PHOTOREGULATING FLUORESCENCE AND SELF-ASSEMBLY IN THIN FILMS USING DITHIENYLETHENE MOLECULAR SWITCHES

by

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B.Eng. South China University of Technology, 1992

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ABSTRACT

Photoresponsive materials have attracted attention from both fundamental and practical points of view. Dithienylethenes (DTEs) are one of the most promising classes of photoresponsive compounds for applying to optical memory and optical switching technologies. Regulating fluorescence intensity is one of the most attractive goals for using molecular devices because of the high sensitivity, high resolution, fast response time and high contrast provided by fluorescence technology. A hybrid system containing a Zn-bis(amidine) fluorescent dye covalently joined to two photochromic dithienylethene (DTE) units was prepared using a concise synthetic route. The photoregulated quenching of the fluorescence from the metal complex by switching the DTE between its two isomers was achieved. The fluorescence quenching can be attributed to intramolecular energy transfer or photoinduced electron transfer. Calculations suggest the latter is the more likely quenching mechanism. UV-Vis absorption and emission spectroscopy showed that the fluorescence switching process has little effect on the photocyclization process and the fluorescence could be turned “on” and “off” for ten cycles without notable side products appearing. This photochromic behaviour plus its excellent thermal irreversibility make it an excellent candidate for non-destructive read out application and biological fluorescence labelling applications.

The changes in the geometrical structure of the photoresponsive DTE backbone was explored for potential use in vesicle-based drug delivery applications by evaluating whether the changes can be used to effect the packing of the molecule within a membrane
structure. Two photoresponsive DTE derivatives were decorated with fatty acids to investigate this phenomenon. By giving them amphiphilic properties thin films of both compounds were prepared as Langmuir layers and the changes in surface pressure as a function of photoswitching were studied. Although one of the two derivatives showed excellent photochromic properties, the changes between the structures of the ring-open and ring-closed isomers of the DTE were not significant enough to be useful in drug delivery.
To my parents, Zhao Kesen and Wang Dilai,

and my husband Meitao Wan and daughter Nora Wan who have loved and supported me throughout this degree
ACKNOWLEDGEMENTS

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<tr>
<td>CH$_3$CN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>AcOH</td>
<td>acetic acid</td>
</tr>
<tr>
<td>Anal. Calcd.</td>
<td>analytical calculated</td>
</tr>
<tr>
<td>Å</td>
<td>Angstroms</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
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<tr>
<td>BODIPY</td>
<td>4,4-difluoro-4-bora-3a,4a-diaza-s-indacene</td>
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<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>cm</td>
<td>centimetres</td>
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<td>δ</td>
<td>chemical shift</td>
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<td>CD</td>
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<tr>
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<td>coupling constant</td>
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<td>dichloromethane</td>
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<tr>
<td>Et$_2$O</td>
<td>diethyl ether</td>
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<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DPPA</td>
<td>diphenylphosphorazine</td>
</tr>
<tr>
<td>DTE</td>
<td>dithienylethene</td>
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<tr>
<td>d</td>
<td>doublet</td>
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<td>ethanol</td>
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<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared</td>
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<td>e. g.</td>
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<td>h</td>
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<tr>
<td>IRF</td>
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<tr>
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<td>mg</td>
<td>milligram</td>
</tr>
<tr>
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</tr>
<tr>
<td>mmHg</td>
<td>millimetres of mercury</td>
</tr>
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<td>millimoles</td>
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<tr>
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<td>minutes</td>
</tr>
<tr>
<td>ε</td>
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<tr>
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<td>multiplet</td>
</tr>
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<td>integer</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>NBS</td>
<td>n-bromosuccinimide</td>
</tr>
<tr>
<td>n-BuLi</td>
<td>n-butyllithium</td>
</tr>
<tr>
<td>NCS</td>
<td>n-chlorosuccinimide</td>
</tr>
<tr>
<td>NHE</td>
<td>normal hydrogen electrode</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>O</td>
<td>open</td>
</tr>
<tr>
<td>ORD</td>
<td>optical rotatory dispersion</td>
</tr>
<tr>
<td>PSS</td>
<td>photostationary state</td>
</tr>
<tr>
<td>PET</td>
<td>photoinduced electron transfer</td>
</tr>
<tr>
<td>PMMA</td>
<td>polymethylmethacrylate</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>Q</td>
<td>quencher</td>
</tr>
<tr>
<td>Φ</td>
<td>quantum yield</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>sec</td>
<td>seconds</td>
</tr>
<tr>
<td>SiO₂</td>
<td>silicon dioxide</td>
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<tr>
<td>s</td>
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</tr>
<tr>
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<td>tert-butyllithium</td>
</tr>
<tr>
<td>TBAI</td>
<td>tetrabutyl ammonium iodide</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>thin layer chromatography</td>
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<td>Et₃N</td>
<td>triethylamine</td>
</tr>
<tr>
<td>PPh₃</td>
<td>triphenylphosphine</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>ultraviolet-visible</td>
</tr>
<tr>
<td><em>in vacuo</em></td>
<td>under vacuum</td>
</tr>
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<td>λ</td>
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<tr>
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</tr>
<tr>
<td>wt.%</td>
<td>weight percent</td>
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</table>
1 Introduction to Photochromic Molecular Switches

1.1 Description of Photochromic Molecular Switches

Molecular switches are compounds that reversibly interconvert between two
different isomers using external stimuli such as heat, light, electricity and the presence of
chemical reagents. Each of the isomers has different properties and the switching of
these properties are of interest for the electronics and optical memory device industries as
well as many others. Photochromic systems are a particular class of molecular switches
whose reversible switching process is based on light-induced interconversions between
two isomers having two different absorption spectra. Photochromic systems are
particularly attractive for materials science applications because the light stimulus can be
easily tuned and focused. In addition to the changes in the absorption spectra, there are
other physical properties that are modified as the states of photochromic compounds are
interconverted including fluorescence intensity, refractive index, oxidation/reduction potential, magnetic properties and chiroptical properties. Chiroptical is a term referring to the optical techniques (using refraction, absorption or emission of anisotropic radiation) for investigating chiral substances (e.g. measurements of optical rotation at a fixed wavelength, optical rotatory dispersion (ORD), circular dichroism (CD), and circular polarization of luminescence (CPL)). The ability to vary these physical properties can be applied to various photonic devices such as erasable optical memory and photo-optical switch components.
1.2 Classes of Photochromic Compounds

