O (27a) were collected by filtration, then rinsed with cold water and air-dried. Yield: 0.72 g, 35% (theory: 50%). $^1$H NMR (500 MHz, DMSO-$d_6$): δ = 9.00 (d, $J = 5.4$ Hz, 1H), 8.67 (d, $J = 8.1$ Hz, 1H), 8.59 (d, $J = 8.1$ Hz, 1H), 8.38 (d, $J = 5.4$, 2H), 8.22 (dd, $J = 8.1$ Hz, $J = 8.1$ Hz, 1H), 8.00 (d, $J = 6.7$ Hz, 2H), 7.99 (dd, $J = 8.1$ Hz, 8.1 Hz, 1H), 7.92 (d, $J = 7.4$ Hz, 1H), 7.88 (dd, $J = 6.7$ Hz, 6.7 Hz, 2H), 7.59 (dd, $J = 7.4$ Hz, 7.4 Hz, 1H), 7.47 (dd, $J = 7.4$ Hz, 7.4 Hz, 3H), 7.39 (dd, $J = 7.4$ Hz, 7.4 Hz, 2H), 5.48 (s, 1H). $^{13}$C NMR (125
MHz, DMSO-$d_6$: $\delta = 168.7, 165.4, 157.0, 156.8, 153.3, 152.5, 152.3, 138.0, 137.9, 137.7, 132.3, 129.3, 128.2, 128.1, 127.7, 126.2, 124.0, 123.8, 76.9$. The tartrate salt was dissolved in methanol, and was converted to $\Lambda$-[Ru(bpy)$_2$(py)$_2$](PF$_6$)$_2$ by precipitation with the addition of a saturated aqueous solution of NH$_4$PF$_6$. Then $\Lambda$-[Ru(bpy)$_2$(py)$_2$](PF$_6$)$_2$ was purified by metathesis with an acetone solution of tetrabutylammonium chloride to precipitate the chloride salt $\Lambda$-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ (27c). CD (CH$_3$CN, $\lambda$, nm, ($\Delta$e, M$^{-1}$·cm$^{-1}$)): 250 (−9.5), 278 (−13.1), 294 (+115.5), 364 (−16.3), 445 (−3.9), 502 (+1.4), 524 (+1.2).

$\Lambda$-[Ru(bpy)$_2$(BiBzImH$_2$)](PF$_6$)$_2$ (A-20). Bibenzimidazole (5) (0.11 g, 0.47 mmol, excess) was suspended in 20 mL of ethylene glycol and degassed for 15 min under nitrogen, then heated at 150 °C until it dissolved. Then the solution was cooled to 120 °C, and $\Lambda$-[Ru(bpy)$_2$(py)$_2$][(-)-O,O'-dibenzoyl-L-tartrate] (0.29 g, 0.25 mmol) was added. The mixture was heated at 120 °C for 8 h. The resulting deep red-brown solution was cooled, diluted with 30 mL of water, and filtered to remove the excess bibenzimidazole. A saturated aqueous solution of NH$_4$PF$_6$ was added dropwise to the above filtrate to precipitate the crude Ru complexes. The crude was collected by filtration and air-dried (0.17 g, crude yield: 90%). The crude product, which contained $\Lambda$-20a and $\Lambda\Lambda$-22, was deprotonated by NaOCH$_3$/methanol to get the mixture of $\Lambda$-21 and $\Lambda\Lambda$-22 (see the procedure of $\Lambda$-21). $\Lambda$-21 was not soluble in acetone and was separated by filtration. $\Lambda\Lambda$-22 remained in the acetone solution as the PF$_6$− salt. Then the pure deprotonated complex $\Lambda$-21 was suspended in methanol, and acidified by
adding concentrated HCl to get $\Lambda$-[Ru(bpy)$_2$(BiBzImH$_2$)]Cl$_2$ ($\Lambda$-20). Diethyl ether was added dropwise to precipitated out $\Lambda$-20. It was purified by dissolving in methanol and metathesis with a saturated aqueous solution of NH$_4$PF$_6$ to convert to the PF$_6^-$ salt $\Lambda$-[Ru(bpy)$_2$(BiBzImH$_2$)](PF$_6$)$_2$. $^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ = 8.88 (d, $J$ = 8.1 Hz, 1H), 8.78 (d, $J$ = 8.1 Hz, 1H), 8.25 (dd, $J$ = 8.1 Hz, 8.1 Hz, 1H), 8.06 (dd, $J$ = 8.1, 8.1 Hz, 1H), 8.01 (d, $J$ = 6.1 Hz, 1H), 7.91 (d, $J$ = 6.1 Hz, 1H), 7.86 (d, $J$ = 8.1, 1H), 7.60 (dd, $J$ = 6.1 Hz, 6.1 Hz, 1H), 7.48 (dd, $J$ = 6.1 Hz, 6.1 Hz, 1H), 7.38 (dd, $J$ = 8.1 Hz, 8.1 Hz, 1H), 7.06 (dd, $J$ = 8.1 Hz, 8.1 Hz, 1H), 5.63 (d, $J$ = 8.1 Hz, 1H). CD (CH$_3$CN, $\lambda$, nm, ($\Delta$ε, M$^{-1}$·cm$^{-1}$)): 238 (-16.8), 254 (40.9), 282 (-124.0), 294 (+185.1), 314 (+64.1), 330 (+85.8), 348 (+78.9), 430 (-26.8), 482 (+7.2).

$\Lambda$-[Ru(bpy)$_2$(BiBzIm)] ($\Lambda$-21). The crude Ru complexes from the above reaction (0.17 g) were added to 20 mL of methanol, and the suspension was degassed for 15 min under nitrogen. NaOCH$_3$ (0.15 g, 2.77 mmol) was dissolved in 5 mL methanol and added to the above suspension dropwise. The color of the solution turned from deep red-brown to purple. The solution was refluxed for 3 h under nitrogen. After the resulting mixture was cooled, the solvent was condensed to a half volume by rotary evaporation. Then the mixture, which contained $\Lambda$-21 and $\Lambda\Lambda$-22, was filtered and rinsed with acetone to provide the pure solid product $\Lambda$-21. Sometimes the solid was difficult to collect by filtration due to the small size, then the following method was applied: the mixture of $\Lambda$-21 and $\Lambda\Lambda$-22 was suspended in acetone. An acetone solution of tetrabutylammonium chloride was added dropwise to precipitate the chloride salt.
ΛΛ-[(Ru(bpy)$_2$)(BiBzIm)]Cl$_2$ (ΛΛ-22) and Λ-21, which were collected by filtration. The solid obtained was suspended in water to dissolve ΛΛ-[(Ru(bpy)$_2$)(BiBzIm)]Cl$_2$ (ΛΛ-22). The deprotonated Λ-21 was not soluble in water, and was separated by filtration. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta = 8.75$ (d, $J = 8.1$ Hz, 1H), 8.64 (d, $J = 8.1$ Hz, 1H), 8.09 (dd, $J = 8.1$ Hz, 8.1 Hz, 1H), 7.94 (d, $J = 6.1$ Hz, 1H), 7.86 (dd, $J = 8.1$, 8.1 Hz, 1H), 7.73 (d, $J = 6.1$ Hz, 1H), 7.49 (dd, $J = 6.1$ Hz, 6.1 Hz, 1H), 7.41 (d, $J = 8.1$, 1H), 7.37 (dd, $J = 6.1$ Hz, 6.1 Hz, 1H), 6.75 (dd, $J = 8.1$ Hz, 8.1 Hz, 1H), 6.45 (dd, $J = 8.1$ Hz, 8.1 Hz, 1H), 5.35 (d, $J = 8.1$ Hz, 1H). $^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta =$ 158.8, 157.6, 157.2, 151.4, 150.8, 148.1, 145.0, 135.2, 134.5, 126.4, 126.3, 123.4, 123.0, 118.6, 118.0, 117.9, 111.1. CD (CH$_3$CN, $\lambda$, nm, ($\Delta\varepsilon$, M$^{-1}$·cm$^{-1}$)): 216 (−74.0), 249 (+31.5), 264 (50.8), 285 (−29.7), 299 (+157.3), 319 (+61.6), 322 (+62.5), 398 (−32.3), 467 (−10.1), 543 (+7.1).

ΛΛ-[(Ru(bpy)$_2$)(BiBzIm)](PF$_6$)$_2$ (ΛΛ-22). For the above deprotonation reaction, the product which was soluble in water is ΛΛ-[(Ru(bpy)$_2$)(BiBzIm)]Cl$_2$. It was precipitated by metathesis with a saturated aqueous solution of NH$_4$PF$_6$ to convert to the PF$_6^-$ salt ΛΛ-[(Ru(bpy)$_2$)(BiBzIm)](PF$_6$)$_2$. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta =$ 8.79 (d, $J = 8.1$ Hz, 1H), 8.76 (d, $J = 8.1$ Hz, 1H), 8.15 (dd, $J = 8.1$ Hz, 8.1 Hz, 1H), 8.06 (d, $J = 8.1$, 1H), 8.06 (dd, $J = 8.1$ Hz, 8.1 Hz, 1H), 7.68 (d, $J = 6.1$ Hz, 1H), 7.52 (dd, $J = 6.1$, 6.1 Hz, 1H), 7.36 (dd, $J = 6.1$, 6.1, 1H), 6.66 (dd, $J = 6.1$, 3.4 Hz, 1H), 5.54 (dd, $J = 6.1$, 3.4 Hz, 1H). $^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta =$ 159.4, 157.8, 157.6, 152.9, 151.0, 144.9, 136.4, 136.2, 127.2, 126.6, 123.6, 123.5, 121.1, 113.7. MALDI-
TOF \((m/z)\) (PF\(_6^−\) salt): 1367 \([M + H_2O]^+\), 1205 \([M – 1PF_6]^+\). CD (CH\(_3\)CN, \(\lambda\), nm, (\(\Delta\varepsilon, M^{-1}\cdot cm^{-1}\))): 214 (−59.4), 248 (−39.4), 302 (+106.2), 317 sh (+71.2), 346 (+61.5), 405 (−38.9), 449 (−26.0), 524 (+25.1).

