DESIGN AND PHOTOCHEMICAL STUDIES OF ZEOLITE-BASED ARTIFICIAL PHOTOSYNTHETIC SYSTEMS

DISSERTATION

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* * * * *

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ABSTRACT

The work described in this thesis describes steps towards building a zeolite-membrane based photochemical assembly, which can be used for developing a hydrogen evolving artificial photosynthetic system. We adopted the membrane system of natural photosynthesis in our artificial photosynthesis system to separate photochemically generated redox species. For photochemical applications, membranes without any intercrystal pinholes and grain boundaries are preferred since these defects introduce non-shape selective pathway for molecules to pass through the membrane. Also the membrane needs to be mechanically stable for assembly and operation of the system. To prepare zeolitic membranes for artificial photosynthetic systems, hydrothermal synthesis of zeolitic membranes was studied and an optimized synthesis procedure was developed. The films formed were typically 10 µm thick and made up of 4-5 µm spherical zeolitic crystals. However, intercrystalline defects were observed in zeolitic films made by hydrothermal synthesis and the films were not mechanically stable for photochemical applications. To address these issues, novel secondary treatment method to prepare zeolitic membranes was developed. Positive-type photoresist was used to fill nano to micrometer size pinholes that are generated during zeolite membrane casting. With this method, membrane leaking was reduced to 0.05% while zeolitic surface and pores were still accessible to molecules. For photochemical studies, photoresist-coated zeolitic
membrane was used as a host for electron acceptor molecules and provided a route for charge propagation by electron hopping across the membrane. Since acceptor molecules are separated from donor molecules by a membrane, back electron transfer is prohibited and permanent charge separation can be achieved.

Ruthenium dyad molecules were utilized as photosensitizers in our artificial photosynthetic system. To improve the efficiency of synthesis and photo electron transfer reaction, we synthesized and developed new ruthenium dyad molecules, [(bpy)$_2$Ru(dmb-L or L’-4DQ)], which have conjugated bridge L or L’ between the ruthenium donor and bipyridinium acceptor. Using modified “ship in a bottle” method, the dyad molecules were partially entrapped in pores of zeolite Y. Spectroscopic and photochemical studies were conducted to test the efficiency of photo electron transfer reactions using these dyads.

The zeolitic membranes and ruthenium dyad photosensitizers developed in this study can be utilized as a solar energy conversion assembly for photolytic splitting of water into hydrogen and oxygen with proper catalysts such as platinium (Pt) and/or ruthenium oxide (RuO$_2$).
Dedicated to my parents
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# TABLE OF CONTENTS

| Chapter |
|------------------|---|
| Abstract | ii |
| Dedication | iv |
| Acknowledgments | v |
| Vita | vii |
| List of Tables | x |
| List of Figures | xi |
| Chapters: |
| 1. Introduction | 1 |
| Natural photosynthetic systems | 1 |
| Artificial photosynthetic systems | 3 |
| Electron donor: Ru(bpy)$_3^{2+}$ | 3 |
| Electron transfer reactions of Ru(bpy)$_3^{2+}$ and viologen | 5 |
| Zeolite | 7 |
| Zeolite as heterogeneous supports | 8 |
| Photochemical systems using zeolites | 10 |
| Scope of this work | 11 |
| References | 14 |
| 2. Synthesis and mechanistic studies of free-standing zeolitic films | 27 |
| Introduction | 27 |
| Experimental section | 30 |
| Results | 33 |
| Synthesis of chabazite-type film | 33 |
| Synthesis of P-type zeolitic film | 39 |
| Discussion | 41 |
| Synthesis of chabazite-type film | 41 |
| Synthesis of P-type zeolitic film | 46 |
| Conclusion | 48 |
| References | 49 |
3. Charge transport through a novel zeolite Y membrane by a self exchange process ................................................................. 71
   Introduction ........................................................................................................ 71
   Experimental section .......................................................................................... 73
   Results ......................................................................................................................... 80
      Synthesis of zeolite Y nanocrystals ................................................................. 80
      Zeolite coating on polymer or glass substrates ................................................. 82
      Membrane fabrication on alumina substrate ..................................................... 83
      Leak properties of the photoresist-coated membrane ...................................... 84
      Ion exchange properties of the photoresist-coated membrane ...................... 85
      Charge transport studies with the photoresist coated membrane .................. 88
   Discussion ............................................................................................................ 92
      Synthesis of nanocrystalline zeolites ............................................................... 92
      Membrane preparation ...................................................................................... 93
      Membrane properties .......................................................................................... 95
      Photo-induced charge transport through zeolitic membrane ......................... 99
   Conclusion ............................................................................................................ 104
   References ........................................................................................................... 106

4. Synthesis and photochemical studies of zeolite surface-bound ruthenium photosensitizers ................................................................. 133
   Introduction ......................................................................................................... 133
   Experimental section .......................................................................................... 136
   Results ......................................................................................................................... 146
      Synthesis and photochemical studies of
      \([\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^2+ \cdot \text{Y} \) .......................................................... 148
      Synthesis and photochemical studies of
      \([\text{Ru(bpy)}_2(\text{dmb-L’-4DQ})]^3+ \cdot \text{Y} \) .......................................................... 159
   Discussion ............................................................................................................ 166
      Syntheses and structures of zeolite bound dyads ............................................. 166
      Emission of ruthenium complexes with olefinic bridge .................................. 168
      Photolysis and electron transfer reaction of zeolite bound dyads .................... 170
   Conclusion ............................................................................................................ 176
   References ........................................................................................................... 178

Bibliography ............................................................................................................. 222
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Properties of commonly used zeolites</td>
<td>8</td>
</tr>
<tr>
<td>2.1</td>
<td>Effects of temperature on zeolitic film formation</td>
<td>34</td>
</tr>
<tr>
<td>2.2</td>
<td>Composition examined for forming chabazite-type film</td>
<td>38</td>
</tr>
<tr>
<td>2.3</td>
<td>Composition examined for forming P-type zeolitic film</td>
<td>39</td>
</tr>
<tr>
<td>4.1</td>
<td>UV-Vis absorption data of ruthenium compounds</td>
<td>149</td>
</tr>
<tr>
<td>4.2</td>
<td>Emission data of ruthenium compounds</td>
<td>150</td>
</tr>
<tr>
<td>4.3</td>
<td>Electrochemical data of bipyridinium acceptors</td>
<td>152</td>
</tr>
<tr>
<td>4.4</td>
<td>Electrochemical data of ruthenium compounds</td>
<td>153</td>
</tr>
<tr>
<td>4.5</td>
<td>Emission data of ruthenium compounds</td>
<td>162</td>
</tr>
<tr>
<td>4.6</td>
<td>Electrochemical data of ruthenium compounds</td>
<td>163</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>“Z scheme” of Natural photoelectron transfer</td>
<td>16</td>
</tr>
<tr>
<td>1.2</td>
<td>Photochemical architecture for natural photosynthesis</td>
<td>17</td>
</tr>
<tr>
<td>1.3</td>
<td>Number of publications related to Ru(bpy)$_3^{2+}$</td>
<td>18</td>
</tr>
<tr>
<td>1.4</td>
<td>Structure of Ru(bpy)$_3^{2+}$</td>
<td>18</td>
</tr>
<tr>
<td>1.5</td>
<td>Molecular Orbital diagram for Ru(bpy)$_3^{2+}$</td>
<td>19</td>
</tr>
<tr>
<td>1.6</td>
<td>Absorption and emission spectra of Ru(bpy)$_3^{2+}$</td>
<td>19</td>
</tr>
<tr>
<td>1.7</td>
<td>Jablonski diagram for the ground state processes for Ru(bpy)$_3^{2+}$</td>
<td>20</td>
</tr>
<tr>
<td>1.8</td>
<td>Structures and redox potentials of bipyridine electron acceptors</td>
<td>20</td>
</tr>
<tr>
<td>1.9</td>
<td>Electron transfer from Ru(bpy)$_3^{2+}$ to methyl viologen (MV$^{2+}$)</td>
<td>21</td>
</tr>
<tr>
<td>1.10</td>
<td>Photosystem involving Ru(bpy)$_3^{2+}$ and MV$^{2+}$ for water splitting</td>
<td>22</td>
</tr>
<tr>
<td>1.11</td>
<td>Structure of zeolitic framework</td>
<td>23</td>
</tr>
<tr>
<td>1.12</td>
<td>Electron relay systems in zeolite</td>
<td>24</td>
</tr>
<tr>
<td>1.13</td>
<td>Photo electron transfer reaction with powder type zeolite sample</td>
<td>25</td>
</tr>
<tr>
<td>1.14</td>
<td>Zeolite-based water splitting system</td>
<td>26</td>
</tr>
<tr>
<td>2.1</td>
<td>Structure of chabazite</td>
<td>51</td>
</tr>
<tr>
<td>2.2</td>
<td>Structure of P-type zeolite</td>
<td>52</td>
</tr>
<tr>
<td>2.3</td>
<td>NMR spectrum of Dab-4Br</td>
<td>53</td>
</tr>
</tbody>
</table>
2.4 Temperature profile of heating procedure for the synthesis of chabazite film (a) 90°C heating (b) 103°C heating (c) step heating .......................... 54
2.5 XRD patterns of products formed from 90°C synthesis .......................... 55
2.6 Morphology of crystals in chabazite films ......................................... 56
2.7 Side view of a chabazite film formed at 90°C........................................ 57
2.8 SEM picture of powder on the bottom of reaction bottle fromed by 90°C heating .................................................................................. 58
2.9 SEM pictures of films formed upon (a) 90°C; (b) 103°C, and (c) step-heating procedures ................................................................. 59
2.10 XRD pattern of powder recovered from bottom of the reaction bottle in 103°C synthesis ................................................................. 60
2.11 Optical micrograph of a piece of film recovered from the step-heating procedure ................................................................. 61
2.12 XRD patterns of products formed from step heating ......................... 62
2.13 (a) Top and (b) side views of chabazite films formed from step heating procedure ................................................................. 63
2.14 SEM pictures of zeolitic films during synthesis ................................. 64
2.15 Structural arrangements of (a)chabazite and (b)gmelinite .................. 65
2.16 Zeolite film growth during synthesis ................................................. 66
2.17 XRD pattern of (a) P-type zeolitic film (b) Sodalite powder formed by the synthesis without Dab4-Br (C) zeolite P-sodalite mixture film ...... 67
2.18 Side view of a P-type thick zeolitic film ........................................... 68

xii
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.19</td>
<td>Top views of dense side of the P-type zeolitic films</td>
</tr>
<tr>
<td>2.20</td>
<td>Top views of loose side of the P-type zeolitic films</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic of a two-compartment cell</td>
</tr>
<tr>
<td>3.2</td>
<td>NMR spectrum of 4DQ$^{2+}$</td>
</tr>
<tr>
<td>3.3</td>
<td>NMR spectrum of mono substituted PVS</td>
</tr>
<tr>
<td>3.4</td>
<td>NMR spectrum of PVS</td>
</tr>
<tr>
<td>3.5</td>
<td>XRD pattern of synthesized nano Y zeolitic powder</td>
</tr>
<tr>
<td>3.6</td>
<td>SEM of zeolite Y nanocrystals (a) before sonication (b) after 3 hours of sonication</td>
</tr>
<tr>
<td>3.7</td>
<td>Nanocrystalline Zeolite Y synthesized with Ludox (a) SEM micrograph (b) X-ray powder diffraction</td>
</tr>
<tr>
<td>3.8</td>
<td>Acrylic copolymer substrate</td>
</tr>
<tr>
<td>3.9</td>
<td>Zeolitic layer on Acrylic copolymer substrate (a) low resolution (b) high resolution SEM</td>
</tr>
<tr>
<td>3.10</td>
<td>Nanocrystalline Y layer on ITO coated glass substrate</td>
</tr>
<tr>
<td>3.11</td>
<td>Commercial alumina substrate (a) Top view (b) Side view</td>
</tr>
<tr>
<td>3.12</td>
<td>Zeolitic films with different thickness (a) 2.5 μm (b) 1 μm (c) 0.5 μm</td>
</tr>
<tr>
<td>3.13</td>
<td>Zeolitic layer on alumina substrates formed by spin coating (a) one cycle of spin coating (b) Three cycles of spin coating</td>
</tr>
<tr>
<td>3.14</td>
<td>SEM pictures of photoresist coated zeolite Y membrane-After development (a) Top view (b) Side view</td>
</tr>
<tr>
<td>3.15</td>
<td>Fluorescence intensity of Rhodamine dye 123 at 525 nm</td>
</tr>
</tbody>
</table>
3.16 Fluorescence spectra of rhodamine dye leaking through membranes …… 124
3.17 MV$^{2+}$ ion exchange experiment with photoresist-coated zeolite membrane ……………………………………………………………………………………………………… 125
3.18 MV$^{2+}$ ion exchange experiment across the photoresist-coated zeolite membrane ……………………………………………………………………………………………………… 126
3.19 Charge transport through a zeolite Y membrane …………………………… 127
3.20 Measure of PVS$^\ast$ generation at the zeolite side …………………………… 128
3.21 Measure of the change of PVS$^\ast$ upon photolysis ………………………… 129
3.22 Structures of Faujasite ………………………………………………………… 130
3.23 Patterning with positive and negative resists ……………………………… 131
3.24 Photoresist coating process …………………………………………………… 132
4.1 Structures and redox potentials of bipyridine electron acceptors ……….. 180
4.2 Structures of ligand dmb-L-dmb and dmb-L’-dmb …………………… 181
4.3 Synthesis of [Ru(bpy)$_2$(dmb-L-dmb)]$^{2+}$ ……………………………………… 182
4.4 NMR spectrum of (dmb-L-dmb) ligand ……………………………………… 183
4.5 NMR spectrum of [Ru(bpy)$_2$(dmb-L-dmb)]$^{2+}$ ……………………………… 184
4.6 Synthesis of [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$ ……………………………………….. 185
4.7 NMR spectrum of [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$ ……………………………… 186
4.8 Preparation of C$_4$H$_8$Br$_2$-Y …………………………………………………….. 187
4.9 Synthesis of [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$-Y ……………………………………… 188
4.10 NMR spectrum of compound extracted from
4.11 UV-Vis absorption spectra of (a) ligand (dmb-L-dmb) (b) I: Ru(bpy)$_3$(PF$_6$)$_2$
II: Ru(bpy)$_2$(dmb-L-dmb)(PF$_6$)$_2$ III: Ru(bpy)$_2$(dmb-L-4DQ)(PF$_6$)$_4$ 
……………………………………………………………………………….. 190
4.12 UV-Vis absorption spectra of Ru(bpy)$_2$(dmb-L-4DQ)(PF$_6$)$_4$ extracted from 
Ru(bpy)$_2$(dmb-L-4DQ)$^{4+}$-Y in CH$_3$CN 
……………………………………………………………………………….. 191
4.13 Diffuse Reflectance UV-Vis spectrum of Ru(bpy)$_2$(dmb-L-4DQ)$^{4+}$-Y 
……………………………………………………………………………….. 191
4.14 Emission spectra of ruthenium compounds I: Ru(bpy)$_3$(PF$_6$)$_2$ II:
Ru(bpy)$_2$(dmb-L-dmb)(PF$_6$)$_2$ III: Ru(bpy)$_2$(dmb-L-4DQ)(PF$_6$)$_4$ 
……………………………………………………………………………….. 192
4.15 Emission spectra with solid samples of I: Ru(bpy)$_3^{2+}$-Y 
II: [Ru(bpy)$_2$(dmb-L-dmb)]$^{2+}$-Y III: [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$-Y 
……………………………………………………………………………….. 192
4.16 Cyclic voltammetry data of MV(PF$_6$)$_2$ 
……………………………………………………………………………….. 193
4.17 Cyclic voltammetry data of 3DQ(PF$_6$)$_2$ 
……………………………………………………………………………….. 193
4.18 Cyclic voltammetry and DPV data of 4DQ(PF$_6$)$_2$ 
……………………………………………………………………………….. 194
4.19 Cyclic voltammetry data of Ru(bpy)$_3$(PF$_6$)$_2$ 
……………………………………………………………………………….. 194
4.20 Cyclic voltammetry data of Ru(bpy)$_2$(dmb-L-dmb)(PF$_6$)$_2$ 
……………………………………………………………………………….. 195
4.21 Cyclic voltammetry data of (dmb-L-dmb) 
……………………………………………………………………………….. 195
4.22 Cyclic voltammetry data of Ru(bpy)$_2$(dmb-L-4DQ)(PF$_6$)$_4$ 
……………………………………………………………………………….. 196
4.23 Photoelectron transfer scheme of EDTA-Ru(bpy)$_2$(dmb-L-4DQ)$^{4+}$-Y 
……………………………………………………………………………….. 197
4.24 Diffuse reflectance UV-Vis absorption spectra according to the photolysis of 
EDTA-Ru(bpy)$_2$(dmb-L-4DQ)$^{4+}$-Y solid 
……………………………………………………………………………….. 198
4.25 Photoelectron transfer scheme of Ru(bpy)$_2$(dmb-L-4DQ)$^{4+}$-MV$^{2+}$-Y 
……………………………………………………………………………….. 199
4.26 Diffuse reflectance spectra of Ru(bpy)$_2$(dmb-L-4DQ)$^{4+}$-Y upon ion exchange with MV$^{2+}$ and exposure to the ambient light ........................................... 200

4.27 Photoelectron transfer scheme of Ru(bpy)$_2$(dmb-L-4DQ)$^{4+}$-MV$^{2+}$-Y in PVS aqueous solution ................................................................. 201

4.28 The growth of PVS$^{\bullet}$ during photolysis of Ru(bpy)$_2$(dmb-L-4DQ)$^{4+}$-3DQ$^{2+}$-Y in aqueous solution of PVS .................................................... 202

4.29 The growth of PVS$^{\bullet}$ during photolysis of (a) Ru(bpy)$_2$(dmb-L-4DQ)$^{4+}$-3DQ$^{2+}$-Y (b) Ru(bpy)$_2$(dmb-L-4DQ)$^{4+}$-Y in aqueous solution of PVS ..... 203

4.30 The growth of PVS$^{\bullet}$ during photolysis of Ru(bpy)$_3^{2+}$-4DQ$^{2+}$-Y in aqueous solution of PVS ............................................................. 204

4.31 Synthesis of dmb-L’-dmb ligand ....................................................... 205

4.32 NMR spectrum of 4’-Methyl-2,2’-bipyridyline-4-carbaldehyde ............206

4.33 NMR spectrum of 4-(Bromomethyl)-4’-methyl-2,2’-bipyridine ...............207

4.34 NMR spectrum of ((4-(4’-methyl)-2,2’-bipyridyl)methyl)triphenyl phosphonium bromide ................................................................. 208

4.35 NMR spectrum of dmb-L’-dmb .......................................................... 209

4.36 Synthesis of [Ru(bpy)$_2$(dmb-L’-dmb)]$^{2+}$ ........................................... 210

4.37 NMR spectrum of [Ru(bpy)$_2$(dmb-L’-dmb)$^{2+}$](PF$_6$)$_2$ ....................... 211

4.38 Synthesis of Ru(bpy)$_2$(dmb-L’-4DQ)$^{4+}$ ........................................... 212

4.39 NMR spectrum of Ru(bpy)$_2$(dmb-L’-4DQ)(PF$_6$)$_4$ in CD$_3$CN .............. 213

4.40 Synthesis of [Ru(bpy)$_2$(dmb-L’-4DQ)]$^{4+}$-Y ....................................... 214

xvi
4.41 UV-Vis absorption spectra of [Ru(bpy)$_3$](PF$_6$)$_2$ and [Ru(bpy)$_2$(dmb-L’-dmb)](PF$_6$)$_2$ …………………………………………………………………………………… 215

4.42 Emission spectra of ruthenium compounds I:Ru(bpy)$_3$(PF$_6$)$_2$ II: Ru(bpy)$_2$(dmb-L’-dmb)(PF$_6$)$_2$ ……………………………………………………………… 215

4.43 UV-Vis absorption spectra of I:Ru(bpy)$_3$(PF$_6$)$_2$ II: Ru(bpy)$_2$(dmb-L’-4DQ)(PF$_6$)$_4$ in CH$_3$CN solutions ……………………………………………………………… 216

4.44 Emission spectra of ruthenium compounds I:Ru(bpy)$_3$(PF$_6$)$_2$ II:
Ru(bpy)$_2$(dmb-L’-4DQ)(PF$_6$)$_4$ in CH$_3$CN solutions …………………………… 216

4.45 Cyclic voltammetry data of [Ru(bpy)$_2$(dmb-L’-dmb)](PF$_6$)$_2$ …………… 217

4.46 Cyclic voltammetry data of [Ru(bpy)$_2$(dmb-L’-4DQ)](PF$_6$)$_4$ …………… 217

4.47 UV-Vis absorption spectra of solutions during photolysis of
[Ru(bpy)$_2$(dmb-L’-4DQ)]$^{4+}$-3DQ$^{2+}$-Y in PVS solution …………………………… 218

4.48 The growth of PVS$^{*+}$ during photolysis of (a) Ru(bpy)$_2$(dmb-L’-4DQ)$^{4+}$
3DQ$^{2+}$-Y (b) Ru(bpy)$_2$(dmb-L’-4DQ)$^{4+}$-Y in aqueous solution of PVS …. 219

4.49 The growth of PVS$^{*+}$ during photolysis of Ru(bpy)$_2$(dmb-L’-4DQ)$^{4+}$
-3DQ$^{2+}$-Y in aqueous solutions of PVS-long time photolysis ………………. 220

4.50 Intramolecular electron transfer reactions in [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$ … 221
CHAPTER 1

INTRODUCTION

NATURAL PHOTOSYNTHETIC SYSTEMS

Natural photosynthesis can be defined as the utilization of solar light energy by plant cells for the biosynthesis of cell components. Natural photosynthesis provides energy for green plants and other photosynthetic autotrophs as well as for nearly all heterotrophic organisms through the operation of food chains. Fossil fuels such as coal, petroleum and natural gas are also produced by photosynthesis since they are decomposition products of biological materials generated by photosynthetic organisms.

The overall photosynthetic process in plants consists of the formation of carbohydrates by the reduction of carbon dioxide. (eq 1.1)

\[
\text{h} \text{\[n\CO_2 + n\H_2O \rightarrow (CH_2O)_n + n\O_2 \quad \Delta G^\circ=114 \text{ kcal when } n=1 \ (1.1)\]
}

In this reaction, light energy is utilized to oxidize water and to reduce CO₂. Therefore photosynthesis can also be viewed as conversion of light energy to chemical energy by photochemical architecture in plants. Reaction (1.1) is a combination of two chemical
processes. One is production of oxygen from water (reaction (1.2)) and the other is reduction of CO\textsubscript{2} to carbohydrates. (reaction(1.3)) Both reactions require the transfer of four electrons.

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+ \quad (1.2)
\]

\[
4\text{e}^- + 4\text{H}^+ + \text{CO}_2 \rightarrow (\text{CH}_2\text{O}) + \text{H}_2\text{O} \quad (1.3)
\]

Since two photons are required for the transfer of one electron, eight photons are needed for the reduction of one CO\textsubscript{2} molecule.

The energy diagram of photosynthetic electron transport via photosystems I and II is shown as “Z scheme” in Figure 1.1. The overall photosynthesis in green plants can be summarized in three steps. First step is the light absorption by the chlorophyll photosensitizers, which are P700 and P680 in photosystem I and II, respectively. Second step is the electron transfer from these excited photosensitizers to proteins and enzymes. Finally, oxidation and reduction will happen on either side of the biological membrane. On the oxidation side, water will be oxidized to oxygen to reduce oxidized photosensitizer P680. On the reduction side of a membrane, reduced NADPH will be used to reduce CO\textsubscript{2} and other acceptors. The energy diagram also shows that the back electron transfer reaction is thermodynamically favorable. The unique spatial arrangement of photosensitizers and electron carriers in natural photosynthetic architecture prevents this energy wasting backward reaction. Also biological membrane keeps the charge separated species separately in opposite sides of the membrane. Figure 1.2 shows the photochemical architecture for natural photosynthesis.
ARTIFICIAL PHOTOSYNTHETIC SYSTEMS

As shown in previous section, natural photosynthesis is a very clean and efficient way of generating or storing energy. To construct an artificial photosynthetic system which can generate and store energy like natural photosynthetic system, we need three elements: Electron relay system, which includes photosensitizer and electron acceptors, membrane or heterogeneous support to prevent recombination of redox species and photocatalysts for final oxidation and reduction reactions. The preparation and properties of these elements and the design for the zeolitic artificial photosynthetic system will be discussed in this section.

Electron donor: Ru(bpy)$_3^{2+}$ [1]

The photochemistry of the tris(bipyridine) ruthenium(II) dication, Ru(bpy)$_3^{2+}$, has been an exciting field of chemical study. Long-lived excited state of Ru(bpy)$_3^{2+}$ has attracted much interest in the field of inorganic synthesis, spectroscopy and electron transfer chemistry. More than 3000 publications concerning the chemistry Ru(bpy)$_3^{2+}$ and its derivatives have appeared in the literature since 1980. Figure 1.3 shows that interest in this complex still continues, producing more than hundred publications each year.

Ru(bpy)$_3^{2+}$ is a complex of ruthenium(II) in the octahedral symmetry D$_3$.(Figure 1.4) According to the molecular orbital structure of the complex shown in Figure 1.5, the ground state of Ru(bpy)$_3^{2+}$ is $t_{2g}^6$, where $t_{2g}$ and $e_g$ levels originate from the 4d orbitals of ruthenium metal. The $t_{2g} \rightarrow e_g$ transition is a weak Laporte forbidden absorption. Excitation of an electron from a $t_{2g}$ orbital into a $\pi^*$-antibonding orbital on the bpy ligand results in an allowed $d \rightarrow \pi^*$ MLCT (metal to ligand charge transfer) transition ($\varepsilon=20,000$
M$^{-1}$cm$^{-1}$). Excited states resulting from MLCT transitions are particularly interesting since they frequently undergo electron transfer reactions. The absorption and emission spectrum of Ru(bpy)$_3^{2+}$ in aqueous solution are shown in Figure 1.6. The intense absorption band at 452 nm is due to this MLCT transition where an electron is promoted from the metal centered t$_{2g}$ orbital into a ligand centered $\pi^*$ orbital. Solutions of Ru(bpy)$_3^{2+}$ show an orange-yellow emission due to a broad band centered around 600nm. The spectroscopic data and kinetic features of the excited state of Ru(bpy)$_3^{2+}$ can be explained by a schematic Jablonski diagram in Figure 1.7. Direct excitation to the triplet state (A$_1T_1$) is a forbidden process, but the triplet state can be populated by an allowed excitation to the singlet state (A(S$_1$)), followed by a fast intersystem crossing to the triplet. The rate constant (k$_{isc}$) for this intersystem crossing is high, leading to a quantum yield for the phosphorescence of 0.042. The emission quantum yield is given by the equation (1.4).

$$\phi_{phos} = \eta_{isc} k_p T_1$$  \hspace{1cm} (1.4)

where $\eta_{isc}$ is the efficiency of population of the emitting excited state, and is given by:

$$\eta_{isc} = k_{isc} / (k_{isc} + k_f + k_{ic})$$  \hspace{1cm} (1.5)

where the lifetime of the emitting excited state is given by

$$\tau_1 = 1 / (k_p + k_{ic}')$$  \hspace{1cm} (1.6)

With a triplet state lifetime of 0.62 microseconds and quantum yield of 0.042, the excited state Ru(bpy)$_3^{2+*}$ can be formed easily and utilized in a wide range of electron transfer reactions.
Electron transfer reactions of Ru(bpy)$_3^{2+}$ and viologen acceptors

The electron transferred from ruthenium t$_{2g}$ orbital to the empty $\pi^*$ orbital of the bpy ligand due to MLCT transition can be used for further electron transfer reactions to other electron acceptors. (eq. 1.7)

$$\text{Ru(bpy)}_3^{2+*} + A \rightarrow \text{Ru(bpy)}_3^{3+} + A^- \quad (1.7)$$

Various electron acceptors have been used in previous studies. Organic bipyridinium ions were utilized in the present study due to its redox potentials and chemical structures. As shown in Figure 1.8, these bipyridinium electron acceptors have redox potentials between $-0.35\text{V}$ and $-0.65\text{V}$ [2,3]. The $\text{Ru(bpy)}_3^{2+/3+}$ redox potential is $-0.87\text{V}$. So the redox potential of these bipyridine compounds lie in the range of good electron acceptors for ruthenium photosensitizer. Also, 2DQ$^{2+}$, 3DQ$^{2+}$ and 4DQ$^{2+}$ carry two positive charges, which is convenient for ion exchange into zeolitic pores. The sizes of these molecules are smaller than the window of zeolite Y supercages.

Figure 1.9 shows the photoinduced electron transfer reaction between Ru(bpy)$_3^{2+}$ and methyl viologen cation (MV$^{2+}$). Ru(bpy)$_3^{2+}$ absorbs light and becomes an excited electron donor, Ru(bpy)$_3^{2+*}$ (eq.1.8). The excited electron can be transferred to MV$^{2+}$ acceptor, which will produce reduced acceptor and oxidized electron donor (eq. 1.9). As Figure 1.9 describes, the back electron transfer from MV$^{•+}$ to Ru(bpy)$_3^{3+}$ is thermally favorable reaction (eq. 1.10). In fact, back electron transfer is as fast as the forward electron transfer according to previous studies [4,5]. In CH$_3$CN, k and k$_r$ are $2.4 \times 10^9 \text{M}^{-1}\text{s}^{-1}$ and $8.3 \times 10^9 \text{M}^{-1}\text{s}^{-1}$, respectively. In aqueous solution, the corresponding values are $5.6 \times 10^9 \text{M}^{-1}\text{s}^{-1}$ and $2.4 \times 10^9 \text{M}^{-1}\text{s}^{-1}$, respectively. To prevent this thermal back electron
transfer reaction, sacrificial electron donors such as EDTA and triethanolamine (TEA) can be used to reduce $\text{Ru(bpy)}_3^{3+}$ to $\text{Ru(bpy)}_3^{2+}$ (eq. 1.11).

$$\text{Ru(bpy)}_3^{2+} \xrightarrow{hv} \text{Ru(bpy)}_3^{2+*} \quad (1.8)$$

$$\text{Ru(bpy)}_3^{2+*} + \text{MV}^{2+} \xrightarrow{k} \text{Ru(bpy)}_3^{3+} + \text{MV}^{**} \quad (1.9)$$

$$\text{Ru(bpy)}_3^{3+} + \text{MV}^{**} \xrightarrow{k} \text{Ru(bpy)}_3^{2+} + \text{MV}^{2+} \quad (1.10)$$

$$\text{Ru(bpy)}_3^{3+} + \text{EDTA} \rightarrow \text{Ru(bpy)}_3^{2+} + \text{EDTA}^- \quad (1.11)$$

In these systems where EDTA or TEA are used as sacrificial electron donors, the oxidation products EDTA$^+$ or TEA$^+$ decompose irreversibly. The reduced methyl viologen (MV$^{++}$) can be used to convert water into hydrogen in cooperation with colloidal platinium(Figure1.10)[3].