Azobenzenes, spiropyrans, fulgides and diarylenes are four major photochromic systems that have been extensively studied in the past decades (see Table 1.2.1). The photochromic properties of azobenzenes arise from the cis-trans isomerization of the N=N bond. The changes in the case of the spiropyrans are a result of bond rearrangement (ring-opening and ring-closing). These two compounds are not thermally stable in one of their forms (the cis form for azobenzenes and the ring-closed form for spiropyrans) and spontaneously revert back to their initial states in the dark. Fulgides and diarylenes are based on pericyclic electrocyclic reactions. These two systems are thermally stable in both of the forms and do not undergo reactions in the dark. In addition to thermal stability, fatigue resistance, which is defined as the number cycles of a photochromic compound can undergo before the absorption spectrum of the first state isomer has decreased to 80%, is particularly important for these systems to be used in reversible data storage application. The excellent thermal stability and high fatigue resistance make diarylenes particularly appealing for use in optoelectronic devices and optical memory media.
Table 1.2.1 Classes of Photochromic Systems

<table>
<thead>
<tr>
<th>classes</th>
<th>Class 1: cis-trans isomerization</th>
<th>Class 2: bond rearrangement</th>
<th>Class 3: pericyclic reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>compound</td>
<td>azobenzene</td>
<td>spiropyran</td>
<td>fulgide</td>
</tr>
<tr>
<td>reactions</td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
</tr>
<tr>
<td>properties</td>
<td>low thermal stability of cis-isomer</td>
<td>low thermal stability of closed form, low fatigue resistance</td>
<td>low fatigue resistance because E-form converts to unproductive Z-form</td>
</tr>
</tbody>
</table>

1.3 Dithienylethene (DTE) Derivatives

The first example of thermally irreversible photochromic diarylethenes was reported by Irie and Mohri in 1988.\textsuperscript{24} Since then, various types of diarylethenes having thiophene, furan, indole, selenophene, and thiazole aryl groups have been prepared.\textsuperscript{1,4} Most of these derivatives show thermally irreversible (both isomers are thermally stable at ambient temperature) and fatigue-resistant properties. Among these DTE derivatives, those with an octofluorocyclopentene ring containing the central alkene of the photoactive hexatriene (‘X’ = F in Table 1.2.1) show excellent thermal stability and remarkable fatigue resistance.\textsuperscript{24-29} More details regarding this structure are discussed in the following section.
1.3.1 Thermal Irreversibility

Diarylethenes are compounds having a 1,3,5-hexatriene molecular framework with two phenyl or heterocyclic five-member rings. Calculations on diarylethene derivatives with phenyl, pyrrolyl, furyl and thienyl groups reveal that the thermal stability (ring-opening) depends on the ground-state energy difference between the ring-open and ring-closed isomers.\(^{22}\) It was found that the smaller the difference in the ground-state energy between the two isomers, the more stable was the ring-closed isomer. The energy differences for diarylethene derivatives containing phenyl groups were calculated to be the biggest while the differences for those containing thienyl groups were the smallest. This energy difference correlated well with the changes in resonance stabilization energy. The result is that introducing thiophene rings which have the smallest change in aromaticity upon ring-closing will produce the most thermally stable photochromic diarylethene compounds.\(^{22}\) The first reported example of a DTE derivative did not return to its initial ring-open isomer when kept in the dark for more than 3 months even at 80 °C.\(^{24}\)

1.3.2 Fatigue Resistance

DTE derivatives are known for their high fatigue resistance. It has been reported that some DTE derivatives can undergo up to \(10^4\) cycles without any significant degradation of their structures.\(^{24,30-33}\) Replacing the thiophene rings with benzothiophene rings can achieve this high fatigue resistance due to the prevention of formation of photo-oxidized side-products.\(^{30,31,34}\)
1.3.3 Facile Modification of the DTE Backbone

One of the reasons that the DTE structure is attractive as a molecular switch is the ease with which the backbone can be modified. The groups labelled as ‘R1’ and ‘R2’ in Table 1.2.1 are the ones that are commonly functionalised to obtain the desired DTE derivatives (Figure 1.3.1). The ring-closed form has a linear conjugated backbone so extending the conjugation by ring closing reactions has a significant effect on their optical and electronic properties based on the ‘R1’ and ‘R2’ groups.

Figure 1.3.1 Dithienylethene derivatives
2 Photoregulating Fluorescence

2.1 Applications for Photoregulating Fluorescence

There have been numerous reports that describe how the photoregulation of fluorescence can be potentially used as the read-out signal in non-destructive data storage applications.\(^\text{1,2,35-40}\) In this application, light is used to control the interconversion between fluorescent “on” states and non-fluorescent “off” states of photochromic compounds. Switching fluorescence emission is considered a promising method for non-destructive read-out application not only because the fluorescence signals can be readily and sensitively (down the single molecule) recognized but also because the small number of photons required for their excitation induces few side effects to spoil the digitalized signals.\(^\text{41}\)

Regulating of fluorescence can also be potentially used in biological fluorescence labelling. Fluorescent probes are placed in a particular cell component or membrane to report on events such as the tracking of cellular structures and functions. Turning the fluorescent probe “on” and “off” can be used to confirm their presence at labelled sites.\(^\text{42}\) When multiprobes are used in a biological cell, the photochromic fluorescent probe could be selectively turned off in order to view the rest of probes more clearly. For example, two colors of fluorescence probes are used. One is green and another one is red. The red one can be turned off when the amounts of the green fluorescence probes are too low to be seen easily due to the large noise. For biological application, fluorescence switching should be reversible and provide high contrast.
The other potential application of photoregulating fluorescence is in confocal imaging. Comparing to conventional epifluorescence microscopy, confocal imaging can offer better resolution by illuminating a single point of the specimen at any one time with a focussed beam and by the use of blocking a pinhole aperture in a conjugate focal plane to the specimen. With normal fluorescence microscopy, one cannot resolve deep structures within a specimen because of light emitted and scattered by the out-of-plane tissue. By placing a small aperture in the light path at points confocal to the focal point within the specimen, almost all of the out-of-focus fluorescence is blocked, allowing detection of just the point of interest (Figure 2.1.1). Better resolution can be achieved by arranging two light sources. One light source projects a ring around a spotlight which induces fluorescence while the light that is the ring quenches fluorescence and makes the spot size smaller (Figure 2.1.2). 43,44

![Confocal microscope](image)