\(\Lambda_4\)-[(Ru(bpy)\(_2\))\(_4\)(bis(BiBzIm))](PF\(_6\))\(_4\) (\(\Lambda_4\)-Ru\(_4\)-25). Bis(bibenzimidazole) (14) (0.050 g, 0.11 mmol) was suspended in 10 mL of ethylene glycol (10% water), degassed for 20 min under nitrogen, and then heated at 150 °C for 2 h to dissolve bis(BiBzImH\(_2\)) (14). Then the above solution was cooled to 120 °C, and \(\Lambda_4\)-[Ru(bpy)\(_2\)(py)\(_2\)] \([-\text{O,0′-dibenzoylL-tartrate}]\) (27a) (0.54 g, 0.47 mmol) was added. The reaction was heated at 120 °C for 8 h. The resulting deep red-brown solution was cooled, diluted with 10 mL water and filtered to remove the insoluble part which may have. Then a saturated aqueous solution of NH\(_4\)PF\(_6\) was added dropwise to precipitate the complex. The crude solid was collected by filtration (320 mg). 160 mg of the crude product was dissolved in a minimum of acetonitrile, and chromatographed over a neutral alumina column (21 cm in length, 17 mm in diameter). The first deep red broad band was collected. The eluate was concentrated to around 25 mL by rotary evaporation, and then diethyl ether was added dropwise to precipitate the desired complex. Yield: 73%. MALDI-TOF \((m/z)\): 2551 \([M – 1PF_6]^+\), 2406 \([M – 2PF_6]^+\), 2261 \([M – 3PF_6]^+\), 2116 \([M – 4PF_6]^+\). Anal. Calcd for C\(_{108}\)H\(_{78}\)F\(_{24}\)N\(_{24}\)P\(_4\)Ru\(_4\)·4H\(_2\)O: C, 46.86; H, 3.13; N, 12.14. Found: C, 46.66; H, 2.72; N, 12.17. CD (CH\(_3\)CN, \(\lambda\), nm, (\(\Delta\varepsilon, M^{-1}\cdot cm^{-1}\))):
$M^{-1}\text{cm}^{-1})$: 213 (−94.7), 240 (+37.9), 252 (−30.9), 282 (+75.1), 297 (+53.5), 309 sh (+56.7), 351 (+107.2), 417 (−84.7), 531 (+33.0).

$\Lambda_8$-[(Ru(bpy)$_2$)(tetra-BiBzIm)](PF$_6$)$_8$  (As-Ru$_8$-26). Tetra(bibenzimidazole) (19) (0.050 g, 0.054 mmol) was suspended in 25 mL of ethylene glycol, degassed for 20 min under nitrogen, and then heated at 170 °C for 8 h to dissolve the tetra(BiBzImH$_2$) ligand. Eventually it was still partially dissolved due to the rigid structure of the ligand. Then the suspension was cooled to around 100 °C, $\Lambda$-[Ru(bpy)$_2$(py)$_2$] [(−)-O, O'-dibenzoyl-L-tartrate]-12H$_2$O (27a) (0.516 g, 0.45 mmol) was added and heated at 150 °C for 2 h. NaOCH$_3$ (58 mg, 1.07 mmol) was added to facilitate the fully deprotonation. Then the solution was heated at 150 °C for another 14 h. The deep red-brown solution was cooled, diluted with around 20 mL water, and filtered to remove the insoluble part. A saturated aqueous solution of NH$_4$PF$_6$ was added dropwise to the filtrate to precipitate the complex. The solid crude product (300 mg) was collected by filtration. 150 mg of the crude product was dissolved in a minimum of acetonitrile, and purified by chromatography with a neutral alumina column (21 cm in length, 17 mm in diameter) using an acetonitrile solution of NH$_4$PF$_6$ as an eluent. The major portion stayed on the top of the column and was eluted slowly by a saturated acetonitrile solution of NH$_4$PF$_6$. The eluate was concentrated to around 10 mL by rotary evaporation and then ether was added dropwise to precipitate the desired complex. Yield: 55%. MALDI-TOF ($m/z$): 5308 [M − 1PF$_6$]$^+\,$, 5154 [M − 2PF$_6$]$^+\,$, 4999 [M − 3PF$_6$]$^+\,$, 4582 [M − 6PF$_6$]$^+\,$, 4431 [M −
7PF₆]⁺, 4278 [M − 8PF₆]⁺. Anal. Calcd for C₂₁₆H₁₅₄N₄₈P₈F₄₈Ru₈: C, 48.13; H, 2.88; N, 12.47. Found: C, 43.07; H, 2.68; N, 11.05. CD (CH₃CN, λ, nm, (Δε, M⁻¹·cm⁻¹)): 210
(−23.0), 242 (+35.5), 257 (+17.2), 284 (+70.9), 349 (+32.6), 432 (−34.2), 532 (+10.1).

[Ru(bpy)₂(R,R-dach)](PF₆)₂ (30).⁶⁷,⁶⁹ rac-[Ru(bpy)₂(py)₂]Cl₂ (27) (100 mg, 0.16 mmol) and (1R,2R)-1,2-diaminocyclohexane (R,R-dach) (31) (50 mg, 0.44 mmol) were added to 4 mL of ethylene glycol (10% water). The solution was heated at 120 °C for 4 h, then cooled, diluted with 6 mL of H₂O, and filtered. A saturated aqueous solution of NH₄PF₆ was added dropwise to the filtrate until no more precipitate formed. The solid was collected by filtration, redissolved in acetonitrile, and reprecipitated by addition of diethyl ether. Yield: 80%.

Λ-[Ru(bpy)₂(R,R-dach)](PF₆)₂ (30a).⁶⁷,⁶⁹ Λ-[Ru(bpy)₂(py)₂][(-)-O,O’-
dibenzoyl-L-tartrate]⋅12H₂O (27a) (150 mg, 0.13 mmol) and R,R-dach (31) (50 mg, 0.44 mmol) were added to 4 mL of ethylene glycol (10% water). The solution was heated at 120 °C for 4 h, then cooled, diluted with 6 mL of H₂O and filtered. A saturated aqueous solution of NH₄PF₆ was added dropwise to the filtrate until no more precipitate formed. The solid was collected by filtration. Yield: 70%, Λ/RR > 98% de.

¹H NMR (500 MHz, acetonitrile-d₃, aromatic region): 9.10 (d, J = 6.1 Hz, 2H), 8.49 (d, J = 8.1 Hz, 2H), 8.32 (d, J = 8.1 Hz, 2H), 8.17 (ddd, J = 7.7 Hz, 7.7 Hz, 1.3 Hz, 2H), 7.83–7.78 (m, 4H), 7.62 (d, J = 6.1 Hz, 2H), 7.14 (ddd, J = 6.7 Hz, 6.7 Hz, 1.3 Hz, 2H).

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PART IV

CROSSLINKED POLYETHYLENIMINE BASED FLAME RETARDANTS
CHAPTER 10
INTRODUCTION

10.1 Polymers and Flame Retardants

Polyethylene and polypropylene are the typical examples of polymers that undergo scission at random locations on the main chain to yield many smaller molecular fragments during burning. They melt, drip and decompose upon combustion and burn completely with very little char formation (carbonized polymer residue). The commercial use of this type of polymers requires that they exhibit selected degrees of flame retardancy. The potential markets for flame retarding polymers are very large. There are four major application areas. First is the electrical and electronic supplies, such as printed circuit boards, internal wires, cables, and the polymeric connectors for TV sets, etc. These materials must meet flammability standards. Second is the construction materials such as furniture cushions and carpets, etc. The third one is the transportation area. For example, polymer components of the interior of mass transit vehicles (airplane, buses, subways) must meet flammability standards. The fourth area is the fabrics and apparel such as workers’ clothing in specific industries. The $2.1 billion global market for flame retardants is experiencing double-digit growth across nearly all applications in 2002.
The flame retardancy of polymers is usually achieved through the use of additives. There are several types of flame retardants: 1) fillers, for example adding clays to dilute polymers and reduce the flammability; 2) alumina trihydrate (Al$_2$O$_3$·3H$_2$O) or magnesium hydroxide, which can decompose and produce water vapor as the incombustible gas to lower the oxygen concentration at the flame front and result in flame snuffing due to lack of oxygen; 3) halogenated compounds, forming highly active fragments during combustion, which enter gas or vapor phase to react with oxygen and therefore acts as potent flame retardants; 4) solid phase char formation flame retardants, such as phosphorus, boron, sulfur, silicon compounds, polynuclear aromatics and intumesce.\textsuperscript{87}

Nonhalogenated, phosphorus-based flame retardant additives have been growing faster than traditional brominated formulations. The use of traditional halogenated flame retardants has been limited due to the formation of extremely toxic halogenated dioxins or dibenzofurans.\textsuperscript{88,89} Environmentally friendly products, such as halogen-free flame retardants and organic heat stabilizers, are among the market niches that plastics additives producers are targeting for growth. Among alternative possibilities intumescent materials have gained considerable attention because they provide fire protection with minimum of overall health hazard. The term intumescent refers to the formation of a foamed char during burning of a polymer formulation.\textsuperscript{90} Intumescent systems decompose on heating with formation of a large amount of thermally stable residue ("char"). This char should be able to act as a thermal shield for heat transmission from the flame to the polymer and as a physical barrier hindering
diffusion of volatiles towards the flame and of oxygen towards the polymer. “Intumescent” chars resulting from a combination of charring and foaming of the surface of the burning polymers may be able to produce an effectively insulating multicellular structure.

Typically, an intumescent system contains three main ingredients, a char former (carbonific, typically pentaerythritol), a blowing agent (spumific, typically melamine), and an acidic catalyst to catalyse the dehydration (phosphorus derivative, typically ammonium polyphosphate) to induce carbonization of the char former. The fire retardant properties of small molecule organophosphorus compounds have been recognized and developed over a number of years and have thus found use as intumescent additives in a variety of polymer materials. The commercially available examples are given in Figure 10.1. Ammonium polyphosphate (Exolit 422, Hoechst) is used as an intumescent fire retardant for thermoplastics such as polypropylene, as is the Great Lakes Chemicals product Char-Guard CN329. Generally, organophosphorus fire retardants promote the formation of large amounts of char. However, typical systems require high loading of the three additives, which results in significantly diminished mechanical properties. Moreover, the additives in many cases add cost and additional problems such as reduced processability. For example, polypropylene has been effectively flame retarded with intumescent systems, but at high loadings of 30 to 50 parts per 100 parts of polymer. It is highly desirable to design the three components into a single molecule. This approach has been the subject of extensive work over many years. For example, Halpern developed a series of pentaerythritol phosphates which are
char-forming, self-catalyzing and intumescent (e.g. Char-Guard CN 329). They are phosphate dimelamine salt and melamine phosphate prepared from pentaerythritol, melamine, and POCl₃, which are sufficiently thermally stable for processing in thermoplastics. They are effective fire retardants for polypropylene at concentrations \( \geq 20\% \), which are more efficient than conventional halogen-Sb retardants, and have a less adverse effect on physical properties.

