Synthesis and Characterization of Stilbenoids and Their Aza-Analogs as Photoluminescent Materials for the Detection of Nerve Agent Mimics

Chun Wang
Western Michigan University

Follow this and additional works at: http://scholarworks.wmich.edu/dissertations
Part of the Chemistry Commons

Recommended Citation
http://scholarworks.wmich.edu/dissertations/927
SYNTHESIS AND CHARACTERIZATION OF STILBENOIDS AND THEIR AZA-ANALOGS AS PHOTOLUMINESCENT MATERIALS FOR THE DETECTION OF NERVE AGENT MIMICS

by

Chun Wang

A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Department of Chemistry
Dr. Ekkehard Sinn, Advisor

Western Michigan University
Kalamazoo, Michigan
December 2007

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
SYNTHESIS AND CHARACTERIZATION OF STILBENOIDS AND THEIR AZA-ANALOGS AS PHOTOLUMINESCENT MATERIALS FOR THE DETECTION OF NERVE AGENT MIMICS

Chun Wang, Ph.D.
Western Michigan University, 2007

A novel series of stilbenoids and their aza analogs were synthesized, characterized and used as photoluminescent components in the detection of nerve agents. Their structure-property relationship was elucidated through UV-visible and fluorescence spectroscopy. The research in this thesis is driven by the hypothesis that the two-block sensor system consisting of a receptor incorporated ruthenium complex and a fluorescent signal molecule of stilbenoids, is capable of detecting chemical warfare agents. The sensor anchored onto nanoparticles and subsequently the nanoparticles were arranged through mediated self-assembly. While photo-induced electron transfer is a well-known mechanism for sensor design, the described system showed that photo-induced electron transfer between the ruthenium complex and the anionic bonded stilbenoid was not promising for molecular sensor construction. On the other hand, the analogs of stilbene compounds, aza stilbenes are excellent receptor-signal integrated sensor materials. The described work will show that silica nanoparticle-promoted self-assembly of organic monolayer provides a method to study the photo physical properties of the organized structures.
INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI Microform 3293184
Copyright 2008 by ProQuest Information and Learning Company.
All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
ACKNOWLEDGEMENTS

First of all, I would like to thank my advisor Dr. Subra Muralidharan, for his kind support, guidance, encouragement and advice.

I am grateful to my chair committee Dr. Ekkehard Sinn for being the first reader of my thesis, and to my committee members, Dr. Sherine Obare, Dr. Yirong Mo and Dr. Nora Berrah, for thoroughly reading and correcting my thesis.

I’m particularly grateful to the academic and support staff at the Department of Chemistry, Western Michigan University, for providing me the means to learn and understand.

I had the good fortune to work with Dr. Murali’s research group. Thanks to my group members, for their scientific discussions and supportive collaboration. I thank Nayane Udawatte for the help with optical measurements. I would like to thank Shankar Varaganti and Kim Junhyung for helping me to obtain the TEM images.

I also would like to express my gratitude to Dr. Sherine Obare’s group, to let me use their laboratory in the last semester, and Dr. Mo’s group for providing computer assistance.

Finally, I am forever indebted to my family from China, for their understanding, endless patience and support.

Chun Wang
# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ................................................................................................ ii

LIST OF TABLES ........................................................................................................ vi

LIST OF FIGURES ....................................................................................................... vii

LIST OF SCHEMES .................................................................................................... xi

CHAPTER

I. INTRODUCTION ...................................................................................................... 1

1.1 Nerve agents and their toxicities ........................................................................ 1

1.2 Current approaches to the detection of nerve agents ......................................... 4

1.3 Purpose of this research .................................................................................... 6

1.4 Central hypothesis ............................................................................................ 7

References ................................................................................................................... 14

II. SYNTHESIS AND CHARACTERIZATION OF STILBENOIDS:
THE SIGNAL MOLECULES .......................................................................................... 17

2.1 Introduction ........................................................................................................ 17

2.2 Results and Discussion ....................................................................................... 19

2.2.1 Synthesis ....................................................................................................... 19

2.2.2 Spectroscopy characterization ....................................................................... 32

2.2.3 Discussion ..................................................................................................... 33

2.3 Conclusion ........................................................................................................... 36

2.4 Experimental section ......................................................................................... 37

References ................................................................................................................... 53
Table of Contents—continued

CHAPTER

III. DIPYRIDOPHENAZINE INCORPORATED RUTHENIUM (II) BIPYRIDINE COMPLEXES: THE RECEP'TORS ............................................. 57

3.1 Introduction ........................................................................................................... 57
3.2 Results and discussion ........................................................................................ 59
   3.2.1 Synthesis of dipyridophenazine ruthenium (II) bipyridine complexes ........... 59
   3.2.2 Characterizations ........................................................................................ 62
3.3 Conclusion ............................................................................................................ 74
3.4 Experimental section ........................................................................................... 74
References ................................................................................................................... 78

IV. FABRICATION AND CHARACTERIZATION OF THE TWO BLOCK SENSOR SYSTEM ........................................................................................................... 80
4.1 Introduction ........................................................................................................... 80
4.2 Results and discussion ........................................................................................ 81
   4.2.1 Interactions between DCP and individual signal and receptor molecules .......... 81
   4.2.2 Interactions between DCP and the mixture of
       [Ru(bpy)2dppp3](PF6)2 complex and stilbenoid molecule 7 ............................. 83
   4.2.3 Fabrication of silica nanoparticle assembled sensor (1) and its characterization 87
4.3 Conclusion ............................................................................................................ 99
References ................................................................................................................. 101

V. STYRYLPYRIDINES AS INTEGRATED RECEPTOR AND SIGNAL MOLECULES ................................................................. 103
Table of Contents—continued

CHAPTER

5.1 Introduction .........................................................................................................103

5.2 Results and discussion ......................................................................................106
  5.2.1 Synthesis ................................................................................................... 106
  5.2.2 Structural determination .......................................................................... 108
  5.2.3 Characterizations of 32 and 33 ............................................................. 112
  5.2.4 Sensing of DCP and HCl ................................................................. 118
  5.2.5 Silica nanoparticle effect on the sensor properties ......................... 123
  5.2.6 Color observations on sensing of DCP and HCl ......................... 132

5.3 Conclusion ..........................................................................................................133

5.4 Experimental section .........................................................................................134

References .................................................................................................................137

VI. SUMMARY AND OUTLOOK ........................................................................... 140

APPENDICES

A. Spectra of Chapter II .................................................................................. 145
B. Spectra of Chapter III .............................................................................. 174
C. Spectra of Chapter V ................................................................................. 184
# LIST OF TABLES

2.1 Summary of stilbenoids synthesized .................................................................................. 30

2.2 UV-visible absorption, emission and excitation maxima of the stilbenoids ..... 33

3.1 Spectroscopic characteristics of the ligands and their complexes (CH$_3$CN, 25 °C) ............................................................................. 64

3.2 Stern-Volmer association constants of [Ru(bpy)$_2$(dppz)](PF$_6$)$_2$ and [Ru(bpy)$_2$(dppp3)](PF$_6$)$_2$ (CH$_3$CN, 25 °C) ......................................................... 73

4.1 Stern-Volmer association constants of sensor 1 ................................................................. 96

5.1 Solvent effect on the absorption and emission maxima of 32 and 33 ............... 114

5.2 Absorption and emission maxima of 32 and 33 and their complexes with HCl and DCP ................................................................. 131

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
LIST OF FIGURES

1. 1 Structures of the most important nerve agents ....................................................... 2
1. 2 Structures of nerve agent simulants ........................................................................ 4
1. 3 The construction of the two-block system ............................................................. 8
1. 4 Nanoparticle mediated self-assembly of stilbenoid monolayer ........................... 9
1. 5 The construction of single molecular system .......................................................... 10
2. 1 Structures of stilbenoids .......................................................................................... 17
2. 2 Side chain influence on the fluorescence .............................................................. 34
2. 3 Normalized emission spectra of a) 4 & 5 and b) 6 & 7. ......................................... 34
2. 4 Emission spectra of upper: 4 & 6 (left) and normalized 4 & 6 (right); lower: 5 & 7 (left) and normalized 5 & 7 (right) ................................................... 36
3. 1 Ligand structure responsible for light-switch ...................................................... 58
3. 2 Schematic demonstration of the MLCT light-switch process ............................... 58
3. 3 Structures of [Ru(bpy)$_2$(dppz)]$^{2+}$ and [Ru(bpy)$_2$(dppz)]$^2$. ......................... 59
3. 4 UV-visible spectrum of [Ru(bpy)$_2$dppz] (PF$_6$)$_2$ ............................................... 62
3. 5 UV-visible spectrum of [Ru(bpy)$_2$(dppp)$_3$](PF$_6$)$_2$ ........................................... 63
3. 6 DCP effect on the luminescence of dppz (upper) and Stern-Volmer’s relationship (lower) ................................................................. 66
3. 7 DCP effect on the luminescence of [Ru(bpy)$_2$dppz](PF$_6$)$_2$ (upper) and Stern-Volmer relationship (lower) ................................................................. 67
3. 8 HCl effect on the luminescence of [Ru(bpy)$_2$(dppz)](PF$_6$)$_2$(upper) and Stern-Volmer relationship (lower) ................................................................. 68
3. 9 DCP effect on the fluorescence of dppp3 ............................................................... 69
3.10 HCl effect on the fluorescence of dppp3 ............................................................... 70
List of Figures—continued

3.11 Emission of \([\text{Ru(bpy)}_2\text{dppp3}](\text{PF}_6)_2\) ................................................................. 70
3.12 Influence of DCP on the luminescence of \([\text{Ru(bpy)}_2\text{dppp3}](\text{PF}_6)_2\) (upper) and the Stern-Volmer relationship (lower) ....................................................... 71
3.13 HCl effect on the luminescence of \([\text{Ru(bpy)}_2(\text{dppp3})](\text{PF}_6)_2\) (upper) and Stern-Volmer relationship (lower) ................................................................. 72

4.1 Influence of DCP on the fluorescence of compound 7 (upper) and the Stern-Volmer relationship (lower) ................................................................. 82
4.2 Effect of DCP on the luminescence of 7 + 31, a) emission intensity; b) Stern-Volmer plot .................................................................................................................. 84
4.3 Structure of MPS-PPV and MV\(^{2+}\) .................................................................................. 86
4.4 TEM images of 35-40 nm diameters of silica nanoparticles ........................................ 88
4.5 TEM images of silanized silica nanoparticles .................................................................. 89
4.6 Effect of DCP on the fluorescence of 7-SiO\(_2\) (a) and the Stern-Volmer relationship (b) ................................................................. 91
4.7 Emission spectra of (a) 7-SiO\(_2\), (b) 31 and (c) 7-SiO\(_2\) + 31 ............................................ 93
4.8 Schematic representation of nanoparticle promoted organized structure of the two-block system .......................................................................................... 94
4.9 a) Interactions between DCP and (31 + 7-SiO\(_2\)), and b) The Stern-Volmer relationship at 631 nm ................................................................. 95
4.10 Emission spectra of silica nanoparticle assembled stilbenoid 1 and its mixture with complex 31 .................................................................................. 97
4.11 Schematic demonstration of the ion pair formation between a) 7-SiO\(_2\) and 31, and b) 1-SiO\(_2\) and 31 ............................................................................... 98

5.1 Polar solvent induced n, π*-π, π* inversion .................................................................. 104
5.2 Polar solvent does not invert the energy states when π, π* is the lowest excited state .................................................................................. 105
5.3 \(^1\)H NMR of 32 .............................................................................................................. 109
List of Figures—continued

5. 4 X-ray crystal structure of 32 ................................................................. 110
5. 5 \textsuperscript{1}H NMR of 33 ........................................................................... 111
5. 6 UV-vis of 32 left) in Hexane and right) in Acetonitrile ......................... 112
5. 7 Emission of 32 left) in Hexane and right) in Acetonitrile ......................... 112
5. 8 UV-vis of 33 left) in Hexane and right) in Acetonitrile ......................... 113
5. 9 Excitation of 33 left) in Hexane and right) in Acetonitrile ..................... 113
5.10 Emission of 33 left) in Hexane, right) in Acetonitrile ............................ 113
5.11 Orbital and state description of n, π, π* state switching as a result of vibrational motion ....................................................................................... 115
5.12 Temperature influence to excitation of 32 (in Acetonitrile) ..................... 116
5.13 Temperature effect on emission of 32 (in Acetonitrile) ......................... 116
5.14 Temperature effect on the excitation spectra of 33 (in Acetonitrile) ....... 117
5.15 Temperature effect on emission of 33 in Acetonitrile ........................... 118
5.16 DCP and HCl effect to the UV-vis spectra of 32 and 33 ......................... 119
5.17 DCP and HCl effect on the emission spectra of 32 and 33 ................. 120
5.18 Relationship between fluorescence of 33 and [DCP] ............................ 122
5.19 Relationship between fluorescence of 33 and [HCl] ............................ 122
5.20 IR of 32 (left) and 32-SiO\textsubscript{2} (right) ................................................. 124
5.21 Left: 33, right: 33-SiO\textsubscript{2} ...................................................................... 125
5.22 DCP and HCl effect on the UV-vis spectra of 32 and 32-SiO\textsubscript{2} ........ 126
5.23 DCP and HCl effect on the emission spectra of 32 and 32-SiO\textsubscript{2} ...... 127
5.24 DCP and HCl effect on the UV-vis spectra of 33 and 33-SiO\textsubscript{2} ...... 128
5.25 DCP and HCl effect on the emission spectra of 33 and 33-SiO\textsubscript{2} ......... 129
List of Figures—continued

5.26  Color change observation on addition of DCP, from left to right, 33, 33 + DCP, 33-SiO₂, 33-SiO₂ + DCP ............................................................... 132

5.27  Color change on addition of HCl: Left 33 and 33 + HCl; right, 33-SiO₂ and 33-SiO₂ + HCl ................................................................. 132

6.1  Schematic demonstration of solid state full sensor .............................................. 144
LIST OF SCHEMES

1. 1 Reactions between the enzyme and acetylcholine .................................................. 3
1. 2 Irreversible reaction between the enzyme and a nerve agent .................................. 3
1. 3 Intramolecular cyclization upon exposure to nerve agents ..................................... 6
1. 4 Protonation of pyridyl fluorophore by HCl ............................................................ 12
1. 5 Interaction of pyridyl fluorophore with DCP ......................................................... 12
2. 1 Horner-Wadsworth-Emmons reaction .................................................................. 20
2. 2 Mechanistic demonstration of Heck reaction ......................................................... 21
2. 3 Synthesis of 4-(4-formylstyryl)benzoic acid (1) ................................................... 22
2. 4 4-(4-(4-sulfobutoxy)styryl)benzoic acid (2) ........................................................... 23
2. 5 Synthesis of 3-(4-(4-sulfobutoxy)styryl)benzaldehyde (4) .................................. 24
2. 6 Synthesis of 4-(4-(4-sulfobutoxy)styryl)benzaldehyde (5) .................................. 25
2. 7 Synthesis of 3-(4-(4-sulfobutoxy)styryl)benzaldehyde (6) .................................. 26
2. 8 Possible approaches to build up distyryl benzene skeleton ................................... 28
2. 9 Synthesis of 4-(4-(4-sulfobutoxy)styryl)benzaldehyde (7) ................................. 29
3. 1 Synthesis of dipyrido[3,2-a;2',3'c]phenazine (dppz) ........................................... 60
3. 2 Synthesis of [Ru(bpy)2dppz] (PF6)2 ....................................................................... 60
3. 3 Synthesis of dppp3 ................................................................................................. 61
3. 4 Synthesis of [Ru(bpy)2dppp3] (PF6)2 ..................................................................... 62
4. 1 Equilibrium between receptor-stilbene adduct and receptor-DCP adduct ........... 85
4. 2 Synthesis of nanoparticle ....................................................................................... 87
List of Schemes—continued

4. 3 Silanization of silica nanoparticle ................................................................. 88
4. 4 Formation of Schiff's base between silanized silica and stilbenoid ............ 90
5. 1 Schematic procedure for 32 ........................................................................... 106
5. 2 Synthesis of 33 ............................................................................................ 108
5. 3 Schiff's base formation between 32 and amino-terminated silica nanoparticle ........................................................................................................... 123
SYNTHESIS AND CHARACTERIZATION OF STILBENOIDS AND THEIR AZA-ANALOGS AS PHOTOLUMINESCENT MATERIALS FOR THE DETECTION OF NERVE AGENT MIMICS

Chun Wang, Ph.D.

Western Michigan University, 2007

A novel series of stilbenoids and their aza analogs were synthesized, characterized and used as photoluminescent components in the detection of nerve agents. Their structure-property relationship was elucidated through UV-visible and fluorescence spectroscopy. The research in this thesis is driven by the hypothesis that the two-block sensor system consisting of a receptor incorporated ruthenium complex and a fluorescent signal molecule of stilbenoids, is capable of detecting chemical warfare agents. The sensor anchored onto nanoparticles and subsequently the nanoparticles were arranged through mediated self-assembly. While photo-induced electron transfer is a well-known mechanism for sensor design, the described system showed that photo-induced electron transfer between the ruthenium complex and the anionic bonded stilbenoid was not promising for molecular sensor construction. On the other hand, the analogs of stilbene compounds, aza stilbenes are excellent receptor-signal integrated sensor materials. The described work will show that silica nanoparticle-promoted self-assembly of organic monolayer provides a method to study the photo physical properties of the organized structures.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
CHAPTER I

INTRODUCTION

1.1 Nerve agents and their toxicities

The continuing war on terror has resulted in a push for the scientific community to develop new and innovative detection methodologies for chemical warfare (CW) agents. These new techniques need to meet the demands of high selectivity and sensitivity, short analysis time, and the ability to detect the toxins in a real world environment. Chemical warfare agents are classified by their mechanism of action\cite{1} and include blood agents such as hydrogen cyanide, blister agents including nitrogen and sulfur mustards, and nerve agents.

Nerve agents acquired their name because they affect the transmission of nerve impulses in the nervous system\cite{2}. All nerve agents belong chemically to the group of organophosphorus compounds. They are stable, easily dispersed, highly toxic and have rapid effects both when absorbed through the skin or inhaled through respiration\cite{3}.

There are two main classes of nerve agents, the G-series and V-series. The G-series is named for their origins in World War II Germany and include tabun, sarin, and soman. The V-series agents include VX, VE, VG and VM. The structures of the nerve agents are shown in Figure 1.1
The mechanism of attack of nerve agents is to disrupt the enzyme acetylcholinesterase by reacting with a serine residue at the active site. This causes the neurotransmitter acetylcholine, to build up in the synapse resulting in uncontrollable muscle contractions. The toxic effect of nerve agents depends on the substance inhibiting the enzyme acetylcholinesterase in the cholinergic nerve system. This enzyme is responsible for breaking down the signal substance acetylcholine, a process requiring two steps acetylation by means of a serine in the active site and hydrolysis, as demonstrated in Scheme 1.1
Scheme 1.1 Reactions between the enzyme and acetylcholine

When the phosphorus atom of the nerve agent covalently binds to a serine hydroxyl group (-OH) in the active site of acetylcholinesterase, the enzymes are irreversibly inhibited, Scheme 1.2

Scheme 1.2 Irreversible reaction between the enzyme and a nerve agent

As a result, acetylcholine builds up in the body, because the covalently bonded enzyme can no longer interact with its normal substrate, acetylcholine. The victim acquires several symptoms including headache, weakness, nausea, vomiting, diarrhea, bronchoconstriction, cardiac arrhythmia, convulsion, and respiratory failure.

Among the nerve agents, soman is the most potent inhibitor of acetylcholinesterase. A concentration of $10^{-9}$ M is sufficient to inhibit the enzyme by more than 50 per cent within 10 minutes.