The other effective method to slow the back electron transfer reaction is utilization of heterogeneous support. Large number of supports including micelles[6], vesicles[7], Nafion[8], silica gel[9], zeolites[4, 10-16], clays[17], and semiconductors[18] were studied. Among them, zeolites have well-defined microporous structures in which photosensitizers and electron acceptors can be spatially arranged. Also, positively charged viologen cations can be ion exchanged into zeolite pores easily. Several of zeolite-based charge separation systems have been investigated and found to be effective for the generation of long-lived charge separated species [4,8,10-14,19,20].
Zeolite

Zeolites are crystalline aluminosilicates with chemical composition $M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$. The three-dimensional structure of zeolite is made up of corner sharing $SiO_4$ and $AlO_4$ tetrahedra, with exchangeable cations ($M^+$) occupying extra framework positions to neutralize charge [21]. The zeolitic frameworks are composed of Si-O-Si bonds or Si-O-Al bonds. Al-O-Al bonds are not formed due to the unfavorable close proximity of negative charges. The presence of Al in zeolite framework leads to a charged framework and ion-exchange capabilities. The Si/Al ratio can vary from 1 to $\infty$, the latter representing pure silica polymorph. If the ratio is close to 1, the framework has a rather high negative charge and the zeolite is highly hydrophilic. On the other hand, a high Si/Al ratio leads to hydrophobic zeolite with no ion exchange sites. Interconnecting channels and cages make up the internal structure of zeolites. Frameworks with over 100 different structures have been synthesized and many more are possible [13]. Figure 1.11 shows the figurative construction of four different zeolite frameworks that contain sodalite cage. The sodalite unit is found in the SOD, LTA, EMT and FAU frameworks. Table 1.1 lists characteristic features of commonly used zeolites including their void volumes and the kinetic diameter of molecules that can enter the porous structure.

Barrer’s pioneering work in the 1940’s and 1950’s demonstrated that a wide range of zeolites could be synthesized from aluminosilicate gels [22]. In a typical hydrothermal synthesis procedure, a solution of alumina in excess of a base such as sodium hydroxide is mixed with a sol or solution of a silica component. In some cases, addition of templating agents such as tetra alkyl ammonium salts results in desirable framework of
zeolites. The reaction mixture forms a thick gel that crystallizes over some synthetic period when maintained at about 100°C. The product in this typical Na₂O-SiO₂-Al₂O₃-H₂O system depends on the gel composition, the nature of the reagents, and the crystallization conditions [23].

<table>
<thead>
<tr>
<th>Type</th>
<th>Unit-cell compound</th>
<th>Pore structure</th>
<th>Typical Si/Al ratio</th>
<th>Kinetic diameter / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Na₁₂[(AlO₂)₁₂(SiO₂)₁₂]·27H₂O</td>
<td>3D, 4.1 Å</td>
<td>1.0</td>
<td>0.39</td>
</tr>
<tr>
<td>X</td>
<td>Na₈₆[(AlO₂)₈₆(SiO₂)₁₀₆]·264H₂O</td>
<td>3D, 7.4 Å</td>
<td>1.0-1.5</td>
<td>0.81</td>
</tr>
<tr>
<td>Y</td>
<td>Na₅₆[(AlO₂)₅₆(SiO₂)₁₃₆]·250H₂O</td>
<td>3D, 7.4 Å</td>
<td>&gt;1.5-3</td>
<td>0.81</td>
</tr>
<tr>
<td>L</td>
<td>K₉[(AlO₂)₉(SiO₂)₂₇]·22H₂O</td>
<td>1D, 7.1 Å</td>
<td>2.6-3.5</td>
<td>0.81</td>
</tr>
<tr>
<td>Mordenite</td>
<td>Na₈[(AlO₂)₈(SiO₂)₄₀]·24H₂O</td>
<td>1D, 7.1Å</td>
<td>4.7-5</td>
<td>0.63</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>(TPA,Na)[(AlO₂)(SiO₂)₃₀]·10H₂O</td>
<td>3D, 5.4*5.6 Å</td>
<td>10-100</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>5.1*5.5 Å</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1 Properties of commonly used zeolites

**Zeolites as heterogeneous supports**

As mentioned previously, zeolites have long been exploited as supports or hosts for catalysis or photochemical studies. There are several different strategies to introduce and assemble molecules into the zeolite interior. Positively charged species can be ion-exchanged into the zeolite from solution if they are small enough to enter the ring openings. Many inorganic complexes such as Ru(NH₃)₆³⁺ as well as organic cations such as viologens can be readily exchanged into the zeolite. For neutral molecules, the molecules can be introduced into zeolite structures via the vapor phase or a solvent. Sometimes molecules larger than ring openings of zeolites need to be assembled within
zeolitic pores. “Ship in a bottle” synthesis has been successfully used for this purpose. This procedure typically includes steps to obtain the necessary building blocks into the supercage, followed by appropriate treatment to synthesize the desired complex. One of the commonly used syntheses is the incorporation of Ru(bpy)$_3^{2+}$ in zeolite Y. Zeolite Y possesses a framework which consists of supercages of 13 Å diameter and each of which is connected to four adjacent supercages by openings having 7-8 Å windows.[19] These large structures and strong hydrophilicity of faujasite type zeolite makes the material especially useful for catalysis or photochemical applications. Ru(bpy)$_3^{2+}$ has a dimension of 12 Å, and cannot be introduced into zeolitic pores due to the size limitation of zeolite Y. The following scheme has been adapted from the pioneering work of Lunsford and co-workers [24].

Ion exchange: $[\text{Ru(NH}_3)_6]^{3+} + \text{Na-Y} \rightarrow [\text{Ru(NH}_3)_6]^{3+} - \text{Na-Y}$

Vaporization: $[\text{Ru(NH}_3)_6]^{3+} - \text{Na-Y} + \text{bipyridine} \xrightarrow{\text{heat}} [\text{Ru(NH}_3)_6]^{3+} - \text{bipyridine-Na-Y}$

Synthesis: $[\text{Ru(NH}_3)_6]^{3+} - \text{bipyridine-Na-Y} \xrightarrow{\text{heat}} [\text{Ru(bpy)}_3]^{2+} - \text{Na}^+ - \text{Y} + \text{N}_2\text{H}_4 + \text{side products}$

Purification: $[\text{Ru(bpy)}_3]^{2+} - \text{Na}^+ - \text{Y} \rightarrow \text{Soxhlet extraction and ion-exchange.}$

Utilization of these methods to introduce and assemble molecules into zeolite channels is essential for photochemical applications of zeolitic materials as hosts or supports.
Photochemical systems using zeolites

Using the methods discussed before, complex electron-transfer systems have been arranged in zeolite pores and channels. These zeolite-based electron transfer systems resulted in permanent charge separation. Dutta and co-workers surrounded the encapsulated Ru(bpy)$_3^{2+}$ in zeolite with N,N'-tetramethylene-2,2'-bipyridinium (4DQ$^{2+}$, E° = -0.65 versus NHE) viologen cations [10]. Ru(bpy)$_3^{2+}$ were introduced in the supercages of zeolite Y by ship-in-a- bottle synthesis and viologen cations were completely ion exchanged into all existing supercages except those cages that contain Ru(bpy)$_3^{2+}$. The zeolitic sample, Ru(bpy)$_3^{2+}$-4DQ$^{2+}$-Y, was suspended in a solution of propylviologen sulfate (PVS, E° = -0.4 versus NHE) upon irradiation of the suspension in a deaerated environment, PVS$^•^-$ radical formation was observed. Figure 1.12 describes the electron relay in Ru(bpy)$_3^{2+}$-4DQ$^{2+}$-Y in PVS solution. The excited photosensitizer, Ru(bpy)$_3^{2+}$, will reduce 4DQ$^{2+}$ in neighboring supercages and form bipyridinium radical cation, 4DQ$^{•^+}$. Electron hopping can occur between neighboring bipyridinium molecules, leading to long-lived charge separation. If the charge migrates to the surface of zeolite, then a directional electron transfer to PVS can occur. The formation of PVS$^•^-$ will lead to repulsion from the zeolite framework and thereby permanent charge separation.

Zeolitic photoelectron transfer systems using dyad photosensitizers have also been studied by Mallouk and co-workers[14]. A three-component system, consisting of Ru(bpy)$_3^{2+}$-nDQ$^{2+}$ dyad and benzyl viologen, BV$^{2+}$, as the secondary electron acceptor was used for charge separation. Ru(bpy)$_3^{2+}$ moiety of the dyad is too large to enter the zeolite cages and stays ion zeolitic surface while the nDQ$^{2+}$ moiety is exchanged through
the 7.1 Å of zeolite L. Upon photoexcitation, an electron cascade occurs from Ru\(^{2+*}\) to DQ\(^{2+}\) by intramolecular electron transfer and to BV\(^{2+}\) by intermolecular electron transfer. A lifetime of 37 μs was measured for Ru\(^{3+}\)-nDQ\(^{2+}\).....BV\(^{4+}\) charge separated state, with a quantum yield of 17%. Mallouk and co-workers also studied the electron transfer reactions in a series of dyads, Ru(bpy)\(_3\)\(^{2+}\)-(CH\(_2\))\(_n\)-MV\(^{2+}\), exchanged onto the surface of large-pore zeolites [20]. The rate of forward electron transfer from photoexcited donor to acceptor decreases with increasing spacer length, n. The back electron transfer reaction is approximately 10\(^5\) times slower for Ru(bpy)\(_3\)\(^{2+}\)-(CH\(_2\))\(_n\)-MV\(^{2+}\) dyads on the zeolite surface than in solution. Addition of another donor, D‘, to the suspension leads to a long-lived charge separated species between D‘ and MV\(^{2+}\).

**SCOPE OF THIS WORK**

The work described in this thesis was aimed at building a zeolite based photochemical system, which can be used for hydrogen evolving artificial photosynthetic system. Based on previous studies, we utilized the ruthenium dyad molecule as a photosensitizer. To improve the efficiency of synthesis and photo electron transfer reaction, we synthesized and developed new ruthenium dyad molecules, [(bpy)\(_2\)Ru(dmb-L or L’-4DQ)], which have conjugated bridge L or L’ between the ruthenium donor and bipyridinium acceptor. Using modified “ship in a bottle” method, the dyad molecules are partially entrapped in pores of zeolite Y. Spectroscopic and photochemical studies were conducted to test efficiency of photo electron transfer reactions using these dyads, [(bpy)\(_2\)Ru(dmb-L or L’-4DQ)].
We also adopted the membrane system of natural photosynthesis in our artificial photosynthesis system. As figure 1.13 describes, it is possible that the reduced acceptor, $A^-$, in the solution reacts with oxidized photosensitizer, $D^+$, on the surface of zeolitic particles and undergoes the energy wasting back electron transfer reaction in powder system. If membrane type of zeolite is used as hosts for electron transfer reaction, back electron transfer reaction can be retarded and photocatalysts can be introduced to the artificial photosynthesis system to generate hydrogen from reduced acceptor. For photochemical applications, membranes without any inter crystal pinholes and grain boundaries are preferred since these defects introduce non-shape selective pathway for molecules to pass through the membrane. Also the membrane needs to be mechanically stable for easy operation of the system. To prepare zeolitic membranes for artificial photosynthetic systems, hydrothermal synthesis of zeolitic membranes was studied and an optimized synthesis procedure was developed. The films formed are typically 10 $\mu$m thick and made up of 4-5 $\mu$m spherical zeolitic crystals. However, intercrystalline defects were observed in zeolitic films made by hydrothermal synthesis and the films were not mechanically stable enough for photochemical applications. To address these issues, a novel secondary treatment method to prepare zeolitic membranes was developed. Positive-type photoresist was used to fill nano to micrometer size pinholes that are generated during zeolite membrane casting. With this photoresist-coating method, membrane leaking was reduced to 0.05% while zeolitic surface and pores are still accessible to molecules.
Photoresist-coated zeolitic membrane is used as a host for acceptor molecules and provides a route for charge propagation by electron hopping across the membrane. Since acceptor molecules are separated from donor molecules by a membrane, back electron transfer can be prohibited and permanent charge separation is achieved.

The zeolitic membranes and ruthenium dyad photosensitizers developed in this study can be utilized as a solar energy conversion assembly for photolytic splitting of water into hydrogen and oxygen if proper photocatalysts such as platinium (Pt) or ruthenium oxide (RuO₂) are combined. Figure 1. 14 represents optimized design of zeolitic artificial photosynthetic system for hydrogen evolution.
REFERENCES


5. Kalyanasundaram, K. Coordination Chemistry Reviews 1982, 46, 159-244.


Figure 1.1 “Z scheme” of natural photoelectron transfer
Figure 1.2 Photochemical architecture for natural photosynthesis
Figure 1.3 Number of publications related to Ru(bpy)$_3^{2+}$

Figure 1.4 Structure of Ru(bpy)$_3^{2+}$
Figure 1.5 Molecular Orbital diagram for Ru(bpy)$_3^{2+}$

Figure 1.6 Absorption and emission spectra of Ru(bpy)$_3^{2+}$
Figure 1.7 Jablonski diagram for the ground and excited state processes for Ru(bpy)$_3^{2+}$

Figure 1.8 Structures and redox potentials of bipyridine electron acceptors. $E^0$ is versus NHE.
Figure 1.9 Electron transfer from Ru(bpy)$_3^{2+*}$ to methyl viologen (MV$^{2+}$)
Figure 1.10 Photosystem involving Ru(bpy)$_3^{2+}$ and MV$^{2+}$ for water splitting
Figure 1.11 Structure of zeolitic framework
Figure 1.12 Electron relay systems in zeolite

- *Ru(bpy)_3^{2+} E^o=-0.87V
- 4DQ^{2+} E^o=-0.65V
- PVS E^o=-0.41V
- Ru(bpy)_3^{2+} E^o=1.25V
- Eo=-0.41V
Figure 1.13 Photo electron transfer reaction with powder type zeolite sample
Figure 1.14 Zeolite-based water splitting system
CHAPTER 2

SYNTHESIS AND MECHANISTIC STUDIES OF FREE-STANDING ZEOLITIC FILMS

INTRODUCTION

Zeolitic membranes have received considerable attention because of their molecular sieving ability and long-term stability to high temperature and chemicals [1-5]. In present study, zeolitic membranes are used as heterogeneous media for photochemical applications. As discussed in previous chapter, molecules such as viologen electron acceptors will be ion-exchanged into zeolitic pores. For this purpose, the pore size and ion exchange capacity of the zeolite needs to be large enough. Gmelinite, zeolite L, faujasite and mordenite satisfy these requirements. Most zeolite membranes reported to date are composed of MFI-type zeolite layers. Zeolite A, faujasite and a few other types of zeolite membranes have also been studied. Zeolite membranes can be classified as either free-standing or supported membranes. Various kinds of support materials
including porous alumina, metallic plate or mesh and porous glass have been utilized for supported zeolitic membranes.

Several methods exist for preparation of zeolite films. One of the common methods is direct synthesis on substrates under hydrothermal conditions. Substrates are typically immersed in the reaction mixture, and in some cases, the reaction container itself can act as a substrate. Various zeolites have been grown on the surfaces of organic polymers [6-9], porous alumina, glasses [10-12], and metals [7,13] using direct film synthesis on substrates. The use of seeded substrates formed by depositing preformed crystals on substrates or laser ablation followed by further hydrothermal growth also allows for continuous film formation [14,15]. Nanocrystalline zeolites coated via a sol-gel method to make transparent films have been reported [16].

Zeolitic membranes have been studied for molecule-selective separations, catalytic reactions, zeolite electrodes and sensors. For some applications and mechanistic studies, free-standing zeolite films are of interest, and several examples have been reported [5]. ZSM films of thickness 20-250 µm have been grown on Teflon and silver surface, and can be readily removed from the substrate [6-8]. Synthesis of self-supporting films of zeolite NaA on polyethylene has also been reported [9].

As discussed before, zeolitic membranes will be used as hosts for photo electron transfer reactions in present study and gmelinite is one of the zeolites which satisfies size limitations and ion exchange capacity. The preparation of one-crystal thick, free-standing gmelinite film was reported by Anderson et al [8] with the (001) planes of the film oriented perpendicular to the substrate. Therefore we adopted the same strategy to
prepare free-standing gmelinite film. However, the resulting products were free-standing chabazite films or P-type zeolitic films. Due to the small pores of these zeolites, chabazite and P-type zeolite cannot be used for photochemical applications. We continued the investigation on these zeolitic films to study membrane formation mechanism and optimized condition of zeolitic membrane synthesis.

Chabazite is a small pore size zeolite (dehydrated chabazite has apertures of 0.38 x 0.38 nm), with Si/Al ratio around 2 [17]. The structure and channels of chabazite are described in Figure 2.1. As anticipated from its high Al content, chabazite is hydrophilic. The aluminosilicate framework of chabazite consists of D6R units (double hexagonal rings) arranged in layers in the sequence of ABCABC [18]. Cation exchange properties of chabazite have been extensively studied [19]. Its preferential ion-exchange towards cesium and strontium, isotopes of which are present in nuclear waste is of significant interest for nuclear remediation [20]. Chabazite has also been used as shape selective catalysts for methyl amine synthesis [21].

Despite numerous studies on chabazite, little is known about the films of chabazite except for examples of composite films with polymers or other zeolites. The preferential size-selective reactivity of ammonia (2.6Å) over tributyl amine (8.1Å) on acidic chabazite/silica films was reported by Bein et al [22]. Recently, Salomon et al. reported the synthesis of mordenite/ZSM-5/chabazite composite membrane on tubular α-alumina support [23]. Because of the high hydrophilicity, this composite membrane was used for the separation of water from ternary mixtures and showed a water/propanol selectivity as high as 149.
P-type zeolite, another small pore zeolite, has a gismondine-like framework with intersecting channels of 0.31 x 0.44 nm and 0.26 x 0.49 nm in (100) and (010) directions, respectively [18]. (Figure 2.2) Eight-membered oxygen rings define these channels. P-type zeolite membranes were hydrothermally synthesized on porous α-alumina supports and applications for separating small gas or liquid molecules were investigated [24,25]. However, formation of free-standing P-type zeolite film was not reported.

In this study, we present the hydrothermal synthesis of free-standing, small pore zeolite films such as chabazite and P-type zeolite grown on polypropylene surfaces. A novel hydrothermal treatment was developed to form the optimum zeolitic film. The morphology of resulting zeolite films were investigated using electron microscopy. The influence of the synthesis parameters on the film formation and the mechanism of the crystal growth are discussed. Since these films are not suitable for photo electron transfer experiments, zeolitic membranes for photochemical application will be discussed in chapter 3 along with photochemical experiments.

EXPERIMENTAL SECTION

**Synthesis of Dab-4Br polymer for structure directing agent** Dab-4Br, a polymer formed from 1,4-diazabicyclo (2.2.2) octane (Dabco, Aldrich) and 1,4-dibromobutane (Aldrich), was used as structure directing agents for the present work. Dab-4Br has previously been utilized for a structure-directing agent for a number of zeolites including chabazite, mordenite and gmelinite [8,26]. The polymers had a molecular weight estimated to be *ca.* 10,000 and were synthesized according to the
procedure outlined by Daniels et al.[26] For example, 1.84g of Dabco was dissolved in 20 ml of DMSO (dimethyl sulfoxide) at 45°C. To this stirred solution, 3.6g of 1,4-dibromobutane were added dropwise. The temperature was controlled to below 70 °C. After 1 hour the temperature was raised to 110 °C and maintained for 6h. Stirring was stopped and the mixture was left to cool overnight. The resulting solid was filtered and extensively washed with ether and methanol followed by drying in air.

Proton chemical shifts of the synthesized polymer were measured on a Bruker DRX 500MHz NMR spectrometer. In addition to Dabco protons at about 4.1 ppm, the protons on the α and β carbons linking these Dabco units were observed at 3.8 and 2.0 ppm, respectively. Acquired NMR spectrum with the polymer is shown in Figure 2.3. Dab-4Br polymer has the following structure.

![Structure of Dab-4Br polymer](attachment:image.png)

**Synthesis of Chabazite-type Films** The primary composition of the reaction mixture to prepare chabazite-type films was SiO$_2$:Al$_2$O$_3$=15, Na:SiO$_2$= 1.2, R: SiO$_2$=0.16, H$_2$O: SiO$_2$=26, where R represents the Dab-4 unit. Crystallization experiments with various amounts of Dab-4Br polymer as well as varying SiO$_2$/Al$_2$O$_3$ ratios have been performed to investigate the effects of these parameters on film formation. Gels were prepared by mixing colloidal silica (Ludox HS-40, Du Pont) with aqueous solutions of Dab-4 Br polymer in a 125 ml of polypropylene or Teflon bottle followed by the addition of NaOH.
(Mallinckrodt) and NaAlO$_2$ (Strem Chemicals) aqueous solutions. For example, 3.972g of Dab-4Br polymer was dissolved in 29.5g of distilled water in a reaction bottle. To this, 22.5g of Ludox HS-40 was added and mixed by shaking for 10 seconds. 1.881g of NaAlO$_2$ and 6.179g of NaOH was dissolved in 27.9g of distilled water and this solution was added to the silica mixture. The reaction mixture was shaken for 2 minutes and heated in an oil bath. The bottles were cleaned with 49 % hydrofluoric acid and rinsed with large amount of distilled water prior to use.

Three temperature profiles were followed for the crystallization, 90°C, 103°C and a ‘step heating’ procedure. The ‘step heating’ involved 40 hours of heating at 90 °C followed by 2 hours of heating at 103 °C (obtained via a heating rate of 1°C/10min). The oil bath was then cooled to 90°C and maintained for 1 hour. (Figure 2.4)

Zeolitic films and crystals were formed simultaneously on the wall and on the bottom of the bottle, respectively. Both were collected and washed with distilled water for analysis. The films were calcined at 500 °C for 18 hours to remove trapped structure-directing agent.

**Synthesis of P-type Zeolitic Films** The composition of the reaction mixture to prepare P-type zeolitic films was SiO$_2$:Al$_2$O$_3$=15, Na:SiO$_2$= 8.4, R: SiO$_2$=0.16, H$_2$O: SiO$_2$=217, where R represents the Dab-4 unit. It is a similar composition to the composition for the synthesis of chabazite-type films except the dilution and higher Na concentration. For example, 0.3972g of Dab-4Br polymer was dissolved in 29.5g of distilled water in a reaction bottle. To this, 2.25g of Ludox HS-40 was added and mixed by shaking for 10 seconds. 0.188g of NaAlO$_2$ and 4.95g of NaOH was dissolved in 27.9g of distilled water
and this solution was added to the silica mixture. The reaction mixture was shaken for 2 minutes and heated in an oil bath. Crystallization experiments without Dab-4Br polymer have been performed to investigate the role of the polymer structure directing agents on film formation. Also syntheses with different amount of NaOH was tried to study the effect of Na cation and basicity. Synthesis gel settled down on the bottom of a reaction bottle 15 minutes after thermal treatment began and upper solution was clear until the end of the reaction.

Thick zeolitic films were formed on the bottom of the bottle in this case. The films were collected and washed with distilled water.

**Analytical Procedures** X-ray diffraction (XRD) patterns for membranes and crystals were obtained using Rigaku-D-Max-2B X-ray diffractometer with nickel-filtered CuK$_\alpha$ ($\lambda = 1.5405$ Å) radiation. The morphology of the zeolite was characterized by scanning electron microscopic method (SEM), using a Jeol JSM-820 electron microscope. Prior to the examination, the samples were mounted with double-sided carbon paste tape on copper pegs and coated with a film of evaporated gold.

**RESULTS**

**Synthesis of Chabazite-type film** In order to investigate the effect of the synthesis temperature on the zeolite film formation, three different hydrothermal treatments were examined, constant heating at 90°C, constant heating at 103°C and a step heating.
procedure (described in experimental section and Figure 2.3). The film formation by each method is summarized in table 2.1.

<table>
<thead>
<tr>
<th></th>
<th>Crystal size</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low temp (90°C)</td>
<td>7-9 µm</td>
<td>90 hrs</td>
</tr>
<tr>
<td>Step heating</td>
<td>4-6 µm</td>
<td>44 hrs</td>
</tr>
<tr>
<td>High temp (103°C)</td>
<td>1-3 µm</td>
<td>30-40 hrs</td>
</tr>
</tbody>
</table>

Table 2.1 Effects of temperature on zeolitic film formation

In all cases, the initial reaction mixture was cloudy and thick, but became homogeneous after mixing and a solid started to settle down 1-2 hours after heating. In the case of constant heating at 90°C, a film became visible on the polypropylene wall surrounding the solution after about 45 hours and became continuous around the bottle after 90 hours. The XRD patterns of the film and crystals formed in the same reaction are presented in Figure 2.5 (a)-(c). Figure 2.5 (a) corresponds to the diffraction pattern of the film. Comparing with the data in the literature [26,27], the film is mainly chabazite with traces of gmelinite intergrowths (The three most characteristic lines (2θ values) of gmelinite are 21.7°, 27.7° and 7.4°). Figure 2.5 (b) corresponds to the XRD pattern of the powdered film and is identical to the intact film in Figure 2.5 (a). This indicates no preferred orientation of the crystals in the film. The XRD pattern of the powder recovered from the bottom of the reaction bottle is shown in Figure 2.5 (c). The peaks from chabazite are marked as C, and those from gmelinite are marked as G. The crystals on the bottom are mainly gmelinite, while the membrane is dominantly chabazite.
From the SEM of the film shown in Figure 2.6, it appears that the film consists of spherical agglomerates of almond-shaped crystals made up of a collection of smaller crystallites, often present as interpenetrating twins. Aggregates were also reported for Al-enriched chabazite [28]. Near-chabazite zeolite K-G [29], and the gmelinite films [8] have very similar morphology as in the present case. Yamazaki and Tsutsumi also reported the formation of cabbage-like crystals consisted of mixed crystals of gmelinite and chabazite [30]. They reported that the areas corresponding to the veins are made of chabazite and the whole globe is formed by gmelinite. In our experiments, the sizes of the spherical crystals were about 7-9 µm. Figure 2.7 is a side view of the film and shows that it consists of a dense layer followed by several layers of loosely packed particles. Dense layer was facing polypropylene wall during the synthesis while loose layer was facing solution. Figure 2.8 shows the morphology of zeolite powder formed at the same time. The shape of crystallites is clearly different from that of film. The agglomerates were planar while the aggregates for chabazite film were spherical. The sizes of agglomerates were 0.3-0.4 µm, which were much smaller than the size for film crystals.

Upon synthesis at 103°C, the film formation is complete after 30-40 hours of heating and is not thick enough to be detached from the wall of the bottle. For SEM analysis, the bottle with the film was cut and the surface of the film was coated with gold. As shown in Figure 2.9(b) the size of spherical crystals in the film is 1-2 µm, less than the 7-9 µm size observed at 90°C. The XRD pattern of the film was that of chabazite (similar to Figure 2.5a) while the powder obtained at 103°C indicate the formation of
mainly gmelinite. (Figure 2.10) Comparing with Figure 2.5(c) the portion of gmelinite increased.

The step heating method involved heating at 90 °C for 40 hours, followed by a temperature increase to 103 °C with a heating rate of 1°C/ 10 min and maintained for 2 hours. Upon temperature increase, a portion of the deposits floated up and the solution became cloudy. Rapid film formation on the wall could be visually observed during the 2-hour heating period. The oil bath was cooled to 90°C, and maintained for 1 hour. A continuous film covering the walls of the reaction bottle was formed. Pieces of film could be readily removed and an optical micrograph of such a piece is shown in Figure 2.11. If the heating was continued at 90°C, the films fell apart after total heating period of 90-100 hours.

The XRD patterns of films formed by step heating procedure are shown in figure 2.12. The XRD pattern of the film is identical to those shown in Figure 2.5(a), indicating that chabazite-type film is produced. The ground-up powder of the film resulted in the same pattern as the intact membrane, which implies that the crystals in the film have random orientation. It was also observed from the XRD that the deposits at the bottom of the reaction vessel included substantial amounts of amorphous material after 45 hours of heating even though the membrane is completely crystalline. Figure 2.12(c) shows significant background originated by amorphous materials. The crystalline peaks are mixture of chabazite and gmelinite. In case the heating was continued at 90°C, the film fell apart, but the deposits became more crystalline and were dominantly gmelinite.
The step heating treatment produced continuous, uniform and one to two crystal thick (about 10\(\mu\)m) zeolitic films. The SEM images of the top and side views of the resulting film are shown in Figure 2.13. The size of the spherical crystals in the film is about 4-6 \(\mu\)m in this case. Because the film is thin and crystalline, it is fragile when dried, but malleable when it is wet. The films can be stored for a long period of time (more than 2 months). The structure-directing agent can be removed by calcination at 500°C for 18 hours. By inspecting the SEM image, we observed no cracks generated by the calcination process.

To study the possibility of generating supported film in this system, a Teflon or polypropylene slab (20mm x 80mm x 2mm) was inserted in the synthesis solution before the hydrothermal treatment. The slab was inserted vertically in the center of the reaction bottle. Continuous film formation was not observed either on the inserted slabs or on the walls of reaction bottle. 