![Reaction structures](image)

Figure 10.1 Examples of Commercially Available Organophosphorus Fire Retardants

![Chart](image)

Chart 10.1

Our goal is to design a new series of intumescent flame retardant additives with low cost based on high molecular weight polyethylenimine (commercial name “Lupasol”) (33). Using Lupasol as a flame retardant has not been reported, but it could be potentially a good flame retardant because of its high thermal stability. Also, it
contains a large mole fraction of nitrogen. It has been shown that nitrogen rich compounds perform better flame retardancy.\textsuperscript{93} The disadvantage of Lupasol is that it is gooey liquid which is difficult to process. Our investigation is trying to change it into free flowing powder form by crosslinking reactions, at the same time, maintain the flame retardant property, so that it can be used as an additive to make flame retardant polymers.

Pyromellitic dianhydride (PMDA) (34) was chosen as one potential crosslinking agent. It is a very commonly used, inexpensive aromatic crosslinking agent for polymers. In this study, Lupasol was crosslinked by various amounts of PMDA. The crosslinked product was converted to phosphates and sulfates by reacting with phosphoric acid or sulfuric acid. These products were characterized by elemental analysis, FTIR and thermogravimetric analysis. Flammability was evaluated by measuring the limiting oxygen index (LOI). It turns out that they are non-halogenated, enviromental friendly, low smoke level and cost effective intumescent flame retardants for polyolefins.

\textbf{10.2 Methods for the Measurement of Flame Retardancy and Thermal Stability}

\textit{10.2.1 Limiting Oxygen Index Test (ASTM D-2863-97)}

Limiting oxygen index method measures the minimum oxygen concentration to support candle-like flaming combustion of materials in a flowing mixture of oxygen and nitrogen. It describes the tendency of a material to sustain a flame, and is widely used as
a tool to investigate the flammability of polymers. It provides a convenient and reproducible means of determining a numerical measure of flammability.

The oxygen index apparatus (Figure 10.2) is designed to allow a candle-like burning of the specimen in a slowly rising mixture of oxygen and nitrogen. In the test, a specimen is placed in the holder at the center of the base of the test column. The flow valves are adjusted to obtain the desired initial oxygen concentration and total flow rate. The oxygen and nitrogen flow into the dispersion chamber and through the glass bead bed. The gases thus are mixed and dispersed evenly over the cross section of the test column. The specimen is ignited so the entire top tip of the specimen is burning like a candle. A gas flame at the end of a tube with a small orifice is used to ignite the specimen.

For physically self-supporting plastic specimens (5” long, 1/4” wide and 1/8” thick), the oxygen concentration is above the oxygen index if the specimen burns for at least 3 minutes after the igniter is removed, or if the specimen burns down 50 mm. The concentration is below the oxygen index if the specimen stops flaming before the criteria (3 min. or 50 mm) are satisfied. The procedure is repeated with a new specimen and a higher or lower oxygen concentration until the lowest concentration of oxygen that will satisfy the criteria is determined. The concentration in percentage is reported as the oxygen index. ASTM Standard D 2863-97 specifies that the difference between oxygen concentrations that will and will not pass the criteria should be reduced to 0.2 percent or less. The entire procedure is repeated for three total gas flow rates between 3 and 5 cm per second. The average of the three results is usually reported. The
effectiveness of fire retardants is measured by the change in the critical oxygen concentration that they induce as a function of their concentration.

Figure 10.2 Diagram of the Limiting Oxygen Index Flammability Test Apparatus

The limiting oxygen index (LOI) or oxygen index (OI), is defined as:

\[ \text{LOI} = \frac{100 \, V_o}{V_o + V_N} \]  
(equation 10.1)

where LOI is the oxygen concentration, in percent by volume; \( V_o \) and \( V_N \) are the minimum oxygen concentration in the inflow gases required to pass the “minimum burning length” criteria and the nitrogen concentration in the inflow gases respectively.

Limiting oxygen index is more commonly reported as a percentage rather than fraction.
Since air comprises about 20.95% oxygen by volume, any material with a limiting oxygen index less than this will burn easily in air. Conversely, the burning behavior and tendency to propagate flame for a polymer with a limiting oxygen index greater than 20.95 will be reduced or even zero after removal of the igniting source. Self-sustaining combustion is not possible if LOI > 100, such values are not physically meaningful. Materials satisfying LOI < 20.95 are “flammable” and LOI > 100 are “intrinsically non-flammable” respectively. Materials with a LOI > 28 are generally self-extinguishing; with 20.95 < LOI < 28 are being “slow-burning”. Some typical LOI values of the commercially available polymers are listed in the Table 10.1.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyolefins (polyethylene, polypropylene)</td>
<td>17.4</td>
</tr>
<tr>
<td>Flame-retarded polyolefins</td>
<td>24-28</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>18.1</td>
</tr>
<tr>
<td>Flame-retarded polystyrene</td>
<td>27-30</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>24-29</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>95.0</td>
</tr>
</tbody>
</table>

10.2.2 Thermogravimetric Analysis (TGA)

The fire retardation of plastic materials is generally achieved by incorporating fire-retardant additives into the plastic during processing. Since processing requires that
the additives withstand temperatures up to above 200 °C, intumescent systems without sufficient thermal stability cannot be incorporated into a number of plastics. Thermogravimetric Analysis (TGA) was used as the major tool in this research to study the thermal stability of the flame retardants. TGA measures weight changes in a material as a function of temperature (or time) under a controlled atmosphere. Its principal usages include the measurement of a material's thermal stability and composition. TGA suspends a sample on a highly sensitive balance over a precisely controlled furnace. Usually the heating rates of 10–20°C/min are used to look for broad decomposition stages. In this study, a slower heating rate of 5°C/min is appropriate due to the intumescent properties of the flame retardants. They foam up upon heating, so the slow heating rate provides the smooth TGA curves. Sample sizes are usually kept as small as possible, within the limits of the apparatus this is usually around 10 mg per run. This reduces bulk effects and at higher heating rates avoids thermal gradients being set up within the sample. The instruments allow for temperatures up to 1000 °C. In this study, the weight loss of the flame retardants vs. the increase of the temperature under nitrogen atmosphere were recorded. The temperature at 5% weight loss and 50% weight loss, as well as the char yield at 800 °C were analyzed.
11.1 Synthesis of Pyromellitic Dianhydride Crosslinked Lupasol (35)

11.1.1 Determinination of the Degree of Crosslinking and Reaction Conditions

To crosslink Lupasol (33) into a free flowing powder, a different percentage of the crosslinking agent, pyromellitic dianhydride (PMDA (34)), was applied in the crosslinking reactions (Scheme 11.1, Table 11.1). The crosslinked product was represented by the empirical formula: \((C_2H_5N)_1(C_{10}H_4O_6)_x\) (35) on the basis of the elemental analysis. \((C_2H_5N)_1\) represents one mole of the repeat unit \((CH_2CH_2NH)\) in the Lupasol long chain. \((C_{10}H_4O_6)_x\) represents the crosslinking agent PMDA (34). X is the molar ratio of the crosslinking agent PMDA compared to the mole of the repeat unit in Lupasol, which indicates the degree of crosslinking. A minimum of the PMDA is required to crosslink in order to keep the organic component to a lower limit, due to the high flammability of the organic compounds. The lowest amount of the PMDA studied was 3% (35a), but they are not enough to crosslink all the Lupasol, rendering the sticky property of the crude crosslinked product and difficulties in the separation from the solvent by filtration due to the hydrophilicity. The excess uncrosslinked Lupasol was washed away during the work up procedure. Then the actual degree of crosslinking was found to be 6.5%, which is higher than the theory.
Scheme 11.1 Synthesis of the Crosslinked Lupasol by PMDA (35)

5% PMDA was applied for the crosslinking of Lupasol under different temperatures and times (35b–d). On the basis of the yield and the empirical formula, the products obtained from a low temperature (60 °C, product 35b) and a short reaction time (7 h, product 35c) showed higher degree of crosslinking in the empirical formulas than the theory, and the yield lower than 100%, indicating the incomplete crosslinking of all the Lupasol by PMDA. Therefore, the excess of uncrosslinked Lupasol was washed away during the work up procedure.

5% PMDA crosslinked Lupasol cured at 100–110 °C for around 24 h (35d) gave the product with a char yield of 22.5%, indicating the significant enhanced thermostability at 800 °C (Table 11.2). With the addition of 5% PMDA, the actual degree of crosslinking is around 8–10% (x is in the range of 0.080–0.090).

7.5% PMDA crosslinked Lupasol cured at 60–70 °C for around 24 h (35e) gave the product with no char left at 800 °C, indicating the incomplete crosslinking at 70 °C.
Table 11.1 Crosslink of Lupasol by PMDA

<table>
<thead>
<tr>
<th>amount of crosslinking agent added</th>
<th>reaction temp, time and yield</th>
<th>crude product</th>
<th>empirical formula of the crosslinked product</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% PMDA (35a) 105 °C 20 h</td>
<td>Very sticky, difficult to work up due to the hydrophilicity, 10% H₂SO₄ solution help to separate</td>
<td>Sulfate obtained, (C₂H₅N)₁(C₁₀H₄O₆)₀.065(H₂SO₄)₀.44</td>
<td></td>
</tr>
<tr>
<td>5% PMDA (35b) 60 °C, 40 h, yield: 93%</td>
<td></td>
<td>(C₂H₅N)₁(C₁₀H₄O₆)₀.082</td>
<td></td>
</tr>
<tr>
<td>5% PMDA (35c) 100−130 °C, 7 h, yield: 74%</td>
<td>Not as sticky as 3% PMDA crosslinked product</td>
<td>(C₂H₅N)₁(C₁₀H₄O₆)₀.093</td>
<td></td>
</tr>
<tr>
<td>5% PMDA (35d) 90–105°C, 26 h, yield: 100%</td>
<td></td>
<td>(C₂H₅N)₁(C₁₀H₄O₆)₀.086</td>
<td></td>
</tr>
<tr>
<td>7.5% PMDA (35e) 60–70 °C, 24 h, yield: 88%</td>
<td>Not sticky, easy work up</td>
<td>(C₂H₅N)₁(C₁₀H₄O₆)₀.099</td>
<td></td>
</tr>
<tr>
<td>10% PMDA (35f) 105 °C, 26 h, yield: 100%</td>
<td>Not sticky, easy work up</td>
<td>(C₂H₅N)₁(C₁₀H₄O₆)₀.128</td>
<td></td>
</tr>
</tbody>
</table>

Table 11.2 Thermal Stability of Lupasol (33) and Crosslinked Lupasol (35)

<table>
<thead>
<tr>
<th>sample</th>
<th>T (°C), at 5% Wt. Loss</th>
<th>T (°C), at 50% Wt. Loss</th>
<th>char yield, at 430 °C (%)</th>
<th>char yield, at 800 °C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lupasol (33)</td>
<td>288</td>
<td>387</td>
<td>0</td>
<td>–</td>
</tr>
<tr>
<td>(C₂H₅N)₁(C₁₀H₄O₆)₀.093 (35e)</td>
<td>140</td>
<td>364</td>
<td>40</td>
<td>25.1</td>
</tr>
<tr>
<td>(C₂H₅N)₁(C₁₀H₄O₆)₀.086 (35d)</td>
<td>154</td>
<td>336</td>
<td>30</td>
<td>22.5</td>
</tr>
<tr>
<td>(C₂H₅N)₁(C₁₀H₄O₆)₀.099 (35e)</td>
<td>199</td>
<td>466</td>
<td>53</td>
<td>0</td>
</tr>
<tr>
<td>(C₂H₅N)₁(C₁₀H₄O₆)₀.128 (35f)</td>
<td>153</td>
<td>366</td>
<td>41</td>
<td>28.6</td>
</tr>
</tbody>
</table>
10% PMDA crosslinked Lupasol cured at 100–110 °C for around 26 h (35f) gave the product with a char yield of 28.6%, which is more thermally stable than 5% PMDA crosslinked Lupasol (35d). But from the empirical formula, around 12.8% Lupasol was crosslinked by PMDA. The degree of crosslinking is too high, which introduced too much organic portion. Therefore, the addition of 10% PMDA is not appropriate.