Diisopropyl fluorophosphate (DFP), dimethy methylphosphosphate (DMMP), and diethyl chlorophosphate (DCP, shown in Figure 1.2, are frequently used as nerve agent simulants, because they have similar reactivity, but lack the efficacy of typical
nerve agents and hence are good model compounds to examine the effectiveness of
the designed sensor toward nerve gases. The research conducted herein uses DCP as
the nerve agent stimulant.

\[
\begin{align*}
\text{Diethyl chlorophosphate (DCP)} & \quad \text{Dimethyl methylphosphate (DMMP)} \\
\text{(H}_3\text{C)}_2\text{HCO-} & \quad \text{O-CH(}\text{CH}_3\text{)}_2
\end{align*}
\]

\[
\text{Diisopropyl fluorophosphate (DFP)}
\]

**Figure 1.2 Structures of nerve agent simulants**

1.2 Current approaches to the detection of nerve agents

There are numerous instrumental approaches which have successfully been
applied to the detection of nerve agents, such as high-speed gas chromatography,\(^4\text{-}^6\)
electrochemical detection,\(^7\text{-}^{13}\) microbiosensor,\(^14\) photoacoustic spectroscopy,\(^15\text{,}^{16}\)
and mass spectrometry.\(^6\text{,}^{17\text{-}19}\)

The fluorescence chemosensor have that focus mainly on the molecular
chemistry of receptor design\(^{20,\text{,}21}\) and construction of photo-induced energy or
electron transfer system\(^{22,\text{,}23}\) have received considerable attention. The binding
event is typically monitored by changes in color, fluorescence intensity or both.\(^{24}\)
Colorimetric detection was one of the earliest methods devised for nerve agent detection. Rueggeberg et al.\cite{Rueggeberg2007} took advantage of the oxidation of amine bases by organophosphates to produce a color change. More recently, Anslyn and colleagues showed that a hypsochromic shift of approximately 50 nm was observed when an oxime and hydrozone indicator molecule react with nerve agent simulants.\cite{Anslyn2010}

Chemical derivatization of nerve agents to produce fluorescent molecules is also possible and has been demonstrated by a number of groups. Gehauf and Goldenson developed a fluorescent assay for organophosphates using indole and sodium perborate.\cite{Gehauf2015} The indole is oxidized in the presence of perborate and organophosphates to produce indoxyl, a fluorescent precursor to indigo, which emits light between 460-490 nm when excited at 365 nm.

Zhang and Swager\cite{Zhang2017} developed a fluorescent ratiometric chemosensor for the detection of organophosphate and organophosphonate nerve agents that, in effect, mimic the toxic pathway of organophosphate nerve agents in their reaction with the active center of acetylcholinesterase. The authors utilized an intramolecular cyclization reaction that results in the generation of rigid planar chromophores with high emission efficiency. The reaction scheme is shown in Scheme 1.3.

Although Swager's indicator compound provides a method to detect nerve agents, its sensitivity is limited by the rotation of the pyridine before ring closing, which affects the efficiency of the cyclization.
1.3 Purpose of this research

The crucial recognition events of chemistry, biology, and materials science occur in a much smaller world than the one we are accustomed to. Information about these events can be conveniently transmitted to us via light signals emitted by purposed-built molecular devices. Besides the sensory role, such molecular devices also have potential for information processing since their emission can be switched between two distinguishable states by environmental stimulation.

Molecular fluorescence or luminescence for sensing and switching can be made highly sensitive down to the single molecule. Furthermore, many of the structural features which control the fluorescence efficiency have been delineated, such as double-bond torsion, low energy n, π* levels, and opportunities for photoinduced electron transfer or energy transfer. Therefore, considerable
opportunities exist for modulating these structures via chemical or physical means at the molecular level.

Our approaches are through synthetic and analytic methods to fluorescent chemosensors. Two types of sensorial systems are proposed: The design of system 1 is based on the construction of a photoinduced electron transfer systems with: (i) large light absorptivity for effective light harvesting or high sensitivity for input light; (ii) superior excited state properties to increase the efficiency of energy transfer to the acceptor unit; (iii) suitable functional groups for the connection of the photosensitizing unit(s) and fluorescent molecule; and (iv) suitable functional group for the assembly of a nanoscale system. Two-blocks, receptor and signal, are included in system 1. System 2 is a single molecular system, which is based on the consideration of integration of receptor and signal functions into one molecule.

1.4 Central hypothesis

The two types of sensor systems have been developed. The two-block system is depicted in Figure 1.3 and the single molecular system is in Figure 1.5.
The central hypothesis of the two-block system includes:

1) Polypyridine ruthenium(II) complex with an ancillary ligand is capable of responding the binding of certain target substrates through metal-ligand charge transfer (MLCT);
2) Fluorescence of both the complex and the stilbenoid can be varied due to photoinduced electron transfer between the stilbenoid and the ruthenium complex.

3) Nanoparticle can mediate the self assembly of covalently bonded stilbenoid molecules attached to their surface, making it possible to study the optical properties of the organized molecules.

As demonstrated in Figure 1.1, the two-block system consists of a receptor molecule (ancillary ligand incorporated ruthenium complex, block 1) and a signal molecule (stilbenoids, block 2). The function of the receptor molecule is to bind to the substrate and in turn, transmit the binding event to the signal molecule. The advantage of the two block sensor system is that there is flexibility in sensing different substrates, which is easily achieved by simply switching the receptors.

Ruthenium bipyridine complex(es) were chosen for incorporating receptor molecule(s) because of their high stability, high fluorescence quantum yield and high sensitivity toward substrates. It is known that \([\text{Ru(bpy)}_2(\text{dppz})]^2+\) showed moderate emission in acetonitrile and ethanol, but no emission in water or in the presence of a
proton donor such as acetic acid. This was ascribed to the protonation of the dppz nitrogen, which caused effective dissipation of the dppz-localized metal ligand charge transfer (MLCT) excited state. This result prompted us to investigate the light switching effect by complexation or protonation of the dppz type ligand in [Ru(bpy)₂dppz]²⁺.

Stilbenoids were used as the fluorescence molecules because of their efficient light emitting properties, the flexibility of conjugated length based band gap, and the ease of modification with functional groups make them excellent choice for device fabrication.

![Diagram of molecular system](image)

where n = 1, 2

**Figure 1.5** The construction of single molecular system

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
As demonstrated in Figure 1.5, the single molecular system combined the receptor and indicator in one molecule. The guiding principle for the design of the single molecular system was that the covalent bonding of the connected chemical device was necessary to obtain a stable arrangement and direct response to binding events. Employment of pyridine as the basic moiety for pH sensors was reported previously.\textsuperscript{[32-35]} Aza aromatics are dual functional molecules since they contain both of the receptors and the signal functions into one molecule. This suggests, making the synthetic approach of sensing toxics simple and efficient.

Central hypothesis for sensor 2:

\textit{Aza stilbenes are molecules with combined receptor and signal functions; their "on" or "off" properties as sensor materials can be obtained through delicately synthetic approaches.}

Protonation or Lewis acid complexion of the pyridyl group is expected to inhibit the deactivating effect of the n, \pi* state. If the n, \pi* state is the lowest singlet excited state in a molecule, it will potentially increase the contribution of the radiative pathway,\textsuperscript{[36, 37]} in other words, it could result in fluorescence enhancement. If the singlet excited state energy levels are reversed, the interaction is expected to quench the fluorescence.
The pyridyl group can form cationic pyridinium adducts with diethylchlorophosphate (DCP) in the following manner:

Therefore, an aza stilbene molecule can work both as receptor and indicator for certain substrates. Since the $\pi, \pi^*$ energy in conjugated oligomer strongly depends on the conjugation length, it can be controlled by strategically adjusting the structure of the aza aromatic compounds.

The objectives of this research are to develop efficient fluorescent chemosensor(s) for nerve agent detection, through synthetic chemistry incorporating analytical techniques; and to study the structure-property relationship of the stilbene containing molecules.
The work in this research project includes the synthesis of stilbenoids and their aza analogues, characterization of their fluorescence properties, and application of these compounds as photoluminescent components in the detection of nerve agent mimics.
References


CHAPTER II

SYNTHESIS AND CHARACTERIZATION OF STILBENOIDS: THE SIGNAL MOLECULES

2.1 Introduction

By stilbenoid compounds we mean systems that are made up of stilbene units, ranging from monomer I, 2-diphenylethene, (E)-I, (Z)-II through oligophenylenevinylene (OPV), III as a representative, to poly(phenylenevinylene) (PPV) IV in Figure 2.1.

Stilbene containing polymer based chemical sensors are widely studied\textsuperscript{[1-3]}, due to their strong luminescence properties. The luminescence efficiency is related to the delocalization of electronic structure. A vast number of studies on oligomers confirm that the electronic states in a polymer have limited delocalization, and the electronic structure of a given polymer is often determined by 7-13 repeating units.\textsuperscript{[4-7]} Consequently, the investigation of well-defined oligomers is of considerable

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structures_of_stilbenoids.png}
\caption{Structures of stilbenoids}
\end{figure}
importance since it can provide an insight into the structural and electronic properties of the related polymeric materials.\textsuperscript{[4,8]} In addition, the ease of obtaining oligomers of high purity and fabricating oligomers onto certain surfaces offers advantages for using functionalized oligomers as an active component for device applications, such as light emitting diodes\textsuperscript{[9,11]}, light modulators\textsuperscript{[11]} and field-effect transistors.\textsuperscript{[12,13]}

Except the conjugated length in $\pi$-conjugated polymers which are responsible for the ultimate optical and electronic properties, the subtle modification of the monomeric unit can often lead to a dramatic change in the physical properties of a polymer such as energy gap or fluorescence efficiency. As a result, knowledge of the structure-property relationship will certainly be important and useful for the exploration and development of better molecular based materials.

Because of planarity and rigidity of the phenylenevinylene units which are responsible for its unique functional properties, the higher homologues of oligophenylenevinlenes are highly insoluble.\textsuperscript{[14]}

Our interest is to synthesize the substituted bi-functional stilbene oligomers, in which one functional group binds covalently to the surface of silica nanoparticles, while the other functional group connects by ionic bonding to the the receptor (s) incorporated molecules in the sensor systems. In this chapter, several stilbenoids with two and three phenyl rings were synthesized. Our attempt to make longer 4, 4'-disubstituted oligomers of phenylene vinylenes was hampered by their insolubility. Although side substituted oligomers containing up to 11 phenyl rings were synthesized, their pi-conjugation backbones were twisted out of co-planarity.\textsuperscript{[15]} On
the other hand, substituents incorporated at the end of the conjugated position of the main chain, i.e. 4,4'-positions can shift the HOMO-LUMO energy level by electronic effect and thus alter the HOMO-LUMO energy gap of an oligomer. This provides a mean to tune the energy gap leading to a change in optical and electronic properties of an oligomer.\[16\]

The preparative characterizations of the synthesized stilbenoids were conducted, through fluorescence measurements, to their potential sensorial material applications.

2.2 Results and Discussion

2.2.1 Synthesis

The methods for the synthesis of stilbenoid compounds can be classified into two groups. On one hand are those in which the stilbene units arise directly during the construction of the carbon skeleton by formation of single or double carbon-carbon bonds, such as Wittig reaction,\[17-19\] Horner-Wadsworth-Emmons reaction,\[57-59\] Peterson reaction,\[23-26\] Julia reaction,\[27-29\] McMurry reaction,\[30, 31\] and Heck reaction\[32-38\] etc. On the other hand are methods in which the carbon skeleton is first constructed and the olefin double bonds are subsequently introduced.

A number of synthetic approaches were applied to synthesize the molecules described.

(1) Horner-Wadsworth-Emmons (HWE) coupling of aryl phosphonates to aromatic aldehydes, since it favors the formation of E-alkenes,\[39-42\] and the byproduct
dialkylphosphate salt can be easily removed by aqueous extraction, as showing in

**Scheme 2.1**

\[
\begin{align*}
\text{Ar}^1\text{P(OEt)}_2^- & + \text{Ar}^2\text{CHO} \xrightarrow{\text{Base}} \text{Ar}^1-\text{Ar}^2^- + \Theta^\circ \text{P(OEt)}_2^- \\
\text{Ar} & = \text{aryl, vinyl}
\end{align*}
\]

(2) Heck coupling of p-halobenzaldehydes to terminal styrenes, offers excellent compatibility with many functional groups.\(^{[43,44]}\) Indeed, the relatively mild conditions of the Heck reaction are particularly suitable for the preparation of alkoxy silane conjugated.\(^{[45,46]}\)

To better manipulate the Heck reaction, let us take a look at each stage of the mechanistic cycle:

While choosing starting aryl halide, we selected aryl bromide. It is well known that the oxidative addition of the Pd (0) to the aryl halide is the rate control step in the Heck reaction, C-X bond strength is reflected in the ability of aryl halides to undergo oxidative addition with palladium (0) complex: \(\text{ArCl} < \text{ArBr} < \text{ArI}\). ArI is usually more expensive than ArBr.

Attempts to optimize the reaction conditions for the Heck coupling of an aryl halide with an olefin showed that tri-o-tolylphosphine was superior to triphenylphosphine in terms of yields. The applicable temperature ranges between 100 °C and 140 °C. At low temperature no product can be detected within 5 h, whereas
black palladium quickly precipitates above 140 °C. Freshly distilled DMF proved to be the solvent of choice since it is sufficiently polar, and has a boiling point above the required temperature range.

To an equimolar solution of an aldehyde and the corresponding phosphonate in anhydrous THF, was slowly added 1.2 equiv. of a suitable base (NaH, t-BuOK or TBD) at room temperature. After stirring for 3 hrs, the solution was quenched with water. The crude product was collected by suction filtration or extracted twice with CH$_2$Cl$_2$, dried over MgSO$_4$ and evaporated to dryness.

**General procedure for Heck reaction:**

---

Scheme 2.2  Mechanistic demonstration of Heck reaction

To an equimolar solution of an aldehyde and the corresponding phosphonate in anhydrous THF, was slowly added 1.2 equiv. of a suitable base (NaH, t-BuOK or TBD) at room temperature. After stirring for 3 hrs, the solution was quenched with water. The crude product was collected by suction filtration or extracted twice with CH$_2$Cl$_2$, dried over MgSO$_4$ and evaporated to dryness.

**General procedure for Heck reaction:**
A mixture of aryl halide, vinyl benzene (1.1 equivalent of aryl halide), Pd(OAc)$_2$ (2 mol% of aryl halide), tri-o-tolylphosphine (4 mol% of aryl halide), and Et$_3$N (1.5 equivalent of aryl halide) in DMF was heated to 110 °C~140 °C. The reaction was monitored by TLC. The mixture was passed through a celite pad. Water was added and the mixture was extracted with CHCl$_3$. The organic layer was washed with brine, dried over anhydrous MgSO$_4$, and the solvent was evaporated under reduced pressure to give a crude product. The crude product was purified by chromatography on silica gel with CHCl$_3$.

2.2.1.1 4-(4-formylstyryl)benzoic acid (1)

![Scheme 2.3 Synthesis of 4-(4-formylstyryl)benzoic acid (1)]

is synthesized through the Horner-Wadsworth-Emmons reaction of the intermediate phosphonate with terephthalaldehyde-monoacetal. The phosphonate 8 was synthesized by the Michaelis-Arbuzov reaction$^{[20, 47]}$ of α-bromobenoic acid with triethylphosphine under reflux in toluene, as shown in scheme 2.3.
2.2.1.2 4-(4-(4-sulfobutoxy)styryl)benzoic acid (2)

The synthetic steps were schematically demonstrated in Scheme 2.4. The 4-hydroxylbenzaldehyde was protected with tri-isopropylsilane chloride\[48\] leading to the formation of 9. The stilbene intermediate 10 was afforded through the Horner-Wadsworth-Emmons reaction of the protected aldehyde 9 with 1 equivalent of 8 and 2.2 equivalent of 1, 5, 7-triazabicyclo[4.4.0]dec-5-ene (TBD) in THF.\[19\] The protecting group was removed efficiently with trace amount of TBAF in THF.
afforded 11. The final product 2 was successfully synthesized by the reaction of 11 with 1 equivalent of 4-butanesultone, and 1.1 equivalent of cesium carbonate in DMF, after NaOH, t-BuOK, NaH, and KOH failed.

2.2.1.3 3-(4-(4-sulfobutoxy)styryl)benzaldehyde (4) and 4-(4-(4-sulfobutoxy)styryl)benzaldehyde (5)

Scheme 2.5 Synthesis of 3-(4-(4-sulfobutoxy)styryl)benzaldehyde (4)

Compound 4 was synthesized by the steps shown in Scheme 2.5. The hydroxyl group of 4-bromophenol was protected with triisopropylsilane chloride

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
affording 12, followed by the Heck reaction\textsuperscript{32, 33, 49} of 12 with 1 equivalent of 4-vinylbenzaldehyde, 1.5 equivalent of triethylamine, 2 mol % of Pd(OAc)_2 and 4 mol% of tri-o-tolyphosphine to give the stilbene intermediate 13. Deprotecting of the silyl ether with tetra-butyl ammonium fluoride resulted in the precursor product 14. The final product 4 was obtained in a similar fashion as that of the final step in getting product 2.

The synthesis of 5 is shown in Scheme 2.6:

\textbf{Scheme 2.6 Synthesis of 4-(4-(4-sulfobutoxy)styryl)benzaldehyde (5)}

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
The synthetic procedure of 5 is similar with that of 4, except that para-olefin 15 was made from the aldehyde through the Wittig reaction.

2.2.1.4 3-(4-(4-sulfobutoxy)styryl)benzaldehyde (6) and 4-(4-(4-sulfobutoxy)styryl)benzaldehyde (7)

Scheme 2.7 Synthesis of 3-(4-(4-sulfobutoxy)styryl)benzaldehyde (6)
The synthesis of 6 began with 4-bromobenzylbromide. The phosphonate 18 was afforded by the Michaelis-Arbuzov reaction,\textsuperscript{[50]} followed by the Horner-Wadsworth-Emmons reaction of 18 and 9 to give the stilbene intermediate 19. The Heck reaction was used to form the distyrylbenzene intermediate 20. The deprotection of silyl ether and the functionalization with the sulfonic group were carried out as above.

When we came to the design of the synthetic routes for 7, there were several combinations to form the distyryl benzene skeleton 25, as shown in Scheme 2.8.

\[ \text{OTIPS} \quad + \quad \text{Br} \quad \text{CHO} \quad \rightarrow \quad \text{OTIPS} \quad \text{CHO} \]

\[ \text{25} \]
Scheme 2.8  Possible approaches to build up distyryl benzene skeleton 25

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
All of the three methods are experimentally practical, but resulted in different yields of a) 59%, b) 69%, and c) 47%. Because the oxidative addition of the aryl bromide to the Pd atom is the rate control step in the Heck reaction, consequently, the electron-withdrawing group on the aryl bromide enhances the rate of the oxidative addition. We adapted method b) for the completion of 7, because the intermediates were favored in the key transformation step. In fact, rout b) resulted in the highest yield of the three routes. The synthetic sequences of 7 were outlined in Scheme 2.9.

**Scheme 2.9 Synthesis of 4-(4-(4-sulfobutoxy)styryl)benzaldehyde (7)**

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
4-vinylbenzyl chloride was converted into 4-vinylbenzyl 22 iodide with NaI in 2-butanone under dark condition. Michaelis-Arbuzov reaction was conducted under dark condition to convert 22 into phosphonate 23. Similar procedures of 6 were used to finish the synthesis of 7.