**Figure 2.1.1** Confocal microscope
2.2 Fluorescent Photochromic Compounds

Fluorescent photochromic compounds have been reported over the past decades. The fluorescence change of the two states of these compounds is normally due to the structural, conjugation and polarity changes. The fluorescence is favored in more rigid structures (less energy of the excited state is lost as heat), longer conjugation (smaller energy gap between HOMO and LUMO; π electron activity increase) and less polar compounds (less energy of the excited state is lost to the environment for less polar compounds). Dithienylethenes exist in two conformations: parallel with mirror symmetry and antiparallel with C2 axis of symmetry (Figure 2.2.1). Antiparallel is the productive conformation for cyclization. Dithienylethenes are normally not fluorescent or are very weakly fluorescent because only the parallel conformation is involved in fluorescence and rotation between C2-C3 (and C1-C7) in the open form is thought to increase the rate of radiationless transition to the ground state.
2.3 Hybrids of Non-Fluorescent Photochromic Compounds and Fluorescent Dyes

Unlike the intrinsically fluorescent photochromic compounds, most compounds are either fluorescent but not photochromic or photochromic but not fluorescent. Therefore, the hybrid system containing a non-fluorescent photochromic compound and a fluorescent dye is in large demand. Many examples approaching this concept have been reported over the past decades. In these hybrid systems, the fluorescence of the fluorescent dyes can be turned “on” and “off” by the photochromic moiety. This design has been implemented either with dyads such as dihydroazulene-anthracene, fulgido-binaphthol, spiropyran-porphyrin, diarylethen-anthracene, and pyrazoline-azobenzene, in which a single photochromic compound is paired to a single fluorescent dye, or triads such as diarylethene-anthracene-diarylethene, spiropyran-fluorescein-
spiropyran and spiropyran-perylene-diimide-spiropyran, in which a single fluorescent dye bridges two identical photochromic compounds. Triads such as oligothiophene-diarylethene-oligothiophene, porphyrin-diarylethene-porphyrin and BODIPY-diarylethene-BODIPY, in which a single photochromic compound bridges two fluorescent dyes have also been reported. In addition, a combination of a porphyrin and four dithienylethenes has been developed to investigate its interesting properties. For the triads with two identical DTE units and the last example with four identical DTE units, only one of the two units and two of the four units were photocyclized during the irradiation, respectively. Although the significant work has been done to improve the fluorescence quenching efficiency, many examples are restricted by low fluorescence intensity contrast ratio, which is defined as the ratio of fluorescence intensity between fluorescence “on” and “off” states. The goal of this project is to synthesize a bistable fluorescent photochromic system with high fluorescence contrast ratio by covalently joining a highly fluorescent dye and a photoresponsive DTE compound as shown in Figure 2.3.1.

![Figure 2.3.1](image)

**Figure 2.3.1** A fluorescent photochromic system joined by a fluorescent dye F and a photochromic moiety Q. Q₁ and Q₂ are two different states of Q.
2.4 Design of a Novel Hybrid System Containing a Non-Fluorescent Photochromic Compound and a Fluorescent Dye

2.4.1 Possible Quenching Pathways

The design of the hybrid system is based on examining the absorption spectra and redox potential of the two states of the photochromic compound with respect to the optical and electronic properties of the fluorescent dye. Correspondingly, Energy Transfer and Electron Transfer are two possible quenching pathways for the photoregulation of fluorescence of these hybrid systems.

In Energy Transfer, the emission bands of the fluorescent dye and the absorption bands of only one of the two states of the photochromic component should overlap significantly as indicated in Figure 2.4.1. When the photochromic component Q is in the $Q_1$ state, there is no overlap between the emission band of the fluorescent dye $F$ and the absorption band of the photochromic component $Q_1$. Irradiation with UV light can induce a decrease in the intensity of the high-energy absorption band and corresponding appearance of new absorption band in the near-UV and visible regions of the spectra because the photochromic component $Q_1$ is converted to the component $Q_2$. Therefore there is overlap between the emission band of the fluorescent dye $F$ and the absorption band of the photochromic component $Q_2$. The emission energy of the fluorescent dye $F$ can be intramolecularly transferred to the photochromic component $Q_2$. The excited state of the photochromic component $Q_2$ is generated, which relaxes back to the ground state through non-emission route. As a result, the fluorescence of a hybrid system containing the photochromic component $Q$ and fluorescent dye $F$ is quenched when the photochromic component is in $Q_2$ state (Figure 2.4.2). The original state $Q_1$ can be
regenerated again by irradiation with visible light. Therefore the fluorescence of this hybrid system can be modulated by UV and visible light via Energy Transfer.

![Diagram](image)

**Figure 2.4.1** The absorption spectra of the photochromic component Q and the emission spectrum of the fluorescent component F. Q₁ and Q₂ are the photochromic component Q in two different states. The shaded area is the overlapping between the absorption band of the photochromic component Q₂ and the emission band of the fluorescent component F.

![Diagram](image)

**Figure 2.4.2** Energy Transfer. Q₂ and Q₂* is the photochromic component in ground state and excited state, F and F* is the fluorescent dye in ground state and excited state.
In Electron Transfer, the change of the oxidation and/or reduction potential between the two states of the photochromic component can be used to activate or suppress the intramolecular electron transfer process. The excited electron in the fluorescent dye can transfer to empty orbital of the LUMO of only one state of the photochromic component or the electron from the HOMO of only one state of the photochromic component can fill the hole of the excited fluorescent dyes. Therefore the fluorescence is quenched as shown in Figure 2.4.3. The fluorescent dye F can be an electron donor or electron acceptor depending on the LUMO and HOMO levels of the fluorescent dye F and photochromic component Q. For the first case, when the HOMO of the F is higher than the LUMO of photochromic component Q2, the F can be an electron donor. The excited electron of the F can then transfer to the Q2. The fluorescence of the F is quenched by the Q2. The excited state of the Q2 is generated, which relaxes back to the ground state by non-emission route. In contrast, when the HOMO of the F is lower than the LUMO of photochromic component Q1, the electron can not transfer to the Q1. The fluorescence of the F cannot be quenched by the Q1. For the second case, when the LUMO of the F is lower than the HOMO of photochromic component Q2, the F can be an electron acceptor. The empty hole of the F in the excited state can then be filled by the electron from the HOMO of the Q2. The fluorescence of the F is quenched by the Q2. In contrast, when the LUMO of the F is higher than the HOMO of photochromic component Q1, the hole cannot be filled by the electron from the Q1. The fluorescence of the F cannot be quenched by the Q1. Since photochromic component Q can be converted between the two different states Q1 and Q2 with different
HOMO and LUMO, the fluorescence of a hybrid system containing the photochromic component $Q$ and fluorescent dye $F$ can be modulated via Electron Transfer.