In conclusion, the crosslinking reaction with 5% PMDA curing at 100–110 °C for around 24 h (35d) is appropriate to meet the requirement of low crosslinking agent and reach the improved thermostability.

11.1.2 Characterization of the Crosslinked Lupasol (35d)

The solid-state $^{13}$C NMR (Figure 11.1) of the crosslinked Lupasol (35d) was performed to confirm the formation of the amide-linkage in the crosslinked Lupasol. The peaks centering at 49 ppm are the carbons on the Lupasol long chain. The peaks at 138 ppm are the carbons on the aromatic rings of PMDA. The peaks at around 170 ppm are the carbons on the carbonyl groups either as carboxylic acids or amides.

From the FTIR study, the band at 1653 cm$^{-1}$ indicates the presence of the carbonyl groups (C=O) in the crosslinked Lupasol due to the formation of the amide and carboxylic acid functionality.
11.1.3 Thermostabilities of Lupasol (33) and Crosslinked Lupasol (35)

The TGA of Lupasol shows that the polymer degraded completely to volatiles by 420 °C, leaving no char residue. However, after it was crosslinked with 5% PMDA, the char yield at 420 °C was 32% and at 800 °C was 22% (Figure 11.2). The LOI of PMDA crosslinked Lupasol was around 23 (Table 11.6). The thermostability at high temperature and the flame retardancy were greatly enhanced by the crosslinking with PMDA.
However, this crosslinked Lupasol 35 is not satisfying for flame retarding polymers due to the relatively low LOI. The burning behavior of PMDA crosslinked Lupasol (35) is shown in Figure 11.3. The sample bar burned with large orange flame (Fig 11.3, b). On the removal of the flame, the bar was anti-glowing (Fig 11.3, c), self
extinguished within 1 minute, and the smoke was evolved. There was char foaming up around two times as large as the original sample, with no dripping.

11.2 Discovery of Sulfates with Improved Flame Retardancy

The Lupasol was a nitrogen rich polymer with quite amount of the free amino groups in the long chain. This structure feature leads to the hydrophilic properties of Lupasol itself and the PMDA crosslinked product (35). If the degree of crosslinking is too low (such as 3% PMDA), the crosslinked product was very difficult to be separated from the solvent such as methanol. 10% Sulfuric acid solution was mixed with the PMDA crosslinked product. It was gratifying to find that the acid treatment was not only helpful for the isolation of the crosslinked product, but also rendered improved flame retardancy of the isolated sulfate. It self-extinguished right on the removal of the flame with a low smoke level. From the elemental analysis, the empirical formula of the product was determined, which indicates the degree of crosslinking by the sulfuric acid due to the protonation of the amino groups on the Lupasol chain. This observation gave us some useful information—the formation of the sulfate of 35 would be a good way to make flame retardant. Thus, a series of sulfates were synthesized and their flame retardancies were tested.

11.2.1 Synthesis of the Sulfates (36)

The crosslinked product \((C_2H_8N)_{1}(C_{10}H_4O_6)_x\) (35) was treated with various concentrations of sulfuric acid to obtain a series of corresponding sulfates (36) as shown
in Scheme 11.2. The sulfates were represented by the empirical formula 
\((C_2H_5N)_1(C_{10}H_4O_6)_x(H_2SO_4)_y\) based on the elemental analysis. \((C_2H_5N)_1\) represents one mole of the repeat unit \((CH_2CH_2NH)\) in the Lupasol long chain. \((C_{10}H_4O_6)_x\) represents the crosslinking agent PMDA. \(X\) represents the degree of crosslinking by mole ratio compared to the mole of the repeat unit in Lupasol. \((H_2SO_4)_y\) represents the degree of crosslinking of \(H_2SO_4\) on the Lupasol long chain by mole ratio. \(Y\) is in the range of 0–0.50. The maximum of \(y\) is 0.50, since one mole of \(H_2SO_4\) can protonate two nitrogen atoms on two repeat units.

Scheme 11.2 Synthesis of the Sulfates (36)

\[
(C_2H_5N)_1(C_{10}H_4O_6)_x(H_2SO_4)_y
\]
11.2.2 Burning Behavior of the Sulfates (36)

The burning behavior of the sulfates is shown in Figure 11.4. The sample was easily ignited, and burned with pale orange flame. On the removal of the flame, it was anti-glowing, self-extinguished immediately, a small amount of gray color smoke suppressed within 5 seconds, and the char foamed up two times than the original sample, with no dripping.

![Figure 11.4 Burning Behavior of the Sulfates (36)](image)

Figure 11.4 Burning Behavior of the Sulfates (36)

a) Before applying the flame to the sample bar. b) During the burning on the flame. c) Intumescent char left after the removal of the flame.

11.2.3 Thermostability and Flammability of the Sulfates (36)

Interestingly, the structure, the thermal stability and the flammability of the sulfates were related closely with the reaction time in the sulfuric acid solution (Scheme 11.3, Table 11.3). The calculated formulas based on the elemental analysis of the sulfates (Table 11.3) showed that with the extension of the reaction time in sulfuric acid, the degree of crosslinking with PMDA (x value in the formula) decreased, while the percentage of the sulfuric acid increased from 0.26–0.49 (y value in the formula). This is probably because the crosslinked amide bonds were hydrolyzed by the sulfuric acid with the extended reaction time.
Figure 11.5 TGA Curves of PMDA Crosslinked Lupasol (35) and the Sulfate (36b)
Solid line: 36b. Dashed line: 35

Scheme 11.3 Formation of Sulfates under the Different Reaction Times

\[
\begin{align*}
(C_2H_5N)_1(C_{10}H_4O_6)_{0.093} + 0.77 \text{ equiv } H_2SO_4 & \quad \xrightarrow{15 \text{ min}} \quad (C_2H_5N)_1(C_{10}H_4O_6)_{0.082} (H_2SO_4)_{0.26} \\
(C_2H_5N)_1(C_{10}H_4O_6)_{0.086} + 0.42 \text{ equiv } H_2SO_4 & \quad \xrightarrow{75 \text{ min}} \quad (C_2H_5N)_1(C_{10}H_4O_6)_{0.064} (H_2SO_4)_{0.36} \\
(C_2H_5N)_1(C_{10}H_4O_6)_{0.128} + 1.17 \text{ equiv } H_2SO_4 & \quad \xrightarrow{10.5 \text{ h}} \quad (C_2H_5N)_1(C_{10}H_4O_6)_{0.061} (H_2SO_4)_{0.49}
\end{align*}
\]

It is clear from the thermal analysis data that with the increase of the reaction time, the S/N ratio increased, the decomposition occurred at the lower temperature, and the less char left at 800 °C. This suggests that the sulfates formed under longer reaction
times are less thermally stable. Especially \(36c\), which burned with no residue left at 800 °C, was formed by the reaction for 10.5 h in 10% sulfuric acid. It has the highest S/N ratio and lowest crosslinking by PMDA among the three samples. When it was burning in the LOI test chamber, there was a large amount of light brown smoke evolved, and eventually no char was left, which was not expected. The possible reason for the lower amount of char left for the higher S/N ratio product is that the sulfuric acid is too strong and breaks the crosslinked amide bonds either by acid catalyzed hydrolysis or by thermal pyrolysis during burning. Then there was no more crosslinking between the Lupasol long chains so that all the samples burned into low molecular weight volatile fragments.

### Table 11.3 Thermal Stability and Flammability of the Sulfates (36)

<table>
<thead>
<tr>
<th>formulation</th>
<th>S/N mole ratio</th>
<th>reaction time in 10% sulfuric acid solution</th>
<th>T, °C at 5% Wt. loss</th>
<th>T, °C at 50% Wt. loss</th>
<th>char yield at 800 °C (%)</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{C}_2\text{H}_5\text{N})<em>1(\text{C}</em>{10}\text{H}_4\text{O}<em>6)</em>{0.082} (\text{H}_2\text{SO}<em>4)</em>{0.36}) ((36a))</td>
<td>0.26</td>
<td>15 min</td>
<td>181</td>
<td>350</td>
<td>28.5</td>
<td>–</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5\text{N})<em>1(\text{C}</em>{10}\text{H}_4\text{O}<em>6)</em>{0.064} (\text{H}_2\text{SO}<em>4)</em>{0.36}) ((36b))</td>
<td>0.36</td>
<td>75 min</td>
<td>192</td>
<td>330</td>
<td>24.3</td>
<td>46.0</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5\text{N})<em>1(\text{C}</em>{10}\text{H}_4\text{O}<em>6)</em>{0.061} (\text{H}_2\text{SO}<em>4)</em>{0.49}) ((36c))</td>
<td>0.49</td>
<td>10.5 h</td>
<td>147</td>
<td>290</td>
<td>0</td>
<td>53.1</td>
</tr>
</tbody>
</table>

For the sulfates, the conclusions are: the crosslinking is very important to promote the char in order to have good flame retardancy; high S/N ratio will lead to the
break down of the crosslinked bonds when burning, which is not expected. This suggests that the reaction time of 10–15 minutes is enough to form the crosslinked sulfates with low S/N ratio.