### Table 2.1

**Summary of stilbenoids synthesized**

<table>
<thead>
<tr>
<th>Number</th>
<th>Stilbenoids</th>
<th>Structure</th>
<th>1,2-ethylenediyl Formation Method</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-(4-formylstyryl)benzoic acid</td>
<td><img src="image1" alt="Structure" /></td>
<td>Horner-Wadsworth-Emmons (HWE)</td>
<td>79.1%</td>
</tr>
<tr>
<td>2</td>
<td>4-(4-(4-sulfobutoxy)styryl)benzoic acid</td>
<td><img src="image2" alt="Structure" /></td>
<td>HWE</td>
<td>48.4%</td>
</tr>
</tbody>
</table>
Table 2.1—Continued

<table>
<thead>
<tr>
<th></th>
<th>Structure</th>
<th>Method</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>4-(4-(4-sulfobutoxy-2,6-dimethyl)styryl)benzaldehyde</td>
<td>HWE</td>
<td>Could not be isolated</td>
</tr>
<tr>
<td>4</td>
<td>3-(4-(4-sulfobutoxy)styryl)benzaldehyde</td>
<td>Heck</td>
<td>50.5%</td>
</tr>
<tr>
<td>5</td>
<td>4-(4-(4-sulfobutoxy)styryl)benzaldehyde</td>
<td>Heck</td>
<td>50.4%</td>
</tr>
<tr>
<td>6</td>
<td>3-(4-(4-sulfobutoxy)distyryl)benzaldehyde</td>
<td>HWE, Heck</td>
<td>35.2%</td>
</tr>
<tr>
<td>7</td>
<td>4-(4-(4-sulfobutoxy)distyryl)benzaldehyde</td>
<td>HWE, Heck</td>
<td>37.4%</td>
</tr>
</tbody>
</table>
2.2.2 Spectroscopy characterization

It is worth mentioning that isomerization of stilbene can start from either the \textit{cis} or the \textit{trans} geometry. After excitation, the molecule undergoes rotation about its ethylene bond. When rotated through about 90° from either the \textit{cis} or \textit{trans} conformation, stilbene arrives at a minimum of potential energy, from which it decays to the ground state through nonadiabatic transitions. After decay to the ground state, the molecule can follow a trajectory which leads to the formation of a product, or alternatively a trajectory which leads back to the reactant. Results indicate an energy barrier of 0.15 eV in the isolated molecule for the \textit{trans-to-cis} occurs,\textsuperscript{[51, 52]} but a barrier of no more than 0.05 eV for \textit{cis-to-trans}.\textsuperscript{[53, 54]} Consequently, photoisomerization proceeds much faster from the \textit{cis-to-trans} than the reverse, in roughly 0.3-0.5 ps versus 10-20 ps.\textsuperscript{[55-57]}

In our experiments, the stereo selective Wadsworth-Emmons-Wittig and Heck reactions were used as key steps to synthesize all \textit{trans} carbon-carbon double bonds of stilbenoids, so the \textit{cis} isomers were neglected in the products. The isomerization of the stilbenoids during fluorescence measurement was not concerned.

The optical properties of compounds 1 through 7 were characterized by spectroscopy of UV-visible, excitation, and fluorescence, summarized in Table 2.2; see Appendix A for spectra.
Table 2.2

UV-visible absorption, emission and excitation maxima of the stilbenoids

<table>
<thead>
<tr>
<th>Stilbenoids</th>
<th>UV-vis (nm)</th>
<th>Emission (nm)</th>
<th>Excitation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>335</td>
<td>434</td>
<td>368</td>
</tr>
<tr>
<td>2</td>
<td>339</td>
<td>440</td>
<td>368</td>
</tr>
<tr>
<td>4</td>
<td>301</td>
<td>490</td>
<td>309</td>
</tr>
<tr>
<td>5</td>
<td>320</td>
<td>361</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>350</td>
<td>485</td>
<td>363</td>
</tr>
<tr>
<td>7</td>
<td>360</td>
<td>544</td>
<td>383</td>
</tr>
</tbody>
</table>

2.2.3 Discussion

2.2.3.1 Effect of the side chain on the fluorescence

By comparing the fluorescence spectra of 5 and its precursor 17, as shown in Figure 2.2, the chain effect to the fluorescence was negligible, indicating that the etherification of the phenol did not disrupt the HOMO-LUMO level of the π-conjugated system.
2.2.3.2 Effect of the positions of the substituents

Figure 2.2 Side chain influence on the fluorescence

Figure 2.3 Normalized emission spectra of a) 4 & 5 and b) 6 & 7
Compounds 6 and 7 have a similar structure except for the position of the aldehyde group substitution on the end ring of each compound. As shown in Figure 2.3 (b), the position of the aldehyde group at para position (7) shifted the emission maxima to 544 nm, from the meta position 450 nm of 6. This result was probably caused by the disruption of the coplanarity of the aldehyde group substitution on the meta position. For the two phenyl ring oligomers 4 & 5, the position of the aldehyde group did not significantly affect the emission maximum.

2.2.3.3 Effect of the conjugated length

Notably, there were dramatic increases in the fluorescence intensity moving from two-phenyl-ring oligomers to the three-phenyl-ring oligomers. This trend was not affected by the aldehyde group position on the end ring, as shown in Figure 2.4. The emission band sequentially shifted to longer wavelength with an extension of the conjugation length for the para-disubstituted oligomers 5 and 7, and the reverse for meta-substituted oligomers 4 and 6. The reason was the disruption of the coplanarity by the meta-substituent, as discussed in 2.3.1.2.
2.3 Conclusion

A novel homologous series of bi-functional oligophenylenevinylene containing up to three phenyl rings were synthesized. We have exposed that the substituents at the para position of the end ring does not disrupt the co-planarity of the pi-conjugated backbone; the fluorescence intensity increases as the extension of conjugation; the tether on the phenoxy does not interrupt the $\pi-\pi^*$ energy level of the conjugated system. These structure-property relationships are important for the future design of organic light emitting materials.

Figure 2.4 Emission spectra of upper: 4 & 6 (left) and normalized 4 & 6 (right); lower: 5 & 7 (left) and normalized 5 & 7 (right)
2.4 Experimental section

$^1$H NMR spectra were recorded with 400 MHz and $^{13}$C NMR spectra were obtained with a 100 MHz JEOL Eclipse nuclear magnetic resonance spectrometer, with tetramethylsilane (TMS) as an internal standard. Chemical shifts are given as $\delta$ values (ppm) and coupling constants $J$ are given in Hz. Melting points were taken using a Thomas-Hoover Unimelt instrument and reported in degree Celsius. FT-IR spectra were recorded on a Bruker Equinox 55 and Perkin Elmer 1710 Fourier Transform Infrared Spectrometers. A Perkin-Elmer Lambda 35 spectrophotometer was used for the absorption measurements. The fluorescence spectra were measured by an Edinburgh Instrument F900 spectrofluorometer. Fluorescence lifetimes were measured on the same machine, using the single photon counting method. For the room temperature spectroscopic measurements in the solution, the sample was dissolved in acetonitrile, unless the solvent was specified. LC-MS data were collected on a Shimadzu LCMS-2010EV High-Performance liquid chromatograph/mass spectrometer, with atmospheric pressure chemical ionization (APCI) method.

The above described instruments and methods are used through over the research project.
4-((ethoxyphosphono)methyl)benzoic acid (8) Triethyl phosphite (2.7 ml, 15.5 mmol) and alpha-bromo-p-toluic acid (3g, 14 mmol) were combined with toluene (20 ml) and heated under reflux for 12 hours. The mixture was allowed to slowly cool to room temperature. The product which crystallized from the solution was collected by suction filtration, washed with petroleum ether and dried under reduced pressure. 8 (3.5g, 92%) was obtained as a pure white crystalline solid. $^1$H NMR (400 MHz, CDCl$_3$): 8.011 (d), 7.375 (d), 4.050 (q), 3.285 (d), 1.240 (t). 13C: 169.85, 137.14, 130.32, 129.92, 129.03, 62.76, 34.60, 33.24, 16.38.

4-(4-formylstyryl)benzoic acid (1) To a solution phosphonate 8 (1g, 3.7mmol) and terephthalaldehyde-mono-acetal (0.73ml, 3.7mmol) in THF, t-BuOK (0.988g, 8.8mmol) was added slowly under nitrogen at room temperature. After stirring for 3h, the solution was quenched with water. 6N HCl was added drop wise until pH=2. The
solution continued to be stirred for 12 h. THF was removed via rotary evaporator. The product was collected by suction filtration, washed thoroughly with ether and water and air dried overnight. 0.8g pure product 1 was collected in yellow powder, yield 86%. $^1$H NMR (400 MHz, DMSO-d$_6$): 10.0087 (s), 7.98 (d), 7.95 (d), 7.87 (d), 7.78 (d), 7.57 (d), 7.52 (d). $^{13}$C: 193.00, 167.59, 143.18, 141.39, 136.00, 131.40, 130.70, 130.40, 127.92, 127.52.

4-triisopropylsiloxylbenzaldehyde (9) The reactants, 4-hydroxybenzaldehyde (2g, 16.4mmol), TIPSCI (3.47ml, 19.6mmol) and imidazole (1.34g, 19.6mmol) were dissolved in DMF and stirred for 12 hrs at room temperature; water was added and the solution was extracted with ether. The organic layer was dried with magnesium sulfate, solvent was removed by rotation evaporation, and 4.37g of the silyl ether product 9 (4.55g, 100%) was collected as pale oil. $^1$H NMR (400 MHz, CDCl$_3$): 1.1 (t, 18H), 1.28 (m, 3H), 6.96 (d, 2H), 7.77 (d, 2H), 9.87 (s, 1H).
4-(4-triisopropylsiloxyl)styrylbenzoic acid (10) To an solution of aldehyde 9 (1g, 3.6mmol) and phosphonate 8 (0.98g, 3.6mmol) in anhydrous THF was added 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (1.2g, 8.64mmol) at room temperature. After stirring for three 3h, the solution was quenched with water. THF was removed via rotary evaporator. The crude product was extracted with CH$_2$Cl$_2$ twice, dried with MgSO$_4$, and dried using evaporation. Column chromatography on silica gel with CHCl$_3$ yielded product 10. (1.04g, 73%). $^1$H NMR (400MHz, CDCl$_3$): 1.07 (t, 18H), 1.12 (m, 3H), 6.88 (d, 2H), 6.99 (d, 1H), 7.23 (d, 1H), 7.41 (d, 2H), 7.61 (d, 2H), 7.84 (d, 2H), 9.98 (s, 1H).

4-(4-hydroxyl)styrylbenzoic acid (11) 10 (1g, 4.2mmol) was dissolved in THF, 1.1 equivalent of tetra butyl ammonium fluoride (TBAF) (1M in THF, 2.8 ml, 2.8mmol)
was added drop wise through an additional funnel, and the mixture was stirred for 5
minutes and quenched with acetic acid/ether solution. THF was removed under
vacuum. After this, ether was added, 11 was precipitated out and was collected by
filtration. (0.55g, 90%) $^1$H NMR (400MHz, DMSO-d$_6$): 6.79 (d, 2H), 7.09 (d, 1H),
7.31 (d, 1H), 7.48 (d, 2H), 7.65 (d, 2H), 7.91 (d, 2H), 9.7 (s, 1H). $^{13}$C NMR
(400MHz, DMSO-d$_6$): 116.21, 124.58, 126.53, 128.26, 128.92, 129.31, 130.33,
131.66.

$\text{COOH}$

$\text{SO$_3$H}$

4-(4-(4-sulfobutoxy)styryl)benzoic acid (2) Cesium carbonate (0.41g, 1.26mmol)
was added in solution of 11 (0.5g, 2.1mmol) in DMF, after stirring for 15 minutes, 4-
butanesultone (0.26ml, 2.52mmol) was added, the mixture was stirred for overnight
and quenched with HCl/ether. The product was collected by filtration as yellow
powder. (0.7g, 88.7%) $^1$H NMR (400MHz, DMSO-d$_6$): 1.76 (m, 4H), 2.50 (t, 2H),
3.99 (t, 2H), 6.98 (d, 2H), 7.18 (d, 1H), 7.36 (d, 1H), 7.58 (d, 2H), 7.68 (d, 2H), 7.92
(d, 2H). $^{13}$C NMR (400MHz, DMSO-d$_6$): 22.42, 28.54, 51.63, 67.98, 115.28, 116.22,
124.58, 125.48, 126.68, 128.82, 130.34, 131.65, 142.62, 158.41, 167.73.
4-bromobenzyl triisopropylsilyl ether (12) The procedure for silyl ether formation was similar with that of 9. $^1$H NMR (400MHz, CDCl$_3$): 1.08 (t, 18H), 1.22 (m, 3H), 6.75 (d, 2H), 7.31 (d, 2H).

3-(4-triisopropylsiloxy)styrylbenzaldehyde (13) A mixture of 12 (2g, 6mmol), 3-vinyl benzaldehyde (0.8ml, 6.6mmol), Pd(OAc)$_2$ (27mg, 0.12mmol, 2mol% of 12), tri-o-tolylphosphine (73mg, 0.24mmol, 4 mol% of aryl halide), and Et$_3$N (1.25ml, 9mmol, 1.5 equivalent of aryl halide) in DMF was heated to 110 °C~140 °C for 24hrs. The yellow to brown solution was cooled to room temperature and filtered through celite pad. Water was added and the mixture was extracted with CHCl$_3$. The organic layer was washed with brine, dried over anhydrous MgSO$_4$, and the solvent was evaporated under reduced pressure to give a crude product. The crude product was purified by chromatography on silica gel with CHCl$_3$ to afford 13. (1.39g, 61%)
3-(4-hydroxyl)styrylbenzaldehyde (14) Similar to 11. $^1$H NMR (400MHz, DMSO-$d_6$): 6.78 (d, 2H), 7.13 (d, 1H), 7.29 (d, 1H), 7.47 (d, 2H), 7.75 (t, 1H), 7.87 (d, 1H), 8.08 (s, 1H), 9.70 (s, 1H), 10.03 (s, 1H). $^{13}$C NMR (400MHz, DMSO-$d_6$): 116.17, 124.34, 127.38, 128.29, 128.74, 130.09, 130.69, 132.41, 137.23, 139.18, 158.23, 193.83.

3-(4-(4-sulfobutoxy)styryl)benzaldehyde (4) Similar to 2. $^1$H NMR (400MHz, DMSO-$d_6$): 1.11 (m, 4H), 2.49 (t, 2H), 3.99 (t, 2H), 6.97 (d, 2H), 7.23 (d, 1H), 7.33 (d, 1H), 7.59 (d, 2H), 7.77 (d, 1H), 7.90 (d, 1H), 8.12 (s, 1H), 10.04 (s, 1H).
4-vinylbenzyl triisopropylsilyl ether (15) 9 (1g, 3.6mmol), CH$_3$PPh$_3$Br (1.285g, 3.6mmol) and 1, 5, 7-triazabicyclo[4,4,0]dec-5-ene (TBD, 0.1g, 4.32mmol) were added in THF, the mixture was refluxed for 12 hrs under stirring, water was added and extracted with ether, the organic layer was dried with magnesium sulfate and ether was removed by rotation evaporation. The residue was purified by column chromatography with chloroform affording 15. (0.82g, 82.5%) $^1$H NMR (400MHz, CDCl$_3$): 1.08 (t, 18H), 1.23 (m, 3H), 5.12 (d, 1H), 5.61 (d, 1H), 6.64 (q, 1H), 6.83 (d, 2H), 7.26 (d, 2H).

4-(4-triisopropylsilyl)styrylbenzaldehyde (16) A mixture of 4-bromobenzaldehyde (0.925g, 5mmol), 15 (1.38g, 5mmol), Pd(OAc)$_2$ (22.5mg, 2 mol% of aryl halide), tri-o-tolylphosphine (60.9mg, 4 mol% of aryl halide), and Et$_3$N (1.05 ml, 1.5 equivalents of aryl halide) in DMF was heated to 110 °C~140 °C. The reaction was monitored by TLC. The mixture was passed through a celite pad. Water
was added and the mixture was extracted with CHCl₃. The organic layer was washed with brine, dried over anhydrous MgSO₄, and solvent was evaporated under reduced pressure to give a crude product. The product was purified by chromatography on silica gel with CHCl₃, affording 16 (1.39g, 73%) ¹H NMR (400MHz, CDCl₃): 1.08 (t, 18H), 1.23 (m, 3H), 6.89 (d, 2H), 7.00 (d, 1H), 7.20 (d, 1H), 7.41 (d, 2H), 7.61 (d, 2H), 7.84 (d, 2H), 10.02 (s, 1H). ¹³C NMR (400MHz, CDCl₃): 12.77, 18.00, 116.04, 120.39, 125.23, 126.67, 128.28, 130.35, 132.02, 144.00, 191.72.

4-(4-hydroxystyryl)benzaldehyde (17) Synthetic procedures were similar to that of 11. ¹H NMR (400MHz, DMSO-d₆): 6.80 (d, 2H), 7.13 (d, 1H), 7.39 (d, 1H), 7.49 (d, 2H), 7.76 (d, 2H), 7.76 (d, 2H), 7.88 (d, 2H), 9.75 (s, 1H), 9.96 (s, 1H). ¹³C NMR (400MHz, DMSO-d₆): 116.24, 124.46, 127.05, 128.16, 129.11, 130.61, 132.71, 135.09, 144.38, 158.62, 192.86.
4-(4-(4-sulfobutoxy)styryl)benzaldehyde (5) Synthetic procedures were similar to that of 2. $^1$H NMR (400MHz, DMSO-d$_6$): 1.79 (m, 4H), 2.47 (t, 2H), 4.00 (t, 2H), 6.98 (d, 2H), 7.21 (d, 1H), 7.44 (d, 1H), 7.60 (d, 2H), 7.78 (d, 2H), 7.89 (d, 2H), 9.97 (s, 1H).

Diethyl(4-bromophenyl)methylphosphonate (18) 4-bromobenzyl bromide (2g, 8mmol) and triethylphosphite (1.4ml, 8mmol) were heated to 160 °C in a heavy-duty distillation apparatus for 3hrs, cooling down to room temperature and resulting in 18 (2.33g, 95%) $^1$H NMR (400MHz, CDCl$_3$): 1.24 (m, 6H), 3.07 (d, 2H), 4.01 (q, 4H), 7.17 (d, 2H), 7.42 (d, 2H). $^{13}$C NMR (400MHz, CDCl$_3$): 16.48, 32.67, 34.05, 62.30, 131.55, 131.74.
(4-bromostyryl)phenyl triisopropylsilyl ether (19) TBD (0.54g, 3.9mmol) was added slowly to a solution of 18 (1g, 3.25mmol) and 9 (0.9g, 3.25mmol) in THF. After stirring for 5hrs, the mixture was quenched with water. THF was removed under vacuum evaporation. The residue was poured into water. The product 19 was collected by filtration and washed with ether, resulting in a white solid (1.1g, 78.5%).

$^1$H NMR (400MHz, CDCl$_3$): 1.09 (t, 18H), 1.12 (m, 3H), 6.85 (q, 2H), 6.89 (d, 1H), 7.03 (d, 1H), 7.33 (d, 2H), 7.37 (q, 2H), 7.45 (d, 2H).

$^{13}$C NMR (400MHz, CDCl$_3$): 12.77, 13.49, 120.30, 121.00, 125.34, 127.80, 129.19, 130.04, 131.80, 136.86.

3-(4-(4-triisopropylsilyl)distyryl)etherbenzaldehyde (20) The procedure was similar to 13. $^1$H NMR (400MHz, DMSO-d$_6$): 1.034 (m, 21H), 6.79 (d, 2H), 7.03 (d, 1H),
7.24 (d, 1H), 7.43 (m, 4H), 7.63 (m, 4H), 7.80 (d, 1H), 7.94 (d, 1H), 8.15 (s, 1H), 10.05 (s, 1H).

4-(4-(4-hydroxy)distyryl)benzaldehyde (21) Similar to 11. \(^1\)H NMR (400MHz, DMSO-d\(_6\)): 6.79 (d, 2H), 7.04 (d, 1H), 7.20 (d, 1H), 7.40 (s, 2H), 7.45 (d, 2H), 7.58 (d, 2H), 7.65 (d, 2H), 7.81 (d, 1H), 7.95 (d, 1H), 8.15 (s, 1H), 9.64 (s, 1H), 10.06 (s, 1H).

3-(4-(4-sulfobutoxy)distyryl)benzaldehyde (6) Similar to 2. \(^1\)H NMR (400MHz, DMSO-d\(_6\)): 1.76 (m, 4H), 2.46 (m, 2H), 3.99 (t, 2H), 6.95 (d, 2H), 7.11 (d, 1H), 7.27
(d, 1H), 7.42 (s, 2H), 7.54 (d, 2H), 7.64 (m, 4H), 7.81 (d, 1H), 7.95 (d, 1H), 8.16 (s, 1H), 10.06 (s, 1H).

4-vinylbenzyl iodide (22) Sodium iodide (2g, 13.3 mmol) and 15 ml of 2-butanone were added to a dry flask which was purged with argon. 4-vinylbenzyl chloride (0.4ml, 2.8mmol) was syringed into the reaction mixture. The reaction was stirred for 8h in the dark under nitrogen at room temperature. The solvent was removed by rotary evaporation. The residue was extracted with ether and washed three times with 20ml of water each time. The organic layer was dried over MgSO₄. The solvent was removed under vacuum to produce 22 (0.63g, 92%) as a brown oil. £H NMR (400MHz, CDCl₃) 4.46 (s, 2H), 5.25 (d, 1H), 5.75 (d, 1H), 6.68 (q, 1H), 7.35 (s, 4H).