In order to evaluate the range of compositions from which the chabazite-type films could be formed, a series of experiments with varying \(\text{SiO}_2/\text{Al}_2\text{O}_3\) ratios (5-15) at a fixed Dab4-Br concentration as well as varying the Dab4-Br/\(\text{SiO}_2\) ratio (0-0.24) at fixed \(\text{SiO}_2/\text{Al}_2\text{O}_3\) were done. Table 2.2 shows the results of these experiments. At a fixed concentration of Dab4-Br, good quality chabazite-type films were only formed with \(\text{SiO}_2/\text{Al}_2\text{O}_3\) ratio of 15. At this \(\text{SiO}_2/\text{Al}_2\text{O}_3\) ratio, good quality chabazite-type films were obtained as long as the Dab4-Br/\(\text{SiO}_2\) was kept within the range of 0.08-0.16. No differences in the detachable films are observed via powder diffraction. At the lower Dab4-Br/\(\text{SiO}_2\) ratio, the zeolite powders formed were zeolites Y and P along with gmelinite and chabazite,
<table>
<thead>
<tr>
<th>Run</th>
<th>Composition</th>
<th>Film quality</th>
<th>Film composition</th>
<th>Crystals on the bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 a</td>
<td>SiO(_2)/Al(_2)O(_3)=5</td>
<td>No membrane</td>
<td></td>
<td>Zeolite Y</td>
</tr>
<tr>
<td>2</td>
<td>SiO(_2)/Al(_2)O(_3)=7</td>
<td>No membrane</td>
<td></td>
<td>Zeolite Y</td>
</tr>
<tr>
<td></td>
<td>.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>SiO(_2)/Al(_2)O(_3)=1</td>
<td>No membrane</td>
<td></td>
<td>Zeolite Y + chabazite</td>
</tr>
<tr>
<td>4</td>
<td>SiO(_2)/Al(_2)O(_3)=1</td>
<td>Good yield,</td>
<td>Chabazite -type</td>
<td>Gmelinite + chabazite</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>detachable</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 b</td>
<td>R/SiO(_2)=0.00</td>
<td>No membrane</td>
<td></td>
<td>Zeolite Y</td>
</tr>
<tr>
<td>6</td>
<td>R/SiO(_2)=0.08</td>
<td>Good yield,</td>
<td>Chabazite -type</td>
<td>Zeolite Y,P+</td>
</tr>
<tr>
<td></td>
<td></td>
<td>detachable</td>
<td></td>
<td>Gmelinite + chabazite</td>
</tr>
<tr>
<td>7</td>
<td>R/SiO(_2)=0.10</td>
<td>Good yield,</td>
<td>Chabazite -type</td>
<td>Zeolite Y,P+</td>
</tr>
<tr>
<td></td>
<td></td>
<td>detachable</td>
<td></td>
<td>Gmelinite + chabazite</td>
</tr>
<tr>
<td>8</td>
<td>R/SiO(_2)=0.12</td>
<td>Good yield,</td>
<td>Chabazite -type</td>
<td>Zeolite Y,P+</td>
</tr>
<tr>
<td></td>
<td></td>
<td>detachable</td>
<td></td>
<td>Gmelinite + chabazite</td>
</tr>
<tr>
<td>9</td>
<td>R/SiO(_2)=0.16</td>
<td>Good yield,</td>
<td>Chabazite -type</td>
<td>Gmelinite + chabazite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>detachable</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>R/SiO(_2)=0.18</td>
<td>Small yield,</td>
<td>Chabazite -type</td>
<td>Gmelinite + chabazite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>detachable</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>R/SiO(_2)=0.20</td>
<td>Small yield,</td>
<td>Chabazite -type</td>
<td>Gmelinite + chabazite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>detachable</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 c</td>
<td>R/SiO(_2)=0.16</td>
<td>Small yield,</td>
<td>Amorphous</td>
<td>Gmelinite+chabazite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>detachable</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>R/SiO(_2)=0.24</td>
<td>Small yield,</td>
<td>Amorphous</td>
<td>Gmelinite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>detachable</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Runs 1-4 were done at a fixed concentration of Dab-4Br(R)/H\(_2\)O of 0.006  
\(^b\) Runs 5-11 were done at a fixed SiO\(_2\)/Al\(_2\)O\(_3\) of 15  
\(^c\) Runs 12-13 were done at a fixed SiO\(_2\)/Al\(_2\)O\(_3\) of 30  

**Table 2.2** Composition examined for forming chabazite-type film

38
whereas at the high Dab4-Br/SiO2 of 0.16, the powder was mainly gmelinite, along with chabazite as the secondary phase.

**Synthesis of P-type Zeolitic films**

To extend our knowledge to other kinds of small pore zeolitic films, P-type zeolitic films were prepared by hydrothermal treatment. Synthesis gel settled down on the bottom of a reaction bottle 15 minutes after thermal treatment began. Upper solution was clear until the end of the reaction in this case. After 48 hours of heating at 90°C, crystallization is complete and thick zeolite layer was formed on the bottom of the reaction bottle. The results due to various composition of synthesis solution are summarized in Table.2.3.

<table>
<thead>
<tr>
<th>Run</th>
<th>Composition</th>
<th>Film quality</th>
<th>Composition of zeolite crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 a</td>
<td>Na:SiO2 = 8.4</td>
<td>Good film</td>
<td>Zeolite P</td>
</tr>
<tr>
<td>2</td>
<td>Na:SiO2 = 10.4</td>
<td>Good film</td>
<td>Zeolite P + Sodalite</td>
</tr>
<tr>
<td>3 b</td>
<td>R:SiO2 = 0.16</td>
<td>Good film</td>
<td>Zeolite P</td>
</tr>
<tr>
<td>4</td>
<td>R:SiO2 = 0</td>
<td>No film</td>
<td>Sodalite</td>
</tr>
</tbody>
</table>

a Runs 1,2 were done at a fixed concentration of Dab-4Br(R)/SiO2 of 0.16  
b Runs 3,4 were done at a fixed Na/SiO2 of 8.4

**Table 2.3** Composition examined for forming P-type zeolitic film

The diffraction pattern of the thick film formed by run1 is shown in Fig.2.17(a). Comparing with the data in the literature [31], the film is composed of zeolite P. The five most characteristic lines (2θ values) of zeolite P are 12.4°, 17.7°, 21.6°, 28.1° and 33.38°.
From the SEM of the film shown in Fig. 2.18, it appears that the thickness of the film is about 100-200 μm. The size of film was as big as the size of reaction bottle, which is 4 cm diameter round plate. The film consists of a dense layer at the bottom of the reaction bottle and a loosely packed layer, which faces solution during the synthesis. This is similar to the shape of the chabazite film in Figure 2.7. Figure 2.19 shows the morphology of crystals in dense layer. The dense layer at the bottom is composed of planer crystallites with a grain size of about 0.2-0.3 μm. Some agglomerates of 1 μm zeolite P crystals also exist on the surface of dense layer. The morphology of these agglomerates are similar to highly crystalline low silica NaP [32]. The dense layer on top of the film has an interesting morphology as shown in Figure 2.20. It appeared to be composed of spherical agglomerates of small crystallites as chabazite film. The size of agglomerates is 5-7 μm. Also the loosely packed layer seems to have somewhat regular pores of 10-20 μm size and macroporous structure. The macroporous structure did not rupture even after calcination procedure at 500°C.

In order to study the role of Dab4-Br polymer in this system, same synthesis without the polymer was tried (Run 4). Film formation was not observed. The product was zeolitic powder scattered on the bottom of the reaction bottle. The XRD pattern of the product was mainly sodalite in this case (Fig.2.17(b)). This observation suggests that Dab-4Br has structure directing effect for the zeolite framework as well as affects film formation properties.

The effect of Na cation on the formation of zeolitic membrane was also investigated by changing the amount of NaOH in synthesis solution. When Na: SiO₂
ration is increased to 10.4, zeolitic film was still formed. However, significant amount of sodalite was observed in zeolitic film. Figure 2.17(c) shows the XRD pattern of Zeolite P-sodalite film generated by higher Na content in the synthesis solution. The peaks from sodalite are marked as S and those from P-type zeolite are marked as P.

DISCUSSION

Synthesis of Chabazite-type Films

There are three issues that form the basis of the discussion section. First, our results appear to be different from an earlier report [8] for a similar reaction system. Second, the role of the step heating in producing the optimum uniform thickness film provides clues to the film formation process. Third, the difference between the frameworks formed on the walls (primarily chabazite) with that formed on the bottom (primarily gmelinite) of the reaction vessel is discussed.

Comparison with Previous Study: [8]

Anderson et al. reported the formation of an aligned gmelinite film from a reaction gel of similar composition as in this study and hydrothermal treatment at 90-95°C for 90 hours [8]. They used Teflon bottles and polysulfonated styrene discs as substrates. We repeated our experiments with Teflon bottles and the resulting films show the same XRD pattern and SEM image as those of films grown on polypropylene surface. Therefore, the difference between substrates is not responsible for chabazite versus gmelinite film formation. Anderson et al. reported that the XRD peaks corresponding to (h0l) and (0kl) are absent or considerably reduced in intensity for the synthesized films
and suggested that this was indicative of the (001) planes of gmelinite crystals being preferentially oriented perpendicular to the film plane. In our experiments, the XRD pattern of gmelinite peaks appeared to be changed in intensity by the overlap with chabazite peaks. However, comparison of the XRD patterns of the ground film and the film clearly shows that the crystallites are randomly oriented. It is unclear why our results do not agree with that of Anderson et al.

**Film formation:**

A model for the growth of zeolitic membranes from synthesis mixture has been proposed and the crystallization mechanism has been discussed. Koegler et al. proposed a thin-film growth model for zeolite Si-ZSM-5 [33]. In this mechanism, a precursor gel layer is formed on the surface of the support. Nucleation will occur at the interface of the gel and synthesis solution. The crystals will grow and consume the gel. Nakazawa et al. also reported formation of a gel layer in the early stages of MFI film synthesis [12]. They assumed that the gel layer was caused by hydrolysis and polymerization of silica source and tetrapropyl ammonium structure directing agent. Two crystallization routes were suggested. In one route, spherical composites are formed, enlarged, and aggregated, followed by crystallization. In the other route, the crystallization starts within the gel layer, and the crystals grow out of the gel layer. Mintova et al. also observed a gel-like layer on a quartz plate during the ZSM-5 film synthesis [11].

In our experiments, zeolitic film formation was investigated by SEM and the data contrasting the 90 °C heating with the step heating procedure is shown in Figure 2.14. The SEM micrographs are those of the material on the polypropylene wall (cut out from
different reaction vessels) after the specified heating period. For the sample heated for 20 hours (Fig.2.14a), the polypropylene substrate appeared coated with an amorphous gel layer, with small particles embedded in them. Koegler et al. and Nakazawa et al. reported similar observation about a precursor gel layer [12,33]. After the reaction mixture had been heated for 40 hours (Fig. 2.14b), spherical particles 1-2 µm in diameter are observed in the layer on the substrate. These particles still appeared to be embedded in gel layer. This layer on the polypropylene support was investigated by XRD and no peaks were observed, indicating that the particles were amorphous at this stage. After 45 hours of heating at 90 °C, spherical crystals 4-5 µm in diameter were formed (Fig. 2.14c). These particles were crystalline and bigger than the particles in Fig.2.14b. The crystalline spheres consist of small, almond-shape crystals. These particles eventually grow to form a continuous layer after 90 hours of heating at 90°C. If the synthesis is carried out at 103 °C, the process of film formation is speeded up, but smaller crystals are produced, and the film is not stable enough mechanically.

The step heating method provides an optimum procedure, with the first 40 hours at 90°C producing nuclei in the gel. The rapid temperature rise to 103 °C after 40 hours results in thermal convective forces that release nuclei and nutrients from the gel into solution, which diffuse and grow at a rapid rate on the walls of the reaction container. This process can actually be observed visually, the solution gets cloudy and the film begins to form, and is evident from figure 2.12d. As pointed out by Myatt et al. in their study on zeolite NaA membrane [9], nuclei/colloidal aluminosilicate particles diffuse to the substrate and initiate growth of the film. By comparing figure 7 and 13(b), the film
formed by step heating has more dense and uniform layer. It can be explained by the fact that film is formed by rapid process in step heating and heating is stopped right after the formation of continuous film. Therefore, the crystals formed in the solution could not adhere to the film. This also implies that the loose layer in the film formed by 90°C heating is by the deposition of crystals from the solution. When Teflon or polypropylene slabs were vertically placed in the center of reaction bottle, film formation was not observed either on the inserted slabs or walls of reaction bottle. The inserted slabs seem to affect convective force in the synthesis solution during reaction. Therefore, the flow of nutrients and nuclei could not reach to the walls or plates effectively to form continuous films.

If the step heating procedure is continued, the film becomes thicker and it falls off from the wall. A decrease in film thickness caused by the extended period synthesis time was also observed by Mintova et al [11]. The arrival of nuclei at different times on the wall is consistent with the fact that there is no orientational relationship between the crystallites.

The number of nuclei and growth rate can explain the formation of different sizes of crystals and the change of reaction time from the different heating procedures. With constant heating at 90°C, the rate of nucleation in the precursor gel is slow. Relatively small number of nuclei exists when the crystal growth begins. The distance between nuclei in low temperature heating is longer than other cases. These nuclei will grow and bond to neighboring particles to form continuous layer. Therefore it takes longer and crystal size is bigger. In case of step heating, the reaction mixture has larger number of
nuclei due to the burst of nuclei and nutrients by rapid temperature increase. Since the particles are closer to each other, it can grow to form continuous layer quickly. High temperature heating for 2 hours also accelerates the growth rate. It resulted in more, but smaller crystals in the film. When the oil bath is cooled to 90°C and maintained for 1 hour, the small crystals or nuclei on the wall of the bottle grow more and resulted in continuous film. In the case of constant heating at 103 °C, there is large number of nuclei, which produced smallest crystals among three cases. This also explains the fact that the film with heating at 103°C was too thin to be removed from the bottle and broken during the process. Figure 2.16 describes the mechanism of membrane formation at various temperatures.

Film versus powder composition:

From Table 2.2, it is clear that the presence of Dab4-Br is required to form the chabazite-type film. In its absence, not only the film is not formed, but also no gmelinite or chabazite powder is formed. Also, the composition of the film as measured by powder diffraction appears to be quite invariant even though the types of zeolite formed as powder at the bottom of the bottle varies. Dab4-Br is a structure directing agent for gmelinite 26 and in most cases, gmelinite is the primary powder product. The DABCO unit of the polymer is cylindrical with a diameter of ca 6.1 Å and would thus fit into 7-8 diameter channels of the zeolite. Davis et al. provided direct evidence that the polymer is retained in the pore system of gmelinite and ZSM-12 using magic-angle 13C NMR spectra [34]. Gmelinite is a member of the chabazite zeolite group. It consists of the same secondary building units as that of chabazite, but the framework is slightly different. In
gmelinite, the D6R units are stacked in the sequence of ABAB instead of ABCABC [27]. The structure and stacking of chabazite and gmelinite are described in figure 2.15. Chabazite-gmelinite intergrowths have been reported by several researchers [26,27,29,35] indicating that these two frameworks may share similarly structured nuclei. Moreover, Rollman et al. [26] observed that with increase in Si/Al ratio of the composition, chabazite is the preferred product. For the compositions under which the chabazite-type membrane is formed (Table 2.2), the solutions are always more siliceous than gels and could explain why chabazite is the primary constituent of the film. Films are formed in the clear synthesis solution and powder is formed in the gel settled in the bottom of the reaction bottle. The formation of the film is closely connected with the presence of the Dab4-Br. An amorphous film is observed at the early stages of film growth (Figure 12a). Anderson et al. [8] have proposed that Dab-4 attaches to the walls of the bottle via electrostatic interactions and would be consistent with the present observations. However, with increasing concentrations of Dab4-Br, the yield of the film decreases. This could result form the film becoming too thick and therefore the crystals formed may collapse into solution. Thus, an optimum amount of Dab4-Br is required for adequate film formation.

**Synthesis of P-type Zeolitic films**

P-type zeolite is another kind of small pore zeolite. P-type zeolite film was formed at the bottom of reaction bottle with diluted synthesis solution in this study. Solution side of the film has interesting macroporous structure with pores of 10-20 µm. This seems to be the effect of Dab4-Br polymer. Since Dab-4Br polymer is cationic, there
might be electrostatic force between the polymer and anionic zeolite framework. If zeolite crystals aggregate around the long polymer chain, it might result in unusual microscopic structures. Dab4-Br appeared to “Glue” individual crystals to form film and macroporous structure. When Dab4-Br was not added to the synthesis solution, the product was powdery sodalite. Since both sodalite and P-type zeolite are small pore zeolites, structure directing mechanism of the polymer will be different from the case of gmelinite or ZSM 12. The polymer cannot be retained in the pores of sodalite or P-type zeolite. However, it is evident from this result that Dab4-Br affects zeolite framework structure as well as film formation. Even when organic polymer was removed by calcinations process, the film morphology was not affected by the SEM observation. This implies that small units of zeolite crystals aggregate around the cationic polymer to build the film structure and form chemical bonds between crystals.

Concentration of Na cation also affects product composition. Comparing with the composition of synthesis solution for chabazite film, this synthesis solution has 7 times higher ratio of Na:SiO₂. According to the studies by Clet et al. P-type zeolite and sodalite was main product with higher Na:SiO₂ ratio in the solution while zeoliteY and gmelinite was main product when the ratio of Na:SiO₂ was less than 1.2 [13]. This is comparable with our result. With the solution of Na:SiO₂ = 1.2, the main product was chabazite and gmelinite as discussed previously. When this ratio was increased to 8.4, P-type zeolite was formed. Much higher concentration of NaOH in synthesis solution (Na:SiO₂ = 10.5) resulted in formation of sodalite. Product was still film type zeolite with macroporous structure in the solution side when Dab4-Br was added in the synthesis
solution. The addition of Dab4-Br solution generally leads to film type of zeolite product with various zeolite framework structures. This polymer structure-directing agent can be utilized to other zeolite synthesis system to lead film formation.

CONCLUSION

Free-standing chabazite-type films were synthesized on the walls of polypropylene bottles. The sizes of crystals and reaction time vary according to the reaction temperatures. By following a step heating method, which results in a burst of nuclei and nutrients into solution during the synthesis, uniformly thick self-standing films of chabazite could be produced. Zeolite crystals formed at the bottom of reaction bottle were mainly gmelinite. Different composition of zeolite formation can be explained by the difference of environment where the crystals grow. The mechanism of zeolitic film formation was also investigated and crystal growth in precursor gel layer was observed. Thick film of P-type zeolite can also be formed by hydrothermal treatment in the presence of Dab4-Br polymer. The amount of Na cation in the synthesis solution affects the composition of product. Without Dab-4Br polymer, film formation was not observed. These films of small pore zeolite can be used for separation or sensor for small size molecules.

Although chabazite and P-type zeolite show interesting properties and can be used for separation or sensing applications, these zeolites are not suitable to be used as heterogeneous supports in artificial photosynthetic systems due to the size limitation of zeolitic pores. Therefore, preparation of large pore zeolitic membrane will be discussed in chapter 3 along with photochemical experiments.
REFERENCES


Figure 2.1 Structure of chabazite
Figure 2.2 Structure of P-type zeolite
Figure 2.3 NMR spectrum of Dab-4Br polymer
Figure 2.4 Temperature profile of heating procedure for the synthesis of chabazite film
(a) 90°C heating (b) 103°C heating (c) step heating
Figure 2.5  XRD patterns of products formed from 90°C synthesis:
(a) films from walls of bottle; (b) films ground to powder;
(c) powder recovered from bottom of the reaction bottle
Figure 2.6 Morphology of crystals in chabazite films
Figure 2.7 Side view of a chabazite film formed at 90°C
Figure 2.8 SEM picture of powder on the bottom of reaction bottle formed by 90°C heating
Figure 2.9 SEM pictures of films formed upon (a) 90°C; (b) 103°C, and (c) step-heating procedures
Figure 2.10 XRD pattern of powder recovered from bottom of the reaction bottle in 103 °C synthesis
Figure 2.11 Optical micrograph of a piece of film recovered from the step-heating procedure
Figure 2.12  XRD patterns of products formed from step heating
(a) films from walls of bottle; (b) films ground to powder;
(c) powder recovered from bottom of the reaction bottle
Figure 2.13 (a) Top and (b) side views of chabazite films formed from step heating procedure
Figure 2.14 SEM pictures during synthesis. Results of heating at 90°C for (a) 20 hours; (b) 40 hours; (c) 45 hours; and (d) 90 hours. (e) Step-heating to 103°C beginning at 40 hours and completion at 45 hours.
Figure 2.15 Structural arrangements of (a) chabazite and (b) gmelinite
Figure 2.16 Zeolite film growth during synthesis
Figure 2.17 XRD pattern of (a) P-type zeolitic film (b) Sodalite powder formed by the synthesis without Dab4-Br (C) zeolite P-sodalite mixture film
Figure 2.18. Side view of a P-type thick zeolitic film
Figure 2.19 Top views of dense side of the P-type zeolitic films
Figure 2.20 Top views of loose side of the P-type zeolitic films
CHAPTER 3

Charge Transport through a Novel Zeolite Y Membrane

by a Self Exchange Process

INTRODUCTION

Membranes can keep apart two chemical systems that interfere with each other, yet, allowing for transport of specific species through the membrane. Probably, the most celebrated example of membranes are in biological systems, as in a living cell, where the membrane makes it possible for the cell to survive, by allowing proper nutrients to pass through the membrane [1]. Membranes also find extensive use in technological applications via selective passage of certain molecules, while excluding others [2]. Our interests have been in development of artificial photosynthetic systems, where light activated charge separation can lead to interesting chemistry, including possibly the splitting of water to hydrogen and oxygen [3]. It is well recognized that in order to do so, the photo generated hole and electron need to be spatially separated, and we are examining zeolite membranes towards this end [4].
Zeolitic membranes are an active area of research because of their molecular sieving ability [5]. The potential industrial applications of zeolitic membranes include separations, catalytic reactions, zeolite electrodes, sensors and in ion exchange processes [6]. Several methods exist for the preparation of zeolitic membranes including the direct formation on a substrate using hydrothermal synthesis [7,8] and secondary growth of preformed crystals [9,10]. As described in chapter 2, it is most common to use direct hydrothermal treatment to prepare zeolitic membranes on substrates. However, there were several disadvantages to this approach. Free-standing zeolitic films needed to be peeled off after hydrothermal treatment for any applications unless porous substrates are used. Another problem of this method is the mechanical stability of membranes and formation of non-zeolitic pinholes. Free-standing zeolitic membranes are usually not resistant enough for chemical operations and non-zeolitic pinholes generate pathways that decrease molecular sieving ability of zeolites. In cases where different compositions are to be maintained on two sides of a membrane, pinholes that produce non-shape selective inter-crystal pathways for molecules to traverse the membrane need to be eliminated. It is a challenging task to make thin, mechanically stable and defect-free membrane with access to the pores of the zeolite. Secondary growth [11], use of binders [10,12], polymer blending [13], chemical vapor deposition (CVD)[14] and post-synthetic coking method [15] are reported to block pinholes as well as improve mechanical stability. The secondary growth of preformed crystals seems to be the most frequently used technique for zeolite membrane growth. This method typically involves deposition of a colloidal zeolite suspension of seed crystals on a support followed by hydrothermal treatment that
promote growth of seed crystals. However, secondary growth typically requires careful adjustment of synthesis conditions for each synthesis system. Also, since it requires one or more cycles of hydrothermal treatment, secondary growth needs almost the same period of time and new synthesis solution for each cycle of growth. It has been pointed out that methods such as polymer blending and using a binder to eliminate pinholes introduce the drawback of blocking zeolite surface and pores [16].

Most previous applications of zeolite membranes have focused on separations of gases [5,11]. Our interest is to keep species separated in an aqueous medium with ultrathin (<1 µm) membranes. In this chapter, we report the preparation of membranes using nanocrystalline zeolite Y. The syntheses of other zeolite nanocrystals and use of various support materials will also be summarized. A photoresist treatment that reduces pinholes, but still allows access to the intrazeolitic volume is described. The mechanical stability is improved upon photoresist coating. Leaks through the membrane and its ion exchange properties provided information on the nature of defects and the accessibility to zeolite pores after photoresist coating. The charge propagation by electron hopping through the membrane is demonstrated using the well-studied photochemical Ru(bpy)₃²⁺-bipyridinium ion system [3].

EXPERIMENTAL SECTION

Synthesis of nanocrystalline zeolite Y Nanocrystalline zeolite Y was synthesized from clear solutions of tetramethylammonium (TMA)-aluminate according to the patent literature [17]. TMA-aluminate solution was prepared by dissolving 13.33 g of
Al$_2$(SO$_4$)$_3$·18 H$_2$O in 70ml distilled water followed by the addition of 25 wt% NH$_3$ solution in water to precipitate Al(OH)$_3$. The gel thus obtained was centrifuged and washed repeatedly to remove sulphate ions. 36.46g of 25 wt % TMAOH solution and distilled water was added to the Al(OH)$_3$ cake to obtain a clear solution. To this solution, 0.072g of NaOH in 10ml water was added with mixing followed by the addition of 14.17g of tetraethylorthosilicate (TEOS). A clear synthesis solution has the following molar composition; SiO$_2$:Al$_2$O$_3$=3.4, Na$_2$O:Al$_2$O$_3$=0.045, (TMA)$_2$O:Al$_2$O$_3$=2.5, H$_2$O:Al$_2$O$_3$=370. The synthesis mixture was placed in a Teflon bottle and heated at 100 °C in an oven until white crystals were observed at the bottom of the bottle. After the hydrothermal reaction, the solid was separated by centrifugation, washed several times and ion-exchanged with 1M NaCl solutions. The zeolite was air-dried and calcined at 500°C overnight under a flow of oxygen.

Similar synthesis with different silica source, Ludox, was also tried following patent procedure [17]. Ludox SM silica sol (30% SiO$_2$, Dupont) was de-ionized to a pH of 8.1 with a strong cationic ion-exchange resin in the H$^+$ form (Dowex HCRS-E). The resin was subsequently separated from the silica sol after de-ionization. 13.33 g of Al$_2$(SO$_4$)$_3$·18 H$_2$O was dissolved in 70ml distilled water followed by the addition of 25 wt% NH$_3$ solution. The Al(OH)$_3$ gel thus obtained was centrifuged and washed repeatedly to remove sulphate ions. 36.46g of 25 wt % TMAOH solution and distilled water was added to the Al(OH)$_3$ cake to obtain a clear solution. To this solution, 13.6 g of the partially de-ionized Ludox SM silica sol was added. A clear synthesis solution has the following molar composition; SiO$_2$:Al$_2$O$_3$=3.4, Na$_2$O:Al$_2$O$_3$=0.04, (TMA)$_2$O:Al$_2$O$_3$=2.5,
H$_2$O:Al$_2$O$_3$=370. Synthesis solution was heated and purified as described previously for TEOS synthesis.

**Zeolitic Film Casting** 33mg of calcined, Na$^+$ ion-exchanged zeolite crystals were dispersed in 10ml of distilled water. Dilute zeolite suspensions were used to form thinner zeolite layer. The zeolite suspension was sonicated in a chilled water bath for three hours to break up agglomeration. A 21mm diameter aluminium oxide filter membrane (Anodisc™, Whatman) was used as a substrate. The average thickness of the support was 60µm with pore size of 0.2µm. Zeolite membrane was formed on the surface of alumina support by dropping 0.125ml of nanocrystalline zeolite suspension and air-drying in a covered petridish. A spin coating procedure (1000 rpm, 15 seconds) also worked well. To get a good coverage of zeolite crystals on a substrate, the spin coating procedure needed to be repeated at least three times. Bipyridinium- zeolite membranes were prepared by starting with bipyridinium ion-exchanged zeolite Y nanocrystals. Nanocrystalline zeolite Y was suspended in 0.1M bipyridinium solution and stirred overnight. For complete ion exchange, this procedure was repeated two times.

Acrylic copolymer filtration membrane (Versapore, Gelman Laboratory) was tested for substrate for zeolitic film casting. Versapore has typical thickness of 190 µm and pore size of 3 µm. Indium Tin Oxide (ITO) coated glass slab (Delta Technologies, 7mm x 50mm x 0.7mm) was also used for film casting.

**Photoresist-Coating of the Membrane** A positive photoresist (AZ 7920, Clariant) was coated on the zeolite film by a spin coating method (2000rpm, 30seconds). After solvent evaporation at room temperature, the sample was baked at 80°C for 10 minutes and then
exposed to ultraviolet light (Mercury I-line lamp, 335nm) either from the photoresist side or substrate side for a time period. The developed portion of the photoresist was removed by treatment with the developing solution (AZ 300 MIF developer, Clariant). The time of exposure to the development solution was done in 20 second increments, followed by water rinsing. Completion of the development process was indicated when the color of the rinsed solution was no longer red. The hard baking procedure involved heat treatment of the membrane at 110°C for 10 minutes after the development process.

**Characterization** X-ray powder diffraction (XRD) patterns were recorded with a Rigaku Geigerflex diffractometer using Ni-filtered Cu Kα radiation (40 kV and 25 mA). Particle and film morphology were obtained using a JEOL 820 scanning electron microscope

**Leak Test of the Photoresist-Coated Membrane** The borosilicate glass cell used for these experiments consisted of two halves that were separated by a plastic plate. The zeolitic membrane was attached to the plastic plate by epoxy resin and the plate and the cell parts were secured by two O-rings and a metal clamp. Figure 3.1(a) shows a schematic of the cell. The leaking property of the photoresist-coated membranes was tested using $6.25\times10^{-6}$ M aqueous solution of rhodamine 123 (Molecular Probe). Fluorescence emission of various concentrations of rhodamine 123 solutions was measured prior to leak experiments. To measure the leak through the membrane, rhodamine solution was placed on the zeolite side, while the substrate side was filled with distilled water. The solution in the substrate side was sampled every 30 minutes by removing aliquots and emission spectra were measured at 515 nm using a Spex Fluorolog fluorometer at an excitation wavelength of 480nm. Sampled solutions were returned to
the cell after measurements. Zeolitic membranes without photoresist coating were used to
determine the efficiency of pinhole plugging by the photoresist.

**Ion Exchange Capacity of the Photoresist-Coated Membrane**  
The ion exchange property of the zeolitic membrane was studied by measuring the amount of
methylviologen (1,1’-dimethyl-4,4’-bipyridinium, MV$^{2+}$) that was released into solution
upon exposure to 0.05M NaCl solution. MV$^{2+}$-exchanged zeolitic film was inserted in the
cell and 0.05M NaCl solution was placed in the zeolite side of the cell to ion exchange
the intrazeolitic MV$^{2+}$. The NaCl solution was sampled every 10 or 20 minutes by UV-
visible spectroscopy.

The other series of ion-exchanging experiments were carried out to check if the
zeolitic pores are accessible from substrate side of membrane. MV$^{2+}$-Y membrane was
inserted in the cell and 0.05M NaCl solution was added to the substrate side of the cell.
The NaCl solution was monitored as a function of time. The same experiment was
repeated with a zeolitic membrane without photoresist coating for comparison.