Although the LOI of the sulfates is greater than 45%, which suggests that they could be the flame retardants, no further investigation on the sulfates was carried out because they may evolve sulfuric acid fragments during burning which are strongly acidic and corrosive. For the instrumental and environmental concerns, they are probably not suitable for being the useful flame retardants. Thus, a less corrosive, more environmental friendly acid, phosphoric acid, was chosen in the subsequent study. A series of phosphates of the PMDA crosslinked Lupasol were investigated.

11.3 Phosphates with Further Improved Flame Retardancy

11.3.1 Synthesis of the Phosphates (37)

The crosslinked product \( (C_2H_5N)_1(C_{10}H_4O_6)_{0.086} \) \( (35d) \) was treated with various concentration of phosphoric acid to obtain a series of corresponding phosphates as shown in Scheme 11.4. The phosphates were represented by the empirical formula \( (C_2H_5N)_1(C_{10}H_4O_6)_x(H_3PO_4)_z \) based on the elemental analysis. \( (C_2H_5N)_1 \) represents one mole of the repeat unit \( (CH_2CH_2NH) \) in the Lupasol long chain. \( (C_{10}H_4O_6)_x \) represents the crosslinking agent PMDA. \( X \) represents the degree of the crosslinking by the mole ratio compared to the mole of the repeat unit in Lupasol. \( (H_3PO_4)_z \) represents the amount of the \( H_3PO_4 \) crosslinked on the Lupasol long chain. \( Z \) is the mole ratio compared with the mole of the repeating unit of Lupasol. \( Z \) is in the range of 0–0.50.
The maximum of $z$ is 0.50 theoretically, since one mole of $H_3PO_4$ can protonate two nitrogen atoms on two repeat units.

**Scheme 11.4 Synthesis of the Phosphates (37)**

\[
\text{(C}_2\text{H}_5\text{N})_1 (\text{C}_10\text{H}_4\text{O}_6)_x (\text{H}_3\text{PO}_4)_z
\]

11.3.2 Burning Behavior of the Phosphates (37)

The burning behavior of the phosphates (37) is very exciting: after being ignited, it showed the light orange flame when burning (Figure 11.6). On the removal of the flame, it was antiglowing, self extinguished immediately, a small amount of smoke suppressed within 5–10 seconds, and the intumescent char foamed up 10 times larger than the original sample, with no dripping.
Due to the formation of the intumescent char, the good flame retardancy and the environmental friendly feature of the phosphorus compound, further detailed investigation were carried out.

![Figure 11.6 Burning Behavior of the Phosphates (37)](image)

a) Before applying the flame to the sample bar. b) During the burning on the flame. c) After the removal of the flame—the intumescent char formed

### 11.3.3 Reaction Time Determination

The reaction time vs. the thermal stability and the flammability was investigated on the phosphates (37) (Scheme 11.5, Table 11.4).

It appears that an extension of the reaction time decreased the decomposition temperature at 5% weight loss, which means that the decomposition occurred at lower temperature (10–30 °C lower), but the tendency to form the char and the LOI were not changed very much. Phosphoric acid is not so strong to break all the crosslinked amide bonds. The conclusion is that it is necessary to limit the reaction time to 30 minutes to produce the phosphates with the enhanced thermal stability as well as the good flame retardancy.
Scheme 11.5 Formation of the Phosphates Series (37)

\[
\begin{align*}
(C_{2}H_{5}N)_{1} (C_{10}H_{4}O_{6})_{0.086} + 0.082 \text{ equiv } H_{3}PO_{4} & \rightarrow \quad (C_{2}H_{5}N)_{1} (C_{10}H_{4}O_{6})_{0.092} (H_{3}PO_{4})_{0.089} \\
& \quad \text{30 min, 37a-1} \\
& \quad \text{5.5 h, 37a-2} \\
(C_{2}H_{5}N)_{1} (C_{10}H_{4}O_{6})_{0.086} + 0.17 \text{ equiv } H_{3}PO_{4} & \rightarrow \quad (C_{2}H_{5}N)_{1} (C_{10}H_{4}O_{6})_{0.088} (H_{3}PO_{4})_{0.180} \\
& \quad \text{30 min, 37b-1} \\
& \quad \text{5.5 h, 37b-2} \\
(C_{2}H_{5}N)_{1} (C_{10}H_{4}O_{6})_{0.086} + 0.86 \text{ equiv } H_{3}PO_{4} & \rightarrow \quad (C_{2}H_{5}N)_{1} (C_{10}H_{4}O_{6})_{0.080} (H_{3}PO_{4})_{0.512} \\
& \quad \text{30 min, 37c-1} \\
& \quad \text{70 min, 37c-2} \\
(C_{2}H_{5}N)_{1} (C_{10}H_{4}O_{6})_{0.128} + 1.24 \text{ equiv } H_{3}PO_{4} & \rightarrow \quad (C_{2}H_{5}N)_{1} (C_{10}H_{4}O_{6})_{0.091} (H_{3}PO_{4})_{0.493} \\
& \quad \text{10 h, R.T., 37d}
\end{align*}
\]
Table 11.4 Thermal Stability and Flammability of the Phosphates (37) vs Reaction Times

<table>
<thead>
<tr>
<th>formulation</th>
<th>P/N mole ratio</th>
<th>reaction time in various concentration of phosphoric acid solution</th>
<th>T, °C at 5% wt. loss</th>
<th>T, °C at 50% wt. loss</th>
<th>char yield at 800 °C (%)</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>37a–1</td>
<td>0.089</td>
<td>30 min</td>
<td>163</td>
<td>477</td>
<td>15.2</td>
<td>50.0</td>
</tr>
<tr>
<td>37a–2</td>
<td>0.093</td>
<td>5.5 h</td>
<td>155</td>
<td>382</td>
<td>32.1</td>
<td>57.5</td>
</tr>
<tr>
<td>37b–1</td>
<td>0.179</td>
<td>30 min</td>
<td>166</td>
<td>439</td>
<td>34.0</td>
<td>&gt; 70.0</td>
</tr>
<tr>
<td>37b–2</td>
<td>0.181</td>
<td>5.5 h</td>
<td>154</td>
<td>464</td>
<td>29.1</td>
<td>&gt; 70.0</td>
</tr>
<tr>
<td>37c–1</td>
<td>0.512</td>
<td>30 min</td>
<td>191</td>
<td>527</td>
<td>32.8</td>
<td>&gt; 70.0</td>
</tr>
<tr>
<td>37c–2</td>
<td>0.545</td>
<td>70 min</td>
<td>148</td>
<td>467</td>
<td>25.9</td>
<td>&gt; 70.0</td>
</tr>
<tr>
<td>37d</td>
<td>0.493</td>
<td>10 h</td>
<td>178</td>
<td>537</td>
<td>29.6</td>
<td>&gt; 70.0</td>
</tr>
</tbody>
</table>

Figure 11.7 TGA Curves of PMDA Crosslinked Lupasol (35) and the Phosphate (37f)
Solid line: 37f. Dashed line: 35
11.3.4 Flame Retardancy of the Phosphates (37)

The flame retardancy of a series of phosphates was evaluated in terms of the limiting oxygen index (LOI). The results are listed in Table 11.5, Figure 11.7 and 11.8. Some important conclusions may be obtained. (The following investigation was on the phosphates produced in various concentrations of the phosphoric acid for 30 minutes.)

<table>
<thead>
<tr>
<th>formulation</th>
<th>P/N (mole ratio)</th>
<th>LOI</th>
<th>T (°C) at 5% wt. loss</th>
<th>T (°C) at 50% wt. loss</th>
<th>char yield at 800 °C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_2H_5N)_1(C_10H_4O_6)_0.086 (37d)</td>
<td>0</td>
<td>23.0</td>
<td>154</td>
<td>336</td>
<td>22.5</td>
</tr>
<tr>
<td>(C_2H_5N)_1(C_10H_4O_6)_0.093 (H_3PO_4)_0.050 (37e)</td>
<td>0.050</td>
<td>36.0</td>
<td>163</td>
<td>399</td>
<td>22.6</td>
</tr>
<tr>
<td>(C_2H_5N)_1(C_10H_4O_6)_0.092 (H_3PO_4)_0.089 (37f)</td>
<td>0.089</td>
<td>50.0</td>
<td>163</td>
<td>383</td>
<td>33.3</td>
</tr>
<tr>
<td>(C_2H_5N)_1(C_10H_4O_6)_0.088 (H_3PO_4)_0.18 (37g)</td>
<td>0.179</td>
<td>&gt; 70.0</td>
<td>166</td>
<td>439</td>
<td>34.0</td>
</tr>
<tr>
<td>(C_2H_5N)_1(C_10H_4O_6)_0.079 (H_3PO_4)_0.34 (37h)</td>
<td>0.340</td>
<td>&gt; 70.0</td>
<td>182</td>
<td>495</td>
<td>35.3</td>
</tr>
<tr>
<td>(C_2H_5N)_1(C_10H_4O_6)_0.093 (H_3PO_4)_0.40 (37i)</td>
<td>0.397</td>
<td>&gt; 70.0</td>
<td>182</td>
<td>547</td>
<td>37.6</td>
</tr>
<tr>
<td>(C_2H_5N)_1(C_10H_4O_6)_0.080 (H_3PO_4)_0.51 (37j)</td>
<td>0.512</td>
<td>&gt; 70.0</td>
<td>190</td>
<td>527</td>
<td>32.8</td>
</tr>
</tbody>
</table>
Different degrees of flame retardancy were obtained by varying the P/N ratio of the phosphates. The P/N ratio can be tuned by controlling the stoichiometry between $\text{35d}$ and $\text{H}_3\text{PO}_4$ using different concentrations of $\text{H}_3\text{PO}_4$ solution. With the increase of P/N ratio from 0 to 0.179, the LOI increase from 23 to 70. If the P/N ratio is greater than 0.179, the LOI is higher than 70%, which means that the phosphates self-extinguish on the removal of the flame, therefore they are potentially very effective flame retardants. The dotted line in Figure 11.8 shows the extrapolated trend which cannot be tested under the experimental condition: to reach 100% LOI, P/N ratio 0.30 would be estimated. This indicates that only 30% loading of the phosphorus content can give very high flame retardancy! Essentially the phosphates do not burn! (100% LOI could not be measured because it requires the burning in the pure oxygen, which is a very dangerous condition. For the safety concern, this measurement was not allowed at Spartech Polycom Corporation in Arlington, TX. So the highest oxygen level used was 70% for the phosphate LOI measurement).