Diethyl 4-vinylbenzylphosphonate (23) A mixture of 4-vinylbenzyl iodide 22 (0.5g, 2.05mmol) and triethylphosphite (0.36ml, 2.05mmol) was stirred for 6h in the dark under nitrogen at room temperature. The side product, iodoethane, was removed by
rotary evaporation to yield 23 (0.489g, yield 95%) as a pale oil. $^1$H NMR (400MHz, CDCl$_3$): 1.21 (t, 6H), 3.11 (d, 2H), 3.97 (m, 2H), 3.99 (m, 2H), 5.19 (d, 1H), 5.69 (d, 1H), 6.65 (q, 1H), 7.22 (m, 2H), 7.32 (d, 2H). $^{13}$C NMR (400MHz, CDCl$_3$): 16.43, 32.94, 34.31, 113.77, 126.43, 129.96, 131.19, 136.49.

OTIPS

4-(4-vinyl)styrylphenyl triisopropylsilyl ether (24) TBD (0.68g, 4.9mmol) was added slowly to a solution of phosphonate 23 (1g, 3.9mmol) and aldehyde 9 (1.09g, 3.9mmol) in THF. The mixture was stirred for 5h at room temperature, then quenched with water. THF was removed under a vacuum. The residue was extracted twice with 25 ml of ether and washed with water thoroughly. The organic layer was dried over MgSO$_4$. Solvent was removed by rotary evaporation to create 24 (1.16g, yield 78%). $^1$H NMR (400 MHz, CDCl$_3$): 1.06 (m, 18H), 1.12 (m, 3H), 5.22 (d, 1H), 5.74 (d, 1H), 6.71 (q, 1H), 6.85 (d, 2H), 6.93 (d, 1H), 7.05 (d, 1H), 7.37 (m, 4H), 7.44 (d, 2H).
4-(4-(4-hydroxyl)distyryl)benzaldehyde (26) Similar to that of 11. $^1$H NMR (400MHz, DMSO-$d_6$): 6.78 (d, 2H), 7.04 (d, 1H), 7.22 (d, 1H), 7.38 (d, 1H), 7.45 (d, 2H), 7.49 (d, 1H), 7.58 (d, 2H), 7.65 (d, 2H), 7.83 (d, 2H), 7.91 (d, 2H), 9.63 (s, 1H), 9.99 (s, 1H).

4-(4-(4-triisopropylsilyl)ether)distyrylbenzaldehyde (25) The synthetic procedures are similar to that of 16.
4-(4-(4-sulfobutoxy)distyryl)benzaldehyde (7) Similar to that of 2. \(^{1}\)H NMR (400MHz, DMSO-d\(_6\)): 1.74 (m, 4H), 2.50 (t, 2H), 3.99 (t, 2H), 6.95 (d, 2H), 7.12 (d, 1H), 7.27 (d, 1H), 7.39 (d, 1H), 7.50 (d, 1H), 7.54 (d, 2H), 7.61 (d, 2H), 7.66 (d, 2H), 7.83 (d, 2H), 7.93 (d, 2H), 9.98 (s, 1H).
References


Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
CHAPTER III

DIPYRIDOPHENAZINE INCORPORATED RUTHENIUM (II) BIPYRIDINE COMPLEXES: THE RECEPTORS

3.1 Introduction

The polypyridyl Ru(II) complexes are colored due to an intense metal-to-ligand charge transfer (MLCT).\textsuperscript{[1-4]} The complex of the type [Ru(bpy)_2 L]^2^+\textsuperscript{2+}, (bpy = 2,2'-bipyridine, and L = dipyrido[3,2-a:2',3'-c]phenazine(dppz) and its analogues), has been identified as luminescent probes of many aprotic environments.\textsuperscript{[5-7]} In aqueous solution, [Ru(bpy)_2 dppz]^{2+} is essentially non-emissive; however, in the presence of DNA, the molecule intercalates between adjacent base pairs in the double helix and becomes brightly luminescent.\textsuperscript{[8-13]} This behavior, called the “light-switch” effect, is the basis for use of these compounds as probes of non-polar microenvironments. As it turns out, DNA is not the only environment in which the ruthenium dppz type complexes emit, and luminescent excited states are observed in many protic and aprotic solvents.\textsuperscript{[14, 15]} Because of their photophysical properties, dppz-type complex are ideally suited for application as molecular probes.\textsuperscript{[14, 16, 17]}

The light-switch mechanism, according to Brennaman, M. K.,\textsuperscript{[18, 19]} has been attributed to the presence of two metal-to-ligand charge transfer (MLCT) states on the dppz ligand: a bright (luminescent) state associated with the bipyridine (bpy) fragment (red-colored structure) and a dark (non-luminescent) state localized largely on the phenazine (phz) portion (blue-colored structure), as shown in Figure 3.1

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
In aprotic environments, the electron density of the excited state was mainly located on the bpy fragment. In protic or cationic environments, on the other hand, protonation or complexation of the phz nitrogens, the electron density, is localized more on the phz portion of the dppz ligand. Thus, it lowers the energy below that of the bright state, and shuts off the luminescence, as shown in Figure 3.2.

Figure 3.2 Schematic demonstration of the MLCT light-switch process
where A denotes the singlet MLCT state, B refers to the bright triplet MLCT state and C corresponds to the quencher(s) bonded dark state.

In this Chapter, we examine the possibility of adapting the light-switch property of the \([\text{Ru(bpy)}_2\text{dppz}]^{2+}\) type of compounds, for responding to DCP and HCl.
Two of the complexes: \([\text{Ru(bpy)}_2\text{dppz}]^{2+}\) and \([\text{Ru(bpy)}_2\text{dppp3}]^{2+}\) (dppp3 = dipyrido[3,2-a:2',3'-c]pirido-[4,3-b]quinoxaline), as demonstrated in Figure 3.3, were synthesized and characterized in order to find the structure of the receptor effect to the light-switch response of the complexes.

\[ \begin{align*}
\text{Ru} & \quad \text{N} \quad \text{N} \\
\text{N} & \quad \text{N} \quad \text{Ru}^{2+} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N}
\end{align*} \]

\[ \begin{align*}
\text{Ru} & \quad \text{N} \quad \text{N} \\
\text{N} & \quad \text{N} \quad \text{Ru}^{2+} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N}
\end{align*} \]

Figure 3.3 Structures of \([\text{Ru(bpy)}_2\text{dppz}]^{2+}\) and \([\text{Ru(bpy)}_2\text{dppp3}]^{2+}\)

3.2 Results and discussion

3.2.1 Synthesis of dipyridophenazine ruthenium (II) bipyridine complexes

3.2.1.1 Synthesis of \([\text{Ru(bpy)}_2(\text{dppz})](\text{PF}_6)_2\)

The dppz ligand was prepared in a two-step process.\(^{[20]}\) 1, 10-phenanthroline is first oxidized with fuming \(\text{H}_2\text{SO}_4\) and \(\text{HNO}_3\) to the dione \(27^{[11]}\), that then reacts with 1,2-phenylenediamine in ethanol, \(p\)-tolysulfonic acid was used to catalyze the reaction, to afford \(28\) (dppz).\(^{[21]}\)
Scheme 3.1 Synthesis of dipyrido[3,2-a;2',3'c]phenazine (dppz)

Scheme 3.2 Synthesis of [Ru(bpy)$_2$]dppz] (PF$_6$)$_2$

[Ru(bpy)$_2$]dppz](PF$_6$)$_2$ was prepared following procedures in the literature.$^{[22, 23]}$ The desired complex was isolated as the hexafluorophosphate salt by treating with ammonium hexafluorophosphate.
Unfortunately, the dppz bipyridine ruthenium complex has very weak interaction with DCP and HCl. A change in the emitting state is possible since the substituents in the ancillary ligands can alter the π-system to some degree, so that the complex may alter the MLCT.

Dipyrido[3,2-a;2',3'c]-pyrido[4,3-b]quinoxaline (dppp3), with a nitrogen replaced carbon in the phz, may lowers the MLCT state of the complex. On the other hand, it adds another binding site to the substrates. A change in the interaction between the complex and substrates (DCP and HCl) is expected.

3.2.1.2 Synthesis of [Ru(bpy)2(dppp3)](PF6)

Scheme 3.3 Synthesis of dppp3

The dppp3 ligand was prepared from dione 28 and 2,3-diaminepyridine. The procedure was similar to that of dppz.

31 is synthesized similar as 29.
Scheme 3.4 Synthesis of [Ru(bpy)$_2$dpbz] (PF$_6$)$_2$

3.2.2 Characterizations

3.2.2.1 UV-visible spectra

Figure 3.4 shows the UV-visible spectrum of [Ru(bpy)$_2$dpbz] (PF$_6$)$_2$ in CH$_3$CN. Peak positions are listed in Table 3.1. The broad peak in the 400–500 nm regions is readily assigned to an MLCT state. The band in the 350–370 nm region...
arises from the \( \pi - \pi^* \) absorption of dppz. The \( \pi - \pi^* \) transition of the bipyridine ligands, which is located in the upper 200 nm region, has a large absorbance.

![UV-visible spectrum of [Ru(bpy)2(dppp3)](PF6)2](image)

**Figure 3.5** UV-visible spectrum of [Ru(bpy)2(dppp3)](PF6)2

The spectroscopic characteristics of the ligands and their ruthenium complexes were summarized in Table 3.1. See Appendix B for the spectra.
### Table 3.1

Spectroscopic characteristics of the ligands and their complexes (CH$_3$CN, 25 °C)

<table>
<thead>
<tr>
<th></th>
<th>MLCT ($\lambda_{\text{max}}$, nm)</th>
<th>L π-π* ($\lambda_{\text{max}}$, nm)</th>
<th>Bpy π-π* ($\lambda_{\text{max}}$, nm)</th>
<th>Excitation ($\lambda_{\text{max}}$, nm)</th>
<th>Emission ($\lambda_{\text{max}}$, nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dppz</td>
<td>361, 380</td>
<td>272</td>
<td>361</td>
<td>413</td>
<td></td>
</tr>
<tr>
<td>Dppp3</td>
<td>362</td>
<td>270</td>
<td>365</td>
<td>423</td>
<td></td>
</tr>
<tr>
<td>[Ru(bpy)$<em>2$dp pz]$</em>{2}^{2+}$</td>
<td>450</td>
<td>365</td>
<td>284</td>
<td>440</td>
<td>610</td>
</tr>
<tr>
<td>[Ru(bpy)$<em>2$Dppp3]$</em>{2}^{2+}$</td>
<td>440</td>
<td>359</td>
<td>284</td>
<td>440</td>
<td>698</td>
</tr>
</tbody>
</table>

#### 3.2.2.2 Stern-Volmer equation

The details of quenching mechanism are not clear. We expect static quenching by complex formation of either the ligands or ruthenium complexes with DCP. The Stern-Volmer equation 3.1\[^{[24]}\], provide a quantitative measure of the fluorescence quenching:

\[
\frac{F_0}{F} = 1 + K_{sv}[Q]
\]

3.1

The fluorescence intensity upon quencher concentration is derived by consideration of the association constant for complex formation. The constant is given by

\[
K_{sv} = \frac{[F - Q]}{[F][Q]}
\]

3.2
where \([F - Q]\) is the concentration of the complex, \([F]\) is the concentration of uncomplexed fluorophore, and \([Q]\) is the concentration of quencher. If the complexed species is nonfluorescent then the fraction of the fluorescence that remains \((F/F_0)\) is given by the fraction of total fluorophores that are not complexed: \(f = F/F_0\). The total concentration of fluorophore \([F_0]\) is given by

\[
[F_0] = [F] + [F - Q]
\]  

substitute into equation 3.2

\[
K_{sv} = \frac{([F_0] - [F])}{[F][Q]} = \frac{[F_0]}{[F][Q]} - \frac{1}{[Q]}
\]  

By substituting the fluorophore concentration for fluorescence intensity, and rearranging equation 3.4, Stern-Volmer equation 3.1 is obtained.

The DCP binding affinities of the ligands and the complexes were evaluated by monitoring their respective emission properties as a function of DCP concentration.

3.2.2.3 Calculation of Stern-Volmer association constant

3.2.2.3.1 dppz and \([\text{Ru(bpy)$_2$}dppz](\text{PF}_6)_2\).

The emission of dppz in CH$_3$CN was quenched by DCP, as shown in Figure 3.6.
Figure 3.6  DCP effect on the luminescence of dppz (upper) and Stern-Volmer’s relationship (lower)

Apply Stern-Volmer equation 3.1

\[ \frac{F_0}{F} = 1 + Ksv[Q] \]
Plot $F_0/F$ vs. [DCP] (or HCl), the Stern-Volmer association constant $K_{sv}$ of 702/mol was obtained from Figure 3.6.

The DCP effect on the luminescence of $[\text{Ru(bpy)}_2\text{dppz}](\text{PF}_6)_2$ is shown in Figure 3.7.

Figure 3.7  DCP effect on the luminescence of $[\text{Ru(bpy)}_2\text{dppz}](\text{PF}_6)_2$ (upper) and Stern-Volmer relationship (lower)
Free ligands featured a strong fluorescence in the near-UV region that arises from the π-π* state with λ_{max} at 419 nm. In the [Ru(bpy)2dppz](PF6)2 complexes the fluorescence of the ligand dppz was quenched, and it is replaced by a red emission centered at 620 nm, due to the MLCT, as shown in Figure 3.7.

Figure 3.8  HCl effect on the luminescence of [Ru(bpy)2(dppz)](PF6)2 (upper) and Stern-Volmer relationship (lower)
The plot $F_0/F$ at 620 nm vs [DCP] is shown in Figure 3.7. The $Ksv$ was derived from the slope, which was 120/mol. The $Ksv$ indicated that the binding of DCP by the dppz ligand did not affect significantly to the MLCT state of the $[\text{Ru(bpy)}_2\text{dppz}](\text{PF}_6)_2$ complex.

The HCl effect on the fluorescence of the complex is shown in Figure 3.8. The $Ksv$ was 325/mol, which was 2.5 times of the $Ksv$ to DCP. The $Ksv$'s revealed that the sensitivity of the complex to HCl was higher than to DCP.

3.2.2.3.2 dppp3 and $[\text{Ru(bpy)}_2\text{dppp3}]^{2+}$. 

![Figure 3.9 DCP effect on the fluorescence of dppp3](image)

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Replacing one of the carbon atoms with nitrogen on the phenazine ring of the dppz, results in dppp3. Unlike dppz, whose fluorescence decreased as the addition of DCP, addition of DCP or HCl increased the fluorescence of dppp3. From this it was concluded that the structure of the ligand altered its fluorescence property, as shown in Figure 3.6 and Figure 3.9.

Figure 3.10  HCl effect on the fluorescence of dppp3

Figure 3.11  Emission of [Ru(bpy)$_2$dppp3](PF$_6$)$_2$
Figure 3.12 Influence of DCP on the luminescence of [Ru(bpy)$_2$dp$_3$3](PF$_6$)$_2$ (upper) and the Stern-Volmer relationship (lower)
Figure 3.13  HCl effect on the luminescence of [Ru(bpy)$_2$(dppp3)](PF$_6$)$_2$ (upper) and Stern-Volmer relationship (lower)
Although the fluorescence of the free ligand dppp3 increased by the addition of DCP, the fluorescence of its complex, [Ru(bpy)₂(dppp3)](PF₆)₂, was still quenched by DCP, Figure 3.9 and Figure 3.12. The Ksv of [Ru(bpy)₂(dppz)](PF₆)₂ was 605/mol. The sensitivity of [Ru(bpy)₂(dppp3)](PF₆)₂ to DCP, comparing with that of [Ru(bpy)₂(dppz)](PF₆)₂, has doubled, as depicted in Table 3.2.

<table>
<thead>
<tr>
<th></th>
<th>Ksv of DCP (mol⁻¹)</th>
<th>Ksv of HCl (mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="PF%E2%82%86">Ru(bpy)₂(dppz)</a>₂</td>
<td>120</td>
<td>325</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">Ru(bpy)₂(dppp3)</a>₂</td>
<td>605</td>
<td>1338</td>
</tr>
</tbody>
</table>

Free ligands featured a strong fluorescence in the near-UV region that arises from the π-π* state with λ_max at 423 nm. In the [Ru(bpy)₂(dppp3)](PF₆)₂ complexes the fluorescence of the ligand dppp3 again was quenched, and it is replaced by a red emission at 698 nm, due to the MLCT, as shown in Figure 3.11. Notably, the λ_max of emission of the free ligands shifted only slightly (419 nm to 423 nm), from dppz to dppp3. On the other hand, the emission maxima of their complexes shifted from 620 nm to 698 nm. This result indicated that a small perturbation of the energy state of the ligand, could result in a significant change in the MLCT state of a complex. This property made the type of [Ru(bpy)₂L]²⁺ complex excellent as molecular probes.
3.3 Conclusion

Two Ru$^{3+}$ complexes: [Ru(bpy)$_2$dpdz](PF$_6$)$_2$ and [Ru(bpy)$_2$dpdp$_3$](PF$_6$)$_2$ were synthesized and characterized with UV-vis and fluorescence. Their sensitivities to DCP and HCl were measured by Stern-Volmer association constants. We have found that the modified ligand dpdp$_3$, in comparing to dpdz, was more sensitive to both DCP and HCl; our results led to the conclusion that changes in the ancillary ligand could be made with the variation in the excited states of the complex. The complexes are suitable fluorescence probes for DCP and HCl.

3.4 Experimental section

The same instrumental and experimental methods, as described in CHAPTER II, were used for obtaining $^1$H NMR, $^{13}$C NMR, UV-visible, excitation, fluorescence spectra and lifetime.

1,10-phenanthroline-5,6-dione A round bottom flask containing 1,10-phenanthroline (0.335g, 1.6mmol) and potassium bromide (1.9g, 16mmol) was cooled in an ice bath. Concentrated sulfuric acid (6ml) was added dropwise while stirring, followed by slow addition of concentrated nitric acid (3ml). After all of the 1,10-phenanthroline had dissolved in the acid medium, the reaction mixture was heated
to reflux in an oil bath for 3h, and then cooled to room temperature, and the solution was poured into 80ml of water. The resulting yellow solution was neutralized with sodium bicarbonate and extracted with chloroform. The extracts were washed with water and the organic layer was dried with MgSO₄. Solvent was removed under reduced pressure to leave a yellow residue which was recrystallized from ethanol to provide 27 (0.35g, 78%), as yellow needles. \(^1\)H NMR (400MHz, DMSO-\(d_6\)): 8.99 (d, 2H), 8.39 (d, 2H), 7.66 (q, 2H).

**Dipyrido[3,2-a:2',3'-c]phenazine(dppz)** A solution of 27 (0.515 g, 2.45 mmol) with 15 mL of ethanol was added into o-phenylenediamine (0.530 g, 4.91 mmol) in 10 mL of ethanol and trace p-toluene sulfuric acid. The mixture was gently boiled and stirred for 3 hr. Some ethanol was removed, and the mixture was cooled to room temperature. A brown precipitate was obtained and recrystallized from aqueous ethanol to give brown-orange needle 28 (0.511g, yield 74%). \(^1\)H NMR (400MHz, DMSO-\(d_6\)): 9.53 (d, 2H), 9.22 (d, 2H), 8.39 (q, 2H), 8.07 (q, 2H), 7.94 (q, 2H).
[Ru(bpy)₂(dppz)](PF₆)₂. A mixture of dppz (100 mg, 0.326 mmol) and [(bpy)₂RuCl₂] (204 mg, 0.392 mmol) in absolute ethanol (40 mL) was refluxed under nitrogen for 16 h. After cooling, excess NH₄PF₆ was added, and the resulting precipitate was collected and purified by chromatography on Al₂O₃ using CH₃CN/toluene (1:1) to provide an orange-red solid (228 mg, 70%). Recrystallization from CH₃CN/toluene gave [Ru(bpy)₂(dppz)](PF₆)₂ as red crystals. ¹H NMR (400MHz, CDCl₃): 8.75 (d, 1H), 8.63 (d, 1H), 8.34 (overlapping m), 8.13 (t, 1 H), 7.99 (t, 1 H), 7.95-7.2 (overlapping m), 6.95 (d, overlapping t), 6.80 (d, 1 H), 6.48 (s), 6.41 (t), 6.20 (d), 6.01 (t).