Ion exchange across photoresist coated zeolitic membranes was tested with
distilled water, NaCl, Tetramethyl ammonium bromide (TMABr) and Tetrapropyl
ammonium bromide (TPABr) solutions. Na$^+$-Y membrane was inserted in the cell and
10ml of 0.005 M MVCl$_2$ solution was added to the zeolite side of the cell. 10 ml of
distilled water was placed in the substrate side of the cell. Distilled water was sampled
every 30 minutes for UV-Vis absorption measurement. To compare ion exchange rate,
ionic solutions such as NaCl, TMABr and TPABr were placed in the substrate side of the
cell for the measurement.
**Chemicals** (2,2′-bipyridyl) ruthenium(II) chloride hexahydrate (Ru(bpy)$_3^{2+}$, Strem Chemicals), Na$_2$EDTA (GFS Chemicals) and methyl viologen dichloride hydrate (MV$^{2+}$, Aldrich) was purchased with the highest purity available and used as received.

**Viologens**

*N,N’-tetramethyl-2,2’-bipyridinium dibromide (4DQ$^{2+}$)* 4DQ$^{2+}$ was prepared as described by Homer and Tomilson [18]. 2.5g of 2,2’-Bipyridyl and 20ml of 1,4-dibromobutane were heated at 140°C for 6 hours. The solid was filtered, washed with acetone and treated with carbon in methanol. After drying, the solid was reddish. Small amount of hot methanol was added to dissolve red impurities and filtered. 4DQ$^{2+}$ is formed as acidic form, which needs to be neutralized. The white crystals were dissolved in minimum amount of water and neutralized with NaOH until the pH is 7. The precipitated with acetone and yielded white crystals. The NMR spectrum of 4DQ$^{2+}$ is shown in Figure 3.2.

**Propyl Viologen Sulfonate (PVS)** PVS was also prepared following literature procedures with modifications [19]. The reaction consists of the nucleophilic substitution of two equivalents of 1,3-propane sultone by a tertiary amine. 4,4′-bipyridine (1g, 6.4 mmols) was added to 30 ml of CH$_3$CN and refluxed with 1,3-propanesultone (1.95g, 16mmols) for 3 hours. Recovered product was mono substituted
bipyridine (a). The NMR spectrum of mono substituted compound is shown in Figure 3.3. Further substitution was stopped due to the low solubility of polar mono substituted product in organic solvent. To continue substitution reaction, mono substituted product (a) was added to 30 ml of CH$_3$CN and refluxed with 1,3-propanesultone (1.95g, 16mmols) again. 0.2 ml of distilled water was added to increase the solubility of mono-substitute compound. The mixture was refluxed for 3 hours followed by solvent evaporation. The solid was dissolved in a minimum amount of hot water and precipitated with ethanol to be recrystallized. The precipitate was rinsed with ethanol and diethyl ether and dried under vacuum. Figure 3.4 shows the NMR spectrum of PVS. Without the addition of water, PVS was not formed and the mono substituted bipyridine product was recovered even after the second reaction.

**H. Photolysis** The light source was a xenon arc lamp equipped with a water filter, a 420nm cutoff filter, and a mirror that reflects radiation in the range 420-650nm. The power of the radiation incident on the substrate side of the cell was measured by a Coherent 210 power meter and found to be 250 mW/cm$^2$. The cell in Figure 3.1(a) was
modified to that of Figure 3.1(b). One part now had a built-in (1 cm internal length) cuvet for in-situ absorption spectroscopic study. This was necessary because of the extreme oxygen sensitivity of bipyridinium radicals and any transfer to an external cell would have led to radical oxidation. The cell needs to be air tight to prevent oxygen leaking into the cell. Simple gas test was performed by blowing air gas in the cell through the needle in the Teflon cover and immersing the cell in the water. No air bubble was observed, which means that the cell is reasonably air tight even when inside is high pressure. DQ$^{2+}$-Y membrane was inserted in the cell. 17 ml of 0.025M PVS solution was placed in the zeolite side and bubbled with argon. Slight amount of Ru(bpy)$_3^{2+}$ and TEA was added and solution was irradiated for 5 minutes to remove trace oxygen. The concentration of Ru(bpy)$_3^{2+}$ and TEA was $8 \times 10^{-6}$ M and $10^{-3}$ M, respectively. Small amount of PVS radical was generated and reacted with oxygen in the cell, which was monitored by in-situ UV-Vis absorption spectroscopy. After 30 minutes, 10 ml of deoxygenated Ru(bpy)$_3^{2+}$, Na$_2$EDTA and DQ$^{2+}$ solution was added to the substrate side and the solution was irradiated for 80 minutes, during which time the solution on the zeolite side was monitored for PVS radical by UV-visible spectroscopy. The concentration of Ru(bpy)$_3^{2+}$, Na$_2$EDTA and DQ$^{2+}$ in the substrate side was $5 \times 10^{-4}$ M, 0.04M and 0.025M, respectively.

RESULTS

Synthesis of zeolite Y nanocrystals Nano crystalline zeolite Y is synthesized from clear synthesis solution. Clear and homogeneous solution became cloudy 5 days after the heat treatment began. White crystals settled down in 7 days and upper solution became clear.
Solids were recovered after the settling down. Figure 3.5(a) shows the XRD pattern of synthesized zeolite nanocrystals. Comparing with the literature the product is mainly zeolite Y with slight impurities of zeolite A [20]. The strongest peak of zeolite A appears at 7.18° (2θ). The general molar composition of synthesis solution was SiO$_2$:Al$_2$O$_3$=3.4, Na$_2$O:Al$_2$O$_3$=0.045, (TMA)$_2$O:Al$_2$O$_3$=2.5, H$_2$O:Al$_2$O$_3$=370. When increased amount of sodium was used (Na$_2$O:Al$_2$O$_3$=0.05), the amount of zeolite A was increased. Figure 3.5(b) shows the powder diffraction of product with increased amount of sodium in synthesis solution. It has been reported in the literature that relatively high ratio Na$_2$O/Al$_2$O$_3$ ratios favor the formation of large crystals of zeolite A [21]. Our observation of the formation of zeolite A agrees with this report. However, further decrease of sodium content below Na$_2$O:Al$_2$O$_3$=0.045 did not affect the product composition. The scanning electron micrograph of the zeolite showed that the particle size was around 100 nm. Agglomeration of zeolite particles was observed after calcination process, but with extensive sonication, it was possible to break the agglomerates into individual crystallites. Figure 3.6(a) shows the SEM of agglomerated zeolite particles and Figure 3.6(b) is the SEM of nano-sized zeolite crystals after 3 hours of sonication.

With Ludox silica sol as a silica source, the formation of zeolite A was not observed by the same synthesis procedure and the product was pure zeolite Y. Figure 3.7(a) shows the SEM picture of synthesized zeolite powder using Ludox silica sol as a silica source. The size of an individual crystal is 150-200nm, which is bigger than the crystals in Figure 3.6. Also individual crystals show clear octahedral morphology of zeolite Y, as compared to more spherical crystals shown in Figure 3.6. The X-ray powder
diffraction pattern of the same zeolite powder is shown in Figure 3.7(b). Comparing with Figure 3.5, the peaks from zeolite A disappeared and the product is pure zeolite Y.

**Zeolite coating on polymer or glass substrates** Colloidal crystals of zeolite Y synthesized from clear tetramethylammonium aluminosilicate solutions were used as the starting material [17]. Acrylic copolymer filtration membrane (Versapore, Gelman Laboratory) was tested for substrate for zeolitic film casting. Versapore has typical thickness of 190 µm and pore size of 3 µm. Figure 3.8 shows the shape of Acrylic polymer membrane. 20 mg nanocrystalline zeolite Y suspension in 20 ml of distilled water was used for film casting. Suspension was applied on the polymer substrate using a glass disposable pipette and dried overnight. As the water evaporates, zeolite layer was formed on the substrate. The SEM of zeolitic film on polyacrylic substrate is shown in Figure 3.9. The low-resolution figure shows good coverage of zeolite layer on the substrate, but cracks were generated due to solvent evaporation. High resolution SEM in Figure 3.9(b) shows the morphology of nanocrystals in the zeolitic layer. Individual zeolite crystals are in good contact with other crystals in the layer. To check the water stability of zeolitic film, the zeolite-versapore membrane was immersed in distilled water for 24 hours. Loss of zeolite crystals from the film was not observed by electron microscopy.

Indium Tin Oxide (ITO) coated glass slab (Delta Technologies, 7mm x 50mm x 0.7mm) was also used for film casting. Upon the solvent evaporation, continuous zeolitic layer is formed on the substrate. Figure 3.10 shows the nanocrystalline Y layer on the ITO coated glass substrate.
**Membrane fabrication on alumina substrate**  Colloidal crystals of zeolite Y were coated on commercial alumina substrate. Sixty-micron thick porous alumina filter membranes were used as substrates. Their honeycomb pore structure had openings of 0.2 µm. The SEM micrograph of top view and side view of the substrate are shown in Figure 3.11. Zeolitic films on alumina substrates were prepared by either spin coating or solvent evaporation of the sonicated nanocrystalline zeolite Y suspension. Typically, a 0.125ml portion of the suspension of 33mg zeolite particles in 10ml of distilled water formed a 1µm thick zeolite film with 7-8 layers of zeolite nanocrystals. When the suspension was diluted to half concentration, the thickness of the film was reduced to 0.5 µm and 3-4 layers of zeolite nanocrystals. When the casting procedure was repeated two times, 2 µm thick zeolitic film with 15-20 layers of zeolite nanocrystals was obtained. Zeolitic films of different thickness are shown in Figure 3.12. The thickness of zeolite layer could be readily controlled by the number of coatings or by the concentration of zeolite suspension. When zeolitic film is formed by spin coating method, repeated spin coating procedures are required to achieve continuous films on the substrate. Figure 3.13(a) shows a nanocrystalline zeolite Y film generated by one cycle of spin coating (1500 rpm, 10 seconds). The pores of alumina substrate are still visible since zeolitic layer is not continuous. The zeolitic layer formed by three cycles of spin coating procedure shows better coverage of zeolite crystals on a substrate.(Figure 3.13(b))

Positive type photoresist liquid was used to soak through the intercrystalline pores, followed by exposure to ultraviolet radiation. The composition of the photoresist liquid was proprietary, but it is known from the patent literature that it contains an
organic resin, sensitizer, solvents and additives [22]. Photoresist is emulsion type chemical before drying or heating process. Typical treatment for photoresist coating is photoresist coating-solvent drying-soft baking-irradiation-development-hard baking. Photoresist can be applied to a substrate or zeolitic layer by spin coating or dip coating. In this experiment, spin coating method was used. After the irradiation, illuminated photoresist dissolves upon treatment with the development solution. The duration of photoresist exposure to illumination was adjusted in order to remove the photoresist covering the surface of the zeolite crystals while leaving the material in the pinholes and below the surface of the film undeveloped. Figure 3.14 is an SEM image of the top view and the cross-section of a photoresist-coated zeolite Y membrane after development. Top photoresist layer is all removed and zeolite crystals are exposed. The membrane is composed of 7-8 layers of nanometer-sized zeolite crystals on top of the substrate, with a thickness of about 1µm. The side view shows the pores of the substrate. The top view does not show a photoresist layer, and is probably not unexpected since the photoresist penetrates into the membrane.

**Leak Properties of the Photoresist-Coated Membrane** Rhodamin 123 was selected for the leak test since it has a larger kinetic diameter (>10Å) than the 12-membered rings (7.4Å) of the zeolite and can only cross the membrane through the pinholes. The strong fluorescence of Rhodamin makes it easy to detect. The fluorescence intensity of Rhodamine solution at 525nm increases linearly in the range of interest and the fluorescence intensity of Rhodamine 123 solution measured at 525nm is plotted in Figure 3.15. The intensity is proportional to the concentration between 0.00 µM and 0.65 µM.
and the leak measurement falls in this range. Figure 3.16(a) compares the levels of emission due to Rhodamine 123 that have traversed across a non-coated zeolitic membrane and photoresist coated (20 seconds irradiated) membrane. Photoresist coated membrane has less than 0.5% of leaking as compared to non-coated film, which indicates that the photoresist is effectively blocking the pinholes.

In order to optimize the leak properties of the membrane, a series of membranes with different irradiation times were prepared and their leak properties tested. Figure 3.16(b) compares the change in leaking of rhodamin 123 as the irradiation time was increased. Films irradiated for 20 seconds showed comparable leaks to the non-irradiated film whereas films irradiated for 40 or 60 seconds showed considerable more leaking (a factor of four after 3 hours). By virtue of the nature of positive photoresist, longer irradiation times result in solubilization of more photoresist, leading to decrease in the amount of photoresist in the pinholes, and more leaking. Therefore, the optimum duration of illumination appeared to be 20 seconds. Heating the developed membrane to 110°C (hard baking) did not improve the leaking property.

**Ion Exchange Properties of the Photoresist-Coated Membrane** Ion exchanging experiments were carried out to test if the interior of the zeolite was accessible after photoresist coating and development process. First, the ion-exchange capacity of the blank alumina substrate coated with photoresist was examined. The probe for monitoring accessibility was the methylviologen ion (MV$^{2+}$) which has an absorption band at 290 nm and can be readily quantitated. The blank photoresist-coated substrate was placed in a 0.05M MVCl$_2$ solution overnight followed by washing with water. The
amount of ion exchange was investigated by placing the photoresist-coated substrate back in 0.05M NaCl solutions. The NaCl solution did not show any MV$^{2+}$ absorption peak. Therefore, the photoresist and alumina substrate does not have a measurable ion exchange capacity.

For the membranes, the zeolite crystals were ion exchanged with MV$^{2+}$ prior to casting. If zeolitic pores were inaccessible, then MV$^{2+}$ would not be ion exchanged out of the zeolite by Na$^+$ in the solution. Figure 3.17(a) shows the amount of MV$^{2+}$ ion-exchanged into the NaCl solution in contact with zeolitic membrane as a function of time. The kinetics of ion exchange followed a biphasic behavior with rapid exchange over a 20-30 min period followed by a slower exchange process over an hour before steady state was reached. A membrane without any irradiation or irradiated for 20 seconds shows the maximum amount of recovered MV$^{2+}$ and as the irradiation time increased, the recovery decreased. This observation appears contrary to expectation since longer irradiation should remove more photoresist and produce a more accessible membrane. We propose that the lower recovery arises because of less MV$^{2+}$ in the membrane. The development solution contains tetramethylammonium hydroxide (TMAOH) and for samples with longer irradiation times, longer exposure to TMAOH was required to remove the soluble photoresist. During the development process, TMA$^+$ cations can ion exchange into the zeolite, replacing MV$^{2+}$ and the longer the membrane was in TMAOH, the more MV$^{2+}$ will be removed from the zeolite. This was confirmed by re-ion exchanging a 40 s-irradiated membrane with MV$^{2+}$, and recovering the MV$^{2+}$ from the membrane by treatment with NaCl. It was found that the amount of recovered MV$^{2+}$ reached the same
level as a non-irradiated or 20 s-irradiated membrane (data not shown). Figure 3.17(a) also shows that membranes with no irradiation or 20 seconds of irradiation had similar absolute recovery of MV$^{2+}$, indicating that photoresist penetrates through the pinholes, and does not cover the zeolite surface.

The accessibility of molecules within the zeolite from the alumina substrate side of the membrane is shown in Figure 3.17(b). The recovery is low if there is no irradiation. Upon irradiation for 40 seconds, the membrane was as accessible as one without photoresist coating. Thus, it appears that 20 seconds of irradiation from the zeolite side and 40 seconds of irradiation from the substrate side resulted in optimum zeolitic membranes. Such a membrane showed similar leaking (0.5%) as 20-s zeolite-side irradiated membrane (Fig 3.16). Therefore, irradiation from the alumina side removes excess photoresist that has penetrated through the zeolite pinholes into the substrate.

Ion exchange across photoresist coated zeolitic membranes was tested with distilled water, NaCl, tetramethyl ammonium bromide (TMABr) and tetrapropyl ammonium bromide (TPABr) solutions. In zeolite side of the cell, 0.005M MVCl$_2$ solution was placed and water or other ionic solutions were placed in substrate side. The amount of MV$^{2+}$ that pass through the membrane can be measured by the absorption measurement of the solution in the opposite side. The concentration of MV$^{2+}$ in the water or NaCl solution in the substrate side is plotted according to the time of measurement in Figure 3.18 (a). In Run1, 0.005 M MVCl$_2$ solution was placed in the zeolite side and DI water was placed in the substrate side for 2 hours. Membrane and glass cell was thoroughly rinsed with DI water after the Run1. For Run2, 0.005 M MVCl$_2$ solution was
placed in the zeolite side of the same membrane as Run1. 0.005 M NaCl solution was placed in the substrate side of the cell for the measurement. Surprisingly, the concentration of MV$^{2+}$ increased faster in DI water than NaCl solution. (Run1 and Run2 in Figure 3.18(a)) This implicates that MV$^{2+}$ moves across the zeolitic membrane through pinholes by the concentration gradient of two sides as well as by ion exchange process. The same experiments were repeated in Run 3 and Run 4 with DI water and 0.005 M NaCl solution, respectively. The results show the same trend as Run 1 and Run 2, which is faster MV$^{2+}$ transport across the membrane with water in the other side.

TPABr and TMABr solutions were used to study MV$^{2+}$ transport across the membrane while maintaining the same concentration of ionic species in both sides. Tetrapropyl ammonium cation (TPA$^+$) is size excluded from zeolite Y supercages, which prevents ion exchange. Tetramethyl ammonium cation is small enough for ion exchange. When TPABr solution is placed in the substrate side, MV$^{2+}$ ions move across the membrane by diffusion through pinholes. When TMABr is placed in the substrate side, MV$^{2+}$ ions move across the membrane by ion exchange process as well as diffusion through pinholes. The concentration of MV$^{2+}$ in 0.005M TMABr or TPABr solutions in the substrate side is plotted according to the time of measurement in Figure 3.18(b). As expected, the concentration of MV$^{2+}$ in the solution in the substrate side is larger when TMABr is placed in the substrate side. The difference between Run1 and Run2 in Figure 3.18(b) corresponds to the “net” ion exchange of MV$^{2+}$ across the membrane.

**Charge Transport Studies with the Photoresist Coated Membrane** The possibility of charge transport through the zeolitic membranes was investigated by using a reaction that
involves electron transfer by a self-exchange mechanism and initiated by a photochemical process. The photochemical system included a zeolite membrane that was ion-exchanged with the bipyridinium ion \((4DQ^{2+})\). On the substrate side of the membrane, \(Ru(bpby)_3^{2+}\) (5×10^{-4} M), \(DQ^{2+}\) (0.025 M) and \(Na_2EDTA\) (0.04 M) was introduced and on the zeolite side another bipyridinium ion, neutral propyl viologen sulfonate (PVS) solution (0.025 M) was introduced. The basic reactions involved in the process are as follows:

\[
\text{Substrate side: } \quad Ru(bpby)_3^{2+} + DQ_s^{2+} \xrightarrow{hv} Ru(bpby)_3^{2+*} + DQ_s^{2+} \quad (1)
\]

\[
Ru(bpby)_3^{2+*} + DQ_s^{2+} \rightarrow Ru(bpby)_3^{3+} + DQ_s^{**} \quad (2)
\]

\[
Ru(bpby)_3^{3+} + EDTA \rightarrow Ru(bpby)_3^{2+} + EDTA^{ox} \quad (3)
\]

\[
DQ_s^{+} + DQ_z^{2+} \rightarrow DQ_s^{2+} + DQ_z^{**} \quad (4)
\]

\[
\text{Intrazeolitic membrane: } \quad DQ_{iz}^{**} + DQ_{2z}^{2+} \rightarrow DQ_{iz}^{2+} + DQ_{2z}^{**} \quad (5)
\]

\[
\text{Zeolite side: } \quad DQ_{iz}^{**} + PVS \rightarrow DQ_{iz}^{2+} + PVS^{*} \quad (6)
\]

where the subscripts ‘s’ and ‘z’ represent solution and zeolite, respectively.

If charge transport through the zeolite membrane can occur by electron hopping via the self-exchange of ion-exchanged \(DQ^{2+}\), as shown in (5), then illumination of the substrate side of the membrane should lead to creation of PVS radical on the zeolite side of the membrane and measure of this radical was the focus of these experiments. The process is schematically represented in Figure 3.19.
However, there were several problems that needed to be addressed. First, as shown in Figure 3.16, though application of the photoresist decreased the level of leaking through the membrane it did not completely seal it. Second, no matter how tight the seals were of the cell (Figure 3.1b), it was impossible to keep \( \text{O}_2 \) from leaking into the cell and reacting with the bipyridinium radical. The use of sulfites is a frequently used method to remove oxygen from water solutions [23]. To apply this method, sulfite was added in the zeolite side of the cell with PVS solution. PVS\(^*\) radical formation was not observed after photolysis when sulfite was added. It is assumed that sulfite reacts with the reduced species, possibly the second reduction to PVS\(^2-\). Therefore, addition of sulfite ions is not a proper method to remove oxygen in this system. Thus, we needed to come up with an appropriate blank system to demonstrate the influence of leaking and control the effect of oxygen. In order to accomplish that, the blank (or control) membrane we designed was an alumina substrate coated with photoresist alone and cured as described before. For ensuring that \( \text{O}_2 \) leaking into the zeolite side was controlled, a small amount of Ru(bpy)\(\text{3}^{2+}\) \( (8*10^{-6}\text{ M}) \), and triethanolamine (TEA, \( 10^{-3}\text{ M} \)) was introduced into the deaerated PVS solution on the photoresist side and photolyzed for 5-minutes. PVS radical was generated and reacted with oxygen in the system, which was monitored by UV-Vis absorption spectroscopy for 30 minutes. The data shown in Figure 3.20(a) demonstrated that the bipyridinium radical that is produced decays with time, as \( \text{O}_2 \) leaks into the cell. However, the constant presence of radical indicates that \( \text{O}_2 \) is being contained. Figure 3.20(a) also shows that the concentration of Ru(bpy)\(\text{3}^{2+}\) during this time remains constant. After 30 minutes, Ru(bpy)\(\text{3}^{2+}\)- DQ\(\text{2}^{2+}\)- Na\(_2\)EDTA was added to the substrate side (time
indicated by arrow in Figure 3.20) and photolyzed with visible light while the absorption
spectrum of the solution on the zeolite side was monitored for the next 80 minutes. There
is a slight increase in the Ru(bpy)$_3^{2+}$ on the zeolite side due to leaking. The viologen
radical however continues to decrease though there is leak of DQ$^{**}$ through the
membrane and formation of PVS$^{•-}$ on the zeolite side, indicating a continuous oxygen
leak into the cell. Though, it is evident that after 30 minutes the decrease of amount of
PVS$^{•-}$ slowed, because of the DQ$^{**}$ leak. This blank experiment clarifies the nature of the
leaking process both through the membrane and due to O$_2$ leak.

The same experiment was repeated with the photoresist coated DQ$^{2+}$-exchanged
zeolite membrane and the data is shown in Figure 3.20(b). Before the addition of the
Ru(bpy)$_3^{2+}$- DQ$^{2+}$ solution on the substrate side (first 30 minutes), the behavior was very
similar to that of the blank membrane, as far as the leak of O$_2$ into the cell. Figure 3.21
(a) shows the UV-Visible spectra acquired for the first 30 minutes. The peak at 450nm is
the metal to ligand charge transfer (MLCT) absorption by Ru(bpy)$_3^{2+}$. The peaks at
390nm and 605 nm are from PVS$^{•-}$ radicals generated by irradiation. The decrease of
PVS$^{•-}$ radicals was shown by the decrease of intensities of 390nm and 605 nm peaks.
However, after the Ru(bpy)$_3^{2+}$- DQ$^{2+}$- Na$_2$EDTA addition and initiation of photolysis,
there was a linear growth of PVS$^{•-}$ radical on the substrate side beginning at about 45
minutes. Figure 3.21(b) shows the UV-Vis absorption spectra after Ru(bpy)$_3^{2+}$- DQ$^{2+}$-
Na$_2$EDTA was injected to the substrate side. Since the blank sample with similar leak
properties does not show the increase of PVS$^{•-}$ radical, this radical must be forming due
to charge transport across the zeolite membrane.
A similar experiment was repeated with a photoresist coated MV\(^{2+}\)-exchanged zeolite membrane with Ru(bpy)\(_3\)\(^{2+}\) - MV\(^{2+}\) - Na\(_2\)EDTA on the substrate side and the data are shown in Figure 3.20(c). The O\(_2\) leak prior to addition of Ru(bpy)\(_3\)\(^{2+}\) - MV\(^{2+}\) - NaEDTA (first 30 minutes) was somewhat more than the previous two membranes and reflects the variability in controlling the O\(_2\) leak. The leak of Ru(bpy)\(_3\)\(^{2+}\) through the membrane was comparable. However, similar observations as with DQ\(^{2+}\) exchanged zeolitic membrane were made in that the PVS* radical increased dramatically after creation of MV** radical on the substrate side.

DISCUSSION

**Synthesis of nanocrystalline zeolites** Nanocrystalline zeolite Y were synthesized following patent procedures with slight modification. For the synthesis of zeolite Y, Ludox was a better reagent for silica source than TEOS. Correct adjustment of the amount of sodium cations in the synthesis solution appeared to be an important factor to synthesize pure zeolitic species. Figure 3.22 shows the framework of Faujasite zeolite. The size of super cages of zeolite Y are about 13 Å, but the window to the cage is 7 Å, in which viologen molecules can snugly fit. For the applications of charge transfer, we need to ion exchange viologen acceptors such as methyl viologen and 4DQ\(^{2+}\). The size of channels and window of zeolite Y is appropriate for this purpose. Also photo sensitizers, Ru(bpy)\(_3\)\(^{2+}\), and final electron acceptors, PVS, are size excluded from zeolite Y due to their molecular size.
Membrane Preparation

Formation of continuous zeolite layer on various substrates: Suspension of nanocrystalline zeolite was used to prepare continuous zeolitic layer on various substrates. Polymeric substrates (Versapore), Glass substrates (ITO coated glass) and alumina substrates were tested, and good coverage of zeolite crystals was achieved on surfaces of all three substrates. This result implies that nanocrystalline zeolite crystals are useful starting material for film casting on various substrates. Resulting films were stable in water up to 24 hours. Also simple solvent evaporation method using nanocrystalline zeolite suspension can be used for various substrates without any modifications due to the nature of substrates. The other advantage of this method is the control of thickness. As Figure 3.13 shows, zeolite layer with different thickness can be prepared by varying the concentration of zeolite suspension or repeating film casting procedure. Even one crystal layer of zeolitic film can be made by this method. In common secondary growth method, careful adjustment of synthesis time and temperature is required to control zeolite film thickness. Therefore our method is easy and efficient for film preparation.

The zeolite crystals in the layer appeared to bond to each other by Si-O-Si bond. The available hydroxide group on the zeolite surface can bond to Si on the surface of neighboring zeolite crystals, which connects zeolite crystals. The bond between zeolite crystals and substrates are presumably electrostatic force.

Comparing three different substrates, alumina substrate is most useful for our applications. Even though continuous layer is formed on all three substrates, polymer support is not stable at high temperature or harsh chemical environment. ITO coated glass
is not porous so molecules cannot pass through substrates. However, for electrochemical applications, ITO coated glass is an excellent substrate since Indium Tin Oxide is a good conducting material [24]. In this research, zeolite membrane was used for photochemical applications.

**Photoresist Strategy** The strategy that we have taken to make defect-free zeolitic membranes is assembly of crystals on a substrate and sealing the gaps between crystals with filler. Limitations of such methods in the past have been the potential clogging of zeolite pores and covering of zeolite surfaces by the additive [16]. We have circumvented this problem by using photoresist to fill the inter crystal spaces. Photoresist is frequently used for lithography or micro patterning [22]. There are two types of photoresist: positive and negative. Figure 3. 23 shows the photo patterning procedure for the use of positive and negative resist. For positive resists, the resist is exposed with UV light wherever the underlying material is to be removed. In these resists, exposure to the UV light changes the chemical structure of the resist so that it becomes more soluble in the developer. The exposed resist is then washed away by the developer solution, leaving windows of the bare underlying material. The mask therefore contains an exact copy of the pattern, which is to remain on the substrate. Negative photoresist behaves in just opposite manner. Exposure to the UV light causes the negative resist to become polymerized, and more difficult to dissolve. Therefore the negative resist remains on the surface where it is exposed, and the developer solution removes only the unexposed portions. Masks used for negative photoresists, therefore, contain the inverse of the pattern.
Positive photoresists are made up of sensitizers, resins, solvents and additives. The sensitizers are typically diazonaphthoquinones (DNQ) dispersed in a low molecular weight phenolic matrix resin (Novolak). Because of the hydrophobic nature of DNQ, it acts as a dissolution inhibitor of the resin. Upon irradiation, the DNQ is converted to the hydrophilic indenecarboxylic acid which renders the exposed film (sensitizer + resin) soluble in the developer (0.2-0.3 M TMAOH) [25].

Since the photoresist is liquid before the heat treatment, it can flow into pinholes between crystals. Also, the organic resins used in the photoresist are large polymers, which cannot enter the zeolite pores. When the photoresist-coated zeolitic membrane is soft baked at 80°C, the organic resin solidifies and becomes insoluble. Upon irradiation, the exposed photoresist becomes soluble and the development process removes the reacted photoresist, as schematically depicted in Figure 3.24. Another advantage using photoresist besides the simplicity of the coating and development process is that the mechanical stability of membrane is improved. The only other example of using photoresist to fill grain boundaries has been between diamond crystals to achieve a high performance film for an electric device [26].

**Membrane Properties** The duration of illumination time is important for effective pinhole blocking and access to the intrazeolitic volume. This is evident from the ion-exchange experiments with MV$^{2+}$. Based on the amount of zeolite that was used to make the membrane, and assuming a maximum loading of 1.5 molecules of methyl viologen per supercage, we estimate from Figure 3.18 that about 83% of the MV$^{2+}$ is ion-exchanged from the membrane. The recovery of the ion exchange from the uncoated and
photoresist coated zeolitic membranes were comparable indicating that the coating was not blocking zeolite access. Complete exchange of the MV$^{2+}$ from the membrane by 0.1 M NaCl took about 60 minutes before steady state was reached. For the same amount of zeolite in powder form, the process is instantaneous. This is indicative of the fact that ion-exchange only proceeds from the surface layer of zeolite, since the access of NaCl is only limited to this layer. In the particular membranes that we have studied, there are about seven layers of zeolite crystallites, so interparticle ion-exchange needs to occur.