![Figure 2.4.3 Electron Transfer. $Q_1$ and $Q_2$ is the photochromic component in two different states. $F$ and $F^*$ is the fluorescent dye in ground state and excited state.](image)

2.4.2 Synthesis of Phenyl Control, Thiienyl Control and a DTE Carboxylic Acid

Our target compound is a hybrid system 2.14Zn containing a bis(amidine) fluorescent dye and two photochromic dithienylethenes as shown in Figure 2.4.4. The bis(amidine) fluorescent dye 2.0 was an intermediate compound provided by Dr. R. Scheffold et al., whose target compounds from it were Vitamin B$_{12}$-model compounds used as catalyst for in vitro organic reactions. This fluorescent dye 2.0 was synthesized with concise route and high yield of 85%. The reason we choose this dye as our fluorescent dye for this project is because of its strong fluorescence and the possible concise synthetic route to connect the two imine groups to the photochromic component by amide linkages. Diarylethenes were chosen as the photochromic component due to their thermal irreversibility and high fatigue resistance. This target compound contains a metal because employing a metal can not only increase the intensity of the emission and
shift the emission wavelength to longer wavelength\textsuperscript{6,68} but also enhance the photochromism of DTE.\textsuperscript{68} The red shift of the emission wavelength would make the overlap of the emission band of the fluorescent dye and the absorption band of the ring-closed DTE more significant. Before the target compound was made, three control compounds, the phenyl control 2.1\textit{Zn}, the thienyl control 2.5\textit{Zn} and the DTE carboxylic acid 2.12 as shown in Figure 2.4.4 were synthesized to investigate the possibility of the fluorescence quenching of the target compound. UV-Vis absorption, fluorescence and cyclic voltammetry experiments were carried out on the phenyl control 2.1\textit{Zn} and UV-Vis absorption and fluorescence experiments were carried out on the thienyl control 2.5\textit{Zn} for this purpose.

![Chemical structures](image)

\textbf{Figure 2.4.4} Fluorescent dye 2.0, target compounds 2.14\textit{Zn} and control compounds 2.1\textit{Zn}, 2.5\textit{Zn} and 2.12

The ligand 2.1 was synthesized as shown in Scheme 2.4.1 by reacting bis(amidine) with benzoyl chloride. The phenyl control 2.1\textit{Zn} was synthesized by
adding a ZnCl\(_2\) solution to a solution of 2.1 in the presence of Et\(_3\)N. Both 2.1 and 2.1Zn were purified by recrystallization with CH\(_2\)Cl\(_2\) and ether. Column chromatography was not used because the imines are easily hydrolysed on the column.

![Scheme 2.4.1 Synthesis of phenyl control 2.1Zn](image)

The ligand 2.5 and thienyl control 2.5Zn were synthesized in the similar way.

![Scheme 2.4.2 Synthesis of thienyl control 2.5Zn](image)
The DTE carboxylic acid 2.12 was prepared according to literature procedures.\textsuperscript{69}

\begin{align*}
\text{Br} & \quad \rightarrow \quad \text{Br} \\
\text{Cl} & \quad \rightarrow \quad \text{OH} \\
\text{Br} & \quad \rightarrow \quad \text{CO}_2 \\
\text{Br} & \quad \rightarrow \quad \text{Cl} \\
\text{Br} & \quad \rightarrow \quad \text{HO} \\
\text{Br} & \quad \rightarrow \quad \text{CO}_2 \\
\end{align*}

Scheme 2.4.3 Synthesis of a DTE carboxylic acid 2.12

All of the synthesized compounds were characterized by $^1$H NMR spectroscopy.

All new compounds were characterized by $^1$H NMR and $^{13}$C NMR spectroscopy, mass spectrometry, and elemental analysis.

2.4.3 UV-Vis Absorption and Fluorescence Spectroscopy of Thienyl Control 2.5Zn and UV-Vis Absorption Spectroscopy of DTE Carboxylic Acid 2.12

The UV-Vis absorption and emission spectra were measured CH$_2$Cl$_2$ solution of both controls. Both control compounds showed emission properties when excited with appropriate light. UV-Vis absorption spectra of ligand 2.5 showed absorption bands at 258 nm, 291 nm and 373 nm. These three bands shifted to longer wavelengths as
expected: 272 nm, 345 nm and 472 nm for the corresponding Zn complex \textit{2.5Zn}.

Excitation at 475 nm of a CH$_2$Cl$_2$ of \textit{2.5Zn} resulted in an intense emission band at 498 nm. The ring-open form of DTE carboxylic acid \textit{2.12} showed an absorption band at 266 nm while absorption bands at 308 nm, 383 nm and 589 nm corresponded to the ring-closed isomer. The overlap of the emission band of the thienyl control \textit{2.5Zn} and the absorption band of the ring-closed isomer of the DTE carboxylic acid \textit{2.12}, show that the fluorescence of dye component should be quenched by the ring-closed isomer through Energy Transfer, while for the ring-open isomer, the fluorescence should not be quenched because the absorption band of the ring-open isomer is not overlapping with the emission band of the fluorescent dye.
Figure 2.4.5 UV-Vis absorption spectra (blue) and emission spectra (red) of the 2.5Zn and the UV-Vis absorption spectra of the DTE carboxylic acid 2.12 (black). Emission spectra were obtained using 475 nm as the excitation wavelength. Spectra were run using $2 \times 10^{-5} \text{ M (2.12)}$ and $1.3 \times 10^{-5} \text{ M (2.5Zn)} \text{CH}_2\text{Cl}_2$ solution.
2.4.4 Cyclic Voltammetry (CV) of the DTE Carboxylic Acid 2.12 and the Phenyl control 2.12Zn

The last section showed that Energy Transfer is one possible quenching pathway. Photoinduced Electron Transfer (PET) is another possible quenching pathway, which is shown in this section. Our goal of photoregulating fluorescence quenching through electron transfer relies on having a change in the electron accepting or electron donating ability of the ring-open isomer as compared to the ring-closed isomer of the DTE carboxylic acid 2.12. Cyclic voltammograms were obtained for 10^{-3} M CH_2Cl_2 solution of both isomers with 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte (Figure 2.4.6). A glassy carbon working electrode, a silver wire reference electrode and a platinum counter electrode were used. For ring-open isomer of 2.12, the voltammograms show an irreversible oxidation peak at 1.570 V (1.806 versus NHE). For ring-closed isomer of 2.12, two oxidation peaks - one is a reversible peak at 0.703 V (0.939 V versus NHE) and another one is an irreversible peak at 1.224 V (1.460 V versus NHE) - and an irreversible reduction peak at -1.123 V (-0.887 V versus NHE) are shown. Comparing to ring-open isomer of 2.12, the oxidation potentials of the ring-closed isomer is smaller, which makes ring-closed isomer easier to oxidize therefore a better electron donor than the ring-open isomer 2.12.
Figure 2.4.6 Cyclic voltammograms of a CH$_2$Cl$_2$ solution (1.0 x 10$^{-3}$ M) of ring-open isomer of 2.12 (2.12O) and ring-closed isomer of 2.12 (2.12C). The photostationary state of 2.12 was generated with 365 nm light. A glass carbon working electrode, a silver reference electrode and a platinum counter electrode were used. The sweep rate was 300 mv/s. The arrows show directions of the sweep.