![Graph showing LOI as a function of P/N ratio](image)

Figure 11.8 LOI of the Phosphates (37) as a Function of the P/N Ratio
The phosphates produced intumescent char during the burning test, which means that the char former, the blowing agent and the acidic catalyst are in one molecule. This is very exciting. When the phosphates are burning, they evolve very small amount of smoke, which is a very important character. When there is a fire, less smoke will prevent the people from suffocating and let them have more time to escape.

11.3.5 Thermogravimetric Analysis of the Phosphates (37)

The thermal analysis of the phosphates has been studied. The TGA data and graph of the phosphates are shown in Table 11.5 and Figure 11.9. The decomposition temperature at 5% and 50% weight loss and the char yields are increased with the increase of the P/N ratio. The char yield can reach 37.6%, which is high and is a very good character for the intumescent flame retardants. The formation of the phosphates of 35d enhanced the thermal stability both at below 200°C and 800°C. But the temperature
at 5% weight loss is around 180°C. It will limit the usage of the phosphates to be processed only with polyethylene.

11.3.6 Flame Retardancy of Phosphate Blended Polyethylene

The LOI of the low density polyethylene (LDPE) is 17, which means it will continue to burn in the atmospheric conditions. The thermostability of the phosphate blended medium density polyethylene (MDPE) powder (38) was investigated, but the LOI values were not obtained, due to the busy production schedule of Spartech Polycom and the limit of time. The loading of the phosphates in the MDPE and the burning behavior are discussed here.

The MDPE and the phosphates were blended in an extruder. The MDPE was the powder from Aldrich, which is not suitable for the extrusion usage. But the LDPE was temporarily not available. The extruder was used for the small quantity fiber extrusion, which is not appropriate for this study. Several blending experiments with the phosphates were performed as the preliminary results. The thermoanalysis results showed that the MDPE burned with no char left at around 475 °C. The phosphate blended MDPE showed better thermostability. Two examples (39a,b) are shown in the Table 11.6 and Figure 11.10. 54% phosphate blended MDPE (39a) burned with around 16% char left at 800 °C. The sample burned with orange flame, and self-extinguished on the removal of the flame, with the low smoke level.
Table 11.6 Thermoanalysis of MDPE (38) and Phosphate Blended MDPE (39a,b)
(P/N of the Phosphate is 0.545)

<table>
<thead>
<tr>
<th>sample</th>
<th>T (°C), at 5% wt. loss</th>
<th>T (°C), at 50% wt. loss</th>
<th>char yield, at 800 °C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDPE powder 38</td>
<td>330</td>
<td>440</td>
<td>0</td>
</tr>
<tr>
<td>54% phosphate blended MDPE 39a</td>
<td>231</td>
<td>460</td>
<td>16.1</td>
</tr>
<tr>
<td>60% phosphate blended MDPE 39b</td>
<td>231</td>
<td>463</td>
<td>20.8</td>
</tr>
</tbody>
</table>

Figure 11.10 TGA Curves of MDPE (38) and Phosphate Blended MDPE (39a,b)
Solid line: MDPE (38). Dashed line: 54% phosphate blended MDPE (39a).
Dashed dot line: 60% phosphate blended MDPE (39b).

Jateen Gandhi in our research group continued this project. His investigation was on using toluene 2,4-diisocyanate as the crosslinking agent for Lupasol. The crosslinking reaction condition was the same as the PMDA crosslinked Lupasol (curing at 100°C for 24 h). The crosslinked products were converted to the phosphates, then
blended with the LDPE to study the flame retardancy. The LDPE was from the Spartech Polycom and is suitable for the extrusion. According to his results, 40% phosphate blended LDPE gives the LOI of 26. 50% phosphate blended LDPE gives the LOI of 27. They both meet the flame retardant requirement for the commercial use.

11.4 Conclusions

A new intumescent flame retardant system for use in olefinic polymers was discovered by crosslinking polyethylenimine (“Lupasol”) with pyromellitic dianhydride, and then further treating with phosphoric acid to make the phosphate salts. The LOI of the phosphate salts can be greater than 70.0, and the char yield at 800 °C reaches 37.6%, which indicates that they could be very potent flame retardants. The phosphates were blended with polyethylene to show the certain flame retardancy for the commercial use. It turns out that the crosslinking, the reaction time, and the phosphorus content are the three critical factors for the high intumescent flame retardancy.
12.1 General

12.1.1 Reagents and Materials

Polyethylenimine (Aldrich, high molecular weight, $M_w$ 25,000, $M_n$ 10,000), pyromellitic dianhydride (Aldrich, 97%), polyethylene (Aldrich, powder, medium density, density 0.94 g/mL, mp 109−111 °C), $N,N$-dimethylformamide (EM Scientific, 99.8%), phosphoric acid (EM Scientific, 85.0%), sulfuric acid (EM Scientific, 95.0−98.0%) and dichloromethane (EM Scientific, 99.5%) were used as received.

12.1.2 Measurements

12.1.2.1 Elemental Analysis

The elemental analysis was performed at Quantitative Technologies Inc. (QTI) (Whitehouse, NJ). All the phosphates and the sulfates were analyzed under optimum combustion conditions. The solid state $^{13}$C NMR was performed at Bruker BioSpin Corp. FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer with KBr pellets.
12.1.2.2 Flammability test

The Limiting Oxygen Index (LOI) was determined by ASTM D-2863 using a Stanton Redcroft Flammability Unit (Rheometric Scientific) at SPARTEC Polycom Corporation in Arlington, TX. This test method describes a procedure for measuring the minimum concentration of oxygen that will just support flaming combustion in a flowing mixture of oxygen and nitrogen. A small test specimen (5” long, 1/4” wide and 1/8” thick) is supported vertically in a mixture of oxygen and nitrogen flowing upwards through a transparent chimney. The upper end of the specimen is ignited and subsequent burning behavior of the specimen is observed to compare the period for which burning continues. By testing a series of specimens in different oxygen concentrations, the minimum oxygen concentration is determined.

12.1.2.3 Thermostability Test

The thermogravimetric analysis (TGA) measurements were performed using a TA 2050 thermogravimetric analyzer (TA Instruments) at a heating rate of 5 °C/min under nitrogen.

12.2 Synthesis

12.2.1 Synthesis of PMDA Crosslinked Lupasol (35)

The reaction was carried out in a 3000 ml resin flask with neck opening of 4”. The 3-neck head is a separated part and can be easily removed so that the final solid mass can be removed easily from the opening. To this flask equipped with a mechanical stirrer, was added a solution of Lupasol (393.82 g., 9.14 mol) in 600 ml DMF. While
this solution was stirred at 60 °C, a solution of PMDA (104.97 g., 0.48 mol) in 500 ml DMF was added dropwise. After the complete addition, the reaction mixture was cured for 26 h at 100 °C to give yellow solid mass. The solid mass was removed from the flask and transferred to a home use blender to reach 1/3 volume of the blender. Dichloromethane (around 1/3 of the total volume of the blender) was added to this blender to immerse the solid mass. Then the solid mass was pulverized in the blender and at the same time thoroughly washed with dichloromethane. The yellow crosslinking product was collected by filtration, dried to constant weight in a vacuum oven at 75 °C for at least 20 h. Grinding with mortar and pestle is necessary to make it powdered. The product is hygroscopic, so all the measurements were performed right after the product was taken out from the vacuum oven.

Table 12.1 Elemental Analysis of PMDA Crosslinked Lupasol (35)

<table>
<thead>
<tr>
<th>(C$_2$H$_5$N)$<em>x$(C$</em>{10}$H$_4$O$_6$)$_x$</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
</tr>
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<tbody>
<tr>
<td>35b</td>
<td>49.08</td>
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<td>20.35</td>
</tr>
<tr>
<td>35c</td>
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<tr>
<td>35d</td>
<td>52.60</td>
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<tr>
<td>35e</td>
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<td>35f</td>
<td>53.16</td>
<td>7.99</td>
<td>18.98</td>
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12.2.2 Synthesis of the Sulfates of Crosslinked Lupasol (36)

PMDA crosslinked Lupasol (35) was mixed with the sulfuric acid solutions at different concentrations and stirred at room temperature for various period. The light
brown sulfate powder was collected by filtration, washed once with water, and once with methanol. They were dried to constant weight in a vacuum oven at 75 °C for at least 20 h.

Table 12.2 Elemental Analysis of the Sulfates (36)

<table>
<thead>
<tr>
<th>Sulfates</th>
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<th>% H</th>
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<tbody>
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<tr>
<td>36c</td>
<td>30.19</td>
<td>5.80</td>
<td>13.43</td>
<td>15.12</td>
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</tbody>
</table>

12.2.3 Synthesis of the Phosphates of Crosslinked Lupasol (37)

PMDA crosslinked Lupasol (35) was mixed with the phosphoric acid solutions at different concentrations, and stirred at room temperature for a various period of times. The typical example is: PMDA crosslinked Lupasol (35d) (8.15 g. 0.131 mol repeat unit) was mixed with phosphoric acid (4.25%*, 50 mL, 0.0217 mol) and stirred at room temperature for 30 minutes. The light brown phosphate powder (37g) was collected by filtration, washed once with water, once with methanol, and dried to the constant weight in a vacuum oven at 75 °C for at least 20 h.