Interparticle ion-exchange has been noted between mixtures of Li$^+$- and Na$^+$-zeolite A, and the rate was controlled by zeolite crystallite size, and degree of hydration [27]. Small crystals (1-2 $\mu$m) were found to reach equilibrium almost instantaneously upon mixing, whereas larger crystals (20-25 $\mu$m) took 24 hours. In comparison to these studies done with vigorous mixing of powders, if the crystals (1-2 $\mu$m) are simply gently brought together, then the process can take up to 24 hours to come to equilibrium. With the present nanocrystalline zeolite Y membranes, 60 minutes is required to reach equilibrium. This is consistent both from the smaller size of crystallites (~100 nm) as well as the static conditions under which the experiment is done. Thus, the ion-exchange process can be viewed as the first layer of crystallites rapidly exchanging their MV$^{2+}$ with Na$^+$ in solution followed by a slower process of interparticle ion-exchange.

When the ion exchange across the photoresist coated zeolitic membrane was tested, the concentration of MV$^{2+}$ increased faster in deionized water than NaCl solution. (Run1 and Run2 in Figure 3.18(a)) This implies that MV$^{2+}$ ions move across the zeolitic membrane though pinholes as well as ion exchange process. In case of ion
exchange, MV\textsuperscript{2+} cations in the zeolite side solution will be ion exchanged into zeolite particles in the membrane and ion exchanged out to the solution in the opposite side. When deionized water is placed in the opposite side, there is no driving force for further ion exchange. Therefore MV\textsuperscript{2+} ions would stay in zeolite particles. The increase of MV\textsuperscript{2+} in deionized water indicates that MV\textsuperscript{2+} ions diffuse to the other side of the membrane through pinholes. The driving force for this diffusion is concentration gradient.

When 0.005M NaCl solution was placed in the substrate side, the ion exchange can happen, and MV\textsuperscript{2+} cations will exit to NaCl solution by ion exchange mechanism. In this case, the diffusion of MV\textsuperscript{2+} cations through pinholes might be slower than that in the water due to the existence of sodium cations in the other side. The pathway might be blocked by the sodium cations that move to the opposite direction. Even though the ion exchange process helps transport of MV\textsuperscript{2+} cations across the zeolitic membrane, the decrease of diffusion through pinholes might overcome the effect of ion exchange. This explains the slow increase of MV\textsuperscript{2+} in NaCl solution in Figure 3.18(a). These phenomena were reproducible when the experiments were repeated with same membrane in Run3 and Run4 in Figure 3.18(a).

The diffusion in free solution can be described by the Stokes-Einstein equation (eq.3.1) that relates the diffusion coefficient (D\textsubscript{s}) to the molecular radius (r\textsubscript{mol}).

\[
D_s = \frac{kT}{6\pi\eta r_{mol}} \quad \text{(eq.3.1)}
\]

Where k is the Boltzmann constant, T is the Kelvin temperature and \(\eta\) is the viscosity. The denominator \(6\pi\eta r_{mol}\) can be thought of as a molecular-friction coefficient that determines the resistance to diffusion in solution. In the zeolite membranes, this
molecular friction coefficient is larger than in free solution because collisions with the crystalline wall and collisions with other molecules in the narrow pinholes increase the frictional drag [28,29]. When NaCl solution is on the other side, this molecular-friction coefficient will be larger than water case due to the counter diffusion of Na\(^+\) cations. Na\(^+\) cations will diffuse through the membrane to the opposite direction of MV\(^{2+}\). This counter diffusion has two effects. One is the physical blocking of pathway across the membrane and the other is repulsion between two cationic species. Therefore, the diffusion of MV\(^{2+}\) will be slower when NaCl solution is in the opposite side. This effect appeared to overcome the increase of ion exchange, and that is why the slope of Run1 (1.05 \(\mu\)M/ min) is almost two times larger than the slope of Run2 (0.54 \(\mu\)M/min). Ion exchange process can be slow due to the slow interparticle ion exchange discussed above or the competition of Na\(^+\) and MV\(^{2+}\) ion exchange.

TPABr and TMABr solutions were used to study MV\(^{2+}\) transport across the membrane while maintaining the same concentration of ionic species in both sides. In these experiments (Run(1) and Run(2) in Figure 3.18 (b)), blocking of pinholes or repulsion between cationic species by TMA\(^+\) or TPA\(^+\) will be similar, which means that the molecular friction coefficient in eq. 3.1 will be similar except the term molecular radius \(r_{mol}\). The counter diffusion by TPA\(^+\) might be slower due to larger molecular size of the cation. Since TPA\(^+\) is size excluded by zeolitic pores, ion exchange only happens when TMABr solution is placed in the substrate side. As expected, the concentration of MV\(^{2+}\) is larger when TMABr is placed in the substrate side. The difference between
Run1 (slope 0.79 μM/min) and Run2 (slope 0.58 μM/min) in Figure 3.19(b) corresponds to the “net” ion exchange of MV$_2^+$ across the membrane.

**Photo-Induced Charge Transport Through Zeolitic Membrane** Our objective was to examine if charge transport is possible through zeolitic membranes via electron self-exchange of bipyridinium ions. There is enough evidence both in the polymer-based electrochemical and zeolite literature that charge hopping between bipyridinium ions can be efficient. For self-exchange to occur, a proper topological arrangement of the molecules, such that electron exchange can occur between the oxidized and reduced members of the species is required. We are using three dimensional framework of zeolite Y to arrange molecules on a heterogeneous support. Membrane form of the host zeolite support will keep the reduced species separate from oxidized species to prevent energy wasting back electron transfer reaction.

The ability to transport charge by self-exchange at rates significantly higher than physical diffusion has been noted on polymer electrodes [30]. Voltammetric studies have provided estimates of electron self-exchange rates of bipyridinium ions in poly(ethylene glycol) films [31]. For MV$_2^+$, the self-exchange rate constant for MV$_2^+/MV^+$ exchange depended on the ionic strength of the medium, but varied from 8.6 x 10$^4$ to 1.6 x 10$^5$ M$^{-1}$ s$^{-1}$[31].

Yoon et al. noted that carbonylmanganate ions (Mn(CO)P(OPh$_3$)$_3^-$ too large to enter the zeolite can effectively reduce all of the intrazeolitic MV$_2^+$. The proposed mechanism involved reduction of MV$_2^+$ only at the zeolite periphery (about 1% of MV$_2^+$) followed by self-exchange that moved the reduced charge to the interior of the zeolite.
[32]. The complete reduction of all the intrazeolitic viologen in a zeolite crystallite occurred very fast.

Several studies have reported that reduced bipyridinium ions in the zeolite can transport charge via self-exchange and can exchange charge with bipyridinium ions external to the zeolite in solution [33,34]. Furthermore, if the reduction potentials of the bipyridinium ions are chosen so that there is a driving force for electron transfer from the species within the zeolite to the bipyridinium ions in solution, then the process of charge injection into the solution can be enhanced. Thus, by choosing 4-DQ2+ (E=-0.68V) to be the species inside the zeolite and PVS (E=-0.42V) in solution, the yields of charge transfer were higher than if MV2+ (E=-0.44V) was chosen to be the species within the zeolite [33,34].

These previous studies were the basis for the use of photoresist coated DQ2+-Y membrane for electron transport. Photolysis of Ru(bpy)32+ and DQ2+ in the presence of EDTA generates DQ• in solution. These DQ• radicals can exchange charge with DQ2+ on the surface of the zeolite crystals in the membrane, which can then propagate through the membrane by self-exchange and finally transfer charge to PVS in solution on the other side of the membrane. Measurement of the reduced viologen (PVS•−) in solution by UV-visible spectroscopy provides a measure of the charge propagation efficiency.

Even though the membrane we used is almost pinhole-free, it is still not a leak-free membrane. To discount the possibility of the generation of PVS•− radical by the transport of DQ• leaking across the membrane, the blank experiments were done, and clearly establishes that trans membrane charge transfer is occurring.
As electron moves from one side of the membrane to the other side, cation transport needs to occur to maintain charge neutrality. We propose that the Na\(^+\) cation from the sacrificial electron donor (Na\(_2\)EDTA) accompanies the electron, keeping the charge balance. When TEA (triethanolamine) was used for a sacrificial electron donor on the zeolite side, no "net" PVS radical was observed, because of the absence of Na\(^+\) that can accompany the electron transfer.

Ion exchange of intrazeolitic DQ\(^{2+}\) by sodium cation in the solution can take place, which can remove acceptors from the zeolite, decreasing the efficiency of the charge hopping process. Indeed, we found that even though the experiment was started with a loading of 1 DQ\(^{2+}\) per supercage, at the end of the experiment, only about 0.7 molecules of DQ\(^{2+}\) per supercage was left. Though it might appear that at least one viologen molecule per supercage is required for charge hopping to proceed, if charge hopping occurs by a percolation route, then loading levels can be considerably lower. Because of the high loading of the intrazeolitic bipyridinium ions, physical diffusion of the radical across a zeolite particle is expected to be quite small (with diffusion coefficients of 10\(^{-8}\) cm\(^2\)/s or even smaller) [35]. Thus, we can view the process as electron hopping between immobile bipyridinium ions. The diffusion coefficient for such a process is similar to that for polymeric electrodes and is given by

\[ D_{\text{app}} = \frac{k_{\text{ex}} \delta^2 c}{\sigma} \]

where \( k_{\text{ex}} \) is the second-order self-exchange constant, \( \delta \) is the distance between the centers of the bipyridinium ions and \( c \) is the concentration of the redox species. Hui and
Baker have used this model for electron transport through MV$^{2+}$-zeolite Y electrodes [36]. Such a model of charge transport can be viewed as a percolation problem. The supercage arrangement in a zeolite Y crystal is the same as the diamond lattice. The percolation threshold of diamond lattice is 0.428, indicating that when occupancy of sites exceeds this number, there is a cluster extending throughout the crystallite[37]. So, at a loading level of 0.7 DQ$^{2+}$ per supercage, percolative pathways that can promote charge transport via self-exchange will exist. This is also an advantage with a multidimensional zeolite, where three-dimensional connections can provide many trans-membrane pathways, as compared to a one-dimensional zeolite like zeolite L.

Comparison of the rates of PVS$^+$ generation between the DQ$^{2+}$ and MV$^{2+}$ membranes show that these rates are comparable. This is puzzling, considering that there is a stronger driving force for electron transfer between DQ$^{++}$ and PVS as compared to MV$^{++}$ and PVS. These results indicate that the limiting step in the charge transport process is inter-zeolitic self-exchange, since it is known that charge transport within the zeolite for the bipyridinium ions is fast [32]. There are about 7 layers of crystallites that the charge has to propagate through to cross the membrane. At the interface between two crystallites, the charge has to hop between the bipyridinium ions on the two crystallites, and unlike the zeolite interior, where the packing of the ions is dense, there are fewer ions on the crystallite surface. This will slow down the process of charge transport and is the rate-limiting step in the process. Thus, even though there is an enhanced rate of charge transfer between DQ$^{++}$ and PVS for the DQ$^{2+}$ membrane, the inter-particle charge transport in the membrane is sufficiently slow such that the effects of the enhanced rate is
not apparent and is comparable to the MV$^{2+}$ membrane, where there is no driving force for MV$^{**}$ to PVS electron transfer and is via self-exchange.

After formation of the bipyridinium radical in solution on the substrate side of the membrane, there appears to be a 10-minute delay before PVS$^{-}$ radical is found to increase on the zeolite side. The simplest explanation for this observation is that though there is immediate formation of PVS$^{-}$, it is not manifested because of the oxygen leaking in the system. The other possibility is that it takes a certain period during which multiple pathways of charge transport are sampled, before the pathway that leads to formation of PVS$^{-}$ is adopted.

Another possibility for formation of PVS$^{-}$ is that the DQ$^{**}$ or MV$^{**}$ on the zeolite side ion-exchange into the zeolite membrane, replacing the DQ$^{2+}$ or MV$^{2+}$, and eventually these ion-exchanged species penetrate through the membrane and show up on the substrate side and transfer electron to PVS. This mechanism would suggest charge transport via ion exchange rather than electron hopping. However, this is unlikely, because we have determined that in the MV$^{2+}$ system, the concentration of MV$^{**}$ to MV$^{2+}$ on the substrate side is about 0.005, indicating that there is considerably more MV$^{2+}$ and Na$^+$ in the system than there is MV$^{**}$ and therefore the possibility of replacement of MV$^{2+}$ in the zeolite by MV$^{**}$ by ion-exchange is unlikely. Though we have not calculated the amounts of DQ$^{**}$, we expect the scenario to be similar to that of MV$^{2+}$ system.

There are other examples of electron transfer across membranes. Lawson et al. utilized doped polypyrrole film to separate a solution of electron donor from a solution of an electron acceptor [38]. Because the conductive polymer is both electronically and
anionically conductive, the membranes could transport electrons from the donor solution to the acceptor solution, and anions in the opposite direction. Matsumara et al. used conducting polymer films loaded with titanium dioxide or cadmium sulfide particles for photocatalytic electron and proton pumping across the membrane [39]. The electron transfer occurred by the electron flow in these cases, not electron hopping through acceptors. Thus, the data presented in this paper is the first report of electron transfer through a membrane via a charge hopping process.

CONCLUSION

Nanocrystalline zeolite Y were synthesized and used to prepare thin coating of zeolite on various substrates. Zeolite Y was chosen for photochemical applications due to its three dimensional channel structure and size of cages. Uniform and thin zeolite layer can be formed on polymer, ITO-coated glass and alumina substrate. Alumina substrate was chosen for membrane fabrication due to its uniform porosity, thermal stability, and chemical resistance. We have shown that the pinhole defects in a zeolite membrane can be reduced effectively with a positive photoresist coating and development process, and leaves the surface and zeolitic pores accessible, as evidenced from ion-exchange studies. The photoresist coating also improves the mechanical stability of the membrane, which is necessary for applications. The illumination period and development conditions are important factors that need to be optimized to get effective pinhole blocking. This almost leak-free membrane was used to examine photo induced charge transport across the membrane by electron self-exchange of bipyridinium ions within the zeolite. A
photochemical Ru(bpy)$_3^{2+}$-EDTA system was used to initiate the charge transport process. Charge propagation by electron hopping through the zeolitic membrane is demonstrated by measuring the amount of reduced viologen radicals. This is the first example of photoinduced electron transfer through a membrane via a charge hopping process.
References


Figure 3.1 (a) Schematic of a two-compartment cell (b) Modified cell for spectroscopic study. One side has a 1 cm cuvet for absorption measurement.
Figure 3.2 NMR spectrum of 4DQ$^{2+}$
**Figure 3.3** NMR spectrum of mono substituted PVS
Figure 3.4 NMR spectrum of PVS
Figure 3.5 XRD pattern of synthesized nanoY zeolite powders
(a) Na$_2$O:Al$_2$O$_3$=0.045 (b) Na$_2$O:Al$_2$O$_3$=0.05
Figure 3.6 SEM of zeolite Y nanocrystals (a) before sonication (b) after 3 hours of sonication
Figure 3.7 Nanocrystalline Zeolite Y synthesized with Ludox
(a) SEM micrograph (b) X-ray powder diffraction
Figure 3.8 Acrylic copolymer substrate
Figure 3.9 Zeolitic layer on Acrylic copolymer substrate
(a) low resolution (b) high resolution SEM
Figure 3.10 Nanocrystalline Y layer on ITO coated glass substrate
Figure 3.11 Commercial alumina substrate
(a) Top view (b) Side view
Figure 3.12 Zeolitic films with different thickness
(a) 2.5 μm (b) 1 μm (c) 0.5 μm
Figure 3.13 Zeolitic layer on alumina substrates formed by spin coating
(a) one cycle of spin coating (b) Three cycles of spin coating
Figure 3. 14 SEM pictures of photoresist coated zeolite Y membrane - After development
(a) top view (b) side view
Figure 3.15 Fluorescence intensity of Rhodamine dye 123 at 525 nm
(a) Conc. 0-6.5 μM (b) Conc. 0-0.65 μM
Figure 3.16 Fluorescence spectra of rhodamine dye leaking through membranes (a) ○: zeolite membrane without photoresist coating, ●: leaking through photoresist-coated zeolite membrane (b) photoresist-coated zeolite membrane with various irradiation time ○: no irradiation, ●: irradiation for 20s, ▲: irradiation for 20s followed by hard baking, ■: irradiation for 40s, □: irradiation for 60s
Figure 3.17 MV$^{2+}$ ion exchange experiment with photoresist-coated zeolite membrane (a) from zeolite side, ▼: no irradiation ○: irradiation for 20s, ■: irradiation for 40s, Δ: irradiation for 60s. (b) from substrate side, ●: zeolite membrane without photoresist coating, ○: photoresist-coated zeolite membrane without substrate side irradiation, □: substrate side irradiation for 10s, ■: substrate side irradiation for 40s.
Figure 3.18 MV$^{2+}$ ion exchange experiment across the photoresist-coated zeolite membrane (a) ●: Run1 with DI water, ■: Run2 with 0.005 M NaCl, ○: Run3 with DI water, □: Run4 with 0.005M NaCl (b) ●: Run1 with 0.005M TMABr, ■: Run2 with TPABr
Figure 3.19 Charge transport through a zeolite Y membrane.
Figure 3.20 Measure of PVS\textsuperscript{*} generation at the zeolite side. Arrow indicates the point where Ru(bpy)\textsubscript{3}\textsuperscript{2+}-MV\textsuperscript{2+} or DQ\textsuperscript{2+}-EDTA solution is added in the substrate side (a) blank experiment with photoresist coated alumina substrate (b) with photoresist coated zeolite membrane, DQ\textsuperscript{2+} was used for electron relay (c) with photoresist coated zeolite membrane, MV\textsuperscript{2+} was used for electron relay.
Figure 3.21 Measure of the change of PVS\(^{-}\) upon photolysis
(a) Before Ru(bpy)\(_3\)^{2+}-DQ\(^2+\)-EDTA solution is added in the substrate side
(b) After Ru(bpy)\(_3\)^{2+}-DQ\(^2+\)-EDTA solution is added in the substrate side
Figure 3.22 Structure of Faujasite

Faujasite framework viewed along [111]

Faujasite 12-ring viewed along [111]
Figure 3.23 Patterning with positive and negative resists
Figure 3.24 Photoresist coating process
INTRODUCTION

Natural photosynthesis involves the conversion of energy from sunlight to chemicals via a complex array of light harvesting pigments and redox species arranged in a definite spatial manner across membranes [1]. If systems that mimic photosynthesis can be designed, plentiful sunlight reaching the earth's surface can be exploited to generate energy storing chemicals such as hydrogen from water [2].

To construct such an efficient energy conversion system, long-lived charge-separated species need to be generated. The first step for charge separation is light absorption by photosensitizer followed by electron transfer from an electron donor to an electron acceptor. Tris(bipyridine) ruthenium(II) dication, $\text{Ru(bpy)}_3^{2+}$, is widely utilized as a photosensitizer since the excited state of the complex, $\text{Ru(bpy)}_3^{2+*}$, can be formed easily with a long lifetime of 0.62 microseconds and high quantum yield of 0.042.
Bipyridinium compounds (often referred to as viologen) are common electron acceptors for electron transfer reactions with excited Ru(bpy)$_3^{2+}$. The structures of bipyridinium compounds, abbreviations, and redox potentials are represented in Figure 4.1. The redox potential of excited Ru(bpy)$_3^{2+}$ is $-0.87\text{V}$ versus NHE (normal hydrogen electrode). The redox potentials of viologens used in this study lie between $-0.65\text{V}$ and $-0.41\text{V}$ versus NHE, which makes the electron flow from Ru(bpy)$_3^{2+*}$ to the organic acceptors. Also if these acceptors are appropriately arranged, they can be used as second or third electron acceptors for extended supramolecular systems. The electron transfer reactions between Ru(bpy)$_3^{2+}$ and viologen acceptors (A) can be summarized by the following reactions:

$$\text{Ru(bpy)}_3^{2+} \xrightarrow{hv} \text{Ru(bpy)}_3^{2+*} \quad (4.1)$$

$$\text{Ru(bpy)}_3^{2+*} + A \xrightarrow{k} \text{Ru(bpy)}_3^{3+} + A^- \quad (4.2)$$

$$\text{Ru(bpy)}_3^{3+} + A^- \xrightarrow{k_r} \text{Ru(bpy)}_3^{2+} + A \quad (4.3)$$

When the ruthenium photosensitizer absorbs light, the excited molecule, Ru(bpy)$_3^{2+*}$ will be generated (4.1). The next step is the electron transfer to a viologen acceptor in reaction (4.2). Reaction 4.3 is backward electron transfer from a reduced acceptor, A$^-$, to an oxidized electron donor, Ru(bpy)$_3^{3+}$. When the acceptor A is MV$^{2+}$, $k$ and $k_r$ are $2.4 \times 10^9 \text{M}^{-1}\text{s}^{-1}$ and $8.3 \times 10^9 \text{M}^{-1}\text{s}^{-1}$ in CH$_3$CN, respectively. In aqueous solution, the corresponding values are $5.6 \times 10^9 \text{M}^{-1}\text{s}^{-1}$ and $2.4 \times 10^9 \text{M}^{-1}\text{s}^{-1}$, respectively [3,4]. Therefore, the energy wasting reverse reaction, back electron transfer, needs to be delayed for an efficient charge separation.
Heterogeneous supports including micells [5], vesicles [6], silica gel [7], clays [8] and zeolites [3, 9, 10, 11] have been studied to slow the back electron transfer in \( \text{Ru(bpy)}_3^{2+} \) and viologen system. Among them, zeolites have well-defined microporous structures in which photosensitizers and electron acceptors can be arranged. Also positively charged viologen cations can be ion exchanged into zeolite pores easily. Several of zeolite-based charge separation systems have been investigated and found to be effective for the generation of long-lived charge separated species. Dutta and coworkers reported series of studies which explored the utility of zeolite entrapped \( \text{Ru(bpy)}_3^{2+} \) for photoinduced charge separation [9, 11-13]. The formation of methyl viologen radicals (MV\(^{\cdash+}\)) upon irradiation of \( \text{Ru(bpy)}_3^{2+} \) loaded zeolite particles were observed in these studies. The back electron transfer between \( \text{Ru(bpy)}_3^{3+} \) and MV\(^{\cdash+}\) is retarded to some extent within the zeolite framework. Zeolite-based systems with alkyl spacer groups between photosensitizer and acceptor ends have been explored for photoinduced electron transfer reactions [14, 15]. In these cases, dyad molecules are synthesized in solution and ion-exchanged on the surface of zeolites. The intramolecular electron transfer reactions between \( [(\text{bpy})_3\text{Ru}]^{2+} \) sensitizer and viologen acceptor were investigated and the back electron transfer was \( 10^5 \) times slower than in solution.

In this study, we designed a system in which \( [(\text{bpy})_2\text{Ru(dmb})]^{2+} \) (dmb= 4,4\-'-dimethyl-2,2\-'-bipyridine) is covalently bonded to diquat acceptors in the zeolite pores. The dyad molecules are incorporated in zeolite by a modified ship-in-a-bottle synthesis. The strategy for this synthesis was the incorporation of alkyl dihalides in the zeolite followed by the reaction with \( [(\text{bpy})_2\text{Ru(dmb-(L or L\,\prime)-dmb})]^{2+} \) in the solution where L
or L’ is a conjugated link between two dmb groups as shown in Figure 4.2. The pyridine nitrogens in dmb ligand react with dihalide units and resulted in [(bpy)$_2$Ru(dmb-(L or L’)-4DQ)]$^{4+}$ (4DQ$^{2+}$ = N,N’-tetramethylene-2,2’-bipyridinium) dyads partially incorporated in zeolites. To improve the efficiency of light absorption, ruthenium units of the dyads stay on the surface of zeolites, while viologen acceptor units are in the supercages of zeolite Y. This geometry is also desirable for reduction of Ru$^{3+}$ after the electron transfer. Ru$^{3+}$ needs to be accessible to the catalysts and water to be reused as an electron donor. The permanent charge separation from [(bpy)$_2$Ru(dmb)]$^{2+}$ photosensitizer bound to zeolite to propylviologen sulfonate (PVS) acceptors in solution was achieved through intrazeolitic electron transfer using consecutive intermolecular electron transfer reactions to second and third viologen acceptors.

EXPERIMENTAL SECTION
The synthetic methods of compounds, [(bpy)$_2$Ru(dmb-L or L’-4DQ)]$^{4+}$ and [(bpy)$_2$Ru(dmb-L or L’-4DQ)]$^{4+}$-Y were developed by Dr. Amitava Das. The solid state photolysis data and NMR spectra of ligand (dmb-L’-dmb) were provided by Dr. Yanghee Kim.

Chemicals and materials Zeolite Y (LZY-52) was donated from Union Carbide. Prior to use, zeolite Y was ion exchanged with 2M NaCl solutions and calcined at 500°C to remove any impurities. This zeolite was activated in vacuum at 500°C overnight. Tetrahydrofuran (THF) and hexane was refluxed over potassium metal and distilled immediately before use. Acetonitrile and diisopropylamine were dried with CaH$_2$. All
other solvents were used as received. Lithium diisopropylamide (LDA) was prepared in situ from equimolar amounts of butyllithium (Aldrich) and diisopropylamine (Aldrich). \(N,N'\text{-tetramethyl-2,2'-bipyridinium dibromide (4DQ}^{2+}\text{)}\) was synthesized as described by Homer and Tomilson [16] and in the previous chapter. Propyl Viologen Sulfonate (PVS) was also prepared following literature procedures [17] and previous chapter. \((2,2'\text{-bipyridyl})\text{ruthenium(II) chloride hexahydrate (Ru(bpy)}_3^{2+}, \text{Strem Chemicals)}, \text{cis-dichlorobis(2,2'-bipyridine)ruthenium(II) dihydrate ( (bpy)}_2\text{RuCl}_2, \text{Strem chemicals)}, \quad \) 

\(4,4'\text{-dimethyl-2,2'-bipyridine (dmb, Aldrich)}, \text{1,4-dibromo butane, terephthaldicarboxaldehyde (Aldrich), phosphoryl chloride (Aldrich), AIBN (Lancaster) and methyl viologen dichloride hydrate (MV}^{2+}, \text{Aldrich) was purchased with the highest purity available and used as received. N-bromosuccinimide (NBS, Aldrich) was recrystallized prior to use.}

**Synthesis of 1,4-bis[2-(4'-methyl-2,2'-bipyrid-4-yl)ethenyl]benzene (dmb-L-dmb)**

The ligand was prepared according to the literature method with slight modifications [18]. To a THF solution of dmb(1 equiv, 20mmol, 3.685g), cooled to 0°C, a solution of LDA (1 equiv, 20 mmol) was added dropwise. The solution immediately turned to the deep purple color of the dmb anion. After one hour of stirring, terephthalaldehyde (0.5 equiv, 10mmol, 1.34g) dissolved in THF was added to the dmb solution dropwise. The reaction mixture was allowed to warm to room temperature and stirred until the deep purple color of the anion disappeared followed by the quenching with water. After solvent evaporation, the crude dialcohol product was dissolved in chloroform and purified by the solvent extraction procedure using chloroform and water. To a solution of
the dialcohol (1 equiv, 10mmol) dissolved in pyridine, a pyridine solution of phosphoryl chloride (2 equiv, 20mmol, 3.1g) was added for dehydration. The solution was stirred for 2 hours and evaporated to dryness. The crude dehydration product was purified by solvent extraction and chromatography. $^1$H NMR (CHCl$_3$) $\delta$ 8.60 (d-d), 8.27(s), 7.59(s), 7.49(s), 7.38(d-d), 7.16(m), 2.46(s)

**Synthesis of [Ru(bpy)$_2$(dmb-L-dmb)](PF$_6$)$_2$** [Ru(bpy)$_2$(dmb-L-dmb)](PF$_6$)$_2$ was prepared by refluxing [(bpy)$_2$RuCl$_2$] (1 equiv, 0.14mmol, 74mg) with excess amount of dmb-L-dmb (3 equiv, 0.42mmol, 0.20g) to prevent formation of dinuclear complex. The dmb-L-dmb ligand was completely dissolved in CHCl$_3$ and [(bpy)$_2$RuCl$_2$] was added to the solution. The reaction mixture was refluxed for 7 hours. The initial dark purple solution turned to the red color of [Ru(bpy)$_2$(dmb-L-dmb)](Cl)$_2$ as the reaction progresses. The crude product was evaporated to dryness. The red solid was dissolved in water and filtered to remove excess dmb-L-dmb ligand. The crude product was precipitated with aqueous NH$_4$PF$_6$ to form [Ru(bpy)$_2$(dmb-L-dmb)](PF$_6$)$_2$. The collected solid was purified by chromatography on neutral alumina (Grade III) using CH$_2$Cl$_2$ (85%)- CH$_3$OH (15%) mixtures as eluent. $^1$H NMR (CD$_3$CN) $\delta$ 8.50 (m), 8.21(s), 7.95(m), 7.65(m), 7.46(m), 7.28(m), 7.18(m), 2.50(s), 2.38(s)

**Synthesis of [Ru(bpy)$_2$(dmb-L-4DQ)](PF$_6$)$_4$** (dmb-L-4DQ = 1-[2-(4'-methyl-2,2'-bipyrid-4-yl)ethenyl]- 4-[2-(4’-methyl-N,N'-tetramethylene-2,2’-bipyrid-4-yl)ethenyl]benzene) [Ru(bpy)$_2$(dmb-L-4DQ)](PF$_6$)$_4$ was synthesized by the reaction of [Ru(bpy)$_2$(dmb-L-dmb)](PF$_6$)$_2$ (28 $\mu$mol, 33mg) and 1, 4-dibromobutane(6.1 mg, 28$\mu$mol). Reaction was performed in 3:1 acetonitrile/toluene mixed solvent. The reaction
mixture was refluxed for 2 days and dried. The crude product is redissolved in acetonitrile followed by the addition of NH₄PF₆. The mixture was stirred for 15 minutes at room temperature and excess PF₆ salt was removed by solvent extraction. The product was purified by chromatography on neutral alumina (Grade III) using acetonitrile (70%)-Toluene(30%) mixtures as eluent. ¹H NMR (CD₃CN) δ 8.50 (m), 8.21(s), 7.95(m), 7.65(m), 7.46(m), 7.46 (m), 7.28(m), 7.18(m), 2.50(s), 2.38(s), 1.21(s), 0.85(s)

**Preparation of C₄H₈Br₂-Y** Activated zeoliteY (1g) and 1,4-dibromo butane (0.4mmol, 86mg) was stirred overnight in dried hexane. The zeolite was washed thoroughly with hexane after the reaction. Loading was limited to 0.8 mole equivalent of 1,4-dibromobutane per one mole of supercages in zeolite.