A cyclic voltammogram was obtained for a CH$_2$Cl$_2$ solution of phenyl control 2.12Zn (10$^{-3}$ M) with 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte (Figure 2.4.7). A glassy carbon working electrode, a platinum reference electrode with 0.1 M TBAI and 0.05 M I$_2$ in CH$_3$CN as the inner solution and platinum counter
electrode were used. The voltammogram shows a reversible reduction peak at -1.016 V (-0.945 V versus NHE).

![Cyclic voltammogram of a CH₂Cl₂ solution of 2.1Zn (10⁻³ M) with 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte. A glass carbon working electrode, a platinum reference electrode with 0.1 M TBAI and 0.05 M I₂ in CH₂CN as inner solution and a platinum counter electrode were used. The sweep rate was 100 mV/s. The arrow shows the direction of the sweep.](image)

**Figure 2.4.7** Cyclic voltammogram of a CH₂Cl₂ solution of 2.1Zn (10⁻³ M) with 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte. A glass carbon working electrode, a platinum reference electrode with 0.1 M TBAI and 0.05 M I₂ in CH₂CN as inner solution and a platinum counter electrode were used. The sweep rate was 100 mV/s. The arrow shows the direction of the sweep.

### 2.4.5 Free Energy of PET Calculations

To relate the change in oxidation potential/reduction potential between the ring-open isomer and ring-closed isomer of the DTE carboxylic acid 2.12 to the difference in efficiency in PET, the free energies of PET in kilocalories per mole were calculated using the Rehm equation⁷⁰ as follows:
\[ \Delta G_{\text{PET}} = (\Delta G_{A^{-}D^{+}}) - w_p - \Delta G_{00} = 23.06[E^0(D^{+}/D) - E^0(A/A^-)] - w_p - \Delta G_{00} \]

Equation 2.4.1 Rehm equation used to calculate the free energies of PET with energy diagram for PET shown above.

Where \( E^0(D^{+}/D) \) is the oxidation potential which refers to the electromotive force of removing an electron from a donor D and \( E^0(A/A^-) \) is the reduction potential which refers to the electromotive force of adding an electron to an acceptor A. Redox potentials are obtained from the CV experiments on both DTE carboxylic acid 2.12 and phenyl control 2.1Zn and are measured in volts (V) and are listed as vs. the reference electrode NHE. \( w_p \) is the attractive Coulombic force that will draw the two ions D\(^+\) and A\(^-\) closer together and result in a release of energy. \( w_p \) is derived from Coulomb's law as follows:

\[ w_p = 332(z_D^+)(z_A^-)(d_{cc}/\varepsilon_s) \]

Equation 2.4.2 Equation used to calculate the attractive Coulombic force between two ions D\(^+\) and A\(^-\).

Where \( z_D^+ \) and \( z_A^- \) are the charges on the molecules, \( d_{cc} \) is the center-to-center separations distance in Å between the two ions, in this case, approximated with the models created by the program of Spartan™ ’02 for Macintosh,\(^7\) and \( \varepsilon_s \) is the static dielectric constant of the solvent, in this case, dichloromethane (CH\(_2\)Cl\(_2\)). \( \Delta G_{00} \) is the
change in free energy (kcal/mol) of the electron donor upon excitation with light and is calculated as follows:

\[
\Delta G_{00} = EN_A = h\epsilon N_A/\lambda
\]

**Equation 2.4.3** Equation used to calculate the change in free energy of the electron upon excitation with light

Where \( E \) is the energy in kcals/mol of the light used for excitation, in this case the wavelength \( \lambda \) is 475 nm. \( h \) is Planck constant, \( 6.626 \times 10^{-34} \) J s, \( c \) is the speed of light, \( 2.9979 \times 10^8 \) m/s and \( N_A \) is Avogadro’s number, \( 6.02214 \times 10^{23} \) mol\(^{-1}\).

According to the above equations, the free energy of PET between \( \textbf{2.1Zn} \) and ring-open isomer of \( \textbf{2.12O} \) and ring closed isomer \( \textbf{2.12C} \) is calculated as follows:

\[
E = h\epsilon /\lambda \\
= [(6.626 \times 10^{-34} \text{ J s})(2.9979 \times 10^8 \text{ m/s})] / 0.000000475 \text{ m} = 4.18 \times 10^{-19} \text{ J}
\]

\[
\Delta G_{00} = EN_A = (4.18 \times 10^{-19} \text{ J})(6.02214 \times 10^{23} \text{ /mol})
\]

\[
= 2.52 \times 10^5 \text{ J/mol}
\]

\[
= 60.2 \text{ kcal/mol}
\]

\[
w_p (\textbf{2.1Zn:2.12O}) = 332(z_D^+)(z_A^-)/(d_{ee}c_e)
\]

\[
= 332(1)(-1)/[(10.4665)(9.08)]
\]

\[
= -3.49 \text{ kcal/mol}
\]

\[
w_p (\textbf{2.1Zn:2.12C}) = 332(z_D^+)(z_A^-)/(d_{ee}c_e)
\]

\[
= 332(1)(-1)/[(10.7885)(9.08)]
\]
\[ \Delta G_{\text{PET}}[2.12\text{O}(\text{Donor}):2.1\text{Zn}(\text{Acceptor})] = -3.39 \text{ kcal/mol} \]

\[ \Delta G_{\text{PET}}[2.12\text{C}(\text{Donor}):2.1\text{Zn}(\text{Acceptor})] = 23.06[(1.806) - (-0.945)] - (-3.49) - 60.2 \]

\[ = 6.73 \text{ kcal/mol} \]

The calculated negative value of the free energy for PET indicated that the quenching reaction was thermodynamically favourable for the ring-closed isomer of the DTE carboxylic acid 2.12 as the electron donor and the fluorescent dye phenyl control 2.1Zn as the electron acceptor. While for the ring-open isomer, the free energy for PET is 6.73 kcal mol\(^{-1}\), which indicated that electron was not likely to transfer from the fluorescent dye to the photochromic moiety. Therefore the fluorescence would not be quenched by this mechanism.