Dipyrido[3,2-a;2',3'-c]-pyrido[4,3-b]quinoxaline (dppp3) The synthetic procedure is similar to that of dppz. The yield was 88%. ¹H NMR (400MHZ,
DMSO-d$_6$): 7.99 (m, 2H), 8.30 (d, 1H), 9.00 (d, 1H), 9.27 (t, 2H), 9.54 (d, 2H), 9.84 (s, 1H).

The procedure is similar to that for [Ru(bpy)$_2$(dppz)](PF$_6$)$_2$.

$^1$H NMR (400MHz, DMSO-d$_6$): 7.40 (t, 2H), 7.60 (t, 2H), 7.76 (d, 2H), 7.82(d, 2H), 0.10 (m, 2H), 8.14 (t, 2H), 8.25 (t, 2H), 8.29 (t, 2H), 8.43 (d, 1H), 8.89 (t, 4H), 9.13 (d, 1H), 9.63 (d, 2H), 9.98 (s, 1H).
References


Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
CHAPTER IV

FABRICATION AND CHARACTERIZATION OF THE TWO BLOCK SENSOR SYSTEM

4.1 Introduction

Construction of efficient photo-induced electron (energy) transfer systems has been the subject of intense studies because of their important role in various rapidly developing fields like sophisticated molecular sensors,[1, 2] artificial solar energy harvesting systems,[3, 4] and molecular-level devices for nanoscale electronics.[5-10]

Molecular system composed of photosensitizing receptor units and various connecting units for efficient and long-distance energy transfer have been reported.[11, 12] In this chapter, we will demonstrate a molecular sensor system, which is composed of ruthenium complex incorporated receptor as a photosensitizing building block, and silica nanoparticle assembled stilbenoid as a signal block. The two blocks are connected through ion pairs between the metal center of the ruthenium complex and the anion group of the stilbenoid.

Modification of the surface of nanoparticles is a suitable method to constrain a set of fluorescent units into an organized network. Fluorescent molecule modified nanoparticles are in fact very promising for the design of labels and sensors for the relative ease of synthesis and for their peculiar properties. Covalently grafting[13] on the nanoparticles is necessary to obtain a stable arrangement and avoid structural
reorganization due to redistribution of the fluorescent molecules on the particle surface. Silica nanoparticles can be prepared in a very straightforward way, and their surface can be easily modified by means of alkoxy silane derivatives. This versatility makes silica nanoparticles as good choices for a network of fluorescent moieties. Fluorescent molecule coated silica nanoparticles constitute a suitable system to characterize intermolecular photophysical processes at their surface, avoiding any interference from the particle nucleus.

We demonstrate here how the silica nanoparticle mediated self-assembly technique enables multi-function components organized into aligned structures, and optical identification through the close-packed nanostructure.

4.2 Results and discussion
4.2.1 Interactions between DCP and individual signal and receptor molecules

Before testing the sensitivity of the full sensor to DCP, we tested the individual compound: \([\text{Ru(bpy)}_2\text{dppp}3]^+\) \(31\) was used as the receptor incorporated complex, stilbenoid \(7\) was chosen as fluorescence signal molecule.

Stern-Volmer analysis gives insight into the efficiency of fluorescence quenching or energy transfer according to Equation 3.1:

\[
\frac{F_0}{F} = 1 + K_{sv}[\text{DCP}]
\]
Figure 4.1 Influence of DCP on the fluorescence of compound 7 (upper) and the Stern-Volmer relationship (lower)
The details of the quenching mechanism are not clear. We expect static quenching by complex formation to dominate at the experimental range of quencher concentration. \((10^{-5} \text{ to } 10^{-4} \text{ M})\)

DCP effect experiments were carried out in acetonitrile solution by adding to 2 \(\times 10^{-6}\) M of stilbenoid 7 increasing amount of DCP \((C = 10^{-5} \text{ M to } 10^{-4} \text{ M})\)

As seen in Figure 4.1, DCP quenched the fluorescence of compound 7, with Stern-Volmer association constant of 752/mol.

The association constant of \([Ru(bpy)_2dppp_3]^{2+}\) with DCP was obtained from slope of the Stern-Volmer relationship plot in Figure 3.12, which was 605/mol.

4.2.2 Interactions between DCP and the mixture of \([Ru(bpy)_2dppp_3](PF_6)_2\) complex and stilbenoid molecule 7

The mixture of 1:2 of complex 31/ Stilbenoid 7 in acetonitrile solution, with concentration of 1 \(\times 10^{-6}\) M and 2 \(\times 10^{-6}\) M respectively, was aged overnight. 1~5 \(\mu\)l of the stock solution of DCP in acetonitrile of 0.034 M was added to the mixture each time, and the fluorescence spectrum was obtained for each addition of DCP.
Figure 4.2  Effect of DCP on the luminescence of 7 + 31, a) emission intensity; b) Stern-Volmer plot

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
As seen in Figure 4.2 (a), the first 5 µl of 0.034 M DCP increased the emission of the 7 + 31. Further addition of DCP constantly quenched the emission with Stern-Volmer's quenching constant of 880/mol. The change in the fluorescent intensity as we increased the concentration of DCP caught our attention. It may be explained by the proposed mechanism as shown in Scheme 4.1.

where R-S is the adduct of receptor and stilbene derivative, R-DCP is the adduct of receptor and DCP.

\[
R-S + DCP \rightarrow R-DCP + S
\]

Scheme 4.1   Equilibrium between receptor-stilbene adduct and receptor-DCP adduct

There were previous reports on the efficient quenching of fluorescence of poly(2-methoxy-5-propyloxy sulfonate phenylene vinylene (MPS-PPV) by Methyl Viologen (MV$_{2}^{+}$),\(^{14-17}\) which resembled the two moieties in the system of 7 + 31, as depicted in Figure 4.3.
The mechanism of quenching was described as by the formation of complex between MPS-PPV and MV$^{2+}$.[14] There were three binding sites on the receptor. Since 1:2 of the receptor incorporated complex/stilbene derivative 7 was used, there was still one binding site available for DCP. When the first 5 µl of 0.034 M of DCP was added, the concentration of DCP in the solution was $4.18 \times 10^{-5}$ M, while the concentration of the receptor was only $1 \times 10^{-6}$ M. As a result, despite of binding with the third site on receptor, DCP also replaced the stilbene in the receptor-stilbene adductive, as shown in Scheme 4.1. Consequently, the increase of fluorescence at 544 nm, which was caused by the increase of free stilbene derivative 7 as we continued to increase the amount of DCP, the emission at 544 nm decreased, which was in agreement with the observation of the fluorescence quenching of 7 by DCP. (Figure 4.1)
4.2.3 Fabrication of silica nanoparticle assembled sensor (1) and its characterization

4.2.3.1 Preparation of silica nanoparticle

40 nm silica nanoparticles can be made according to Wang et al.[18]

\[
\text{Si(OC}_2\text{H}_5\text{)}_4 + 4\text{H}_2\text{O} \xrightarrow{\text{NH}_3, \text{Alcohol}} \text{Si(OH)}_4 + 4\text{C}_2\text{H}_5\text{OH}
\]

\[
\text{Si(OH)}_4 \xrightarrow{\text{NH}_3, \text{Alcohol}} \text{SiO}_2 \downarrow + 2\text{H}_2\text{O}
\]

Scheme 4.2 Synthesis of nanoparticle

1.5 ml of TEOS (tetra-ethoxysilane), 1.7 ml of ammonia (25 wt %), 1.0 ml of deionized water, and 50 ml of ethanol were introduced into a 250 ml round-bottomed glass flask. After the mixture was stirred at 40 °C for 3 hrs, an additional 1.0 ml of TEOS was added into the system and the reactions were allowed to continue for another 3 hrs. The system was then diluted several (e.g. 10) times with deionized water. Ethanol was removed from the system through a rotary evaporation. By this process, a suspension containing colloidal particles of about 40 nm in diameter was obtained. The size of the nanoparticle was tested by transmission electron microscopy (TEM), in Figure 4.4.
4.2.3.2 Silanization of nanoparticles

Silica-immobilized (3-aminopropyl)-silane was prepared by reacting 0.4 ml of 3-aminopropyltrimethoxysilane with 100 mg of baked silica gel (35-40 nm diameter) in dry toluene for 30 min, filtered, and washed exhaustively with toluene.\textsuperscript{[19]}

\[
\text{Si(OCH}_3\text{)}_3 + \text{NH}_2
\]

\[
\text{HO} - \text{SiO}_2\text{OH} \rightarrow \text{Tolene} \rightarrow \text{NH}_2
\]

\[
\text{SiO}_2
\]

\textbf{Scheme 4.3} Silanization of silica nanoparticle

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
The TEM image of the silanized silica nanoparticles was shown in Figure 4.5

![TEM image of silanized silica nanoparticles](image)

**Figure 4.5** TEM images of silanized silica nanoparticles

4.2.3.3 Fabrication of the two-block sensor system

The formation of the Schiff's base was achieved by reacting the aldehyde group substituted stilbenoid with silanized silica nanoparticles in methanol. The mixture was stirred at 50 °C for 3 hrs. After the condensation the substrates were washed with methanol and sonicated in methanol for 30 min. Finally the substrates were dried under vacuum.\(^{[20]}\)
where \( n = 1 \) or 2

**Scheme 4.4** Formation of Schiff's base between silanized silica and stilbenoid

The two-block sensor was made by mixing the silica nanoparticle assembled stilbenoids with \([\text{Ru(bpy)}_2\text{dppp}3](\text{PF}_6)_2\) in acetonitrile. The construction of full sensor was demonstrated in Figure 1.1.

### 4.2.3.4 Characterizations

To understand the behavior of the nanoparticle organized molecular system, we conducted the following experiments: 1) DCP effect to the fluorescence of 7-SiO₂, Figure 4.6; 2) compare the emission spectra of 7-SiO₂ and 2:1 (concentration) of 7-SiO₂/31, as shown in Figure 4.7.
Figure 4.6 Effect of DCP on the fluorescence of 7-SiO₂ (a) and the Stern-Volmer relationship (b)
The emission data for 7-SiO$_2$ + 31 are shown in Figure 4.7.
Figure 4.7  Emission spectra of (a) 7-SiO₂, (b) 31 and (c) 7-SiO₂ + 31

The fluorescence of the silica nanoparticle-assembled stilbenoid 7 was quenched from $9.45 \times 10^5$ M to $3.1 \times 10^3$ M, about 300 times, by mixing with the ruthenium complex 31. This result was quite different from the behavior of the pure compound 7, while the fluorescence of the 7 was not significantly affected by the complex. The reason can be visualized by Figure 4.8:
Figure 4.8 Schematic representation of nanoparticle promoted organized structure of the two-block system

As shown in Figure 4.8, nanoparticle mediated the self-assembly of the stilbenoids, forming a monolayer with negative charge of the $\text{SO}_3^-$ at the surface. We speculate that the spontaneous formation of a cationic ruthenium complex shell to be primarily the result of cooperative electrostatic forces.
Figure 4.9  a) Interactions between DCP and (31 + 7-SiO₂), and b) The Stern-Volmer relationship at 631 nm
Addition of the ruthenium complex into the stilbenoid increased the association constant from 752 to 880/mol, as seen from Table 4.1, indicating the existing of the interaction between the receptor molecule 31 and the signal molecule 7.

Table 4.1
Stern-Volmer association constants of sensor 1

<table>
<thead>
<tr>
<th></th>
<th>7</th>
<th>31</th>
<th>7 + 31</th>
<th>7-SiO$_2$ + 31</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_{sv}$ (mol$^{-1}$)</td>
<td>752</td>
<td>605</td>
<td>880</td>
<td>1516</td>
</tr>
</tbody>
</table>

The interaction between the ion pairs of the receptor and signal molecule quenched the fluorescence of the signal molecule (Figure 4.9 (c)), making the signal molecule lost its function in the full sensor system. However, the K$_{sv}$ of the silica nanoparticle-assembled two block system at 631 nm was 1516/mol, comparing with 605/mol of free ruthenium complex 31 (Table 4.1), the sensitivity to DCP has been increased by 2.5 times. From the above results, we can conclude that silica nanoparticles can mediate the formation of organized multichromophoric system, making the study of the photobehavior between mutilchromophores possible. In addition, an increased sensitivity can be achieved by forming organized structure. This feature would open up a new perspective in the design of functional nanosystems with great application in the field of fluorescent sensor development.
While quenching of the fluorescence of the signal molecule had happened by nanoparticle-mediated self-assembled multilayer formation, a red shift of the emission maximum from the Ru$^{2+}$ metal central from 698 nm to 631 nm was also observed. This result indicated the interaction between the signal molecule and the receptor molecule was due to photo-induced electron transfer.

![Emission spectra of silica nanoparticle assembled stilbenoid 1 and its mixture with complex 31](image)

Figure 4.10  Emission spectra of silica nanoparticle assembled stilbenoid 1 and its mixture with complex 31

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Figure 4.11  Schematic demonstration of the ion pair formation between a) 7-SiO$_2$ and 31, and b) 1-SiO$_2$ and 31
To investigate the tethered -SO$_3^-$ effect on the formation of ion pairs with cation, we compared the effect with that of stilbenoid 1, in which the carboxylic anion group –COO$^-$ was directly attached on the phenyl ring.

The fluorescence of stilbenoid 1 was quenched from 2 x 10$^6$ to 6.7 x 10$^4$, upon addition of the ruthenium complex. The smaller effect of the complex to 1 than to 7 (30 times vs. 300 times), showing the tethered SO$_3^-$ group was more efficient than COO$^-$ group in terms of forming ion pairs with the oppositely charged complex, as illustrated in Figure 4.11

4.3 Conclusion

An amino-terminated self-assembled monolayer on the silica nanoparticle was covalently fabricated into an organic fluorescent monolayer. A two-block sensor system has been successfully built up by silica nanoparticle promoted ion pair formation between the signal molecules and the receptor molecules.

The designed molecules, both the stilbenoids with tethered sulfonyl group and the receptor incorporated ruthenium bis-bipyridine complex, were proven to be efficient as signal or photosensitizing molecule, respectively. The quenching of fluorescence of the stilbene by ruthenium complex was unexpected. However, the sensitivity of the ruthenium complexes to DCP has been increased in the two-block system. This finding would open up a new perspective in the design of functional nanosystems with great application in the field of fluorescent sensor development.
The interaction between the two-block was due to photo induced electron transfer has been proved. This system can be easily adapted for detection of other toxic chemicals by replacing the receptor in the ruthenium complex.
References


CHAPTER V

STYRYLPYRIDINES AS INTEGRATED RECEPTOR AND SIGNAL MOLECULES

5.1 Introduction

Introduction of a nitrogen atom into the ring noticeably affects the photophysical and photochemical behavior of stilbene. This is probably because of the involvement of \( n, \pi^* \) states, where \( n \) refers to the lone pair on the nitrogen atom. The basic site of aza aromatics makes them excellent candidates for sensor materials. There have been a few examples which employ pyridine as the basic moiety for fluorescence pH sensors.

The fluorescence properties and the photoisomerization mechanism have been interpreted in terms of the competition among the radiative, non-radiative and reactive relaxation processes. Fluorescence emission is one of the ways by which photo excited azastilbene decays to the ground state. In azastilbene derivatives with close-lying \( n, \pi^* \) and \( \pi, \pi^* \) states, the two states are vibronically coupled, an inversion of energy states can be caused by polar solvent, temperature, and Lewis acid-base interactions. This occurs if \( n, \pi^* \) is the lowest singlet excited state. Fluorescence of both neutral and protonated molecules arises from \( \pi, \pi^* \) states and its efficiency is highly affected by the relative energies between \( n, \pi^* \) and \( \pi, \pi^* \) of azastilbenes. Therefore, the substitutions on the aromatic rings and extension of conjugation can be designed in which the molecular systems can be persuaded to
switch "on" their fluorescence if the n, π* state is perturbed such that the lowest energy singlet excited state is of π, π* type.

**Figure 5.1** illustrates this situation in terms of polar solvent bond induced n, π*-π, π* inversion.\(^{19,21}\)

![Energy level diagram](image)

**Figure 5.1  Polar solvent induced n, π*-π, π* inversion**

If the lowest excited state is of n, π* state, protonation or Lewis acid complexion of the pyridyl group is expected to cause inversion of the π, π* state and n, π* state, as shown in **Figure 5.1**. The main deactivation process is through intersystem crossing (ISC) in this case. There would be no inversion if the lowest excited singlet state is already π, π* in a non-polar solvent,\(^{12,16,18}\) as illustrated in **Figure 5.2**, and the main deactivation process of the excited state is through internal conversion (IC).
Figure 5.2  Polar solvent does not invert the energy states when $\pi, \pi^*$ is the lowest excited state

The structural related photo behaviors of aza stilbenes make them good candidates for fluorescence alternation studies. In addition, the presence of the lone-pair electrons on the nitrogen allows the photophysical and photochemical properties of the neutral molecule and their pyridinium complex to be investigated. In this chapter, the synthesis of two styrylpyridines with different conjugation length is reported. The structure-property relationship has been investigated. The possibility of applying these compounds as sensor materials for DCP and HCl are also studied.
5.2 Results and discussion

5.2.1 Synthesis

5.2.1.1 4-((E)-2-(pyridin-4-yl)vinyl)benzaldehyde (32)

![Chemical structure of 32]

32 was prepared in high yield by a Heck reaction of 4-bromobenzaldehyde with 4-vinylpyridine.[22, 23]

The Heck reaction of halobenzaldehyde and styrylpyridine strongly depends on the leaving group,[24] because the oxidative addition of the haloarenes to palladium (0) is in many cases the rate-determining step.[25-28] Along with the consideration of material accessibility and price, we chose bromide. Attempts to optimize the reaction conditions for the Heck reaction of bromo-benzaldehyde and styrylpyridine had shown that tris-o-tolylphosphine was better than triphenylphosphine in terms of yields. The applicable temperature ranges between 100-130 °C, at lower temperature no product was detected within 5 hrs, whereas quickly black palladium precipitates quickly above 135 °C. Freshly distilled DMF was to be the solvent of choice since it

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
is sufficient polar, and has a boiling point above the required temperature range. After cooling to room temperature, the reaction mixture was filtered with celite packed funnel. Water was added into the filtrate and chloroform was added to extract product from reaction mixture. The organic layer was washed with several portions of water and dried with MgSO₄. Chromatography on silica gel with 9:1 of CH₂Cl₂/MeOH allowed the separation of the product from by-products and un-reacted starting materials.

5.2.1.2 Synthesis of 4-(4-(2-(pyridin-4-yl)vinyl)styryl)benzaldehyde (33)

33 was synthesized from 35 and 4-vinylpyridine through the Heck coupling reaction. 18 was obtained from 4-bromo-benzylbromide by a Michaelis-Arbuzov reaction, as described in 2.2.4, Chapter 2. The Wittig-Horner coupling reaction of 34 and teraphthalaldehyde-monoacetal gives an intermediate 4-bromo-stilbene monoacetal. The subsequent deprotection of the intermediate with 6N HCl, [31, 32] (without isolation of the intermediate) resulted in 35. The final product was finished by the Heck reaction of 35 and 4-vinylpyridine, in which the procedures and reactions conditions similar with the Heck reaction described in Chapter 2.

A Perkin-Elmer Lambda 35 spectrophotometer was used for the absorption measurements. The fluorescence spectra were measured by an Edinburgh Instrument F900 spectrofluorometer, and fluorescence lifetimes were measured on the same
machine, using the single photon counting method. For the room temperature spectroscopic measurements in solution, the sample was dissolved in acetonitrile.

Scheme 5.2 Synthesis of 33

5.2.2 Structural determination

32 was recrystallized from benzene. The purity of the white-yellowish solid was checked by $^1$H, $^{13}$C NMR (in DMSO-d$_6$), and the melting point (114.8-115.4 °C).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
$^1$H NMR showed a trans isomer, with coupling constant of 16.1 MHz of the ethylene double bond hydrogen.