**Synthesis of [Ru(bpy)₂(dmb-L-4DQ)]⁺⁺ -Y** [Ru(bpy)₂(dmb-L-4DQ)]⁺⁺ -Y was prepared by the reaction of [Ru(bpy)₂(dmb-L-dmb)](PF₆)₂ (5 µmol, 5.9 mg) and C₄H₈Br₂-Y (1g). Reaction was performed in 3:1 acetonitrile/toluene mixed solvent. The reaction mixture was refluxed for 3 days followed by extensive washing with acetonitrile. The washing was continued till the solvent was free from the red color of Ru(II) complex. Then unreacted dihalide was removed by soxhlet extraction using CH₃Cl as a solvent (for about 7 days). The resulting solid was washed thoroughly with 0.5M NaCl at room temperature followed by sonication at 55 °C. Finally, the solid was washed with distilled water to remove excess NaCl and dried.

**Synthesis of Trans-1,2-bis-[4-(4’-methyl)-2,2’-bipyridyl]ethene (dmb-L’-dmb)** The ligand was prepared according to the literature method [19] with slight modification.
dmb-L’-dmb ligand is formed by the reaction of 4’-methyl-2,2’-bipyridyl-4-carbaldehyde and ((4-(4’-methyl)-2,2’-bipyridyl)methyl)triphenyl phosphonium bromide.

4’-methyl-2,2’-bipyridyl-4-carbaldehyde was made by the reaction of dmb and SeO₂. Dmb (0.9g, 4.84 mmol) and SeO₂ (0.55g, 4.95 mmol) were added to 1,4-dioxane (25ml) and the mixture was refluxed under Ar blanket for a day. The hot solution was filtered to remove black precipitates of Se metal. Hot filtrate was allowed to cool to room temperature, at which most of carboxylic acid crystallizes. These acid crystals were removed by another filtration and solvents in the filtrate were removed by rotary evaporation. The recovered solid was dissolved in ethyl acetate and remaining acid derivative was removed by solvent extraction with 0.1M Na₂CO₃. Ethyl acetate layer was collected. Another solvent extraction step with 0.2M NaHSO₃ took desired aldehyde product to the aqueous phase. The pH of the aqueous phase was adjusted to 9.0 with Na₂CO₃ and the desired product was extracted to CH₂Cl₂ layer. Typical reaction yield was 40% based on the amount of starting material. ¹H NMR (CDCl₃) δ 10.15 (s), 8.85(d), 8.81(s), 8.57(d), 8.24(s), 7.68 (d), 7.18(d), 2.44(s)

The other reactant for the synthesis of (dmb-L’-dmb) is ((4-(4’-methyl)-2,2’-bipyridyl)methyl)triphenyl phosphonium bromide. To prepare ((4-(4’-methyl)-2,2’-bipyridyl)methyl)triphenyl phosphonium bromide, 4-(Bromomethyl)-4’-methyl-2,2’-bipyridine was synthesized by partial oxidation of one of the methyl groups of dmb by N-bromosuccinimide (NBS). 10.1 molar equivalents of NBS were added to the dmb solution of CCl₄. Trace amount of AIBN was added and the mixture was heated for 2 hours under Ar blanket. While refluxed, the reaction vessel was irradiated with 500 W
lamp (Regent, WZ 505). After cooling, the mixture was filtered to remove decomposed product of NBS followed by solvent evaporation. The product was purified by chromatography with SiO2 using 98:2 volume ratio of CH2Cl2-acetone mixture as an eluent. Typical reaction yield was 60-75%. 1H NMR (CDCl3) δ 8.62(d), 8.48(d), 8.35(s), 8.19(s), 7.25(d), 7.08(d), 4.42(s), 2.40(s)

((4-(4’-methyl)-2,2’-bipyridyl)methyl)triphenyl phosphonium bromide is synthesized by the reaction of 4-(Bromomethyl)-4’-methyl-2,2’-bipyridine and triphenyl phosphine. 4-(Bromomethyl)-4’-methyl-2,2’-bipyridine (0.5g, 1.9mmol) and excess PPh3 (5g, 19 mmol) were added to toluene and the solution was heated at 60°C for 2h. The mixture was cooled to room temperature and filtered to yield precipitates ((4-(4’-methyl)-2,2’-bipyridyl)methyl)triphenyl phosphonium bromide. This reaction is almost quantitative. 1H NMR (DMSO) δ 8.63(d), 8.52(d), 8.26(s), 8.19(s), 8.00(d), 7.86(m), 7.38(d), 7.16(d), 5.58(s), 5.51(s), 2.61(s)

4’-methyl-2,2’-bipyridylne-4-carbaldehyde(0.110g, 0.56 mmol) and ((4-(4’-methyl)-2,2’-bipyridyl)methyl)triphenyl phosphonium bromide (0.335g, 0.64 mmol) were reacted to form the ligand (dmb-L’-dmb) in the presence of NaOEt. Initially, 4’-methyl-2,2’-bipyridyline-4-carbaldehyde and ((4-(4’-methyl)-2,2’-bipyridyl)methyl)triphenyl phosphonium bromide were dissolved in ethanol and stirred under Ar blanket at 0°C for 30 minutes. A solution of 0.3M NaOEt in ethanol (20ml) was added dropwise over a 2 min period. The solution was warmed to room temperature after that. After 18h, the volume was reduced to half of the original volume by evaporation and H2O was added to decompose remaining NaOEt. The white powder of (dmb-L’-dmb)
ligand was isolated by filtration. The product was further purified with SiO₂ column chromatography. Hexane-CHCl₃ mixture (1:9, v/v) was used as an eluent in the beginning and the amount of hexane was slowly decreased until pure CHCl₃ was used as an eluent. The composition of eluent was slowly changed to CH₃OH-CHCl₃ by the slow addition of methanol. Typical synthetic yield was 35%. ¹H NMR (CDCl₃) δ 8.65(d), 8.56(s), 8.53(d), 8.23(s), 7.42(s), 7.38(d), 7.15(d), 2.42(s)

**Synthesis of [Ru(bpy)₂(dmb-L’-dmb)](PF₆)₂** [Ru(bpy)₂(dmb-L’-dmb)](PF₆)₂ was prepared by refluxing [(bpy)₂RuCl₂] (1 equiv) with excess amount of dmb-L’-dmb (3 equiv). The dmb-L’-dmb ligand was completely dissolved in EtOH-H₂O mixed solvent (3:1, v/v) and [(bpy)₂RuCl₂] was added to the solution. The reaction mixture was refluxed for 8 hours. The volume of the dark red solution was reduced to approximately 10 ml after reflux. Saturated aqueous solution of KPF₆ was added with stirring to precipitate [Ru(bpy)₂(dmb-L’-dmb)] (PF₆)₂. The mixture was kept refrigerated overnight and filtered. The collected solid was purified by chromatography on silica (Aldrich, grade 922, -200 mesh) using CH₃CN-saturated aqueous solution of NH₄PF₆ (98:2, v/v) as eluent. First major fraction was collected and solvent was removed by rotary evaporator. Dried product was dissolved in minimum volume of CH₃CN and further purified by Al₂O₃ (grade III) column chromatography. CH₃CN-toluene (6:4, v/v) mixture was used as eluent. Generally second fraction is the desired product as well as the major product. ¹H NMR (CD₃CN) δ 8.71(m), 8.65(d), 8.50(m), 8.53(s), 8.40(s), 8.32(s), 8.23(s), 8.0(m), 7.74(d), 7.70(d), 7.63(s), 7.55(m), 7.42(d), 7.28(m), 7.2(m), 7.15(d), 2.60(s), 2.52(s)
Synthesis of \([\text{Ru}(bpy)_2(dmb-L'\text{-}4DQ)](\text{PF}_6)_4\) (dmb-L'-4DQ = Trans-1-[4-(4’-methyl)-2,2’-bipyridyl]-2-[4-(4’-methyl)-N,N’-tetramethylene-2,2’-bipyridyl]ethane) \([\text{Ru}(bpy)_2(dmb-L'\text{-}4DQ)](\text{PF}_6)_4\) was synthesized by the reaction of \([\text{Ru}(bpy)_2(dmb-L'-dmb)](\text{PF}_6)_2\) and 1, 4-dibromobutane. Reaction was performed in 3:1 acetonitrile/toluene mixed solvent. The reaction mixture was refluxed for 2 days and dried. The crude product is redissolved in acetonitrile followed by the addition of \(\text{NH}_4\text{PF}_6\). The mixture was stirred for 15 minutes at room temperature and excess \(\text{PF}_6\) salt was removed by solvent extraction. The product was purified by chromatography on neutral alumina (Grade III) using acetonitrile (70%)-Toluene(30%) mixtures as eluent. \(^1\text{H} \text{NMR} \ (\text{CD}_3\text{CN}) \delta \ 8.71(\text{m}), 8.65(\text{d}), 8.50(\text{m}), 8.53(\text{s}), 8.40(\text{s}), 8.32(\text{s}), 8.23(\text{s}), 8.0(\text{m}), 7.74(\text{d}), 7.70(\text{d}), 7.63(\text{s}), 7.55(\text{m}), 7.42(\text{d}), 7.28(\text{m}), 7.2(\text{m}), 7.15(\text{d}), 3.84(\text{m}), 2.60(\text{s}), 2.55(\text{m}), 2.52(\text{s}), 1.1(\text{m}), 0.85(\text{m}) \)

Synthesis of \([\text{Ru}(bpy)_2(dmb-L'\text{-}4DQ)]^{4+} - \text{Y}\) \([\text{Ru}(bpy)_2(dmb-L'\text{-}4DQ)]^{4+} - \text{Y}\) was prepared by the reaction of \([\text{Ru}(bpy)_2(dmb-L'-dmb)](\text{PF}_6)_2\) and \(\text{C}_4\text{H}_8\text{Br}_2\text{-Y}\). \(\text{C}_4\text{H}_8\text{Br}_2\text{-Y}\) was prepared as described before. Reaction was performed in 3:1 acetonitrile/toluene mixed solvent. The reaction mixture was refluxed for 3 days followed by extensive washing with acetonitrile. The washing was continued till the solvent was free from the red color of Ru(II) complex. Then unreacted dihalide was removed by soxhlet extraction using \(\text{CH}_3\text{Cl}\) as a solvent (for about 7 days). The resulting solid was washed thoroughly with 0.5M \(\text{NaCl}\) at room temperature followed by sonication at 55 °C. Finally, the solid was washed with distilled water to remove excess \(\text{NaCl}\) and dried.
Dissolution of zeolite \([\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^{4+} - \text{Y} \text{ or } [\text{Ru(bpy)}_2(\text{dmb-L’-4DQ})]^{4+} - \text{Y}\) was treated in acidic solution to dissolve zeolite framework and characterize entrapped \([\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^{4+} - \text{Y} \text{ or } [\text{Ru(bpy)}_2(\text{dmb-L’-4DQ})]^{4+} - \text{Y}\). 20ml of 1% HF solution was added to 200 mg of zeolitic sample and stirred for 30 minutes. Zeolite powders were dissolved after stirring and the solution turned pale orange color of Ruthenium complexes. Sufficient amount of KPF₆ was added to the solution to form Ru(bpy)₂(dmb-L-4DQ)(PF₆)₄ or Ru(bpy)₂(dmb-L’-4DQ)(PF₆)₄ followed by the addition of 20ml dichloromethane. The dichloromethane layer turned to the pale orange color due to the ruthenium complexes. The organic layer was collected and dried for spectroscopic studies.

Electrochemistry All electrochemistry measurements were carried out with a Princeton Applied Research model 273 potentiostat linked to EG&G PARC model 250 software. Cyclic voltammetry, differential pulse voltammetry were run in acetonitrile with 0.10M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. A freshly polished platinium disk electrode (2mm diameter, CH instruments) was used as a working electrode and platinium wire electrode was used as a counter electrode. The reference electrode was a Ag electrode with a potential of 0.48 V versus ferrocenium/ferrocene (Fc/Fc⁺) couple in acetonitrile as an standard. All potentials reported here are versus the Fc/Fc⁺ couple unless mentioned otherwise.

Photolysis The light source was a xenon arc lamp equipped with a water filter, a 420nm cutoff filter, and a mirror that reflects radiation in the range of 420-650nm. The
power of the radiation incident on the substrate side of the cell was measured by a Coherent 210 power meter and found to be 250 mW/cm².

For solid state photolysis with sacrificial electron donor, a pellet of $[\text{Ru} (\text{bpy})_2 (\text{dmb-L-4DQ})]^{4+}$-Y was immersed in 1M Na$_2$EDTA solution for 5 minutes. The pellet was dried under vacuum for 48 hours. This Na$_2$EDTA-$[\text{Ru} (\text{bpy})_2 (\text{dmb-L-4DQ})]^{4+}$-Y pellet was placed in an anaerobic diffuse reflectance cell in a dry box and photolyzed with a xenon arc lamp. The growth of 4DQ$^{2+}$ radical ($4\text{DQ}^{2+}/4\text{DQ}^{2-}$) was monitored with a diffuse reflectance UV-Vis spectrophotometer (Shimadzu, UV-2501PC with a ISR-2200 integrating sphere attachment).

For solid state photolysis, fifty milligrams of $[\text{Ru} (\text{bpy})_2 (\text{dmb-L-4DQ})]^{4+}$-Y were ion exchanged twice with a 0.1M solution of MV$^{2+}$ overnight and dried under vacuum for 48 hours. This $[\text{Ru} (\text{bpy})_2 (\text{dmb-L-4DQ})]^{4+}$-MV$^{2+}$-Y powder was placed in an anaerobic diffuse reflectance cell in a dry box and exposed to the ambient light. The growth of methylviologen radical (MV$^{++}$) was monitored with a diffuse reflectance UV-Vis spectrophotometer. After the exposure to the room light, the solid sample was re-ion exchanged with NaCl solution to study the recovery of ruthenium compound.

For suspension photolysis, fifty milligrams of $[\text{Ru} (\text{bpy})_2 (\text{dmb-L-4DQ})]^{4+}$-Y were ion exchanged twice with a 0.1M solution of N,N’-trimethylene-2,2’-bipyridinium ions (3DQ$^{2+}$) overnight. 10 mg of $[\text{Ru} (\text{bpy})_2 (\text{dmb-L-4DQ})]^{4+}$-3DQ$^{2+}$-Y and 10 mg of PVS were placed in an NMR tube and degassed water was distilled over to the tube. Freeze-pump-thaw cycle was repeated three times to deoxygenate the sample completely. The tube was sealed and photolyzed, and the growth of PVS radical in solution was monitored.
with a UV-Vis spectrophotometer. The amount of PVS radical was calculated by using beer’s law, \( A = \varepsilon b c \). Calibrated value for \( b \) for the photolysis tube is 0.32 cm. Same photolysis experiment was repeated with \([\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+\) and PVS suspension without 3DQ\(^{2+}\) ion exchange for comparison.

Same suspension photolysis experiments were conducted with samples of \([\text{Ru(bpy)}_3]^{2+}\)-Y and \([\text{Ru(bpy)}_2(\text{dmb-L’-4DQ})]^4^+\)-Y.

RESULTS

I. Synthesis and photochemical studies of \([\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+\)-Y

Synthesis of \([\text{Ru(bpy)}_2(\text{dmb-L-dmb})](\text{PF}_6)_2\) and \([\text{Ru(bpy)}_2(\text{dmb-L-4DQ})](\text{PF}_6)_4\)

(dmb-L-dmb) ligand was prepared as described in the literature with slight modifications [18]. The synthetic scheme is shown in Figure 4.3 along with metallation procedure. \(^1\)H NMR of (dmb-L-dmb) is shown in Figure 4.4. NMR and mass spectral analysis matches with literature data [18], which proves the formation of the ligand.

\([\text{Ru(bpy)}_2(\text{dmb-L-dmb})](\text{PF}_6)_2\) was synthesized by the reaction of \([\text{((bpy)}_2\text{RuCl}_2]\) with (dmb-L-dmb) ligand as shown in Figure 4.3. Excess amount of ligand (3 equiv) was used to prevent the formation of binuclear complexes. \(^1\)H NMR in Figure 4.5 and mass analysis results confirmed the formation of \([\text{Ru(bpy)}_2(\text{dmb-L-dmb})](\text{PF}_6)_2\) complex.

\([\text{Ru(bpy)}_2(\text{dmb-L-4DQ})](\text{PF}_6)_4\) was synthesized by the reaction of \([\text{Ru(bpy)}_2(\text{dmb-L-dmb})](\text{PF}_6)_2\) and 1, 4-dibromobutane as shown in Figure 4.6. This NMR spectrum of \([\text{Ru(bpy)}_2(\text{dmb-L-4DQ})](\text{PF}_6)_4\) in CD\(_3\)CN is shown in Figure 4.7. \(^1\)H
NMR in acetonitrile-d solvent showed two additional methylene peaks at 1.21 ppm and 0.86 ppm, which confirmed that the available nitrogen in dmb end of the compound are linked by four methylene groups from 1,4-dibromobutane.

**Synthesis and properties of [Ru(bpy)₂(dmb-L-4DQ)]⁴⁺ - Y** Zeolite Y was impregnated with 1,4-dibromobutane as shown in Figure 4.8 prior to the synthesis of [Ru(bpy)₂(dmb-L-4DQ)]⁴⁺ - Y. [Ru(bpy)₂(dmb-L-4DQ)]⁴⁺ - Y was prepared by the reaction of [Ru(bpy)₂(dmb-L-dmb)](PF₆)₂ and zeolite-incorporated 1,4-dibromobutane (C₄H₈Br₂-Y) as shown in Figure 4.9.

To investigate the loading level and the integrity of the dyad molecule, [Ru(bpy)₂(dmb-L-4DQ)]⁴⁺ - Y was treated in acidic solution to dissolve the zeolite framework and leave the dyad molecules intact in solution. ¹H NMR spectrum of the extracted complex (Figure 4.10) agrees with that of solution-synthesized [Ru(bpy)₂(dmb-L-4DQ)](PF₆)₄. (Figure 4.7)

Optical Spectroscopic Studies of (dmb-L-dmb), [Ru(bpy)₂(dmb-L-dmb)]²⁺, [Ru(bpy)₂(dmb-L-4DQ)]⁴⁺ and [Ru(bpy)₂(dmb-L-4DQ)]⁴⁺-Y UV-Vis absorption spectrum of (dmb-L-dmb) in CH₃CN is shown in Figure 4.11(a). As described in the literature [18], the ligand has an absorption maximum at 356 nm and exhibits strong emission with a maximum at 420 nm. UV-Vis absorption spectra of [Ru(bpy)₃](PF₆)₂, [Ru(bpy)₂(dmb-L-dmb)](PF₆)₂ and [Ru(bpy)₂(dmb-L-4DQ)](PF₆)₄ in CH₃CN are shown in Figure 4.11(b). The absorption spectrum of [Ru(bpy)₂(dmb-L-dmb)](PF₆)₂ show both intra ligand and metal-to-ligand charge-transfer (MLCT) transitions at 368 nm and 457 nm, respectively. The absorption maximum of the MLCT transition of [Ru(bpy)₂(dmb-
L-dmb\(^{2+}\) is red shifted with 7 nm difference from the absorption maximum of MLCT transition of [Ru(bpy)\(_3\)]\(^{2+}\)(PF\(_6\))\(_2\) at 450nm, which is due to the ligand change from bpy to conjugated ligand,(dmb-L-dmb). The red shift is caused by the lower \(\pi^*\) orbital of the dmb-L-dmb ligand due to conjugation. UV-Vis absorption spectrum of [Ru(bpy)\(_2\)(dmb-L-4DQ)](PF\(_6\))\(_4\) in CH\(_3\)CN also shows the intra ligand and metal-to-ligand charge-transfer (MLCT) transitions at 366nm and 457nm, respectively. The absorption spectrum of [Ru(bpy)\(_2\)(dmb-L-4DQ)](PF\(_6\))\(_4\) did not show any noticeable change from the absorption spectrum of [Ru(bpy)\(_2\)(dmb-L-dmb)](PF\(_6\))\(_2\) as shown in Figure 4.11(b).

Figure 4.12 shows the UV-Vis absorption spectrum of dissolved [Ru(bpy)\(_2\)(dmb-L-4DQ)]\(^{4+}\)-Y. [Ru(bpy)\(_2\)(dmb-L-4DQ)]\(^{4+}\)-Y was treated with acid to dissolve zeolite and leave ruthenium compounds intact. Extracted ruthenium compounds were dissolved in CH\(_3\)CN and the solution was used for spectroscopic analysis. Comparing with the absorption spectrum of solution synthesized [Ru(bpy)\(_2\)(dmb-L-4DQ)](PF\(_6\))\(_4\), it shows the same intraligand and MLCT transitions at 366nm and 457 nm as the solution-synthesized [Ru(bpy)\(_2\)(dmb-L-4DQ)](PF\(_6\))\(_4\). Calculated loading level of [Ru(bpy)\(_2\)(dmb-L-4DQ)]\(^{4+}\) in zeolite Y from absorption study is ca. 1.0*10\(^{-6}\) mole/g zeolite, which is consistent with approximately monolayer coverage of zeolite external surface [14]. The Diffuse Reflectance UV-Vis spectrum of Ru(bpy)\(_2\)(dmb-L-4DQ)(PF\(_6\))\(_4\)–Y is shown in Figure 4.13. The spectrum shows the intraligand and MLCT transitions at 365 nm and 464 nm, respectively. Comparing with the solution-synthesized [Ru(bpy)\(_2\)(dmb-L-4DQ)](PF\(_6\))\(_4\), the diffuse reflectance spectrum of the zeolite-entrapped complex exhibits a slight red shift in the MLCT transition (457 vs 464 nm). This behavior is consistent with that seen...
previously for other zeolite entrapped complexes [20]. The UV-Vis absorption data of ruthenium compounds in solution or bound to zeolite surface are summarized in table 4.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Intraligand Transition maximum</th>
<th>MLCT transition maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)₂]²⁺</td>
<td>450 nm</td>
<td>450 nm</td>
</tr>
<tr>
<td>[Ru(bpy)₂(dmb-L-dmb)]²⁺</td>
<td>368 nm 457 nm</td>
<td></td>
</tr>
<tr>
<td>[Ru(bpy)₂(dmb-L-4DQ)]⁴⁺</td>
<td>366 nm 457 nm</td>
<td></td>
</tr>
<tr>
<td>[Ru(bpy)₂(dmb-L-4DQ)]⁴⁺-Y</td>
<td>366 nm 464 nm</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1 UV-Vis absorption data of ruthenium compounds

The emission spectra of [Ru(bpy)₂(dmb-L-dmb)](PF₆)₂ and [Ru(bpy)₂(dmb-L-4DQ)](PF₆)₄ in CH₃CN solution are shown in Figure 4.14 along with the emission spectrum of [Ru(bpy)₃](PF₆)₂. The quantum yield of [Ru(bpy)₂(dmb-L-dmb)](PF₆)₂ is 5% of the quantum yield of [Ru(bpy)₃](PF₆)₂ when both solutions were excited at 450nm. Emission quantum yields were calculated from the integration of the peak area between 530nm and 700nm in each emission spectrum. The quantum yield is corrected by the absorption intensity of each solution. The percentage calculation is based on the quantum yield of [Ru(bpy)₃](PF₆)₂ in CH₃CN solution which has the same absorption intensity as the solution of interest at 450nm (quantum yield of [Ru(bpy)₃](PF₆)₂ in CH₃CN is considered to be 100% for comparison). The quantum yield of [Ru(bpy)₂(dmb-L-4DQ)](PF₆)₄ is 8% of the quantum yield of [Ru(bpy)₃](PF₆)₂ when both solutions were
excited at 450nm. The emission of the solution of [Ru(bpy)$_2$(dmb-L-4DQ)](PF$_6$)$_4$ is from impurity, possibly from unreacted ruthenium compounds.

The emission spectra of [Ru(bpy)$_2$(dmb-L-dmb)]$^{2+}$-Y and [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$-Y as a solid sample are shown in Figure 4.15 along with the emission spectrum of [Ru(bpy)$_3$]$^{2+}$-Y. The quantum yield of [Ru(bpy)$_2$(dmb-L-dmb)]$^{2+}$-Y is 6% of the quantum yield of [Ru(bpy)$_3$]$^{2+}$-Y when both samples were excited at 450nm. The quantum yield is normalized based on the diffuse reflectance absorption intensity of each sample (quantum yield of Ru(bpy)$_3$$^{2+}$-Y is considered to be 100% for a comparison). The quantum yield of [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$-Y is 10% of the quantum yield of [Ru(bpy)$_3$]$^{2+}$-Y when excited at 450nm. As in the solution sample, the emission of [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$-Y is possibly from unreacted ruthenium compounds.

The emission data of ruthenium compounds in solution or bound to zeolite surface are summarized in table 4.2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Emission Intensity</th>
<th>Emission Maxima</th>
<th>Compound</th>
<th>Emission Intensity</th>
<th>Emission Maxima</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)$_3$]$^{2+}$</td>
<td>100%</td>
<td>605 nm</td>
<td>[Ru(bpy)$_3$]$^{2+}$-Y</td>
<td>100%</td>
<td>620</td>
</tr>
<tr>
<td>[Ru(bpy)$_2$(dmb-L-dmb)]$^{2+}$</td>
<td>5%</td>
<td>612 nm</td>
<td>[Ru(bpy)$_2$(dmb-L-dmb)]$^{2+}$-Y</td>
<td>6%</td>
<td>632</td>
</tr>
<tr>
<td>[Ru(bpy)$_2$(dmb-L-4DQ)]$^{2+}$</td>
<td>8%</td>
<td>612 nm</td>
<td>[Ru(bpy)$_2$(dmb-L-4DQ)]$^{3+}$-Y</td>
<td>10%</td>
<td>620</td>
</tr>
</tbody>
</table>

**Table 4.2** Emission data of ruthenium compounds
Slight red shift of emission maxima due to zeolite ion exchange or binding is observed in all cases. These results are also consistent with the results reported previously for other zeolite-entrapped species [20].

**Electrochemistry** Electrochemical properties of ruthenium complexes and related viologen compounds (Figure 1) were studied. Viologen compounds were used as electron acceptors for photoinduced electron transfer experiments, as described later.

Bipyridinium acceptors are positively charged and the size of molecules is smaller than the window to zeolite supercages (7.4 Å). Due to these features, viologen compounds can be ion exchanged into zeolite pores. The reduction potential of the bipyridinium ion is related to the angle between two pyridinium rings. It is reported in the literature that bigger interplanar dihedral angle usually results in more negative reduction potentials [21]. In the reduced form, the two aromatic rings are forced into a planar configuration to maintain an effective π-π resonance overlap. The methylene chain linking two quaternary nitrogens is longer in 4DQ2+, which causes the bigger distortion of pyridinium rings from planarity as compared to 3DQ2+. In the non-bridged 2,2'-bipyridinium compound like methyl viologen, the distortion is smaller than 3DQ2+ or 4DQ2+. This factor contributes to the more positive reduction potential of methyl viologen acceptor. Table 4.3 shows the reduction potentials of bipyridinium acceptors and dihedral distortion angles between two pyridinium rings. The actual cyclic voltammograms of these acceptors are shown in Figure 4.16-4.18. The reduction potentials of methyl viologen cation (MV2+) measured in our system agree with the values reported in the literature [22].
Bipyridinium acceptors | Reduction potential | Dihedral angle
---|---|---
$\text{MV}^{2+}$ | -0.825 | 37.2°
$\text{3DQ}^{2+}$ | -0.938 | 38.7°
$\text{4DQ}^{2+}$ | -1.030 | 62.2°

[a] As PF$_6^-$ salts. All potentials are versus Fe$^+/\text{Fc}$ in CH$_3$CN solution with 0.1M TBAPF$_6$ as supporting electrolyte $\nu=100$mVs$^{-1}$

Table 4.3 Electrochemical data of bipyridium acceptors

The data for the redox processes in $[\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+$ and $[\text{Ru(bpy)}_2(\text{dmb-L-dmb})]^2^+$ are compiled in table 4.4 together with the corresponding data for $[\text{Ru(bpy)}_3]^2^+$ and $4\text{DQ}^{2+}$ under the same condition. The cyclic voltammograms of $[\text{Ru(bpy)}_3]^2^+$ and $[\text{Ru(bpy)}_2(\text{dmb-L-dmb})]^2^+$ are shown in Figure 4.19 and 4.20, respectively. Cyclic voltammogram of $[\text{Ru(bpy)}_2(\text{dmb-L-dmb})]^2^+$ shows one redox curve at 0.845V and three reduction waves( -1.662V, -1.872V, -2.129V ). By comparison with the voltamograms observed for the model compounds $[\text{Ru(bpy)}_3]^2^+$ and (dmb-L-dmb) (Figure 4.21) ligand under the same condition, the redox curve at 0.845 V can be assigned to metal-centered oxidation ( Ru II to Ru III). The redox curve at $-1.662$ V can be assigned to the reduction of ligand (dmb-L-dmb). The other two reductions are from bpy groups attached to Ru metal.