To compare the HOMO and LUMO energy difference between the phenyl control 2.1Zn and thienyl control 2.5Zn, the molecular models for these two compounds were created as shown in Figure 2.4.8 using program of Spartan\(^{\text{TM}}\) '02 for Macintosh. Equilibrium geometries of the ground states were determined by semi-empirical molecular orbital models calculations. The semi-empirical models were used because these models have proven to be successful for calculations of equilibrium geometries, including the geometries of transition-metal compounds. Detailed procedures for this calculation were shown in Experimental section of this chapter. However HOMO and
LUMO energies for phenyl control $2.1\text{Zn}$ and for thienyl control $2.5\text{Zn}$ could not obtained probably because the program cannot handle this complicated metal complex. Therefore, assuming the energy difference between the two ligands is similar to that between the two metal complexes, HOMO and LUMO energies for ligands $2.1$ and $2.5$ were calculated for comparison. The HOMO and LUMO for $2.1$ are $-8.953$ eV and $-0.854$ eV while for $2.5$ are $-8.837$ eV and $-0.878$ eV respectively. The thienyl one is a better acceptor due to its lower LUMO and a better donor due to its higher HOMO. Also the energies are very close between these two compounds (difference < 3%). Therefore, the same conclusion would be drawn for the donor / acceptor pair of the DTE carboxylic acid $2.1\text{Zn}$ and thienyl control $2.5\text{Zn}$.

Figure 2.4.8 Molecular models of phenyl control $2.1\text{Zn}$ and thienyl control $2.5\text{Zn}$. Equilibrium geometries at the ground state were determined by PM3 calculations using Spartan™ '02 for Macintosh.
2.4.6 Synthesis and Photochromic Reactions of a Novel Hybrid System

2.4.6.1 Synthesis

In analogy to the controls, the imidate 2.14 was prepared as shown in Scheme 2.4.4 by acylating the same bis(amidine) 2.0 with carboxylic acid chloride of DTE acid 2.12.\textsuperscript{69} Zn imidate 2.14Zn was synthesized by adding a ZnCl\textsubscript{2} solution to a solution of 2.14 in the presence of Et\textsubscript{3}N (Scheme 2.4.4). Similar to the two controls, both 2.14 and 2.14Zn were purified by recrystallization (2.14 from mixture of CH\textsubscript{3}OH and CH\textsubscript{2}Cl\textsubscript{2}, 2.14Zn from ethyl acetate).

Both the imidate 2.14 and the Zn imidate 2.14Zn were characterized by \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectroscopy, mass spectrometry and elemental analysis.

\begin{align*}
\text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} \\
\text{Ph} & \quad \text{S} & \quad \text{S} & \quad \text{O} & \quad \text{H} \\
\end{align*}

\text{DMF, (COCl)}_2

\begin{align*}
\text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} \\
\text{Ph} & \quad \text{S} & \quad \text{S} & \quad \text{N} & \quad \text{O} \\
\end{align*}

\text{CH}_2\text{Cl}_2

\begin{align*}
\text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} \\
\text{Ph} & \quad \text{S} & \quad \text{S} & \quad \text{N} & \quad \text{O} \\
\text{N} & \quad \text{N} & \quad \text{N} & \quad \text{N} \\
\text{NH} & \quad \text{N} & \quad \text{N} & \quad \text{N} \\
\end{align*}

\text{Et}_3\text{N, ZnCl}_2

\text{CH}_2\text{Cl}_2, \text{CH}_3\text{CN}

\begin{align*}
\text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} \\
\text{Ph} & \quad \text{S} & \quad \text{S} & \quad \text{N} & \quad \text{O} \\
\text{N} & \quad \text{N} & \quad \text{N} & \quad \text{N} \\
\end{align*}

\text{Scheme 2.4.4 Synthesis of a novel hybrid Zn imidate 2.14Zn}
2.4.6.2 Photochromic Reactions of the Novel Hybrid System 2.14Zn

The photochromic reactions of imidate 2.14 and Zn imidate 2.14Zn are best evaluated by alternately irradiating solutions of the compounds with UV and visible light while monitoring the changes in their UV-Vis absorption spectra. The resulting UV-Vis spectra are shown in Figure 2.4.9 and Figure 2.4.10 using a CH₃CN solution for imidate 2.14 (Figure 2.4.9) and using a CH₂Cl₂ solution for Zn imidate 2.14Zn (Figure 2.4.10). For both compounds, irradiation with 365 nm light induced an immediate decrease in the high-energy absorptions and corresponding appearance of new absorption bands in the visible region of the spectra as the ring-open DTEs were converted to their coloured ring-closed forms (for 2.14, the color changed from colorless to blue while for 2.14Zn the color changed from yellow to dark green). In analogy to the control compounds, the absorption bands shifted to longer wavelength: 283 nm, 374 nm, 609 nm (closed peak) for the imidate 2.14 to 280 nm, 342 nm, 478 nm, 665 nm (closed peak) for the Zn imidate 2.14Zn. It took 9 min to reach photostationary state and 8 min (>557 nm) to restore the original spectra for the imidate 2.14. While for the Zn imidate 2.14Zn, it only took 2.5 min to reach the photostationary state and only 3 min (>525 nm) to regenerate the original spectra.