Figure 5.3 $^1$H NMR of 32

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
The crystal was sent to North Carolina State University for X-ray powder diffraction analysis. The result conformed that the single crystal used in X-ray analysis was representative of the bulk used in optical measurements. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number of CCDC 645774, Private Communications (1078), Y: 2007. Formula: C_{14}H_{11}NO, M = 209 g/mol, Unit cell parameters: a 7.7647(2) b 12.1912(3) c 22.4911(5) orthorhombic, see Appendix D for the space group Pbca. The crystal structure also gave a *trans* isomer, as shown in Figure 5.4.

We were not able to get a single crystal suitable for X-ray diffraction from 33. The structure of 33 was determined by $^1$H NMR, $^{13}$C NMR, IR and LC-MS.
Figure 5.5 $^1$H NMR of 33

$^1$H NMR indicated trans-trans isomer of 33 with coupling constant of 16.5 kHz for the hydrogens of the ethylene bond joined with pyridine ring and 16.4 kHz for the hydrogens of the other ethylene bond.
5.2.3 Characterizations of 32 and 33

5.2.3.1 Solvent influences to absorptions and emissions

Hexane and acetonitrile were chosen as the non-polar and polar solvents for the solvent effect experiments. The solvent effect on the UV-visible spectra of 32 were shown in Figure 5.6, emission in Figure 5.7; UV-vis of 33 in Figure 5.8, excitation in Figure 5.9, and emission in Figure 5.10.

![Figure 5.6: UV-vis of 32 in Hexane and Acetonitrile](image)

**Figure 5.6** UV-vis of 32 left) in Hexane and right) in Acetonitrile

![Figure 5.7: Emission of 32 in Hexane and Acetonitrile](image)

**Figure 5.7** Emission of 32 left) in Hexane and right) in Acetonitrile

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Figure 5.8  UV-vis of 33 left) in Hexane and right) in Acetonitrile

Figure 5.9  Excitation of 33 left) in Hexane and right) in Acetonitrile

Figure 5.10  Emission of 33 left) in Hexane, right) in Acetonitrile
UV-visible absorbance and emission maxima for 32 and 33 in hexane and acetonitrile are summarized in Table 5.1.

### Table 5.1

**Solvent effect on the absorption and emission maxima of 32 and 33**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>32</th>
<th>33</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV-vis</td>
<td>Emission</td>
</tr>
<tr>
<td></td>
<td>λ\text{max} (nm)</td>
<td>λ\text{max} (nm)</td>
</tr>
<tr>
<td>Hexane</td>
<td>321</td>
<td>Undetectable</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>321</td>
<td>475</td>
</tr>
</tbody>
</table>

A peculiar behavior was found for 32, whose absorption spectrum was little affected by the polarity of solvents while the emission spectrum showed “on” by polar solvent and “off” by non-polar solvent. This spectral behavior could indicate that the fluorescence of 32 originates from a state different from that reached by absorption. Both the n, π* and π, π* states are responsible for the absorption but they are too close to be distinguished in the absorption spectra. While the emission from the S\textsubscript{1} state is expected from π, π* in polar solvent and is deactivated by the n, π* vibronic effect through internal conversion (IC) in non-polar solvent.\[20,33]\[15\]

The state inversion of 32 by polar solvent can be schematically illustrated by Figure 5.11.\[15\]
On the other hand, both UV-visible absorbance shifted from 300 to 363 nm, emission from 418 to 450 nm, from n-hexane to acetonitrile, indicating that the excitation and emission were from the same state, \( \pi, \pi^* \) in 33. The excitation in both hexane and acetonitrile looked very similar except a small peak at 308 nm in hexane, and it disappeared in acetonitrile, indicating the weak excitation of \( n, \pi^* \) state in non-polar solvent and no excitation in polar solvent due to its shifting to higher energy. There was no state energy inversion in 33 as in 32.
5.2.3.2 Temperature influence to absorption and emission

**Figure 5.12** gives the excitation of 32 at 0 °C and 25 °C, and emission of temperature effect in **Figure 5.13**.

**Figure 5.12**  Temperature influence to excitation of 32 (in Acetonitrile)

**Figure 5.13**  Temperature effect on emission of 32 (in Acetonitrile)

From **Figure 5.12** and **Figure 5.13**, we can see that there were two absorptions at low temperature (0 °C) which could be assigned as 265 nm for n, π* and 345 for π, π*. As the temperature rose to 25 °C, the two states were mixed into
one state at 345 nm. Interestingly, the emission was not affected by the temperature; both spectra at 0 °C and 25 °C were similar. We conclude that only one state (\(\pi, \pi^*\)) was responsible for the emission. \(32\) has the lowest singlet excited state of \(\pi, \pi^*\) that can be induced from the experimental results.\(^{[16,21]}\)

Temperature effect on the excitation and emission of \(33\) in acetonitrile were illustrated in **Figure 5.14** and **Figure 5.15**, respectively.

![Figure 5.14](image)

**Figure 5.14**  Temperature effect on the excitation spectra of \(33\) (in Acetonitrile)

**Figure 5.14** showed that the temperature did not have much effect on the excitation of \(33\) except the small peak around 300 nm at 0 °C, and it disappeared when the temperature rose to 25 °C. This peak was due to the \(n, \pi^*\) transition. These findings indicated that at low temperature, the energy gaps between \(\pi, \pi^*\) and \(n, \pi^*\) were smaller than at higher temperature.
Figure 5.15  Temperature effect on emission of 33 in Acetonitrile

The increase in temperature shifted the emission maximum of 33 to red slightly. The energy gaps between $\pi$, $\pi^*$ and $n$, $\pi^*$ states were increased as the temperature increased.

5.2.4 Sensing of DCP and HCl

In the entire experiments, UV-visible absorbance was controlled by closing to 0.2, and the concentrations of the substrates were fallen into the range of $10^{-6}$ M.

5.2.4.1 UV-visible spectra

Increasing DCP or HCl caused the decreasing of the absorption at the shorter wavelength 321 nm and the increasing at the longer wavelength 350 nm (Figure 5.16), indicating the deactivation of $n$, $\pi^*$ state and increased contribution of the $\pi$, $\pi^*$ state. The addition of HCl into 33 first lowered the energy of $\pi$, $\pi^*$, shown as a red shift of UV-vis, and further addition of HCl caused the decrease of absorbance, these results
indicated the existing of the lowest $\pi, \pi^*$ singlet state in 33. The addition of DCP gradually shifted the UV-vis to red, showing weaker interaction with 33 than HCl.

5.2.4.2 Emission spectra

DCP and HCl effect on the fluorescence spectra of 32 and 33 are illustrated in Figure 5.17. The fluorescence of 32 increased with the increasing of both DCP and HCl, due to the deactivation of $n,\pi^*$ effect upon formation of the pyridium adductive. Consequently, the increasing contribution of the $\pi,\pi^*$ state made 32 a "turn on" fluorescence sensor material for both DCP and HCl.
As demonstrated in Figure 5.16 and Figure 5.17, the lowest singlet state of 32, which was \( n, \pi^* \) in non-polar solvent such as n-hexane, was not discernible in the absorption spectrum due to the large extinction coefficient of the lowest \( \pi, \pi^* \) transition.\(^{[34]}\) The \( \pi, \pi^* \) state was strongly mixed with the \( n, \pi^* \) transition, dominating the first absorption band. Consequently, the absorption and fluorescence spectra correlated with the lowest \( \pi, \pi^* \) states in both the pyridine and pyridium forms.

**Figure 5.17**   DCP and HCl effect on the emission spectra of 32 and 33

Fluorescence spectra of 33 have maxima located at 450 nm in neutral form and 550 nm in complex form. The complexation shifts the maxima of 33 towards the
red by about 100 nm. As we demonstrated by solvent and temperature effect, the red-shifted excited state was \( \pi, \pi^* \) in nature. The \( n, \pi^* \) state was shifted to higher energy and did not play a significant role on the photochemical behavior of protonated/complexed 33. The quantum yield of the pyridinium form was lower than that of the pyridine form, as seen in Figure 5.17, in agreement with theoretical calculations.\(^{21,35}\) Despite the red shift, complexation also quenched the fluorescence, further proving that the existence of a lowest singlet \( \pi, \pi^* \) state in 33.

5.2.4.3 Discussion

The formation of 1:1 complex between 32 and DCP or 32 and HCl is readily seen from the absorption spectra presented in Figure 5.16, where an isosbestic point is evident at 331 nm for the complex of 32 and DCP, and at 329 nm for the complex formed between 32 and HCl. Similarly, an isoemissive point at 524 nm can be seen in Figure 5.17 for both complex between 33 and DCP, and 33 and HCl, indicating the formation of 1:1 complex between 33 and DCP, as well as 33 and HCl. Consequently, we tried to apply Stern-Volmer's equation (Equation 3.1) to study the quenching mechanism.

\[
\frac{F_0}{F} = 1 + K_{sv}[Q]
\]

Where \( F_0 \) and \( F \) are the fluorescence intensities in the absence and presence of quencher (DCP or HCl in this research), and \([Q]\) is the concentration of a quencher. A linear Stern-Volmer plot is generally indicative of a single class of fluorophores.\(^{36}\)
Figure 5.18  Relationship between fluorescence of 33 and [DCP]

Figure 5.19  Relationship between fluorescence of 33 and [HCl]

Plotting $F_0/F$ at 450 nm (where $F_0$ is the emission intensity of 33, $F$ is the emission intensity of the complex between 33 and DCP, Figure 5.18, or 33 and HCl, Figure 5.19) vs. concentration of DCP or HCl, resulted in a curved relationship,
which indicated DCP or HCl quenched the fluorescence of the neutral form and added emission of the newly formed adducts with 33.\textsuperscript{[18]} The emission intensity of the pyridium form was lower than the pyridine form indicating the internal conversion energy transfer between the singlet $\pi, \pi^*$ states.

5.2.5 Silica nanoparticle effect on the sensor properties

5.2.5.1 Fabrication of silica nanoparticle sensors

The silica nanoparticles with diameter between 35-40 nm and their silanization were the same as described in 4.2.3.1 and 4.2.3.2, Chapter 4. The assembly of 32 on silica nanoparticle through imine bond formation is shown in Scheme 5.3.

\begin{center}
\textbf{Scheme 5.3} Schiff's base formation between 32 and amino-terminated silica nanoparticle
\end{center}
32 was mixed with silanized silica in methanol. After stirring for 3 hr at 50°C under nitrogen, the silica nanoparticle assembled with 32 was obtained by filtration. The excess of 32 was washed off thoroughly with chloroform. The formation of imine bond between 32 and silanized silica was proved by IR, see Figure 5.20. The silica nanoparticle assembled 32 and 33 were abbreviated as 32-SiO₂ and 33-SiO₂, respectively.

![Figure 5.20 IR of 32 (left) and 32-SiO₂ (right)](image)

Since both compound 32 and 33 contain C=N, it is not practical to prove the imine formation between the two compounds and silanized silica by the IR. However, the conversion of aldehyde group into imine can be evident by the disappearances of the typical C=C-H stretch from the carbonyl group around 2700 and 2800 cm⁻¹, as well as the C=O stretch at about 1700. (Figure 5.20)

The fabrication of 33 on silica is similar with above described for 32, and IR spectra were given in Figure 5.21.
The coverage of both 32 and 33 were calculated with UV-visible absorbance, (See Appendix) which were $3 \times 10^{-4}$ mol/g for 32 and $1.182 \times 10^{-4}$ mol/g for 33, which was 100 time higher than micron scale particles.$^{[4,37]}$

The size of the nanoparticle was determined by TEM images, as in Figure 4.4.

5.2.5.2 UV-vis and fluorescence spectra

Silica effect on the UV-vis spectra of 32 and 32-SiO$_2$ are shown in Figure 5.22.

The DCP and HCl effect to the UV-vis of 32-SiO$_2$ followed the same trends, as of pure 32. The effect of the fluorescence was shown to be basically similar to that of 32. The fluorescence increased as the increasing concentration of DCP or HCl, except that the addition of DCP or HCl into 32-SiO$_2$ did not cause any shift of the emission wavelength maximum. The emission maximum of 33 did not shift by DCP.
or HCl, as that of 32 did. Increasing the concentration of DCP or HCl increased the emission of 32-SiO$_2$, which was similar to the behavior of pure 32. The results indicated that 32 possesses the lowest excited state of n, $\pi^*$.  

![Figure 5.22](image_url)  

**Figure 5.22**  DCP and HCl effect on the UV-vis spectra of 32 and 32-SiO$_2$  

As we can see from **Figure 5.22**, the nanoparticle did not cause significant effect on the absorption of 32, but it shorted the lifetime from 7.51 to 2.56 ns for the longer chromophores and from 0.93 to 0.26 ns for the shorter chromophores. (Table
5.2) The two lifetimes meant the ISC was the main deactivation process of 32, which further proved the existence of \( n, \pi^+ \) as the lowest excited state in 32.

**Figure 5.23** DCP and HCl effect on the emission spectra of 32 and 32-SiO\(_2\)

**Figure 5.23** shows DCP and HCl effect on the fluorescence of 32 and 32-SiO\(_2\). From Figure 5.23, we also noticed the different behavior of 32 and 32-SiO\(_2\). Addition of DCP or HCl into acetonitrile solution of 32 shifted the emission maximum from 475 to 419 nm, while there was no shift for silica assembled 32, in which the aldehyde group effect was removed by formation of Schiff’s base with the silanized
nanoparticle. This difference might be due to the aldehyde group effect. Several theoretical calculations have invented on the effect of aldehyde group to aromatic hydrocarbons,\(^{38-41}\) but no report has been seen on aldehyde group effect to aza aromatics. At this stage, we are not clear how the aldehyde group participated in the aromatic conjugated \(\pi\) system, but we did demonstrate the effect of aldehyde group on the fluorescence of aza aromatics.

**Figure 5.24** DCP and HCl effect on the UV-vis spectra of 33 and 33-SiO\(_2\)
As shown in Figure 5.24, addition of DCP or HCl shifted the UV-visible absorption of 33 to 400 nm and had an increase of absorption. The red shift on the absorption spectra demonstrated that protonation with HCl and complexation with DCP lowered the $\pi, \pi^*$ state of 33, indicating that 33 possesses the lowest excited state of $\pi, \pi^*$ state.

Figure 5.25  DCP and HCl effect on the emission spectra of 33 and 33-SiO$_2$
Similarly to the effect on 33, DCP or HCl quenched the fluorescence of 33-SiO₂ (Figure 5.25), and formed pyridium chromophores with emission shifting to red about 100 nm, which in accordance with the UV-visible spectra. The lifetime of 33-SiO₂ was 0.96 ns, compared with 1.27 ns for 33. (Table 5.2) The single lifetime of 33 indicating that the main deactivation process of the excited stated of 33 was through IC, which further confirmed that the lowest excited stated of 33 was of \( \pi, \pi^* \) state.

The absorption and emission maximum of 32 and 33 as well as their nanoparticle assembled states are summarized in Table 5.2.
### Table 5.2

Absorption and emission maxima of 32 and 33 and their complexes with HCl and DCP

<table>
<thead>
<tr>
<th>Compound</th>
<th>Neutral</th>
<th>Protonation</th>
<th>DCP adductive</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorption (nm)</td>
<td>Fluorescence (nm)</td>
<td>Lifetime (ns)</td>
</tr>
<tr>
<td>32</td>
<td>321</td>
<td>475</td>
<td>(\tau_1 = 7.51) (\tau_2 = 0.93) (\chi = 1.526)</td>
</tr>
<tr>
<td>32 + SiO₂</td>
<td>321</td>
<td>475</td>
<td>(\tau_1 = 2.56) (\tau_2 = 0.26) (\chi = 1.116)</td>
</tr>
<tr>
<td>33</td>
<td>360</td>
<td>450</td>
<td>(\tau = 1.27) (\chi = 0.929)</td>
</tr>
<tr>
<td>33 + SiO₂</td>
<td>360</td>
<td>450</td>
<td>(\tau = 0.96) (\chi = 1.224)</td>
</tr>
</tbody>
</table>
5.2.6 Color observations on sensing of DCP and HCl

Figure 5.26 Color change observation on addition of DCP, from left to right, 33, 33 + DCP, 33-SiO₂, 33-SiO₂ + DCP

33 in acetonitrile solution of 2 X 10⁻⁶ M showed blue color under UV light. When 2.5 μl of 0.034 M stock solution of DCP acetonitrile was added, the color changed from blue to green, as shown in Figure 5.26. The color observations were in agreement with the fluorescence spectra, where the addition of DCP shifted the emission maximum from 450 nm to 550 nm. 33-SiO₂ had the same behavioral properties as pure 33, except the solution was not transparent like the free compound 33.

Figure 5.27 Color change on addition of HCl: Left 33 and 33 + HCl; right, 33-SiO₂ and 33-SiO₂ + HCl

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Similarly, Figure 5.27 demonstrates the color changing from blue to green upon addition of HCl into 33 and silica nanoparticle assembled 33.

5.3 Conclusion

We have synthesized two styryl pyridine derivatives: 32 and 33. Their fluorescence properties vary based on different lengths of conjugation. While 32 was found to be a turn “on” sensor for DCP and HCl, 33 was a turn “off” type. Protonation or complexion of 33 causes significant emission maximum shift. The color changes from blue to green at $10^{-5}$ M magnitude of substrate concentration. We rationalize this as the close-lying $n, \pi^*$ and $\pi, \pi^*$ states. The intrinsic properties of 32 and 33 make them excellent sensor materials for acidic substrates.

Nanoparticle did not significantly affect the photo properties of the aza stilbenes. However, silica nanoparticle promoted the formation of organized structure between multichromophores with enhanced fluorescence efficiency. We have also found that the coverage of immobilized molecules on nanoparticle was in the range of $10^{-4}$ mol/g, which was about 100 times greater than that of the micron size particles. It is an excellent choice for molecular sensor material assembly.
5.4 Experimental section

4-[2-(4-pyridyl)ethenyl]benzaldehyde (32): A 100 ml round bottom flask was charged with 4-bromobenzaldehyde (1.85 g, 0.01 mol), 4-vinylpyridine (1.06 g, 0.01 mol), Pd(OAc)$_2$ (0.045 g, 2 X $10^{-4}$ mol), tri-o-tolylphosphine (0.122 g, 4 X $10^{-4}$ mol), Et$_3$N (2.09 ml, 0.015 mol) and 30 ml of DMF. The mixture was purged with nitrogen and heated under nitrogen at 100-110 °C for 24 hrs. The reaction mixture was allowed to cool to room temperature and filtered with celite packed funnel. The solution was extracted with 100 ml of CHCl$_3$ and washed with 200 ml of water for three times. The organic layer was dried with magnesium sulfate. Solvent was removed under vacuum. The crude product was purified on silica gel (CHCl$_3$) yield (1.77g, 85%) pale-yellow powder. $^1$H NMR (400 MHz, DMSO-d$_6$): 10.05 (s, 1H), 8.59 (d, 2H), 7.95 (d, 2H), 7.87 (d, 2H), 7.65 (d, 1H), 7.61 (d, 2H), 7.46 (d, 2H). $^{13}$C NMR: 193.07, 150.75, 144.26, 142.62, 136.32, 132.37, 130.60, 129.95, 128.19, 121.73.

Crystal structural has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 645774. See Appendix
4-(4-bromostyryl)benzaldehyde (34) Solid potassium tetra-butoxide (0.14 g, 1.2 X 10^{-3} mol) was added in small portion into a solution of 18 (0.307 g, 1X10^{-3} mol) in 25 ml of anhydrous THF in a 100 ml round bottom flask. After the generation of hydrogen gas subsided, the reaction was stirred at room temperature for 10 minutes and teraphthaldehyde-mono ethoxide (0.2 ml, 1X10^{-3} mol) was added. The mixture was stirred at room temperature for 3 hrs under nitrogen, 6N HCl was added drop wise until pH = 2. The mixture was stirred for 12 hrs. THF was removed under vacuum, and ether (100 ml) was added. 34 (0.26 g, 90%) was collected as yellow powder through filtration. \(^1\)H NMR (400 MHz, CHCl\(_3\)): 9.99 (s, 1H), 7.87 (d, 2H), 7.64 (d, 2H), 7.50 (d, 2H), 7.40 (d, 2H), 7.18 (d, 1H), 7.12 (d, 1H). \(^{13}\)C: 191.8, 143.1, 135.6, 132.1, 130.9, 130.4, 128.4, 128.1, 127.1, 126.2, 122.6.