(*4.25% H₃PO₄ solution was prepared by taking 2.50 g. of 85% H₃PO₄ (concentrated) solution, and diluting to 50 mL with deionized water.)
Table 12.3 Elemental Analysis of the Phosphates (37)

<table>
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<th>Phosphates</th>
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<th>% P</th>
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<td>3.60</td>
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<td>30.62</td>
<td>5.26</td>
<td>12.78</td>
<td>14.45</td>
</tr>
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</table>
APPENDIX 1

$^1$H, $^{13}$C NMR, AND FTIR SPECTRA OF

2,2'-Bibenzimidazole 5
APPENDIX 2

$^1$H NMR AND FTIR SPECTRA OF

3,3'-Diaminobenzidine 6
APPENDIX 3

$^1$H, $^{13}$C NMR, AND FTIR SPECTRA OF

2-Trichloromethylbenzimidazole 10
in DMSO-d$_6$
Solid in KBr

27/05/2005
APPENDIX 4

$^1$H, $^{13}$C NMR SPECTRA OF

Fluoflavin 11
VIII_JY_Fluorofluoro_Pure_TFA112665-6.jdf

in CF₃COOD

X: parts per Million : 1H

VIII_JY_Fluorofluoro_Pure_TFA112665-6.jdf

X: parts per Million : 1H
APPENDIX 5

$^1$H, $^{13}$C, COSY NMR, ESI MASS, FTIR SPECTRA,
AND X-RAY CRYSTALLOGRAPHY DATA OF

Bis(2,2'-bibenzimidazole) 14
--- ACQUISITION PARAMETERS ---

File Name = V_JY_173_BisBisBisMeH2_D
Author =
Sample ID = 88513131
Context = Single Pulse with Brra
Creation Date = 28-NOV-2004 25:31:57
Revision Date = 5-DEC-2004 13:53:31
Spec Site = Eclips= 500
Spec Type = ESELA-MNR
Data Format = 1C COMPLEX
Dimensions = 1C
Sola Title = 13C
Sola Units = ppm
Sola Delay = 0.8[ms]
Chopper SAMPLE =
NMR Sample = Single pulse dec
Field_strength = 7.0475T05[TT]
IRrr9 = 15[H]
IRrr9_lh = 15[H]
IRrr9_lc = 62[H]
IRrr9lcm = 18[H]
IRrr9Lcm = 32[H]
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Relaxation Delay = 20[s]
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Solvent = TRIFLUOROACETIC
Spinset = 14[H]
Spin Lock P = 65[H]
Spin Lock Att = 15[ms]
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Spin Status = 8231[H]0
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Temp State = THERM OFF
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XPower = 1.0
XProc = 4
XScale = 6.66666667[ppm]
XResolution = 0.67993313[H]z
XRange = 1.66544080[H]z

--- CHART 1 ---

| X : parts per Million : 13C |

--- CHART 2 ---

| X : parts per Million : 13C |
### X-ray Crystallography Data of Bis(2,2′-bibenzimidazole) (14)

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<td>Weights</td>
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Atomic coordinates \([ x \times 10^4]\) and equivalent isotropic displacement parameters \([Å^2 \times 10^3]\). \(U(\text{eq})\) is defined as one third of the trace of the orthogonalized \(U_{ij}\) tensor.

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Symmetry transformations used to generate equivalent atoms:

'(x,y,z) → (1-x,1-y,2-z)
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APPENDIX 6

$^1$H, $^{13}$C, COSY NMR, AND FTIR SPECTRA OF

$[(4-(2-(1H-Benzol[d]imidazol-2-yl)-1H-benzo[d]imidazol-5-
yl)benzene-1,2-diamine)]$ 15
APPENDIX 7

$^1$H, $^{13}$C, COSY NMR, AND FTIR SPECTRA OF

2-(1H-Benzo[\textit{d}]imidazol-2-yl)-5-(1H-benzo[\textit{d}]imidazol-5-yl)

-1H-benzo[\textit{d}]imidazole 16
in CF₃COOD
APPENDIX 8

$^1$H, $^{13}$C NMR, FTIR, AND ESI MASS SPECTRA OF

Tris(2,2'-bibenzimidazole) 17
VI_JY_258_TriperBFC_D2SO4-5.pdf

in D₂SO₄

Filename = VI_JY_258_TriperBFC_D2SO4-5.pdf
Experiment = single pulse expt
Sample = D2B2ACETIC
Solvent = D2B2ACETIC
Creation time = 6-NOV-2004 06:27:09
Modification time = 26-MAY-2005 12:13:55
Current time = 26-MAY-2005 12:13:55

Display mode = single pulse experience
Graph size = 16.94
Dye units = ppm
Dimensions = 1
Site = Eclipse 500
Spectrometer = DEPTA 600

Field strength = 11.749379[T] (500) MHz
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X offset = 1.4559616(9) Hz
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X resolution = 0.01020109(9) kHz
X sweep = 1001020109(9) kHz
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Unblank time = 21(9)

X : parts per Million ; III
APPENDIX 9

$^{1}\text{H}$, $^{13}\text{C}$ NMR, AND FTIR SPECTRA OF

Bis(2-trichloromethylbenzimidazole) 18
$^{1}H$ NMR spectrum of a compound in DMSO-$d_6$.
APPENDIX 10

$^1$H, $^{13}$C NMR, FTIR AND ESI MASS SPECTRA OF

Tetra(2,2'-bibenzimidazole) 19
APPENDIX 11

$^1$H, $^{13}$C NMR, AND FTIR SPECTRA OF
Poly(2,2'-bibenzimidazole) 4a
Filename = VII_JY_150_PolyBisAlm
Author = delta
Experiment = single_pulse.exe
Sample ID = 7618
Solvent = TMS
Creation time = 2-JAN-2005 04:25:25
Revision time = 16-FEB-2005 23:05:48
Current time = 26-APR-2005 21:06:33
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Dim units = [ppm]
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Spectrometer = DELTA NMR
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X freq = 500.199935/21[MHz]
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Total scans = 100
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Recover gain = 16
Relaxation delay = 1[s]
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Goblock time = 2[ms]

$M_n = 19000$
In D$_2$SO$_4$
APPENDIX 12

$^1$H NMR AND FTIR SPECTRA OF

Poly(2,2'-bibenzimidazole) $4b$
APPENDIX 13

$^1$H, $^{13}$C NMR, AND FTIR SPECTRA OF

Poly(2,2'-bibenzimidazole) 4c
[Image of chemical structures and spectra]

**VII_JY_213_PolyBilizedI2_forC_BisCCl3_D2s04-5.pdf**

**X : parts per Million : 1H**

**VII_JY_213_PolyBilizedI2_forC_BisCCl3_D2s04-5.pdf**

**X : parts, per Million : 1H**

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**Data:***

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- **Sample id:** 56773335
- **Solvent:** TRIFLUOROACETIC
- **Creation time:** 5-APR-2015 23:48:26
- **Revision time:** 20-MAY-2015 21:43:55
- **Current time:** 20-MAY-2015 21:19:37
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- **Data format:** ID COMPLEX
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- **Contrast:** 2
- **Dimensions:** x
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- **Spectrometer:** Delta 3000

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- **Temp cu:** 25.6[oc]
- **Dwell_time:** 2[ms]
APPENDIX 14

$^{1}H, ^{13}C$ NMR, AND FTIR SPECTRA OF

Poly(2,2'-bibenzimidazole) 4d
**JEOL**

File name: V2 liberty 139 PolyDMFconex autochirin12223 D25034-4.jpg

**Author**: Delta

Experiment: single pulse exp

Sample id: 0879251

Solvent: ME

Creation time: 21-SEP-2005 08:04:23

Recrystallization time: 7-SEP-2005 22:18:14

Current time: 26-SEP-2005 22:03:44

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**Unblank time**: 2[us]

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in D2SO4
APPENDIX 15

$^1$H AND COSY NMR SPECTRA OF

$\Lambda$-[Ru(bpy)$_2$(BiBzImH)$_2$](PF$_6$)$_2$; $\Lambda$-20

255
APPENDIX 16

$^{1}H$ AND $^{13}C$ NMR SPECTRA OF

Λ-[Ru(bpy)$_2$(BiBzlm)] Λ-21
APPENDIX 17

$^1$H, COSY, $^{13}$C NMR, ESI-MASS, AND DIFFERENTIAL
PULSE VOLTAMMETRY SPECTRA OF

ΔΔ-[(Ru(hpy)$_2$)(BiBzIm)](PF$_6$)$_2$ ΔΔ-22
APPENDIX 18

$^1$H NMR, DIFFERENTIAL PULSE VOLTAMMETRY

SPECTRA OF [(Ru(bpy)$_2$(BiBzIm))(PF$_6$)$_2$] 22
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Quiet Time (s) = 2
Sensitivity (AVV) = 1e-6
Differential Pulse Voltammetry

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Final E (V) = 0.4
Incr E (V) = 0.004
Amplitude (V) = 0.05
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Sample Width (s) = 0.0167
Pulse Period (s) = 0.2
Quiet Time (s) = 2
Sensitivity (AVV) = 1e-6
APPENDIX 19

$^1$H NMR, MALDI-TOF MASS, AND DIFFERENTIAL PULSE VOLTAMMETRY SPECTRA OF

$[(\text{Ru(bpy})_2\text{)}_2\text{bis(BiBzImH}_2\text{)}][(\text{PF}_6)_4 23$
Differential Pulse Voltammetry
APPENDIX 20

$^1$H NMR AND CYCLIC VOLTAMMOGRAM SPECTRA OF

$[(\text{Ru(bpy})_2)(\text{bi(BzIm})] \quad 24$
APPENDIX 21

\(^1\)H NMR, MALDI-TOF MASS AND DIFFERENTIAL PULSE VOLTAMMETRY SPECTRA OF

\([(\text{Ru(bpy})_2\text{)(bis(BiBzIm)})][\text{PF}_6]_4\) 25
Differential Pulse Voltammetry

Potential / V

Current / 1e-6A
APPENDIX 22

$^1$H NMR AND MALDI-TOF MASS SPECTRA OF

$\Lambda_4-[(\text{Ru(bpy})_2)_4(\text{bis(BzIm})_2)](\text{PF}_6)_4 \Lambda_4-\text{Ru}_4-25$
MALDI-TOF REFLECTRON

Original File: E:\Data\tmp\04May\0570457376.ris
This File #2: E:\DATA\ROUTINE\04May\0570457376MS

Comment:

Method: RDE2003K
Mode: Reflectron
Accelerating Voltage: 20000
Gold Voltage: 2.0 V 100 %
Guide Wire Voltage: 0.038 V
Delay: 100 DN
Sample: 05

Laser: 2400
Scans Averaged: 35
Pressure: 5.6 ± 0.7
Low Mass Cut: 400.0
Time of Flight Collector: 180.0 OFF
Negative ions: OFF
Collected: 5/6/04 11:11 AM

Savitsky-Golay Order x 2 Points x 19

\[ \Lambda^+_4Ru^+_2-25 \]
APPENDIX 23

MALDI-TOF MASS SPECTRA AND DIFFERENTIAL PULSE VOLTAMMETRY OF

\[
[(\text{Ru(bpy)}_2)_8(\text{tetra(BzIm)})](\text{PF}_6)_8
\]

26
APPENDIX 24

MALDI-TOF MASS SPECTRA OF

$\Lambda_8-[(\text{Ru(bpy)}_2)_8(\text{tetra(BiBzm)}))(\text{PF}_6)_8 \Lambda_8-\text{Ru}_8-26$
APPENDIX 25

\(^1\text{H AND COSY NMR SPECTRA OF}

[Ru(bpy)_2(py)_2]Cl_2 27
APPENDIX 26

$^1$H AND $^13$C NMR SPECTRA OF

$\Lambda$-[$\text{Ru(bpy)}_2(\text{py})_2][(-)-\text{O}_2\text{O'}\text{-dibenzoyl-L-tartrate}] \textbf{27a}$
\[ \text{di}(\text{Ru(bpy)}_2\text{(py)}_2)[(-)\text{-O,O'}\text{dibenzoyl-L-tartrate}] \]
APPENDIX 27