The irradiation cycles were repeatedly carried out using CH₂Cl₂ solution of 2.14Zn for 10 cycles without any significant decreasing of the absorbance in its UV-Vis absorption spectra (Figure 2.4.10, insert). Exposure to 365 nm light for periods longer than 30 min resulted in the decrease in the intensity of the closed band and the closed band could not return to zero in height after irradiation with visible light.
The photochromic reactions of Zn imidate 2.14Zn were also studied by $^1$H NMR spectroscopy by irradiating a CD$_2$Cl$_2$ solution with 365 nm light in a quartz NMR tube. After 30 min of irradiation, the photostationary state was reached and was identified by $^1$H NMR spectroscopy as consisting of 99% of the ring-closed isomer. The ring-closed isomer could be photobleached (>525 nm) with no observable degradation. $^1$H NMR spectroscopy showed that extended periods of continuous irradiation (2h) of the solution of the photostationary state of 2.14Zn with 365 nm light did not result in any decomposition of the compound. $^1$H NMR spectroscopy also revealed that the cyclization reaction occurred in only one of the DTE moieties (Figure 2.4.11). $^1$H NMR showed only one set of peaks (f, g, h, i, j, k, l) for the two DTE moieties for the ring-open isomer of 2.14Zn but two sets of peaks (f, f', g, g', h, h', i, i', j, j', k, k', k'', l, l', l'') for ring-closed isomer of 2.14Zn. This indicated that the ring-open isomer is symmetric while the ring-closed isomer is not symmetric due to only one of the moieties ring-closing. The reason for four methyl peaks (k', k'', l', k'') of the ring-closed moiety of the ring-closed isomer is because of the diastereomers of the cyclic products. The $^1$H NMR spectra of the ring-closed isomer in CD$_2$Cl$_2$ did not change in the dark for at least 2 weeks. This showed excellent thermal irreversibility of the 2.14Zn.
Figure 2.4.9 Changes in the UV-Vis absorption spectra and emission spectra of a CH$_3$CN solution of 2.14 (1.2 x 10$^{-5}$ M). a) The irradiation at 365 nm for absorption spectroscopy was carried out for 10 sec, 20 sec, 30 sec, 1 min, 1.5 min, 2.5 min, 5.5 min, and 9 min. b) The irradiation at 365 nm for emission spectroscopy was carried out for 10 s, 20 s, 30 s, 1 min, 1.5 min, 2.5 min, 5.5 min, and 9 min. Emission spectra were obtained using excitation wavelength of 472 nm.
Figure 2.4.10 Changes in the UV-Vis absorption spectra and emission spectra of a CH₂Cl₂ solution of 2.14Zn (1.3 x 10⁻³ M, the solution was deoxygenated by nitrogen bubbling and then by freeze-pump-thaw method using liquid nitrogen as cooling bath.) a) The irradiation at 365 nm for absorption spectroscopy was carried out for 2 sec, 5 sec, 10 sec, 20 sec, 30 sec, 1 min, 1.5 min and 2.5 min. b) The irradiation at 365 nm for emission spectroscopy was carried out for 2 sec, 5 sec, 10 sec, and 40 sec. Insert: modulated absorptions at 478 nm (open circles) and emission spectra (black squares) during alternating irradiation at 365 nm (2sec, 5sec, 10sec, 30 sec for absorption and 2s, 5s, 10s, 40s for emission) and >525 nm (3 min for absorption and 6 min for emission). Emission spectra were obtained using excitation wavelength of 470 nm.
Figure 2.4.11 $^1$H NMR (500 MHz) spectra of Zn imidate 2.14Zn (2.3 x 10^{-3} M, CD$_2$Cl$_2$) with irradiation of 365 nm light a) before irradiation, b) after 30 min irradiation, c) after 3 min. irradiation, d) after 120 min. irradiation, e) photo isomerization of Zn imidate 2.14Zn. The protons are labelled on the structure above the spectrum.

In the ring-open isomer 2.14Zn, significant fluorescence intensity at 502 nm when excited at 470 nm was observed. After a solution of 2.14Zn was irradiated with 365 nm light, the fluorescence intensity at 502 nm dropped to almost zero. The original emission spectrum was regenerated when the 2.14Zn was irradiated with light of wavelength greater than 525 nm. However, it was found that irradiation at excitation wavelength 470 nm and emission wavelength 502 nm resulted in a very small amount (1%) of ring-closing and ring-opening reactions. This showed that prolonged excitation at 470 nm on the ring-open isomer would expect to result in fluorescence intensity decreasing due to the ring-closing reaction and prolonged excitation at 470 nm on the ring-closed isomer would expect to result in fluorescence intensity increasing due to the ring-opening reaction.
2.4.7 Thermal Stability Study

It was found that the hybrid 2.14Zn, the phenyl control 2.1Zn and the thienyl control 2.5Zn were very stable in CH₂Cl₂ but not stable in other solvents such as CH₃CN and ethanol in the dark. Therefore, thermal stability studies by UV-Vis absorption spectroscopy were carried out for the Zn imidate 2.14Zn (Figure 2.4.12) and the control 2.5Zn on 100% CH₂Cl₂, 50% CH₂Cl₂ + 50% CH₃CN, 100% CH₃CN and 100% ethanol solutions. The UV-Vis spectrum of 2.14Zn didn’t change in the 100% CH₂Cl₂ solution but kept changing until it reached a new spectrum with two peaks disappearing and a new peak appearing within 3 h for the 100% CH₃CN solution and within 48 h for the 50% CH₂Cl₂ + 50% CH₃CN solution. For the ethanol solution, the trend was the same as the above two solvents but the change was slower. The control 2.5Zn showed the same phenomenon except that the change was much slower. In comparison to the metal-containing compounds, the free-base compounds 2.5 and 2.14 were stable in CH₃CN and a small amount of degradation was observed for the CH₂Cl₂ solution. To investigate the structure of the new compounds produced, ¹H NMR spectra were measured in a NMR tube with 100% CD₂Cl₂ solution of both 2.14Zn and 2.5Zn and the same tube with the same amount of CD₃CN solution added into them within 30 min in the dark. The spectra of 2.14Zn changed with the original bis(amidine) methyl peaks decreasing to almost zero in height and two new downfield single peaks appearing. But this trend was not observed for 2.5Zn. This indicated that the 2.14Zn dissociated in the mixture of CD₃CN and CD₂Cl₂ solvents and the Zn ion might fall off from the complex due to its coordinating to the CN group of the solvent CD₃CN. The two new peaks might be the methyl peaks of the bisamidin moiety of the resulted non-Zn compound 2.14. To prove the above, ¹H NMR spectra was measured in a NMR tube with 100% CD₂Cl₂ solution of 2.14 and the
same tube with 60% of CD$_3$CN added into the tube. The spectra showed the two methyl peaks of the bisamidin moiety are in different region to that of d) in Figure 2.4.12. Therefore the new product is an unknown product and needs to be further characterized.
Figure 2.4.12  a) and b): Change in the UV-Vis absorption spectra of 2.14Zn in a) a CH₃CN solution, at beginning (thick line) and after 4 h (thin line), b) a 50% CH₂Cl₂ + 50% CH₃CN, at beginning (thick line) and after 48 h (thin line). c) and d): Changes in the ¹H NMR spectra of 2.14Zn in c) a CD₂Cl₂ solution d) adding same amount of CD₃CN solvent to the above CD₂Cl₂ solution and waiting for 30 min. The chemical shifts changed from a, b, e, d, e, f of c) to a', b', c', d', e', f' and two new peaks of d). All spectra were measured in the dark.
2.4.8  Lifetime and Quantum Yield of Fluorescence

2.4.8.1  Lifetime

A molecule that has absorbed light energy exists as an unstable excited state and usually loses this energy very rapidly (typically in <1 ns). In most cases, this energy is lost as heat, that is, it is converted into molecular rotations and vibrations. In some molecules, for example, rigid ring systems, rotations and vibrations may be too restricted to allow the excited state to dissipate its energy as heat. In this case the energy of the excited state is lost as emission. Emission of such a large packet of energy (compared with rotational and vibrational quanta) is less frequent and the excited state molecules survive for rather longer (about 10⁻⁹ sec). This is the fluorescence lifetime of the molecule. Mathematically lifetime is defined as the time taken for the fluorescence intensity decay to 1/e of its initial value (e = 2.71828).⁷² The lifetime of 2.14Zn was measured as 1.40 ns by Tamara C. S. Pace from Dr. Cornelia Bohne’s research group of the University of Victoria.⁷³