4-(4-((E)-2-(pyridin-4-yl)vinyl)styryl)benzaldehyde (33) A 100 ml round bottom flask was charged with 35 (0.25 g, 9 X 10^{-4} mol), 4-vinylpyridine (0.096 ml, 9 X 10^{-4}), Pd(OAc)\(_2\) (0.004 g, 1.8 X 10^{-5} mol), tri-o-tolylphosphine (0.011 g, 3.6 X 10^{-5} mol), Et\(_3\)N (0.19 ml, 1.4 X 10^{-3} mol). The mixture was purged with nitrogen and heated under nitrogen at 100-110 °C for 24 hrs. The reaction mixture was allowed to cool to room temperature and filtered with celite packed funnel. The solution was extracted
with 100 ml of CHCl$_3$ and washed with 200 ml of water for three times. The organic layer was dried with magnesium sulfate. Solvent was removed under vacuum. The crude product was purified on silica gel (CHCl$_3$) yield 33 (0.227 g, 81%) as pale-yellow powder. $^1$H NMR (400 MHz, DMSO-d$_6$): 10.00 (s, 1H), 8.56 (d, 2H), 7.93 (d, 2H), 7.85 (d, 2H), 7.71 (s, 4H), 7.58 (m, 3H), 7.53 (d, 1H), 7.44 (d, 1H), 7.32 (d, 1H). $^{13}$C NMR: 192.97, 150.63, 144.9, 143.6, 137.5, 136.6, 135.7, 133.1, 132.0, 130.6, 128.2, 128.0, 127.6, 126.8, 121.5.
References


Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
   1975, London.

   1991, Sausalito.


CHAPTER VI

SUMMARY AND OUTLOOK

Stilbene and its derivatives as optical materials have been extensively explored and investigated for various technologically functional properties for next-generation electronic and optoelectronic applications such as electroluminescent devices, field effect transistors, photovoltaic devices, electro-optic modulators, and solid-state lasers in the past decade. In addition to polymer materials, the use of functionalized \( \pi \)-conjugated molecules and oligomers as active component in device applications such as a light-emitting layer in an organic light-emitting diode (LED), has received considerable attention since these can exhibit unique and interesting optoelectronic properties. In this research project, a novel series of bi-functionalized \( \pi \)-conjugated molecules and oligomers have been designed and synthesized to tune the desirable optical and electronic properties and to enhance the functional properties of the materials. Their structure-property relationships have been established through spectroscopy measurements. The findings are essential and important toward the rational design and optimization of functional molecular materials.

Two aza analogues of stilbenes, with two and three rings, were also synthesized. Protonation with HCl and complexation with DCP effect on the fluorescence of the aza stilbenes were performed. The results indicated that the effect of introducing a nitrogen atom into stilbene on the optical behavior depends on the
relative energy states of n, \( \pi^* \) and \( \pi, \pi^* \). Therefore, the desired optical properties can be obtained by tuning the length of conjugation and the substituents on the ring.

In addition, the ancillary ligand incorporated ruthenium complexes have been found useful as fluorescence probes. Importantly, they can be adapted for the detection of various toxic substances by selection of appropriate receptor molecules (ancillary ligands).

The other results and conclusions from this research project include:

1. Facile synthetic routes to all trans isomers of stilbene derivatives with as long as three phenyl rings have been successfully established and optimized.

2. Cesium carbonate was found to be an especially efficient reagent for the etherification of hydroxyl stilbenes with more than two phenyl rings.

3. The etherification of the phenoxy (ph-OH) with an alkyl tethered SO\(_3^-\) do not disrupt the HUMO-LUMO level of the \( \pi \)-conjugated system.

4. The substituents at the para-position of the end ring do not disrupt the coplanarity of the conjugated system, as those at the meta-position do.
5. The emission band shifted to longer wavelength and the intensity increased with an extension of conjugation length for *para*-substitute oligomers.

6. The effect of introducing a nitrogen atom into stilbene on the photo behavior depends on the length of conjugation and the substituents on the ring. Protonation avoided the deactivating effect of the \( n, \pi^* \) in the styryl pyridine (where \( n, \pi^* \) was the lowest excited state), thus, potentially increased the fluorescence. On the other hand, protonation of distyrylpyridine quenched the fluorescence, in which \( \pi, \pi^* \) was the lowest excited state, and dual fluorescence was observed. Such properties are very promising in development of optical sensors for various applications.

7. Single crystal x-ray structure of 4-((E)-2-pyridin-4-y1)vinylbenzaldehyde has been achieved and deposited at Cambridge Crystallographic Data Centre.

8. Two complexes: \([\text{Ru(bpy)}_2\text{dppz}](\text{PF}_6)_2\) and \([\text{Ru(bpy)}_2\text{dppp3}](\text{PF}_6)_2\) were synthesized. The sensitivity to substrates was found to be tunable by modifying the structure of the ancillary ligand. Dppp3 is efficient to bind with both DCP and HCl.
9. We found that silica nanoparticles mediated monolayer enabled multi-functional components organized into aligned structures, making the optical identification through multi-components possible.

10. The facts that increased efficiency of nanoparticle organized chromophores open up a new perspective in the design of functional nanosystems with great application in the field of fluorescent sensor development.

11. The coverage of immobilized molecules on nanoparticles has been enhanced to $10^4$ mol/g, from $10^6$ mol/g of micron size particles.

It will continue to be our interest to investigate the optical behavior of stilbenoids and analogues related to their structures. This will provide new impetus and ideas for synthesis and materials technology, making it possible to refine ways of either eliminating unwanted radiation effect or increasing the efficiency of the desired optical properties, depending on the type of applications. We will also be interested in exploring the applications of these molecules in other fields, such as optoelectronics, light-emitting diodes (LED's), and field-effect transistors etc. In the near future, we will finish the following works in fulfillment of this research project:

1. The water soluble property of the sulfonyl-bonded stilbenoids would find wide
use in medical diagnostics and biomedical research applications. In fact, these compounds are already in use for imaging cells for the diagnosis of cancer at the School of Molecular Biosciences, Washington State University. Expanding the library of the functionalized stilbenoids will be continued.

2. Since the silica nanoparticle mediated self assembly of the functionalized molecules proved to be ideal for close-packing multilayer formations, the bottom up fabrication of the full sensor on quartz plate, as demonstrated in Figure 6.1, would find them useful for military.

![Figure 6.1 Schematic demonstration of solid state full sensor](image)

3. The pyridine containing receptors are sensitive to both HCl and DCP. At this stage we are not able to selectively detect DCP. Works need to be done on the selectivity of the receptors.
Appendix A

Spectra of Chapter II
<table>
<thead>
<tr>
<th>Numer</th>
<th>Name</th>
<th>Structure</th>
<th>Formular</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-(4-formylstyril)benzoic acid</td>
<td><img src="image" alt="Structure" /></td>
<td>(C_{10}H_{12}O_3)</td>
</tr>
<tr>
<td>2</td>
<td>4-(4-(4-sulfobutoxy)styril)benzoic acid</td>
<td><img src="image" alt="Structure" /></td>
<td>(C_{12}H_{26}O_4S)</td>
</tr>
<tr>
<td>3</td>
<td>4-(4-(4-sulfobutoxy-2,6-dimethyl)styril)benzaldehyde</td>
<td><img src="image" alt="Structure" /></td>
<td>(C_{21}H_{23}O_8S)</td>
</tr>
<tr>
<td></td>
<td>Compound</td>
<td>Structure</td>
<td>Molecular Formula</td>
</tr>
<tr>
<td>---</td>
<td>----------------------------------------------</td>
<td>----------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>4</td>
<td>3-(4-(4-sulfobutoxy)styryl)benzaldehyde</td>
<td><img src="structure_1.png" alt="Structure 1" /></td>
<td>C$<em>{19}$H$</em>{20}$O$_5$S</td>
</tr>
<tr>
<td>5</td>
<td>4-(4-(4-sulfobutoxy)styryl)benzaldehyde</td>
<td><img src="structure_2.png" alt="Structure 2" /></td>
<td>C$<em>{19}$H$</em>{20}$O$_5$S</td>
</tr>
<tr>
<td>6</td>
<td>3-(4-(4-sulfobutoxy)distyryl)benzaldehyde</td>
<td><img src="structure_3.png" alt="Structure 3" /></td>
<td>C$<em>{27}$H$</em>{26}$O$_5$S</td>
</tr>
<tr>
<td></td>
<td>Chemical Structure</td>
<td>Molecular Formula</td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>--------------------------------------------------------</td>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>4-(4-(4-sulfobutoxy)distyryl)benzaldehyde</td>
<td>C_{27}H_{26}O_{3}S</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>4-((ethox phosphono)methyl)benzoic acid</td>
<td>C_{12}H_{17}O_{3}P</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>4-triisopropylsiloxylbenzaldehyde</td>
<td>C_{16}H_{22}O_{3}Si</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4-(4-triisopropylsiloxyl)styrylbenzoic acid</td>
<td>C_{24}H_{32}O_{5}Si</td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Compound Name</td>
<td>Chemical Structure</td>
<td>Molecular Formula</td>
</tr>
<tr>
<td>-----</td>
<td>--------------------------------------------------</td>
<td>--------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>11</td>
<td>4-(4-hydroxy)styrylbenzoic acid</td>
<td><img src="attachment.png" alt="OH" /></td>
<td>C₁₃H₁₂O₃</td>
</tr>
<tr>
<td>12</td>
<td>4-bromobenzyl triisopropylsilyl ether</td>
<td><img src="attachment.png" alt="OTIPS" /></td>
<td>C₁₉H₂₂BrOSi</td>
</tr>
<tr>
<td>13</td>
<td>3-(4-triisopropylsiloxyl)styrylbenzaldehyde</td>
<td><img src="attachment.png" alt="OTIPS" /></td>
<td>C₂₀H₂₅O₂Si</td>
</tr>
<tr>
<td>14</td>
<td>3-(4-hydroxy)styrylbenzaldehyde</td>
<td><img src="attachment.png" alt="OH" /></td>
<td>C₁₃H₁₂O₂</td>
</tr>
<tr>
<td>15</td>
<td>4-vinylbenzyl triisopropylsilyl ether</td>
<td><img src="attachment.png" alt="OTIPS" /></td>
<td>C₁₇H₁₈OSi</td>
</tr>
<tr>
<td></td>
<td>Chemical Structure</td>
<td>Molecular Formula</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>--------------------</td>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>4-(4-trisopropylsilylether)styrylbenzaldehyde</td>
<td>C_{24}H_{32}O_{2}Si</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>4-(4-hydroxystyryl)benzaldehyde</td>
<td>C_{13}H_{12}O_{2}</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Diethyl(4-bromophenyl)methylphosphonate</td>
<td>C_{11}H_{16}BrO_{3}P</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>(4-bromostyryl)phenyl triisopropylsilyl ether</td>
<td>C_{23}H_{35}BrOSi</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chemical Structure</td>
<td>Molecular Formula</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-------------------</td>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>3-(4-(4-trisopropylsilyl)distyryl)etherbenzaldehyde</td>
<td>C\textsubscript{32}H\textsubscript{38}O\textsubscript{2}Si</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>4-(4-(4-hydroxy)distyryl)benzaldehyde</td>
<td>C\textsubscript{23}H\textsubscript{19}O\textsubscript{2}</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>4-vinylbenzyl iodide</td>
<td>C\textsubscript{9}H\textsubscript{9}I</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>Diethyl 4-vinylbenzylphosphonate</td>
<td>C\textsubscript{13}H\textsubscript{19}O\textsubscript{3}P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Structure</td>
<td>Formula</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-----------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td><img src="image1" alt="Structure" /></td>
<td>C&lt;sub&gt;25&lt;/sub&gt;H&lt;sub&gt;34&lt;/sub&gt;OSi</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td><img src="image2" alt="Structure" /></td>
<td>C&lt;sub&gt;25&lt;/sub&gt;H&lt;sub&gt;38&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;Si</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td><img src="image3" alt="Structure" /></td>
<td>C&lt;sub&gt;23&lt;/sub&gt;H&lt;sub&gt;18&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
</tr>
</tbody>
</table>
$^1$H NMR of 1

$^{13}$C NMR of 1
UV-vis of 1

Emission of 1

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Excitation of 1

\[
\begin{array}{c}
\text{Intensity} \\
\hline
10000 \quad 20000 \quad 30000 \quad 40000 \quad 50000 \quad 60000 \quad 70000
\end{array}
\]

\[
\begin{array}{c}
\text{Wavelength nm} \\
300 \quad 320 \quad 340 \quad 360 \quad 380 \quad 400
\end{array}
\]

\[\text{H NMR of 2}\]

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
$^{31}$C NMR of 2

Emission of 2

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Excitation of 2

![Graph of excitation vs wavelength](image)

NMR of 4

![NMR spectrum of 4](image)
UV-vis of 4

Emission spectrum of 4
Excitation spectrum of 4

\[ \text{Intensity} \]

\[ \text{Wavelength (nm)} \]

\[ 260 \quad 280 \quad 300 \quad 320 \quad 340 \quad 360 \quad 380 \quad 400 \]

\[ 0 \quad 500 \quad 1000 \quad 1500 \quad 2000 \quad 2500 \quad 3000 \quad 3500 \quad 4000 \]

\[ \text{NMR of 5} \]

\[ \text{Chemical shift ppm} \]

\[ 0 \quad 2 \quad 4 \quad 6 \quad 8 \quad 10 \quad 12 \]

\[ 12 \quad 10 \quad 8 \quad 6 \quad 4 \quad 2 \quad 0 \]

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
UV-vis spectra of 5

![UV-vis spectrum of 5](image)

Emission spectra of 4 & 5

![Emission spectrum of 4 & 5](image)
Excitation spectra of 4&5

$^1$H NMR of 6

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
UV-vis spectrum of 6

Emission spectrum of 6
$^1$H NMR of 7

UV-vis spectrum of 7
Emission spectrum of 7

\[ \text{Intensity} \]

\[ \text{Wavelength (nm)} \]

\[ \text{1H NMR of 8} \]

\[ \text{Chemical Shift (ppm)} \]

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
$^{1}$$H$ NMR of 9

$^{1}$$H$ NMR of 10

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
$^{1}$$H$ NMR of 11

$^{13}$$C$ NMR of 11

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
$^1$H NMR of 12

$^1$H NMR of 14

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
$^1$H NMR of 15

$^1$H NMR of 16

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
$^{13}$C NMR of 16

$^1$H NMR of 17
$^{13}$C NMR of 17

$^1$H NMR of 18

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
\(^{13}\text{C}\) NMR of 18

\(^{1}\text{H}\) NMR of 19

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
$^{13}$C NMR of 19

$^1$H NMR of 20 (Crude product)
$^1$H NMR of 22

$^1$H NMR of 23
Appendix B

Spectra of Chapter III
<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Structure</th>
<th>Formula</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>1, 10-phenanthroline 5,6-dione</td>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>C_{12}H_{10}N_{2}O_{2}</td>
<td>78%</td>
</tr>
<tr>
<td>28</td>
<td>dipyrido[3,2-a;2',3'c] phenazine (dppz)</td>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>C_{18}H_{10}N_{4}</td>
<td>74%</td>
</tr>
<tr>
<td>29</td>
<td>bis-(bipyridyl) pyrido[3,2-a;2',3'c] phenazo ruthenium hexafluorophosphate</td>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>C_{36}H_{23}F_{12}N_{4}P_{2}Ru</td>
<td>61%</td>
</tr>
<tr>
<td>30</td>
<td>Dppp3</td>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>C_{17}H_{9}N_{3}</td>
<td>88%</td>
</tr>
<tr>
<td>31</td>
<td>bis-(bipyridyl) dppp3 ruthenium hexafluorophosphate</td>
<td><img src="image5.png" alt="Structure 5" /></td>
<td>C_{36}H_{23}F_{12}N_{4}P_{2}Ru</td>
<td>60%</td>
</tr>
</tbody>
</table>

\(^{1}\)H NMR of 27

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
$^1\text{H NMR of 28}$
$^{13}$C NMR of 28

Emission of 28

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
$^1$H NMR of 29

Chemical Shift ppm

$^{13}$C NMR of 29

Chemical Shift ppm
UV-vis of 29

\[
\begin{array}{c}
\text{Intensity} \\
200 & 250 & 300 & 350 & 400 & 450 & 500 & 550 & 600 \\
\end{array}
\]

2.5 \times 10^{-6} \text{ M}

\[
\begin{array}{c}
\text{Wavelength (nm)} \\
200 & 250 & 300 & 350 & 400 & 450 & 500 & 550 & 600 \\
\end{array}
\]

\[1\text{H NMR of 30}\]

\[
\begin{array}{c}
\text{Chemical Shift (ppm)} \\
14 & 12 & 10 & 8 & 6 & 4 & 2 & 0 \\
\end{array}
\]

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
UV-vis of 30

Excitation of 30
$^1$H NMR of 31

UV-vis of 31

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Emission of 31

\[ Emission \text{ of } 31 \]

\[ 10000 \]

\[ 8000 \]

\[ 6000 \]

\[ 4000 \]

\[ 2000 \]

\[ 500 \]

\[ 400 \]

\[ 600 \]

\[ 700 \]

\[ 800 \]

\[ Wavelength \text{ (nm)} \]

\[ 1H \text{ NMR of } 24 \]

\[ 1H \text{ NMR of } 24 \]

\[ Chemical \text{ Shift ppm} \]

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
\(^1\)H NMR of 26
Appendix C

Spectra of Chapter V
<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Structure</th>
<th>Formula</th>
<th>Available Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>4-((E)-2-(pyridine-4-yl)vinyl)benzaldehyde</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>C_{14}H_{11}NO</td>
<td>$^1$H NMR, $^{13}$C NMR, IR, LC-MS, UV-vis, Em, Ex</td>
</tr>
<tr>
<td>33</td>
<td>4-(4-((E)-2-(pyridin-4-yl)vinyl)styryl)benzaldehyde</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>C_{22}H_{17}NO</td>
<td>$^1$H NMR, $^{13}$C NMR, IR, LC-MS, UV-vis, Em, Ex</td>
</tr>
<tr>
<td>34</td>
<td>4-(4-bromostyryl)benzaldehyde</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>C_{13}H_{15}BrO</td>
<td>$^1$H NMR, $^{13}$C NMR, IR, LC-MS, UV-vis, Em, Ex</td>
</tr>
</tbody>
</table>

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
$^1$H NMR of 32

$^{13}$C NMR of 32

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
LC-MS of 32

![LC-MS graph]

IR of 32

![IR graph]
Raman of 32

![Raman Spectrum of 32]

Raman of 32-SiO₂

![Raman Spectrum of 32-SiO₂]
X-Ray crystal structure report

Experimental for C_{14}H_{11}NO (x07088)

Data Collection and Processing. The sample (x07088) was submitted by Chun Wang of the Muralidharan research group at Western Michigan University. The sample was mounted on a nylon loop with a small amount of NVH immersion oil. All X-ray measurements were made on a Bruker-Nonius X8 Apex2 diffractometer at a temperature of 110 K. The unit cell dimensions were determined from a symmetry constrained fit of 9982 reflections with 6.38° < 2θ < 47.14°. The data collection strategy was a number of ω and θ scans which collected data up to 47.32° (2θ). The frame integration was performed using SAINT+. The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.

Structure Solution and Refinement. The structure was solved by direct methods using the SIR92 program. All non-hydrogen atoms were obtained from the initial E-map. The hydrogen atoms were treated in a mixed fashion. The phenyl and aldehyde bound hydrogens were placed at idealized positions and were allowed to refine isotropically. The hydrogens bound to C8 and C9 were placed at idealized positions and were allowed to ride on the parent carbon atoms. This was done because these hydrogen atoms refined to chemically unreasonable positions (see note below.
concerning the final difference Fourier map). The structural model was fit to the data using full matrix least-squares based on F. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using LSTSQ program from NRCVAX, graphic plots were produced using the ORTEP implementation included in the NRCVAX crystallographic program suite. Additional information and other relevant literature references can be found in the reference section of the Facility's Web page (http://www.xray.ncsu.edu).