Cyclic voltammograms of $[\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+$ show one oxidation wave(0.843V) and four reduction waves(-1.25V, -1.706V, -1.899V, -2.128V ) as shown in Figure 4.22. In this case, the voltammetric waves can be assigned to metal-centered
oxidation at 0.843 V (Ru II to Ru III) and a reduction of 4DQ\(^{2+}\) group in (dmb-L-4DQ)\(^{2+}\) ligand (-1.25V). One remaining dmb group in (dmb-L-4DQ) ligand shows a reduction wave at -1.706V. The other two reduction waves at -1.899V and -2.128V are from the reductions of two bipyridyl groups attached to Ru metal.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(bpy)(^{0/-})</th>
<th>(bpy)(^{0/-1})</th>
<th>(bpy)(^{0/-1})</th>
<th>(dmb-L-dmb)</th>
<th>DQ(^{2+/+})</th>
<th>Ru(^{3+/2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)(_3)](^{2+})</td>
<td>-2.178</td>
<td>-1.927</td>
<td>-1.738</td>
<td>-1.03</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>[(bpy)(_2)Ru(dmb-L-dmb)](^{2+})</td>
<td>-2.129</td>
<td>-1.872</td>
<td>-1.662</td>
<td>-2.128</td>
<td>-1.899</td>
<td>-1.706</td>
</tr>
</tbody>
</table>

[a] As PF\(_6^–\) salts. All potentials are versus Fe\(^+/0\) in CH\(_3\)CN solution with 0.1M TBAPF\(_6\) as supporting electrolyte \(\nu=100\text{mVs}^{-1}\)

**Table 4.4. Electrochemical data of Ruthenium Compounds**

The cyclic voltammograms of [Ru(bpy)\(_2\)(dmb-L-dmb)]\(^{2+}\) and [Ru(bpy)\(_2\)(dmb-L-4DQ)]\(^{4+}\) in Figure 4.20 and 4.22 shows broad and quasi reversible redox peaks of bipyridyl ligands. This is the result of the accumulation of the complex on the electrode. The electrodeposition is probably the result of reductive electro polymerization, a process that has been thoroughly studied for Ru(II) diimine complexes having olefinic moieties [18,23,24].
Photolysis The photochemistry of $[\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+ - \text{Y}$ was examined by using a reaction that involves electron transfer by a self-exchange mechanism and initiated by a photochemical process.

The photochemical system included $[\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+ - \text{Y}$ that was treated in Na$_2$EDTA solution. Na$_2$EDTA was adsorbed on the surface of zeolite to be utilized as sacrificial electron donor. This Na$_2$EDTA-$[\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+ - \text{Y}$ zeolite solid sample was irradiated with visible light in an anaerobic environment and the diffuse reflectance UV-Vis spectra were monitored. The basic reactions involved in the process are described in Figure 4.23. The chemical reactions occur as follows:

\[
\begin{align*}
[(\text{bpy})_2\text{Ru}^{2+}(\text{dmb-L-4DQ})^{2+}]_z & \xrightleftharpoons{\text{hv}} [((\text{bpy})_2\text{Ru}^{2+}(\text{dmb-L-4DQ})^{2+})]^z, \\
[(\text{bpy})_2\text{Ru}^{2+}(\text{dmb-L-4DQ})^{2+}]_z & \longrightarrow [(\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L-4DQ})^{+}]_z, \\
[(\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L-4DQ})^{+}]_z + \text{EDTA} & \longrightarrow [(\text{bpy})_2\text{Ru}^{2+}(\text{dmb-L-4DQ})^{+}]_z + \text{EDTA}^+ 
\end{align*}
\]

where the subscripts ‘s’ and ‘z’ represent solution and zeolite, respectively. Figure 4.24 shows the result of a typical photolysis of $[\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+ - \text{Y}$ solid sample. Curve I shows diffuse reflectance spectrum of Na$_2$EDTA-$[\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+ - \text{Y}$ before irradiation. The intraligand and MLCT transitions of the ruthenium compound are observed at 365nm and 464 nm, respectively. Curve II is diffuse reflectance spectrum of Na$_2$EDTA-$[\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+ - \text{Y}$ after 80 minutes of irradiation. The growth of a broad peak at 480nm is observed. The diffuse reflectance spectrum after 130 minutes of
irradiation is shown as curve III in Figure 4.24. After the irradiation, the solid sample is exposed to O₂ to remove radical species. The diffuse reflectance spectrum after oxygen exposure is shown as curve IV. The intensity of the peak at 480nm decreased due to the removal of DQ⁺⁺ by oxygen.

The photo induced electron transfer from the dyad molecule to the acceptor molecules in the zeolite was also investigated. The photochemical system included [Ru(bpy)₂(dmb-L-4DQ)]⁴⁺ -Y that was ion-exchanged with the other bipyridinium ion (MV²⁺). Ion exchanged zeolite solid sample was exposed to room light and the diffuse reflectance UV-Vis spectra was monitored. The basic reactions involved in the process are as follows:

\[
\begin{align*}
[(\text{bpy})_2\text{Ru}^{2+}(\text{dmb-L-4DQ})^2]^z & \xrightarrow{hv} [(\text{bpy})_2\text{Ru}^{2+}(\text{dmb-L-4DQ})^2]^z_x & \quad (1) \\
[(\text{bpy})_2\text{Ru}^{2+}(\text{dmb-L-4DQ})^2]^x & \rightarrow [(\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L-4DQ})^+]_z & \quad (2) \\
[(\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L-4DQ})^+]_z + \text{MV}^{2+} & \rightarrow [(\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L-4DQ})^2]^x_z + \text{MV}^{2+} & \quad (3)
\end{align*}
\]

The scheme of the photo electron transfer reaction is shown in Figure 4.25. Figure 4.26 shows the result of a typical diffuse reflectance spectra of [Ru(bpy)₂(dmb-L-4DQ)]⁴⁺-MV²⁺-Y solid sample. Curve I shows diffuse reflectance spectrum of [Ru(bpy)₂(dmb-L-4DQ)]⁴⁺-Y solid sample before MV²⁺ ion exchange. The intraligand and MLCT transitions of the ruthenium compound are observed at 365 nm and 464 nm, respectively. Curve II is diffuse reflectance spectrum of [Ru(bpy)₂(dmb-L-4DQ)]⁴⁺-MV²⁺-Y after ion
exchange and exposure to ambient light. The growth of MV• can be observed by the

growth of the peaks at 395 nm and 605 nm with exposure to ambient light. The intraligand
and MLCT transitions of [Ru(bpy)₂(dmb-L-4DQ)]⁴⁺ decreased significantly due to the
oxidation of Ru²⁺ metal center to Ru³⁺ in Curve II. Curve III in Figure 4.26 shows the
diffuse reflectance spectrum of the same zeolite sample after re-ion exchange with NaCl
solution. The peaks from MV• disappeared in curve III while the peaks from intraligand
and MLCT transitions of [Ru(bpy)₂(dmb-L-4DQ)]⁴⁺ are recovered.

Transfer of electrons from zeolite to solution to achieve long-lived charge
separation was studied by photolysis of [Ru(bpy)₂(dmb-L-4DQ)]⁴⁺ - Y in neutral propyl
viologen sulfonate (PVS) solution. In this case, zeolite sample was ion exchanged with
3DQ²⁺ prior to irradiation to build an electron relay system.

The basic reactions involved in solution photolysis are as follows:

\[
\begin{align*}
[(\text{bpy})_2\text{Ru}^{2+}(\text{dmb-L-4DQ})^{2+}]_z & \xrightarrow{\text{hv}} [(\text{bpy})_2\text{Ru}^{2+}(\text{dmb-L-4DQ})^{2+}]_z^* \quad (1) \\
[(\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L-4DQ})^{2+}]_z & \rightarrow [(\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L-4DQ})^+]_z \quad (2) \\
[(\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L-4DQ})^+]_z & + 3\text{DQ}^{2+}_z \rightarrow [(\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L-4DQ})^{2+}]_z + 3\text{DQ}^{*+}_z \quad (3) \\
3\text{DQ}^{*+}_z + 3\text{DQ}^{2+}_z & \rightarrow 3\text{DQ}^{2+}_z + 3\text{DQ}^{*+}_z \quad (4) \\
3\text{DQ}^{*+}_z + \text{PVS}_z & \rightarrow 3\text{DQ}^{2+}_z + \text{PVS}^{*-}_z \quad (5)
\end{align*}
\]
The intramolecular electron transfer reaction localizes an electron on the 4DQ$^{2+}$ acceptor end of the dyad. The charge will migrate onto the 3DQ$^{2+}$ acceptors in next cages of zeolite and to the other 3DQ$^{2+}$ acceptors by self-exchange reactions. Charges that migrate onto the zeolite surface can be transferred to PVS in the surrounding solution, resulting in long-lived charge separation. Measurement of the reduced viologen (PVS$^\bullet$) in solution by absorption spectroscopy provides a good measure of the charge separation efficiency. The scheme of the photo electron transfer reaction in PVS solution is shown in Figure 4.27. Figure 4.28 shows the UV-Vis absorption spectra of solution during photolysis of Ru(bpy)$_2$(dmb-L-4DQ)$^{4+}$-3DQ$^{2+}$-Y in aqueous solution of PVS. The peaks at 395 nm and 610 nm are from PVS PVS$^\bullet$ radical and the intensity of peaks increased as photolysis continued. Figure 4.29(a) shows the growth of PVS$^\bullet$ radical in solution for a typical suspension photolysis experiment with [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$-Y. When zeolite sample was ion exchanged with 3DQ$^{2+}$ before irradiation, the sample solution turned blue in an hour and absorption spectra indicated 11.6 nmols of PVS$^\bullet$ radical formation after 3 hours of irradiation and 3.88 nmols after 2 hours of irradiation. Since sacrificial electron donors are not used in this experiment, the maximum possible amount of PVS$^\bullet$ radical is 10 nmols (calculated from the loading level of [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$ in Y). Therefore approximately 100% of yield was achieved in 3 hours upon photoinduced electron transfer. The yield is 30% after 2 hours. Figure 4.29 (b) is the result of similar photolysis experiment without 3DQ$^{2+}$ ion exchange. In this case, the reduced 4DQ$^{4+}$ end in the dyad cannot transfer the electron directly to PVS since two species are spatially
separated by zeolite. Therefore little amount of PVS$^\bullet$ radical was generated (1.9 nmols) after 3 hours of irradiation.

For comparison, photolysis of $[\text{Ru(bpy)}_3]^{2+}$-Y in neutral propyl viologen sulfonate (PVS) solution was studied. The loading level of Ru(bpy)$_3$$^{2+}$ was 1 molecule in 20 supercages of zeolite Y. Ru(bpy)$_3$$^{2+}$-Y was ion exchanged with 4DQ$^{2+}$ prior to photolysis experiment. The photo electron transfer reactions are as follows:

$$[\text{Ru(bpy)}_3]_{\text{z}}^{2+} \xrightarrow{\text{hv}} [\text{Ru(bpy)}_3]_{\text{z}}^{2+\bullet}$$

$$[\text{Ru(bpy)}_3]_{\text{z}}^{2+\bullet} + 4\text{DQ}^{2+}_{\text{z}} \rightarrow [\text{Ru(bpy)}_3]_{\text{z}}^{3+} + 4\text{DQ}^{++}_{\text{z}}$$

$$4\text{DQ}^{++}_{\text{1z}} + 4\text{DQ}^{2+}_{\text{2z}} \rightarrow 4\text{DQ}^{2+}_{\text{1z}} + 4\text{DQ}^{++}_{\text{2z}}$$

$$4\text{DQ}^{++}_{\text{z}} + \text{PVS} \rightarrow 4\text{DQ}^{2+}_{\text{z}} + \text{PVS}^{++}$$

The excited electron from $[\text{Ru(bpy)}_3]^{2+\bullet}$ migrate onto the 3DQ$^{2+}$ acceptors in next cages of zeolite and to the other 3DQ$^{2+}$ acceptors by self-exchange reactions. Charges that migrate onto the zeolite surface can be transferred to PVS in the surrounding solution. Figure 4.30 shows the growth of PVS$^\bullet$ radicals in solution for a typical photolysis experiment with 1 molecule in 20 supercages loading of $[\text{Ru(bpy)}_3]^{2+}$ in zeolite Y. The absorption spectra indicated 12 nmols of PVS$^\bullet$ radical formation after 2 hours of irradiation. The maximum possible amount of PVS$^\bullet$ radical that can be generated from 10 mg of $[\text{Ru(bpy)}_3]^{2+}$-Y when the loading is 1 in 20 supercages is 245 nmols. The yield of photoinduced electron transfer in 2 hours of irradiation is only 4.8% in this case.
Comparing with the yield of photo electron transfer with $[\text{Ru(bpy)}_2(\text{dmb-L-4DQ}^{2+})]^{3+}-\text{Y}$ (30%), the yield is approximately 6 times larger in the new dyad system than in $[\text{Ru(bpy)}_3]^{2+}-\text{Y}$ photo electron transfer.

**II. Synthesis and photochemical studies of $[\text{Ru(bpy)}_2(\text{dmb-L’-4DQ})]^{4+}-\text{Y}$**

Synthesis of $[\text{Ru(bpy)}_2(\text{dmb-L’-dmb})](\text{PF}_6)_2$ and $[\text{Ru(bpy)}_2(\text{dmb-L’-4DQ})](\text{PF}_6)_4$

dmb-L’-dmb ligand is formed by coupling of 4’-methyl-2,2’-bipyridyline-4-carbaldehyde and ((4-(4’-methyl)-2,2’-bipyridyl)methyl)triphenyl phosphonium bromide via the Wittig reaction as described in Figure 4.31.

4’-methyl-2,2’-bipyridyline-4-carbaldehyde (compound I in Figure 4.31) was made by partial oxidation of one of the methyl groups of dmb by SeO$_2$. $^1$H NMR of the product shown in Figure 4.32 agrees with the characterization data of the literature [19].

The other reactant for the synthesis of (dmb-L’-dmb) is ((4-(4’-methyl)-2,2’-bipyridyl)methyl)triphenyl phosphonium bromide (compound III in Figure 4.31). To prepare ((4-(4’-methyl)-2,2’-bipyridyl)methyl)triphenyl phosphonium bromide, 4-(Bromomethyl)-4’-methyl-2,2’-bipyridine (compound II in Figure 4.31) was synthesized by partial oxidation of one of the methyl groups of dmb by N-bromosuccinimide (NBS). $^1$H NMR of the product in Figure 4.33 confirmed the formation of 4-(Bromomethyl)-4’-methyl-2,2’-bipyridine. ((4-(4’-methyl)-2,2’-bipyridyl)methyl)triphenyl phosphonium bromide is synthesized by the reaction of 4-(Bromomethyl)-4’-methyl-2,2’-bipyridine and triphenyl phosphine. The formation of the triphenyl phosphonium bromide salt was nearly quantitative and the $^1$H NMR data of the resulting salt in Figure 4.34 matches with the literature data. [19] dmb-L’-dmb ligand is formed by coupling of 4’-methyl-2,2’-
bipyridyline-4-carbaldehyde and ((4-(4'-methyl)-2,2'-bipyridyl)methyl)triphenyl phosphonium bromide. $^1$H NMR data of the ligand dmb-L’-dmb in Figure 4.35 match with the literature data [19].

$\text{[Ru(bpy)$_2$(dmb-L’-dmb)](PF_6)$_2$}$ was synthesized by the reaction of $[(\text{bpy})_2\text{RuCl}_2]$ with (dmb-L’-dmb) ligand as shown in Figure 4.36. $^1$H NMR shown in Figure 4.37 confirmed the formation of $[\text{Ru(bpy)}_2(\text{dmb-L’-dmb})]$(PF$_6$)$_2$ complex.

$\text{[Ru(bpy)$_2$(dmb-L’-4DQ)](PF_6)$_4$}$ was synthesized to study the spectroscopic properties of $[\text{Ru(bpy)}_2(\text{dmb-L’-4DQ})]^{4+}$ in solution. $[\text{Ru(bpy)}_2(\text{dmb-L’-4DQ})](\text{PF}_6)_4$ was formed by the reaction of $[\text{Ru(bpy)}_2(\text{dmb-L’-dmb})]$(PF$_6$)$_2$ and 1,4 dibromobutane as shown in Figure 4.38. $^1$H NMR in acetonitrile-d solvent showed four methylene peaks, which confirmed that the nitrogen in dmb end of the compound are linked by four methylene groups from 1,4 - dibromobutane. (Figure 4.39)

**Synthesis of $[\text{Ru(bpy)}_2(\text{dmb-L’-4DQ})]^{4+}$ -Y** The complex $[\text{Ru(bpy)}_2(\text{dmb-L’-4DQ})]^{4+}$ -Y was synthesized by the reaction of 1,4- dibromobutane incorporated in zeolite Y and $[\text{Ru(bpy)}_2(\text{dmb-L’-dmb})]^{2+}$ as described in Figure 4.40. To investigate the loading level of the dyad molecule, $[\text{Ru(bpy)}_2(\text{dmb-L’-4DQ})]^{4+}$ -Y was treated in acidic solution to dissolve the zeolite framework and leave the dyad molecules intact in solution. Calculated loading level of $[\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^{4+}$ in zeolite Y from absorption study is ca. 1.4* 10$^{-6}$ mole/g zeolite, consistent with approximately monolayer coverage of zeolite external surface [14].
Optical spectroscopic studies of [Ru(bpy)$_2$(dmb-L'-dmb)](PF$_6$)$_2$ and [Ru(bpy)$_2$(dmb-L'-4DQ)](PF$_6$)$_4$

UV-Vis absorption spectra of [Ru(bpy)$_2$(dmb-L'-dmb)](PF$_6$)$_2$ in CH$_3$CN are shown with the absorption data of [Ru(bpy)$_3$]$^{2+}$ in Figure 4.41. The spectra of [Ru(bpy)$_2$(dmb-L'-dmb)](PF$_6$)$_2$ have metal-to-ligand charge-transfer (MLCT) transitions at 458nm. The intraligand transition, which was seen with [Ru(bpy)$_2$(dmb-L-dmb)](PF$_6$)$_2$ at 360nm, was not observed with [Ru(bpy)$_2$(dmb-L'-dmb)](PF$_6$)$_2$. The maximum MLCT absorption of [Ru(bpy)$_3$](PF$_6$)$_2$ is 450 nm. Therfore MLCT absorption of [Ru(bpy)$_2$(dmb-L'-dmb)]$^{2+}$ is red-shifted from the MLCT absorption of [Ru(bpy)$_3$]$^{2+}$ by 8 nm due to the ligation of (dmb-L'-dmb).

The emission spectra of [Ru(bpy)$_2$(dmb-L'-dmb)](PF$_6$)$_2$ is shown in Figure 4.42 along with the emission spectrum of [Ru(bpy)$_3$](PF$_6$)$_2$. The quantum yield of [Ru(bpy)$_2$(dmb-L'-dmb)](PF$_6$)$_2$ is 6% of the quantum yield of [Ru(bpy)$_3$](PF$_6$)$_2$ when both solutions were excited at 450nm. Emission quantum yield was calculated from the integration of the peak area between 530nm and 750nm in each emission spectrum. The quantum yield is corrected by the absorption intensity of each solution. The percentage calculation is based on the quantum yield of [Ru(bpy)$_3$](PF$_6$)$_2$ in CH$_3$CN solution which has the same absorption intensity as the solution of interest at 450nm. Also, the emission of [Ru(bpy)$_2$(dmb-L'-dmb)](PF$_6$)$_2$ shows maximum at 645nm. The emission maximum of [Ru(bpy)$_3$](PF$_6$)$_2$ is 605 nm. Therefore it is red shifted by 30 nm due to the ligation of (dmb-L'-dmb).

UV-Vis absorption spectrum of [Ru(bpy)$_2$(dmb-L'-4DQ)](PF$_6$)$_4$ in CH$_3$CN is shown in Figure 4.43, which shows the same MLCT absorption at 458 nm as
[Ru(bpy)₂(dmb-L’-dmb)](PF₆)₂. The emission spectra of [Ru(bpy)₂(dmb-L’-4DQ)](PF₆)₄ is shown in Figure 4.44 along with the emission spectrum of [Ru(bpy)₃](PF₆)₂. The emission quantum yield of [Ru(bpy)₂(dmb-L’-4DQ)](PF₆)₄ is 8% of the quantum yield of [Ru(bpy)₃](PF₆)₂ when both solutions were excited at 450nm. The emission of the solution of [Ru(bpy)₂(dmb-L’-4DQ)](PF₆)₄ is possibly from unreacted ruthenium compounds. The emission data of ruthenium compounds in solution are summarized in table 4.5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Emission Intensity</th>
<th>Emission Maxima</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)₃]²⁺</td>
<td>100%</td>
<td>605 nm</td>
</tr>
<tr>
<td>[Ru(bpy)₂(dmb-L’-dmb)]²⁺</td>
<td>6%</td>
<td>643 nm</td>
</tr>
<tr>
<td>[Ru(bpy)₂(dmb-L’-4DQ)]²⁺</td>
<td>8%</td>
<td>648 nm</td>
</tr>
</tbody>
</table>

**Table 4.5** Emission data of ruthenium compounds

**Electrochemistry** The data for the redox processes in [Ru(bpy)₂(dmb-L’-dmb)]²⁺ and [Ru(bpy)₂(dmb-L’-4DQ)]⁴⁺ are compiled in table 4.6 together with the corresponding data for [Ru(bpy)₃]²⁺ and 4DQ²⁺ under the same condition. The cyclic voltammogram of [Ru(bpy)₂(dmb-L’-dmb)]²⁺ is shown in Figure 4.45. Cyclic voltammogram of [Ru(bpy)₂(dmb-L’-dmb)]²⁺ shows one oxidation wave (0.872V) and three reduction waves(-1.588V, -1.844V, -2.054V). The oxidation voltammetric waves can be assigned to metal-centered oxidation (RuII to Ru III). Three reduction waves can be assigned to a
reduction of conjugated (dmb-L'-dmb) ligand at \(-1.588\) V and two reductions from bpy groups attached to Ru metal.

Cyclic voltammograms of [Ru(bpy)₂(dmb-L'-4DQ)]⁴⁺ show one ruthenium oxidation wave (0.884 V) and a non-reversible reduction of 4DQ²⁺ group in (dmb-L-4DQ²⁺) ligand (-1.25 V) as shown in Figure 4.46. The broad reduction peaks between \(-2.0\) V and \(-1.0\) V are from other bipyridine ligands attached to Ru metal.

<table>
<thead>
<tr>
<th>compounds</th>
<th>(bpy)⁰⁻</th>
<th>(bpy)⁰⁻¹</th>
<th>(bpy)⁰⁻¹</th>
<th>(dmb-L'-dmb)</th>
<th>DQ²+/+</th>
<th>Ru⁵⁺/²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)₃]²⁺</td>
<td>-2.178</td>
<td>-1.927</td>
<td>-1.738</td>
<td></td>
<td></td>
<td>0.89</td>
</tr>
<tr>
<td>DQ²⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-1.03</td>
<td></td>
</tr>
<tr>
<td>[(bpy)₂Ru(dmb-L'-dmb)]²⁺</td>
<td>-2.054</td>
<td>-1.844</td>
<td>-1.588</td>
<td></td>
<td></td>
<td>0.872</td>
</tr>
<tr>
<td>[(bpy)₂Ru(dmb-L'-4DQ)]⁴⁺</td>
<td></td>
<td></td>
<td></td>
<td>-1.25</td>
<td></td>
<td>0.884</td>
</tr>
</tbody>
</table>

[a] As PF₆⁻ salts. All potentials are versus Fe⁺/Fc in CH₃CN solution with 0.1M TBAPF₆ as supporting electrolyte \(v=100\) mV/s⁻¹

**Table 4.6 Electrochemical data**

The cyclic voltammograms of [Ru(bpy)₂(dmb-L'-dmb)]²⁺ and [Ru(bpy)₂(dmb-L'-4DQ)]⁴⁺ in Figure 4.45 and 4.46 also show broad and quasi reversible redox peaks of bipyridyl ligands, which were also observed in the cyclic voltammograms of [Ru(bpy)₂(dmb-L-dmb)]²⁺ and [Ru(bpy)₂(dmb-L-4DQ)]⁴⁺. As discussed before, this is the result of the accumulation of the complex on the electrode.
**Photolysis** The photochemistry of [Ru(bpy)$_2$(dmb-L'-4DQ)]$^{4+}$-Y was examined by using a similar reaction as described in previous section. To study electron transfer to solution surrounding zeolite powders and achieve long-lived charge separation, photolysis of [Ru(bpy)$_2$(dmb-L'-4DQ)]$^{4+}$-Y in neutral propylviologen sulfonate (PVS) solution was studied. The basic reactions involved in solution photolysis are similar to the solution photolysis reaction with [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$-Y:

\[
\begin{align*}
((\text{bpy})_2\text{Ru}^{2+}(\text{dmb-L'}-4\text{DQ})^{2+})_z & \xrightarrow{\text{hv}} ((\text{bpy})_2\text{Ru}^{2+}(\text{dmb-L'-4DQ})^{2+})_z \\
((\text{bpy})_2\text{Ru}^{2+}(\text{dmb-L'-4DQ})^{2+})_z & \rightarrow ((\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L'-4DQ})^{+})_z \\
((\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L'-4DQ})^{+})_z & \rightarrow ((\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L'-4DQ})^{+})_z + 3\text{DQ}^{2+}_z \\
3\text{DQ}^{2+}_z + 3\text{DQ}^{2+}_z & \rightarrow 3\text{DQ}^{2+}_z + 3\text{DQ}^{2+}_z \\
3\text{DQ}^{2+}_z + \text{PVS}_z & \rightarrow 3\text{DQ}^{2+}_z + \text{PVS}^{2+}_z
\end{align*}
\]

Measurement of the reduced viologen (PVS$^\bullet$) in solution by absorption spectroscopy provides a good measure of the charge separation efficiency. Figure 4.47 shows the UV-Vis absorption spectra of solution during photolysis of [Ru(bpy)$_2$(dmb-L'-4DQ)]$^{4+}$-3DQ$^{2+}$-Y in aqueous solution of PVS. The peaks at 395 nm and 610 nm are from PVS PVS$^\bullet$ radical and the intensity of peaks increased as photolysis continued. Figure 4.48 shows the growth of PVS$^\bullet$ in solution for a typical photolysis experiment with [Ru(bpy)$_2$(dmb-L'-4DQ)]$^{4+}$-Y. When zeolite sample was ion exchanged with 3DQ$^{2+}$
before irradiation, the sample solution turned blue in 20 minutes and absorption spectra indicated 43.8 nmols of PVS•− radical formation after 3 hours of irradiation (Curve (a) in figure 4.48). Based on the loading level of [Ru(bpy)2(dmb-L′-4DQ)]4+ in Y, 14 nmols of Ruthenium compound are bound to 10 mg of [Ru(bpy)2(dmb-L′-4DQ)]4+-Y sample. Therefore, approximately 3 times of electrons from available Ru2+ was transferred to PVS acceptors in the surrounding solution in 3 hours. Figure 4.48(b) is the result of similar photolysis experiment without 3DQ2+ ion exchange. In this case, the reduced 4DQ•− end in the dyad cannot transfer the electron directly to PVS since two species are spatially separated by zeolite. Therefore small amount of PVS•− radical was generated (2.8 nmols) after 3 hours of irradiation. Comparing with the yield of photo electron transfer with [Ru(bpy)3]3+-Y (4.8 % after 2 hours of irradiation), the yield of photo electron transfer with [Ru(bpy)2(dmb-L′-4DQ2+)]4+-Y (200% after 2 hours of irradiation) is approximately 40 times larger. The yield is also approximately 6.5 times larger than the photo electron transfer with [Ru(bpy)2(dmb-L-4DQ2+)]4+-Y. (30% after 2 hours of irradiation)

The result of suspension photolysis experiment for extended period of time is shown in Figure 4.49. As shown in Figure 4.49, the growth of PVS•− slowed down after 4 hours oh photolysis. The color of solution turned to intense blue after 4 hours and the absorption of light by photosensitizers is reduced as compared to the initial period of irradiation. 128.4 nmols of PVS•− radical was formed after 470 minutes of irradiation. This is almost 9 fold amount of ruthenium photosensitizer in 10 mg of [Ru(bpy)2(dmb-L′-4DQ)]4+-Y sample.
DISCUSSION

Syntheses and structures of zeolite bound dyads The complex [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$ -Y and [Ru(bpy)$_2$(dmb-L'-4DQ)]$^{4+}$ -Y are donor-acceptor dyads partially entrapped in zeolite Y pores. This molecule is designed to improve the electron transfer efficiency and expose ruthenium center to catalysts for further redox reactions after the electron transfer. The viologen end of the molecule is trapped in supercages while the donor end stays on zeolite surface. Conjugated link L or L’ connects donor and acceptor ends of the molecule.

The compounds are synthesized by modified ship-in-a-bottle synthesis. During the synthesis, the dmb end of the reactant is sufficiently small enough to pass through 12-ring openings of zeolite Y, but [Ru(bpy)$_2$(dmb)]$^{2+}$ end is too large to enter zeolitic pores. Then the available nitrogens in dmb end of the ligand (dmb-L-dmb) or (dmb-L’-dmb) react with 1,4-dibromobutane in supercages to produce a diquat acceptor end of the dyad. The size of 4DQ$^{2+}$ moiety is slightly larger (8.2-8.3 Å) than the window of supercages of zeolite Y. Therefore the acceptor ends of the dyad molecules are entrapped in zeolite pores. To remove any compounds on zeolite surface, the product was extensively washed with 0.5M NaCl solutions after the reaction.