$^{1}H$ NMR SPECTRA OF

$[\text{Ru(bpy)}_2(R,R\text{-dach})](\text{PF}_6)_2$ 30
[Ru(bpy)_2(R,R-dach)]^{2+}
APPENDIX 28

$^1$H NMR SPECTRA OF

$\Lambda-$[Ru(bpy)$_2$(R,R-dach)](PF$_6$)$_2$ **30a**
APPENDIX 29

$^1$H NMR SPECTRA OF

(−)-$O,O'$-Dibenzoyl-L-tartaric acid
APPENDIX 30

TGA SPECTRA OF Lupasol and crosslinked
lupasol series 33–39
Sample: LupHigh M.W
Size: 33430 mg
Method: Ramp

TGA

File: C:\\WJ_JY_LupHighMW.001
Operator: Jun
Run Date: 29-Jan-02 18:12

Weight (%)

Polyethylenimine ("Lupasol")

Temperature (°C)

- 288.31°C 5.000% Loss
- 386.65°C 50.00% Loss
- 420.53°C -0.08488%

Universal V2.60 TA Instruments
Sample: II_JY_145
Size: 10.7210 mg
Method: Ramp 5°C/min to 800°C
Comment: 5%PD_LUP

TGA

154.27°C 5.000% Loss
336.40°C 50.00% Loss

(C_2H_3N)_x(C_10H_4O_6)_y 0.085

35d

Residue: 22.52% (2.414mg)

Universal V2.6D TA Instruments
Sample: III_JY_11
Size: 9.3520 mg
Method: Ramp 5°C/min to 800°C
Comment: 5%PD_LUP_4.25%H3PO4_0.5hr

**TGA**

File: III_JY_11_5%PD_4.25%H3PO4...
Operator: Jun
Run Date: 25-Sep-02 17:38

- 166.36°C 5.000% Loss
- 438.75°C 50.000% Loss
- Residue: 34.00% (3.180 mg)

(C2H3N)(C10H4O6)0.088(H3PO4)0.18

Universal V2.6D TA Instruments
Sample: III_JY_22
Size: 9.2010 mg
Method: Ramp 5°C/min to 800°C
Comment: 5%PD_LUP_12.75%H3PO4_3rd

TGA

File: III_JY_22_5%PD_LUP_12.75...
Operator: Jun
Run Date: 16-Oct-02 11:26

181.93°C 5.000% Loss

546.74°C 50.00% Loss Residue: 37.62% (3.461 mg)

(C2H5N)1(C10H4O6)0.063(H3PO4)0.40

Weight (%)

Temperature (°C)

Universal V2.6D TA Instruments
Sample: III_JY_25
Size: 9.8860 mg
Method: Ramp 5°C/min to 800°C
Comment: 5%PD_LUP_17%H3PO4_30min

File: III_JY_25_5%PD_LUP_17%H3...
Operator: Jun
Run Date: 4-Oct-02 17:50

TGA

Weight (%) vs. Temperature (°C)

190.72°C 5.000% Loss
526.93°C 50.00% Loss
Residue: 32.79% (3.242mg)

(C2H5N)3(C10H4O6)0.080(H3PO4)0.51
Sample: II_JY_125
Size: 13.6590 mg
Method: Ramp 5 degC/min to 800°C
Comment:

File: II_JY_125
Operator: Jun
Run Date: 26-Mar-02 13:43

TGA

Universal V2.6D TA Instruments

Temperature (°C)

Weight (%)
Sample: II_JY_153
Size: 14.0240 mg
Method: Ramp 5°C/min to 800°C
Comment: Lup_5%PD_H2SO4_Dryat75°C

File: C:\_III_JY_153-5%PD-H2SO4-Dry75degC-2
Operator: Jun
Run Date: 08-May-2002 10:44
Instrument: 2050 TGA V5.4A

Weight (%) vs. Temperature (°C)

192.57°C 5.00% Loss
330.09°C 50.00% Loss

(C$_2$H$_6$N)$_1$ (C$_{10}$H$_{4}$O$_6$)$_{0.064}$ (H$_2$SO$_4$)$_{0.36}$

Residue: 24.40%
(3.422mg)
Sample: II_JY_205
Size: 10.3900 mg
Method: Ramp 5°C/min to 800°C
Comment: 10%PD_LUP_10%H2SO4

TGA

File: II_JY_205_10%PD_10%H2SO4...
Operator: Jun
Run Date: 28-Aug-02 10:52

Weight (%) vs Temperature (°C)

147.49°C 5.014% Loss
289.78°C 49.90% Loss

(C_H_N)_1 (C_H_o)_0.061 (H_SO)_0.49

Universal V2.6D TA Instruments
Sample: MDPE Powder
Size: 12.9480 mg
Method: 10.00 °C/min RT to 600°C
Comment: Aldrich 05/02

TGA

File: C:\MDPE\MDPE powder.001
Operator: Jun
Run Date: 26-Jul-02 16:56

Weight (%)

0 20 40 60 80 100

Temperature (°C)

0 200 400 600 800

MDPE Powder

Universal V2.6D TA Instruments
Sample: II_JY_250
Size: 14.0410 mg
Method: Ramp 5°C/min to 800°C
Comment: 54.5%FR_II_JY_151P

TGA

File: C:\Jun\MDPE\II_JY_250_54.5%FR_JY151P
Operator: Jun
Run Date: 30-Jul-2002 11:49
Instrument: 2050 TGA V5.4A

Weight (%) vs. Temperature (°C)

- 230.85°C 5.000% Loss
- 459.85°C 50.00% Loss
- Residue: 16.18% (2.271mg)

54% Phosphate Blended MDPE
Sample: II_JY_251
Size: 16.4450 mg
Method: Ramp 5°C/min to 800°C
Comment: 61.5%FR_II_JY_151P

File: C:\..\Jun\MDEP\II_JY_251_61.5%FR_JY151P
Operator: Jun
Run Date: 29-Jul-2002 14:03
Instrument: 2050 TGA V5.4A

TGA

Weight (%)

Temperature (°C)

231.52°C 5.00% Loss
462.60°C 50.00% Loss

Residue:
20.90% (3.437mg)

60% Phosphate Blended MDPE
APPENDIX 31

FTIR SPECTRA OF Lupasol and crosslinked lupasol series 33–37
Polyethylenimine ("Lupasol")

Wavenumber cm⁻¹

Transmittance [%]

D:\OPUS_NT\DATA\Jun\Lupasol2 0 Lupasol2 Viscous Liquid 10/11/2002
(C<sub>2</sub>H<sub>5</sub>N)<sub>1</sub>(C<sub>10</sub>H<sub>4</sub>O<sub>6</sub>)<sub>0.093</sub>(H<sub>3</sub>PO<sub>4</sub>)<sub>0.050</sub>
$(\text{C}_2\text{H}_5\text{N})_1(\text{C}_10\text{H}_4\text{O}_6)_{0.088}(\text{H}_3\text{PO}_4)_{0.18}$

37g
(C_2H_3N)_1(C_{10}H_4O_6)_{0.08}(H_3PO_4)_{0.51}
\((\text{C}_2\text{H}_8\text{N})_1 \ (\text{C}_{10}\text{H}_4\text{O}_8)_{0.082} \ (\text{H}_2\text{SO}_4)_{0.26}\)
The image contains a Fourier transform IR (FT-IR) spectrum of a compound. The peak assignments are as follows:

- 3028.59 cm⁻¹
- 1689 cm⁻¹
- 1477.77 cm⁻¹
- 1107 cm⁻¹
- 857 cm⁻¹
- 577.73 cm⁻¹

The compound is identified as:

\[(\text{C}_2\text{H}_5\text{N})_1 (\text{C}_10\text{H}_4\text{O}_6)_{0.061} (\text{H}_2\text{SO}_4)_{0.49}\]

Wavenumber cm⁻¹ range: 4000 to 500
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BIOGRAPHICAL INFORMATION

Jun Yin was born in Guiyang city of China. In July 1995, she received her Bachelor degree of Engineering in Polymer Science and Materials from Sichuan University in Chengdu city, China. During her undergraduate study, she worked with Professor Wen Xu on a research project investigating the effect of mechanical deformation on changes in morphology and physical/chemical properties of high-density polyethylene (HDPE). The results of this project were presented at the 36th IUPAC International Symposium on Macromolecules (8/4/96–8/9/96 in Seoul, Korea) and the paper entitled “A study on morphology and change in properties of HDPE during pan-milling” was published in the conference proceedings.

Upon her graduation in 1995, she joined the Resin Application Research Institute of Beijing Yanshan Petrochemical Group Co. Ltd. (BYP) in Beijing of China as an application and marketing engineer. BYP is at present the largest producer of ethylene, plastics, resins, synthetic rubber, basic organic chemical raw materials and synthetic fiber carpet in China. She worked on various R&D projects which were primarily about the development of large-scale and more cost-effective manufacturing processes of synthetic resins for various industrial applications, such as developing better anti-aging, anti-fogging and temperature-keeping properties of low-density polyethylene (LDPE) films used in farms located in various weather zones in China.
She also worked on marketing and sales of BYPC’s new and high quality polyethylene and polypropylene products in northeast regions of China.

In 1999, she was granted a full scholarship from the University of Texas at Arlington in Arlington, Texas, and started her Ph.D. program under the guidance of Prof. Ronald L. Elsenbaumer in the Department of Chemistry. Her research topics were in the field of conductive polymers and flame retardants of the polymers. Some of her research results had been published in the following papers: “Efficient Synthesis and Characterization of Novel Bibenzimidazole Oligomers and Polymers as Potential Conjugated Chelating Ligands” *The Journal of Organic Chemistry, 2005, 70*, 9436-9446. “Synthesis and Properties of Multi-nuclear Ruthenium (II) Complexes of Bis(2,2’-bibenzimidazole)” *Synthetic Metals, 2005, 154*, 233-236. In 2005, she received her Ph.D. degree in Chemistry, and concluded all her research work in her Ph.D. dissertation, entitled: “Oligomeric and Polymeric Bibenzimidazole Based Metal Complexes and Crosslinked Polyethyleneimine Based Flame Retardants”. She received the Outstanding Research Award at the Department of Chemistry in 2005.

She is affiliated with the American Chemical Society.

In August 2000, she was married to Dr. Yong He, formally from Nanjing city in China. She still keeps her maiden name because of the Chinese tradition. Her primary interest lies in the scientific research in the field of polymer science and materials. She would like to continue her current research work in academic institutions and research laboratories.