**Note on final difference map:** The final difference map showed three relatively large peaks in the vicinity of carbons C8 and C9. The height of these peaks were 0.73, 0.49, and 0.44 e\(^{-}/\text{Å}^3\), the first of these peaks being about the height typical for a hydrogen atom. The positions of these peaks were not positioned in a chemically reasonable position around these carbons, indicating that they were traces from an unaccounted for disorder or co-crystallized impurity. Attempts to interpret the difference map in a chemically sensible way with regard to either of these two possibilities were unsuccessful. This being said, this X-ray analysis can still be taken as definite proof of structure.
Figure 1. ORTEP drawing of x07088 showing naming and numbering scheme. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

Figure 2. ORTEP drawing of x07088. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.
Figure 3. Stereoscopic ORTEP drawing of x07088. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.
Table 1. Summary of Crystal Data for x07088

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C14H11NO</td>
</tr>
<tr>
<td>Formula Weight (g/mol)</td>
<td>209.25</td>
</tr>
<tr>
<td>Crystal Dimensions (mm)</td>
<td>0.23 × 0.18 × 0.12</td>
</tr>
<tr>
<td>Crystal Color and Habit</td>
<td>colorless prism</td>
</tr>
<tr>
<td>Crystal System</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space Group</td>
<td>Pbca</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>110</td>
</tr>
<tr>
<td>a, Å</td>
<td>7.7646(2)</td>
</tr>
<tr>
<td>b, Å</td>
<td>12.1912(3)</td>
</tr>
<tr>
<td>c, Å</td>
<td>22.4911(5)</td>
</tr>
<tr>
<td>a, °</td>
<td>90.0</td>
</tr>
<tr>
<td>b, °</td>
<td>90.0</td>
</tr>
<tr>
<td>g, °</td>
<td>90.0</td>
</tr>
<tr>
<td>V, Å³</td>
<td>2129.00(9)</td>
</tr>
<tr>
<td>Number of reflections to determine final unit cell</td>
<td>9982</td>
</tr>
<tr>
<td>Min and Max 2q for cell determination, °</td>
<td>6.38, 47.14</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>F(000)</td>
<td>880.50</td>
</tr>
<tr>
<td>r (g/cm)</td>
<td>1.306</td>
</tr>
<tr>
<td>l, Å, (MoKa)</td>
<td>0.71073</td>
</tr>
<tr>
<td>m, (cm⁻¹)</td>
<td>0.08</td>
</tr>
<tr>
<td>Diffractometer Type</td>
<td>Bruker-Nonius X8 Apex2</td>
</tr>
<tr>
<td>Scan Type(s)</td>
<td>omega and phi scans</td>
</tr>
<tr>
<td>Max 2q for data collection, °</td>
<td>47.32</td>
</tr>
<tr>
<td>Measured fraction of data</td>
<td>1.00</td>
</tr>
<tr>
<td>Number of reflections measured</td>
<td>49797</td>
</tr>
</tbody>
</table>
Unique reflections measured 1609
Rmerge 0.026
Number of reflections included in refinement 1378
Cut off Threshold Expression \( \text{Inet} > 1.0 \sigma(\text{Inet}) \)
Structure refined using full matrix least-squares using
Weighting Scheme \( 1/(\sigma^2(F)+0.0005F^2) \)
Number of parameters in least-squares 181
Rf 0.056
Rw 0.078
Rf (all data) 0.066
Rw (all data) 0.079
GOF 2.74
Maximum shift/error 0.000
Min & Max peak heights on final DF Map (e/\AA) -0.30, 0.73

Where:

\[
R_f = \frac{\sum |F_o - F_c|}{\sum F_o} \\
R_w = \left[ \frac{\sum w(F_o - F_c)^2}{\sum F_o^2} \right]^{1/2} \\
\text{GOF} = \left[ \frac{\sum w(F_o - F_c)^2}{\text{(No. of reflns. - No. of params.)}} \right]^{1/2}
\]
Table 2. Atomic Coordinates for x07088

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uiso/equiv</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>0.4393(3)</td>
<td>0.44471(16)</td>
<td>0.91547(8)</td>
<td>0.0531(11)</td>
</tr>
<tr>
<td>C1</td>
<td>0.3956(3)</td>
<td>0.3499(2)</td>
<td>0.91089(12)</td>
<td>0.0427(15)</td>
</tr>
<tr>
<td>C2</td>
<td>0.3906(3)</td>
<td>0.27120(19)</td>
<td>0.96070(10)</td>
<td>0.0323(13)</td>
</tr>
<tr>
<td>C3</td>
<td>0.4319(3)</td>
<td>0.3042(2)</td>
<td>1.01822(11)</td>
<td>0.0347(14)</td>
</tr>
<tr>
<td>C4</td>
<td>0.4265(3)</td>
<td>0.2285(2)</td>
<td>1.06391(12)</td>
<td>0.0389(15)</td>
</tr>
<tr>
<td>C5</td>
<td>0.3776(3)</td>
<td>0.11938(20)</td>
<td>1.05308(11)</td>
<td>0.0380(14)</td>
</tr>
<tr>
<td>C6</td>
<td>0.3365(3)</td>
<td>0.0893(2)</td>
<td>0.99593(12)</td>
<td>0.0404(15)</td>
</tr>
<tr>
<td>C7</td>
<td>0.3440(3)</td>
<td>0.1634(2)</td>
<td>0.95028(13)</td>
<td>0.0388(14)</td>
</tr>
<tr>
<td>C8</td>
<td>0.3665(3)</td>
<td>0.0342(2)</td>
<td>1.09942(13)</td>
<td>0.0496(15)</td>
</tr>
<tr>
<td>C9</td>
<td>0.4214(4)</td>
<td>0.0405(2)</td>
<td>1.15363(13)</td>
<td>0.0478(16)</td>
</tr>
<tr>
<td>C10</td>
<td>0.4023(3)</td>
<td>-0.0486(2)</td>
<td>1.19868(11)</td>
<td>0.0395(14)</td>
</tr>
<tr>
<td>C11</td>
<td>0.4306(4)</td>
<td>-0.0253(2)</td>
<td>1.25703(13)</td>
<td>0.0424(16)</td>
</tr>
<tr>
<td>C12</td>
<td>0.4114(4)</td>
<td>-0.1046(2)</td>
<td>1.29959(13)</td>
<td>0.0429(17)</td>
</tr>
<tr>
<td>N1</td>
<td>0.3659(3)</td>
<td>-0.20781(17)</td>
<td>1.28899(9)</td>
<td>0.0430(13)</td>
</tr>
<tr>
<td>C13</td>
<td>0.3385(3)</td>
<td>-0.2315(2)</td>
<td>1.23161(13)</td>
<td>0.0445(16)</td>
</tr>
</tbody>
</table>

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Ueq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl4</td>
<td>0.3549(3)</td>
<td>-0.1565(2)</td>
<td>1.18600(13)</td>
<td>0.0456(16)</td>
</tr>
<tr>
<td>H1</td>
<td>0.350(3)</td>
<td>0.313(2)</td>
<td>0.8737(11)</td>
<td>0.041(7)</td>
</tr>
<tr>
<td>H3</td>
<td>0.463(3)</td>
<td>0.3793(19)</td>
<td>1.0246(9)</td>
<td>0.026(6)</td>
</tr>
<tr>
<td>H4</td>
<td>0.453(3)</td>
<td>0.247(2)</td>
<td>1.1039(12)</td>
<td>0.046(7)</td>
</tr>
<tr>
<td>H6</td>
<td>0.306(4)</td>
<td>0.011(3)</td>
<td>0.9870(12)</td>
<td>0.068(9)</td>
</tr>
<tr>
<td>H7</td>
<td>0.320(3)</td>
<td>0.141(2)</td>
<td>0.9094(11)</td>
<td>0.056(8)</td>
</tr>
<tr>
<td>H8</td>
<td>0.312</td>
<td>-0.034</td>
<td>1.088</td>
<td>0.0596</td>
</tr>
<tr>
<td>H9</td>
<td>0.478</td>
<td>0.107</td>
<td>1.166</td>
<td>0.0578</td>
</tr>
<tr>
<td>H11</td>
<td>0.467(3)</td>
<td>0.048(2)</td>
<td>1.2696(11)</td>
<td>0.054(8)</td>
</tr>
<tr>
<td>H12</td>
<td>0.433(4)</td>
<td>-0.086(2)</td>
<td>1.3381(14)</td>
<td>0.064(9)</td>
</tr>
<tr>
<td>H13</td>
<td>0.302(4)</td>
<td>-0.309(2)</td>
<td>1.2235(11)</td>
<td>0.059(8)</td>
</tr>
<tr>
<td>H14</td>
<td>0.339(3)</td>
<td>-0.176(2)</td>
<td>1.1457(12)</td>
<td>0.045(7)</td>
</tr>
</tbody>
</table>
Table 3. Anisotropic Displacement Parameters for x07088

<table>
<thead>
<tr>
<th>Atom</th>
<th>$u_{11}$</th>
<th>$u_{22}$</th>
<th>$u_{33}$</th>
<th>$u_{12}$</th>
<th>$u_{13}$</th>
<th>$u_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>0.0665(13)</td>
<td>0.0419(12)</td>
<td>0.0508(13)</td>
<td>0.0070(9)</td>
<td>0.0084(10)</td>
<td>0.0107(10)</td>
</tr>
<tr>
<td>C1</td>
<td>0.0452(16)</td>
<td>0.0453(17)</td>
<td>0.0377(17)</td>
<td>0.0099(13)</td>
<td>0.0016(12)</td>
<td>-0.0020(14)</td>
</tr>
<tr>
<td>C2</td>
<td>0.0362(14)</td>
<td>0.0338(14)</td>
<td>0.0269(14)</td>
<td>0.0044(10)</td>
<td>0.0001(10)</td>
<td>0.0000(11)</td>
</tr>
<tr>
<td>C3</td>
<td>0.0370(14)</td>
<td>0.0309(14)</td>
<td>0.0364(16)</td>
<td>0.0010(11)</td>
<td>0.0001(12)</td>
<td>-0.0048(12)</td>
</tr>
<tr>
<td>C4</td>
<td>0.0428(15)</td>
<td>0.0479(17)</td>
<td>0.0259(15)</td>
<td>0.0079(12)</td>
<td>-0.0022(12)</td>
<td>-0.0011(12)</td>
</tr>
<tr>
<td>C5</td>
<td>0.0364(14)</td>
<td>0.0392(15)</td>
<td>0.0384(16)</td>
<td>0.0056(11)</td>
<td>0.0050(11)</td>
<td>0.0094(12)</td>
</tr>
<tr>
<td>C6</td>
<td>0.0448(16)</td>
<td>0.0322(15)</td>
<td>0.0444(18)</td>
<td>0.0002(11)</td>
<td>-0.0048(12)</td>
<td>0.0003(13)</td>
</tr>
<tr>
<td>C7</td>
<td>0.0440(15)</td>
<td>0.0379(15)</td>
<td>0.0345(17)</td>
<td>0.0057(11)</td>
<td>-0.0054(12)</td>
<td>-0.0064(13)</td>
</tr>
<tr>
<td>C8</td>
<td>0.0469(17)</td>
<td>0.0500(18)</td>
<td>0.0519(19)</td>
<td>0.0061(13)</td>
<td>0.0000(14)</td>
<td>-0.0040(14)</td>
</tr>
<tr>
<td>C9</td>
<td>0.0459(16)</td>
<td>0.0489(17)</td>
<td>0.0487(18)</td>
<td>0.0017(13)</td>
<td>0.0005(14)</td>
<td>-0.0104(13)</td>
</tr>
<tr>
<td>C10</td>
<td>0.0403(16)</td>
<td>0.0403(16)</td>
<td>0.0378(16)</td>
<td>0.0078(12)</td>
<td>0.0054(11)</td>
<td>0.0076(12)</td>
</tr>
<tr>
<td>C11</td>
<td>0.0466(16)</td>
<td>0.0330(15)</td>
<td>0.0476(18)</td>
<td>0.0005(12)</td>
<td>0.0002(13)</td>
<td>0.0005(13)</td>
</tr>
<tr>
<td>C12</td>
<td>0.0558(18)</td>
<td>0.0439(18)</td>
<td>0.0291(17)</td>
<td>0.0013(13)</td>
<td>-0.0037(12)</td>
<td>-0.0043(13)</td>
</tr>
<tr>
<td>N1</td>
<td>0.0519(14)</td>
<td>0.0401(14)</td>
<td>0.0369(14)</td>
<td>0.0008(10)</td>
<td>-0.0003(10)</td>
<td>0.0047(11)</td>
</tr>
<tr>
<td>C13</td>
<td>0.0442(16)</td>
<td>0.0342(16)</td>
<td>0.055(2)</td>
<td>-0.0018(12)</td>
<td>-0.0057(14)</td>
<td>-0.0050(14)</td>
</tr>
<tr>
<td>C14</td>
<td>0.0461(17)</td>
<td>0.062(2)</td>
<td>0.0284(16)</td>
<td>0.0121(13)</td>
<td>-0.0075(12)</td>
<td>-0.0038(14)</td>
</tr>
</tbody>
</table>
Table 4. Bond Lengths for x07088

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1-C1</td>
<td>1.209(4)</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.476(4)</td>
</tr>
<tr>
<td>C1-H1</td>
<td>1.01(3)</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.392(3)</td>
</tr>
<tr>
<td>C2-C7</td>
<td>1.383(3)</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.381(4)</td>
</tr>
<tr>
<td>C3-H3</td>
<td>0.96(2)</td>
</tr>
<tr>
<td>C4-C5</td>
<td>1.405(4)</td>
</tr>
<tr>
<td>C4-H4</td>
<td>0.95(3)</td>
</tr>
<tr>
<td>C5-C6</td>
<td>1.374(4)</td>
</tr>
<tr>
<td>C5-C8</td>
<td>1.474(4)</td>
</tr>
<tr>
<td>C6-C7</td>
<td>1.369(4)</td>
</tr>
<tr>
<td>C6-H6</td>
<td>1.00(3)</td>
</tr>
<tr>
<td>C7-H7</td>
<td>0.98(3)</td>
</tr>
<tr>
<td>C8-C9</td>
<td>1.294(4)</td>
</tr>
<tr>
<td>C8-H8</td>
<td>0.96</td>
</tr>
<tr>
<td>C9-C10</td>
<td>1.493(4)</td>
</tr>
<tr>
<td>C9-H9</td>
<td>0.96</td>
</tr>
<tr>
<td>C10-C11</td>
<td>1.361(4)</td>
</tr>
<tr>
<td>C10-C14</td>
<td>1.395(4)</td>
</tr>
<tr>
<td>C11-C12</td>
<td>1.369(4)</td>
</tr>
<tr>
<td>C11-H11</td>
<td>0.98(3)</td>
</tr>
<tr>
<td>C12-N1</td>
<td>1.328(3)</td>
</tr>
<tr>
<td>C12-H12</td>
<td>0.91(3)</td>
</tr>
<tr>
<td>N1-C13</td>
<td>1.340(4)</td>
</tr>
<tr>
<td>C13-C14</td>
<td>1.381(4)</td>
</tr>
<tr>
<td>C13-H13</td>
<td>1.00(3)</td>
</tr>
<tr>
<td>C14-H14</td>
<td>0.94(3)</td>
</tr>
<tr>
<td>Bond Angle</td>
<td>Value</td>
</tr>
<tr>
<td>------------</td>
<td>--------</td>
</tr>
<tr>
<td>O1-C1-C2</td>
<td>124.4(3)</td>
</tr>
<tr>
<td>O1-C1-H1</td>
<td>126.4(14)</td>
</tr>
<tr>
<td>C2-C1-H1</td>
<td>109.2(13)</td>
</tr>
<tr>
<td>C1-C2-C3</td>
<td>120.8(2)</td>
</tr>
<tr>
<td>C1-C2-C7</td>
<td>119.7(2)</td>
</tr>
<tr>
<td>C3-C2-C7</td>
<td>119.5(2)</td>
</tr>
<tr>
<td>C2-C3-C4</td>
<td>119.4(2)</td>
</tr>
<tr>
<td>C2-C3-H3</td>
<td>118.3(12)</td>
</tr>
<tr>
<td>C4-C3-H3</td>
<td>122.3(12)</td>
</tr>
<tr>
<td>C3-C4-C5</td>
<td>120.8(2)</td>
</tr>
<tr>
<td>C3-C4-H4</td>
<td>122.6(16)</td>
</tr>
<tr>
<td>C5-C4-H4</td>
<td>116.6(16)</td>
</tr>
<tr>
<td>C4-C5-C6</td>
<td>118.5(2)</td>
</tr>
<tr>
<td>C4-C5-C8</td>
<td>124.1(2)</td>
</tr>
<tr>
<td>C6-C5-C8</td>
<td>117.4(2)</td>
</tr>
<tr>
<td>C5-C6-C7</td>
<td>121.1(2)</td>
</tr>
<tr>
<td>C5-C6-H6</td>
<td>119.7(15)</td>
</tr>
<tr>
<td>C7-C6-H6</td>
<td>119.2(15)</td>
</tr>
<tr>
<td>C2-C7-C6</td>
<td>120.7(3)</td>
</tr>
<tr>
<td>C2-C7-H7</td>
<td>118.4(16)</td>
</tr>
<tr>
<td>C6-C7-H7</td>
<td>120.8(16)</td>
</tr>
<tr>
<td>C5-C8-C9</td>
<td>127.2(3)</td>
</tr>
</tbody>
</table>
Table 6. Bond Angles for x07088

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1-C1-C2-C3</td>
<td>2.3(2)</td>
<td>C5-C6-C7-C2</td>
<td>-1.1(2)</td>
</tr>
<tr>
<td>O1-C1-C2-C7</td>
<td>-177.9(6)</td>
<td>C5-C8-C9-C10</td>
<td>178.6(6)</td>
</tr>
<tr>
<td>C1-C2-C3-C4</td>
<td>-179.8(5)</td>
<td>C8-C9-C10-C11</td>
<td>-166.0(6)</td>
</tr>
<tr>
<td>C7-C2-C3-C4</td>
<td>0.4(3)</td>
<td>C8-C9-C10-C14</td>
<td>13.3(3)</td>
</tr>
<tr>
<td>C1-C2-C7-C6</td>
<td>-179.2(6)</td>
<td>C9-C10-C11-C12</td>
<td>178.9(6)</td>
</tr>
<tr>
<td>C3-C2-C7-C6</td>
<td>0.6(3)</td>
<td>C14-C10-C11-C12</td>
<td>-0.5(3)</td>
</tr>
<tr>
<td>C2-C3-C4-C5</td>
<td>-0.9(2)</td>
<td>C9-C10-C14-C13</td>
<td>-178.9(6)</td>
</tr>
<tr>
<td>C3-C4-C5-C6</td>
<td>0.5(3)</td>
<td>C11-C10-C14-C13</td>
<td>0.4(3)</td>
</tr>
<tr>
<td>C3-C4-C5-C8</td>
<td>-179.2(6)</td>
<td>C10-C11-C12-N1</td>
<td>0.3(2)</td>
</tr>
<tr>
<td>C4-C5-C6-C7</td>
<td>0.5(3)</td>
<td>C11-C12-N1-C13</td>
<td>0.0(3)</td>
</tr>
<tr>
<td>C8-C5-C6-C7</td>
<td>-179.8(6)</td>
<td>C12-N1-C13-C14</td>
<td>-0.1(3)</td>
</tr>
<tr>
<td>C4-C5-C8-C9</td>
<td>-10.7(3)</td>
<td>N1-C13-C14-C10</td>
<td>-0.1(2)</td>
</tr>
<tr>
<td>C6-C5-C8-C9</td>
<td>169.7(6)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
UV-vis (black) and emission (blue) of 32

Lifetime decay of 32

\[ t_1 = 7.51 \text{ ns}, t_2 = 0.93 \text{ ns}, x^2 = 1.368, E_x = 321 \text{ ns}, E_m = 425 \text{ nm} \]
$^1\text{H NMR of 33}$

$^{13}\text{C NMR of 33}$

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
IR of 33

IR of 33-SiO₂
LC-MS of 33

UV-vis and emission of 33
Lifetime decay of 33

\[ t = 1.27 \text{ ns}, \chi^2 = 1.193, \text{Ex}=383 \text{ nm}, \text{Em}=465 \text{ nm} \]

Raman of 33
Raman of 33-SiO$_2$

$^{1}$H NMR of 34

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
$^{13}$C NMR of 34

Chemical Shift ppm