To our knowledge, this is the first time that zeolite surface-bound dyad molecule is synthesized by ship-in-a-bottle method. Ion exchange methods have been used previously for preparation of this type of system [14,15]. Ship-in-a-bottle synthesized species have advantages over previous ion exchange method used to form zeolite surface-
bound dyads. First, the final products are permanently trapped in zeolitic cages since smaller fragments such as 1,4-dibromobutane are introduced into zeolitic pores during the synthesis, and built to bigger moieties. It will be beneficial to utilize these species for chemical processes in ionic solutions. Ion exchanged molecules will be removed from zeolite in ionic solution. Second, ship-in-a-bottle synthesis is more flexible for design of molecules. Other fragments can be introduced into zeolitic pores and assembled to bigger molecules while the size limitation for ion exchange method is present. In ion exchange method, the final species or moieties should not be bigger than the window in zeolitic channels. Finally, ship-in-a-bottle method has better control for spatial arrangement of molecules. Since 1,4-dibromobutane is already entrapped in zeolitic pores, only bipyridine ligand penetrated in pores are able to react and form diquat moieties. The extensive washing step with 0.5M NaCl solutions would remove any dyads on zeolite surface if they exist. When dyads are ion exchanged in zeolite, the acceptor diquat ions might remain on zeolite surface. Ion exchange purification step is not possible for this system since it will remove all dyads molecules. Therefore this unique synthesis method for partially entrapped dyad molecules in zeolite can be utilized for broad range of applications. The other advantage of this zeolite surface bound photosensitizer is that ruthenium center of the photosensitizer can be exposed to catalysts. After the photosensitizer is oxidized, it needs to be reduced by catalysts, which was not possible with zeolite encapsulated photosensitizer system. It is possible to combine this system with photocatalysts and reduce the photosensitizer again for further reactions.
**Emission of ruthenium complexes with olefinic bridge** The emission quantum yield of [Ru(bpy)$_2$(dmb-L-dmb)](PF$_6$)$_2$ in CH$_3$CN solution is only 5% of the emission quantum yield of [Ru(bpy)$_3$(PF$_6$)$_2$] in CH$_3$CN solution when excited at 450 nm (Figure 4.14). The emission quantum yield of the similar complex, [Ru(dmb)$_2$(dmb-L-dmb)]$^{2+}$, is less than 0.006 calculated from integrated emission spectra relative to Ru(bpy)$_3$$^{2+}$ in water, which accounts for only 14% of emission quantum yield of Ru(bpy)$_3$$^{2+}$ in water [18]. Emission quantum yield of Ru(bpy)$_3$$^{2+}$ in water is 0.042 at 298 K [25]. The lower emission quantum yield could be due to inefficient intersystem crossing efficiencies to emitting $^3$MLCT state, as explained for low emission quantum yield of [Ru(dmb)$_2$(dmb-L-dmb)](PF$_6$)$_2$ [18]. From the literature, the emission intensity of [Ru(bpy)$_2$(dmb)]$^{2+}$ is as strong as that of Ru(bpy)$_3$$^{2+}$, which means electron delocalization on bpy versus dmb ligand is not responsible for low emission quantum yield of [Ru(bpy)$_2$(dmb-L-dmb)](PF$_6$)$_2$ [26]. The emission of a similar complex [Ru(dmb)$_2$(dmb-(b-b)-dmb)]$^{2+}$, in which the ethenyl groups of the bridge between dmb groups are saturated (where b-b is 1,4-bis[2-(4’-methyl-2,2’-bipyridyl-4-yl)ethyl]benzene), also shows strong emission quantum yield of 0.068 calculated from integrated emission spectra relative to Ru(bpy)$_3$$^{2+}$ in water [18, 25]. The intersystem crossing efficiency, $\eta_{isc}$, of the similar complex [Ru(dmb)$_2$(dmb-L-dmb)]$^{2+}$ is only 0.30 while $\eta_{isc}$ of the alkyl bridge compound, [Ru(dmb)$_2$(dmb-(b-b)-dmb)]$^{2+}$, is 1.0 [18]. Therefore it is assumed that the unsaturated olefinic bridge between the donor and acceptor on the dyad causes weak emission of the molecule due to low intersystem crossing efficiencies for population of the emitting $^3$MLCT state.
The cis-trans isomerization of olefinic bridge can also provide rapid non-radiative decay of absorbed energy. However, this effect appears to be insignificant based on the low emission intensity of zeolite-bound compound, [Ru(dmb)₂(dmb-L-dmb)]²⁺-Y. When the ruthenium complex is bound to zeolite surface, (dmb-L-dmb) ligand will be entrapped in zeolitic channels and cis-trans isomerization will be restricted due to the narrow space in zeolitic channels. If the isomerization is the main cause of low emission, the emission intensity should increase significantly when [Ru(dmb)₂(dmb-L-dmb)]²⁺ is bound to zeolite. The emission of zeolite surface bound [Ru(bpy)₂(dmb-L-dmb)]²⁺ is compared with the emission of zeolite surface bound [Ru(bpy)₃]²⁺ as shown in Figure 4.15. The emission quantum yield of [Ru(bpy)₂(dmb-L-dmb)]²⁺-Y is 6.25% of the emission quantum yield of [Ru(bpy)₃]²⁺-Y. Since the increase of emission quantum yield due to binding to zeolitic pores was not observed, cis-trans isomerization of olefinic ligand is not the main cause of the low emission of [Ru(dmb)₂(dmb-L-dmb)]²⁺.

Similar to [Ru(bpy)₂(dmb-L-dmb)](PF₆)₂, the emission quantum yield of [Ru(bpy)₂(dmb-L’-dmb)](PF₆)₂ is only 6% of the emission quantum yield of [Ru(bpy)₃](PF₆)₂ in CH₃CN solution. The emission quantum yield of the similar complex, [Ru(dmb)₂(dmb-L’-dmb)](PF₆)₂, is less than 0.01, which is only 10% of the emission quantum yield of [Ru(dmb)₃](PF₆)₂ [19]. The emission of similar complex but with a saturated alkyl bridge, [Ru(bpy)₂(dmb-(CH₂)ₙ-dmb)], also shows strong emission [31]. As discussed before, the olefinic bridge between the donor and acceptor on the dyad causes weak emission of the molecule as for [Ru(bpy)₂(dmb-L-dmb)](PF₆)₂. Strouse et al. studied that the trans isomer configuration of (dmb-L’-dmb) is retained in ruthenium
complexes due to the instability of the cis-configuration [19]. Therefore it can be assumed that the trans configuration of (dmb-L'-dmb) will also be retained in

\[ [\text{Ru(bpy)}_2(\text{dmb-L'}-\text{dmb})][\text{PF}_6]_2 \] and nonradiative decay due to cis-trans isomerization of (dmb-L'-dmb) is not responsible for weak emission of \([\text{Ru(bpy)}_2(\text{dmb-L'}-\text{dmb})][\text{PF}_6]_2 \).

**Photolysis and electron transfer reaction of zeolite bound dyads**

**Electron Transfer Processes** Step-by-step electron transfer processes between molecules are studied in solid and suspension photolysis experiments with \([\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+ -\text{Y}\). First, the intramolecular electron transfer from ruthenium metal center to 4DQ\(^2^+\) acceptor was observed by solid photolysis experiment with \(\text{Na}_2\text{EDTA-}[\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+ -\text{Y}\). When sacrificial electron donor (Na\(_2\)EDTA) was present on zeolitic surface, the intramolecular electron transfer reaction was observed by the diffuse reflectance peaks of 4DQ\(^{**}\) as shown in Figure 4.24.

Second, the intermolecular electron transfer from 4DQ\(^{**}\) to MV\(^{2^+}\) in neighboring supercages was observed by the ambient light exposure of \([\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+ -\text{MV}^{2^+}-\text{Y}\) solid sample in Figure 4.26. It is surprising that MV\(^{**}\) radical was formed just by the exposure of the sample to ambient light. Also the decrease of intraligand and MLCT transitions of \([\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+ \) observed upon light exposure is evidence of efficient electron transfer. This decrease is due to the oxidation of the dyad molecule by MV\(^{2^+}\) acceptor in reaction:

\[
[(\text{bpy})_2\text{Ru}^{2^+}(\text{dmb-L-4DQ})^{2^+}]_z \xrightarrow{\text{hv}} [(\text{bpy})_2\text{Ru}^{2^+}(\text{dmb-L-4DQ})^{2^+}]_z
\]  

(1)
After the electron transfer reaction, the dyad molecule will be oxidized to 

\([(\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L-4DQ})^{2+}]_x \rightarrow [(\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L-4DQ})^{3+}]_x \)  

(2)

\([(\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L-4DQ})^{3+}]_x + \text{MV}^{2+} \rightarrow [(\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L-4DQ})^{2+}]_x + \text{MV}^{4+} \)  

(3)

After the electron transfer reaction, the dyad molecule will be oxidized to 

\([(\text{bpy})_2\text{Ru}^{3+}(\text{dmb-L-4DQ})^{2+}]_x \), which does not show the absorption peaks of the Ru(II) complex. After light exposure, \([\text{Ru(bpy})_2(\text{dmb-L-4DQ})]^{5+} - \text{MV}^{4+} - \text{Y} \) was re-ion exchanged with NaCl solution. The intraligand and MLCT transitions of \([\text{Ru(bpy})_2(\text{dmb-L-4DQ})]^{4+} \) was recovered by the re-ion exchange procedure due to the reduction of oxidized dyad as shown in Figure 4.26.

Finally, the solution photolysis results show that the electron relays from \([\text{Ru(bpy})_2(\text{dmb-L-4DQ})]^{4+} \) to 3DQ\(^{2+}\) in zeolite and PVS in surrounding solution occurs and the yield of the photo electron transfer is 6 times larger than the yield of photoelectron transfer with \([\text{Ru(bpy})_3]^{2+} \) photosensitizer. The suspension photolysis results with \([\text{Ru(bpy})_2(\text{dmb-L-4DQ})]^{4+} \) show that the yield of PVS\(^{4+}\) formation is 40 times larger than the yield of photolysis with \([\text{Ru(bpy})_3]^{2+} - 4\text{DQ}^{2+} - \text{Y} \) in PVS solution. The improvement of photo electron transfer yield with dyad comparing with \([\text{Ru(bpy})_3]^{2+} \) photosensitizer can be explained by the retardation of back electron transfer. In general the forward electron transfer reactions will be weakly exoergic and lie in Marcus normal region. The back electron transfer will be highly exoergic and will occur in the Marcus inverted region according to previous studies [27]. In Marcus normal region, as the reaction energy, \(\Delta G^0\), becomes more negative, the electron transfer reaction rate, \(k_e\),
increases. In Marcus inverted region, as $\Delta G^0$ becomes more negative, $k_c$ decreases [28].

In the electrochemical measurement, the reduction of $4\text{DQ}^{2+}$ in $[\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+\text{dyad occurs around } -1.25 \text{ V. This is } -0.20\text{V more negative than free } 4\text{DQ}^{2+/+}\text{redox reaction. The change of redox potential is due to geometrical change of the viologen or attachment of methyl group in } 4\text{DQ}^{2+}\text{ in the dyad molecules. As shown in Figure 4.50, this potential change will move } \Delta G^0\text{ of back electron transfer reaction to more negative region. Since this back electron transfer reaction lies in Marcus inverted region, the reaction rate of back electron transfer will decrease. Therefore the yield of } \text{PVS}^*\text{ formation in suspension photolysis will increase.}

**Electron Transfer Efficiency of Dyads with L and L’ Link**  The suspension photolysis results with $[\text{Ru(bpy)}_2(\text{dmb-L’-4DQ})]^4^+\text{ show that the yield of } \text{PVS}^*\text{ formation is approximately 6.5 times larger than the yield of photolysis with } [\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+\text{-3DQ}^{2+}\text{-Y in PVS solution. The improvement of photo electron transfer yield with } [\text{Ru(bpy)}_2(\text{dmb-L’-4DQ})]^4^+\text{-Y comparing with } [\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+\text{-Y can be explained by the effect of donor-acceptor distance in dyads. From the research on a series of linked tris(2.2’-bipyridine)ruthenium(II)/diquat complexes, the intra molecular electron transfer occurs only from the MLCT states localized on bipyridine ligand which are linked to diquat acceptors [29]. From the structure of the dyad, } [\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^4^+,\text{ the excited electron from ruthenium center should be localized in dmb ligand or (dmb-L-dmb) conjugated ligand before the electron transfer to the diquat acceptor in the molecule. From the electrochemical measurement, the redox potential of the conjugated ligand (dmb-L-dmb) is } -1.588\text{V and the other two bpy ligands were reduced in more}
negative region, -1.844 and -2.054 V. The $\pi$ conjugation of (dmb-L-4DQ)$^{2+}$ decreases the $\pi^*$ energy level of the ligand and the conjugated ligand will be easily reduced. From this result, it is assumed that the major portion of excited electrons resides on a conjugated bridge and transferred to 4DQ$^{2+}$ ligand.

The rate constant ($k_{ET}$) for non adiabatic electron transfer reaction can be described by using a damping factor $\beta$ and a donor-acceptor distance, $r_{DA}$.[32]

$$k_{ET} = A \exp(-\beta r_{DA})$$

In this equation, the rate of electron transfer reaction varies exponentially with the distance between electron donor and acceptor and $\beta$ value decides the distance dependence. In ruthenium dyad molecule, this is the distance between ruthenium metal center and acceptor in the ligand. Yonemoto et al. studied the rate of photoinduced forward and thermal back electron transfer in a series of dyad molecules (bpy)$_2$Ru(dmb-(CH$_2$)$_n$-MV$^{2+}$) [27]. It is observed that the rate of intramolecular forward electron transfer varies exponentially with the number of carbon atoms in the spacer chain up to $n$=5. The rate of back electron transfer, which occurs in the Marcus inverted region, also varies exponentially with $n$, but more weakly than the forward electron transfer rates. $\beta$ values observed by Yonemoto et al. for forward electron transfer and backward electron transfer are 1.38 and 0.66 Å$^{-1}$, respectively [27]. When these dyads are exchanged onto the surface of zeolites, the rate of forward electron transfer from photoexcited ruthenium center to MV$^{2+}$ acceptor also decreases exponentially with increasing the distance between the donor and acceptor [14]. These results implicate that shorter distance between the donor and acceptor speeds up forward electron transfer, while affecting the
back electron transfer relatively less. The structure of [Ru(bpy)$_2$(dmb-L $'$-4DQ)]$^{4+}$ dyad is almost the same structure of [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$ except the absence of benzene group and one of the ethene groups in link L between ruthenium metal center and diquat acceptor. The improvement of photo electron transfer yield is attributed to the effect of shorter distance between Ru$^{2+}$ donor and diquat acceptor in [Ru(bpy)$_2$(dmb-L $'$-4DQ)]$^{4+}$ dyad.

**Recovery of Ru$^{2+}$ in solution.** Photolysis for extended period of time (470 minutes) with [Ru(bpy)$_2$(dmb-L $'$-4DQ)]$^{4+}$ - 3DQ$^{2+}$-Y shows that 128.5 nmols of PVS$^•$ was generated by photo electron transfer after 470 minutes of irradiation (Figure 4.49). This is 9 times larger than the amount of available dyad calculated by the amount of sample and loading level. Considering the fact that sacrificial electron donor was not added to the system, there should be additional electron source in the environment except photoexcited Ru$^{2+}$. Ledney and Dutta proposed reduction of Ru(bpy)$_3^{3+}$ by water when Ru(bpy)$_3^{3+}$ is entrapped within the supercages of zeolite Y [33].

$$\text{Ru(bpy)}_3^{3+} + H_2O \longrightarrow [\text{Ru}^{3+} (\text{bpy})_2 (\text{bpy-H}_2\text{O})]^{3+} \quad (1)$$

$$[\text{Ru}^{3+} (\text{bpy})_2 (\text{bpy-H}_2\text{O})]^{3+} \xrightarrow{\text{OH}} [\text{Ru}^{3+} (\text{bpy})_2 (\text{bpy-OH}^-)]^{2+} + H_2O \quad (2)$$

$$[\text{Ru}^{3+} (\text{bpy})_2 (\text{bpy-OH}^-)]^{2+} \longrightarrow [\text{Ru}^{2+} (\text{bpy})_2 (\text{bpy-OH}^•)]^{2+} \quad (3)$$

$$[\text{Ru}^{2+} (\text{bpy})_2 (\text{bpy-OH}^•)]^{2+} \longrightarrow \text{Ru(bpy)}_3^{2+} + \text{OH}^• \quad (4)$$

$$\text{MV}^{2+} + \text{OH}^• \longrightarrow [\text{MV-OH}]^{2+} \quad (5)$$
Reaction (2) requires basic condition. According to Ledney and Dutta, neutral (pH 7) sample showed 30-50% conversion of \( \text{Ru(bpy)}_3^{3+} \) to \( \text{Ru(bpy)}_3^{2+} \) [33]. Das and Dutta also proposed that hydroxyl radicals formed in reaction (4) react with methyl viologen and form methylviologen-hydroxy intermediate shown as reaction (5) [3]. The environment of electron transfer reaction with \( [\text{Ru(bpy)}_2(\text{dmb-L’-4DQ})]^{4+} - \text{Y} \) is neutral aqueous solution. Therefore it is assumed that similar reaction as (1)-(4) occurs to 
\[ [\text{Ru}^{3+}(\text{bpy})_2(\text{dmb-L’-4DQ}^2+)], \text{which converts Ru}^{3+} \text{to Ru}^{2+}. \]

\[
\begin{align*}
\text{[Ru}^{3+}(\text{bpy})_2(\text{dmb-L’-4DQ}^2+)]^{5+} + \text{H}_2\text{O} & \rightarrow [\text{Ru}^{3+}(\text{bpy})(\text{bpy-H}_2\text{O})(\text{dmb-L’-4DQ}^2+)]^{3+} & (1’)
\text{[Ru}^{3+}(\text{bpy})(\text{bpy-H}_2\text{O})(\text{dmb-L’-4DQ}^2+)]^{5+} & \rightarrow [\text{Ru}^{3+}(\text{bpy})(\text{bpy-OH}')(\text{dmb-L’-4DQ}^2+)]^{4+} + \text{H}_2\text{O} & (2’)
\text{[Ru}^{3+}(\text{bpy})(\text{bpy-OH}')(\text{dmb-L’-4DQ}^2+)]^{4+} & \rightarrow [\text{Ru}^{2+}(\text{bpy})(\text{bpy-OH}^*)(\text{dmb-L’-4DQ}^2+)]^{4+} & (3’)
\text{[Ru}^{2+}(\text{bpy})(\text{bpy-OH}^*)(\text{dmb-L’-4DQ}^2+)]^{4+} & \rightarrow [\text{Ru}^{2+}(\text{bpy})_2(\text{dmb-L’-4DQ}^2+)]^{4+} + \text{OH}^* & (4’)
\end{align*}
\]

Reaction (1’) is nucleophilic attack of water to ligand bpy. Since (dmb-L’-4DQ^2+) is encapsulated inside zeolitic pores, nucleophilic attack to 4DQ^2+ by water is less favorable in this case. Reactions (2’) favors basic reaction condition. As discussed before, 30-50\% conversion of \( \text{Ru(bpy)}_3^{3+} \) was observed even at pH 7. Therefore, recovery of 
\[ [\text{Ru}^{2+}(\text{bpy})_2(\text{dmb-L’-4DQ}^2+)] \] by water is possible in this reaction system. The hydroxyl radical reacts with PVS in solution, similar to reaction (5).
The growth of PVS$^\bullet$ radical in suspension photolysis also means that the intermolecular reverse reaction, electron transfer from PVS$^\bullet$ radical to Ru$^{3+}$, is not as effective as the forward electron transfer reaction. The backward electron transfer reaction between PVS$^\bullet$ radical and Ru$^{3+}$ is as fast as the forward electron transfer reaction in solution [4]. This result is surprising considering the structure of the dyad in zeolites. The electron donor end still stays on zeolite surface in this system and remains accessible to diffusing molecules in solution. It can be explained by prompt conversion of Ru$^{3+}$ to Ru$^{2+}$ by water as described in reactions (1')-(4'). If the oxidized ruthenium photosensitizer reacts with water immediately after the oxidation, the back electron transfer is prohibited and Ru$^{2+}$ metal center can be used as photosensitizer and electron donor again. This is a promising result for the application of this system for water splitting. Recovery of Ru$^{2+}$ electron donor will be possible even without catalysts if this system is used for further applications.

**Conclusion**

A dyad molecule in which [(bpy)$_2$Ru(dmb)]$^{2+}$ is covalently bonded to diquat acceptors in the zeolite pores is synthesized by modified ship-in-a-bottle synthesis. To the best of our knowledge, this is the first example of the formation of partially entrapped dyad molecules in zeolite by ship-in-a-bottle synthesis. The permanent charge separation from ruthenium photosensitizer to the PVS acceptors in solution was achieved through
intramolecular electron transfer and consecutive intermolecular electron transfer reactions to second and third viologen acceptors.

Two kinds of dyad molecules, $[\text{Ru}^{2+}(\text{bpy})_2(\text{dmb-L-4DQ}^2+)]$ and $[\text{Ru}^{2+}(\text{bpy})_2(\text{dmb-L’-4DQ}^2+)]$, were synthesized with different link L and L’. $[\text{Ru}^{2+}(\text{bpy})_2(\text{dmb-L’-4DQ}^2+)]$-Y showed more efficient charge separation due to shorter distance between Ru$^{2+}$ electron donor and diquat acceptor. Recovery of Ru$^{2+}$ after electron transfer was observed in neutral aqueous system. A modification of this system with zeolitic membranes will lead to hydrogen fuel generation from water using sunlight. These possibilities will be tested in future studies.
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Figure 4.1 Structures and redox potentials of bipyridine electron acceptors. $E^0$ is versus NHE.
Figure 4.2 Structures of ligand dmb-L-dmb and dmb-L’-dmb
Figure 4.3 Synthesis of $[\text{Ru(bpy)}_2(\text{dmb-L-dmb})]^{2+}$
Figure 4.4 NMR spectrum of (dmb-L-dmb) ligand
Figure 4.5 NMR spectrum of \([(\text{bpy})_2\text{Ru(dmb-L-dmb)}]^2^+\)
Figure 4.6 Synthesis of $[\text{Ru(bpy)}_2(\text{dmb-L-4DQ})]^{4+}$
Figure 4.7 NMR spectrum of [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$(PF$_6$)$_4$ in CD$_3$CN
Figure 4.8 Preparation of C₄H₈Br₂-Y
Figure 4.9 Synthesis of [Ru(bpy)$_2$(dmb-L-4DQ)]$^{2+}$ - Y
Figure 4.10 NMR spectrum of compound extracted from \([\text{Ru(bpy)}_2(\text{dmb-L-dmb})]^{2+}\cdot\text{Y}^+\) dissolved in CD$_3$CN.
Figure 4.11 UV-Vis absorption spectra of (a) ligand (dmb-L-dmb) in CH$_3$CN (b) 8.6 µM solutions of I:Ru(bpy)$_3$(PF$_6$)$_2$ II: Ru(bpy)$_2$(dmb-L-dmb)(PF$_6$)$_2$ III: Ru(bpy)$_2$(dmb-L-4DQ)(PF$_6$)$_4$ in CH$_3$CN
Figure 4.12 UV-Vis absorption spectra of Ru(bpy)$_2$(dmb-L-4DQ)(PF$_6$)$_4$ extracted from Ru(bpy)$_2$(dmb-L-4DQ)$^{4+}$-Y in CH$_3$CN

Figure 4.13 Diffuse Reflectance UV-Vis spectrum of Ru(bpy)$_2$(dmb-L-4DQ)$^{4+}$-Y
Figure 4.14 Emission spectra of ruthenium compounds I:Ru(bpy)$_3$(PF$_6$)$_2$ II: Ru(bpy)$_2$(dmb-L-dmb)(PF$_6$)$_2$ III: Ru(bpy)$_2$(dmb-L-4DQ)(PF$_6$)$_4$ in CH$_3$CN

Figure 4.15 Emission spectra with solid samples of I:Ru(bpy)$_3$$^{2+}$-Y II: [Ru(bpy)$_2$(dmb-L-dmb)]$^{2+}$-Y III: [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$-Y
Figure 4.16 Cyclic voltammetry data of MV\((\text{PF}_6)_2\) in CH\(_3\)CN solution with 0.1M TBAPF\(_6\) as supporting electrolyte \(v=100\text{mVs}^{-1}\). Reference electrode is Ag/AgCl.

Figure 4.17 Cyclic voltammetry data of 3DQ(\(\text{PF}_6\))\(_2\) in CH\(_3\)CN solution with 0.1M TBAPF\(_6\) as supporting electrolyte \(v=100\text{mVs}^{-1}\). Reference electrode is Ag/AgCl.
**Figure 4.18** Cyclic voltammetry and differential pulse voltammetry data of 4DQ(PF₆)₂ in CH₃CN solution with 0.1M TBAPF₆ as supporting electrolyte \( \nu=100\text{mVs}^{-1} \). Reference electrode is Ag/AgCl.

**Figure 4.19** Cyclic voltammetry data of Ru(bpy)₃(PF₆)₂ in CH₃CN solution with 0.1M TBAPF₆ as supporting electrolyte. \( \nu=100\text{mVs}^{-1} \). Reference electrode is Ag/AgCl.
Figure 4.20 Cyclic voltammetry data of Ru(bpy)$_2$(dmb-L-dmb)(PF$_6$)$_2$ in CH$_3$CN solution with 0.1M TBAPF$_6$ as supporting electrolyte. $\nu$=100mVs$^{-1}$. Reference electrode is Ag/AgCl.

Figure 4.21 Cyclic voltammetry data of (dmb-L-dmb) in CH$_3$CN solution with 0.1M TBAPF$_6$ as supporting electrolyte. $\nu$=100mVs$^{-1}$. Reference electrode is Ag/AgCl.
**Figure 4.22** Cyclic voltammetry data of Ru(bpy)$_2$(dmb-L-4DQ)(PF$_6$)$_4$ in CH$_3$CN solution with 0.1M TBAPF$_6$ as supporting electrolyte. $\nu=100$mVs$^{-1}$. Reference electrode is Ag/AgCl. (a) –2V-2V area (b) –2V-0V area
Figure 4. 23 Photoelectron transfer scheme of EDTA-Ru(bpy)$_2$(dmb-L-4DQ)$^{2+}$-Y
Figure 4.24 Diffuse reflectance UV-Vis absorption spectra according to the photolysis of EDTA-Ru(bpy)$_2$(dmb-L-4DQ)$^{4+}$-Y solid I: before irradiation; II: after 80 minutes of irradiation; III: after 130 minutes of irradiation; IV: after O$_2$ treatment.
Figure 4.25 Photoelectron transfer scheme of Ru(bpy)$_2$(dmb-L-4DQ)$_2$$^{2+}$-MV$^{2+}$-Y
Figure 4.26 Diffuse reflectance spectra of Ru(bpy)$_2$(dmb-L-4DQ)$_4^{4+}$-Y upon ion exchange with MV$^{2+}$ and exposure to the ambient light

I: before MV$^{2+}$ ion exchange
II: after ion exchange with MV$^{2+}$ and exposure to the room light
III: after re-ion exchange with NaCl solution
Figure 4.27 Photoelectron transfer scheme of Ru(bpy)$_2$(dmb-L-4DQ)$^{2+}$-MV$^{2+}$-Y in PVS aqueous solution
Figure 4.28 The growth of $\text{PVS}^\ast$ during photolysis of $\text{Ru(bpy)}_2(dmb-L-4DQ)^{4+}\cdot\text{3DQ}^{2-}\cdot Y$ in aqueous solution of PVS
Figure 4.29 The growth of $\text{PVS}^{\bullet-}$ during photolysis of (a) $\text{Ru(bpy)}_2(\text{dmb-L-4DQ})^{4+}$-$3\text{DQ}^{2+}$-$\text{Y}$ (b) $\text{Ru(bpy)}_2(\text{dmb-L-4DQ})^{3+}$-$\text{Y}$ in aqueous solution of PVS
Figure 4.30 The growth of PVS$^*$ during photolysis of Ru(bpy)$_3^{2+}$-4DQ$^{2+}$-Y in aqueous solution of PVS
Figure 4.31 Synthesis of dmb-L’-dmb ligand
Figure 4.32 $^1$H NMR spectrum of 4'-Methyl-2,2'-bipyridyline-4-carbaldehyde in CDCl$_3$
Figure 4.33: H NMR spectrum of 4-(Bromomethyl)-4'-methyl-2,2'-bipyridine in CDCl₃.
Figure 4.34 $^1$H NMR spectrum of (4-(4'-methyl)-2,2'-bipyridyl)methyltriphenyl phosphonium bromide
Figure 4.35 $^1$H NMR spectrum of dmb-L'-dmb in CDCl$_3$
Figure 4.36 Synthesis of Ru(bpy)$_2$(dmb-L’-dmb)$^{2+}$
Figure 4.37 $^1$H NMR spectrum of Ru(bpy)$_2$(dmb-L'-dmb)(PF$_6$)$_2$ in CD$_3$CN
Figure 4.38 Synthesis of Ru(bpy)$_2$(dmb-L’-4DQ)$^{4+}$
Figure 4.39  $^1$H NMR spectrum of Ru(bpy)$_2$ (dmb-L-4DQ)(PF$_6$)$_4$ in CD$_3$CN
Figure 4.40 Synthesis of $[\text{Ru(bpy)}_2(\text{dmb-L’-4DQ})]^{4+}$ -Y
Figure 4.41 UV-Vis absorption spectra of [Ru(bpy)$_3$](PF$_6$)$_2$ and [Ru(bpy)$_2$(dmb-L'-dmb)](PF$_6$)$_2$ in CH$_3$CN.

Figure 4.42 Emission spectra of ruthenium compounds I:Ru(bpy)$_3$(PF$_6$)$_2$ II: Ru(bpy)$_2$(dmb-L'-dmb)(PF$_6$)$_2$.
**Figure 4.43** UV-Vis absorption spectra of I: Ru(bpy)$_3$(PF$_6$)$_2$ II: Ru(bpy)$_2$(dmb-L’-4DQ)(PF$_6$)$_4$ in CH$_3$CN solutions

**Figure 4.44** Emission spectra of ruthenium compounds I: Ru(bpy)$_3$(PF$_6$)$_2$ II: Ru(bpy)$_2$(dmb-L’-4DQ)(PF$_6$)$_4$ in CH$_3$CN solutions
Figure 4.45 Cyclic voltammetry data of [Ru(bpy)$_2$-(dmb-L’-dmb)](PF$_6$)$_2$ in CH$_3$CN solution with 0.1M TBAPF$_6$ as supporting electrolyte. $\nu$=100mVs$^{-1}$. Reference electrode is Ag/AgCl.

Figure 4.46 Cyclic voltammetry data of [Ru(bpy)$_2$-(dmb-L’-4DQ)](PF$_6$)$_4$ in CH$_3$CN solution with 0.1M TBAPF$_6$ as supporting electrolyte. $\nu$=100mVs$^{-1}$. Reference electrode is Ag/AgCl.
Figure 4.47 UV-Vis absorption spectra of solutions during photolysis of $[\text{Ru(bpy)}_2(\text{dmb-L'-4DQ})]^{4+}-3\text{DQ}^{2+}$ in PVS solution
Figure 4.48 The growth of PVS$^\bullet$ during photolysis of (a) Ru(bpy)$_2$(dmb-L$'$-4DQ)$_{4}^{4+}$-3DQ$_{2}^{2+}$-Y (b) Ru(bpy)$_2$(dmb-L$'$-4DQ)$_{4}^{4+}$-Y in aqueous solution of PVS
Figure 4.49  The growth of PVS\(^*\) during photolysis of Ru(bpy\(_2\))(dmb-L’-4DQ\(^{4+}\)-3DQ\(^{2+}\)-Y in aqueous solutions of PVS-long time photolysis
Figure 4.50 Intramolecular electron transfer reactions in [Ru(bpy)$_2$(dmb-L-4DQ)]$^{4+}$
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Chapter 1


**Chapter 2**


223


224


**Chapter 3**


Chapter 4

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228