In this measurement, the lifetime was measured by time-domain techniques, which measure fluorescence decay curves (fluorescence intensity as a function of time). In order to obtain the fluorescence lifetime, the profile of instrument response function (IRF) (excitation pulse) has to be measured in addition to the fluorescence decay. This is because the lamp (laser) pulse has a finite temporal width, which distorts the intrinsic fluorescence response from the sample. This effect is called convolution. The lifetime is obtained by convoluting the IRF with a single exponential decay function and then comparing the result with the experimental decay.
The lifetimes of fluorescence were measured for two different solutions. In one case, only the ring open isomer was present, since no absorption bands were observed in the visible region of the UV-Vis absorption spectrum. For a second solution, a mixture of ring-open and ring-closed isomers was present. Both solutions were prepared in CH$_2$Cl$_2$ and diluted such that the absorbance at the excitation wavelength was approximately 0.1 and were purged with N$_2$ for at least 20 minutes prior to measuring. In both cases, the fluorescence decay (Figure 2.4.13) was a mono-exponential and the same lifetime was measured ($1.40 \pm 0.05$ ns as an average of two independent experiments), which implies the presence of only one fluorescent species. Since one solution had just ring-open form and the other was a mixture we can conclude that the lifetime is due to the decay of the ring-open form, and that the ring-closed form is non-fluorescent (at least to the limit of their equipment).

There was little change in the absorbance spectra over the course of the experiment, indicating that a minimal amount of switching occurred during the experiment. Excitation at the isosbestic point around 370 nm was also attempted. There were problems with intensity, and good data was not obtainable, however qualitatively the results are the same as those above.
Figure 2.4.13 Time-resolved fluorescence decay of Zn imidate 2.14Zn in CH$_2$Cl$_2$ fit to a mono-exponential function (decay (O), IRF (Δ), fit (-)). The residuals, the difference between the experimental data and the calculated fit, are randomly scattered between −4 and +4 indicating the quality of the fit is good. Excitation was carried out at 470 nm with emission at 502 nm.

2.4.8.2 Quantum Yield

The efficiency of fluorescence is quantified by quantum yield, $\Phi$ where

$$\Phi = \left( \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} \right) \times 100\%$$

The quantum yield strongly depends on the geometry of the measuring system because light emits from the sample in all directions, whereas measurements are made in a single direction and most emitted light is not detected.

The fluorescence quantum yield of the fluorescent switch in CH$_2$Cl$_2$ was also measured by Tamara C. S. Pace$^{74}$ using quinine bisulfate in 0.5 M H$_2$SO$_4$ as a primary standard ($\Phi_r = 0.55$).

The fluorescence quantum yield was calculated using the following relationship:
Equation 2.4.4 Equation used to calculate fluorescence quantum yield

\[
\phi_u = \frac{\phi_s A_s F_s n_s^2}{A_u F_u n_u^2}
\]

where \( \phi \) is the fluorescence quantum yield of the standard (s) or the unknown (u),
\( A \) is the absorbance at the excitation wavelength of the standard (s) or the unknown (u),
\( F \) is the area of the emission spectrum and \( n \) is the refractive index of the solvents for
standard (s) or the unknown (u).

Solutions were prepared in CH\(_2\)Cl\(_2\) and diluted to give a matched absorbance (± 0.005 absorbance units) of approximately 0.1 at the excitation wavelength (320 nm) and
were purged with N\(_2\) for at least 20 minutes prior to measurement. Solutions were diluted
with deaerated solvent to obtain two data points for each measurement. The fluorescence
quantum yield of the Zn imidate 2.14Zn in CH\(_2\)Cl\(_2\) was found to be 0.12 ± 0.02 (average
of two independent experiments). The quantum yield showed no dependence on
concentration.

The measurements were carried out with irradiation at 320 nm for two reasons.
First there is no reliable primary standard for quantum yield determination that can be
excited at 470 nm in their lab. Secondly as 470 nm is very close to the edge of the
emission spectrum, excitation at 470 nm doesn't allow for collection and integration of
the entire fluorescence emission spectrum, which is necessary for determination of the
quantum yield. Since the molecule is switched during the determination of the quantum
yield then the calculated quantum yields will be lower than the true quantum yield. The
samples were handled carefully, and exposure times were kept to a minimum and resulted
in a maximum 10% decrease in absorbance throughout the entire experiment. This would
result in at most 10% error in the calculated quantum yield values, which is within the error determined for the value.

The measured quantum yield is comparable to other fluorescent photochromic systems reported by other authors. For example, Raymo et al reported quantum yield of 0.0009 - 0.18 in their review article. Irie et al and Chen et al recently reported quantum yield of 0.03 - 0.221.

2.4.9 Photochemical Patterning of Thin Films

2.4.9.1 Thin film preparation and photochromic reactions of the thin film

One of the potential applications of the fluorescent photochromic compound is non-destructive read out, in which a thin film is required to perform the reading and writing task in a practical device (i.e. storage media). The Zn imidate 2.14Zn was spin coated onto a quartz substrate for this purpose. Three films were prepared by spin coating CHCl₃ solutions of PMMA (83 mg/ml, 44 mg/ml and 28 mg/ml) and 2.14Zn (12%, 9% and 9% weight ratio) on quartz substrates with size of 2.5 cm x 1.2 cm. Absorption spectra were measured on film 1 (Figure 2.4.14 a), while the emission spectra was measured on films 2 and 3 (Figure 2.4.14). The measurement of absorption spectra on films 2 and film 3 was attempted but the stable absorption spectra were not obtained due the large signal to noise ratio because of the low concentration of the 2.14Zn in the these films. All films were irradiated with 365 nm light to induce ring-closing and photobleached with light greater than 525 nm to regenerate the ring-opening. The films were excited with 470 nm and the intense emission was observed at 499 nm for the ring-open film. For the ring-closed film, the emission was dropped to almost zero in height because of the quenching. The UV-Vis absorption and emission spectra show similar
results to the compound in solutions (Table 2.4.1). However, compared to solution, the fluorescence intensity contrast ratio of the ring-open isomer and the ring-closed isomer is smaller (99:1 for solution and 49:1 for thin film) and the photochromic reaction rate is also lower and the percentage of the ring-closed isomers at photostationary state, which is defined as the percentage of ring-open molecules that undergo an isomerization reaction at a given wavelength, is also less (Figure 2.4.15). The reason for this might be that the rigid solid-state matrix restricts the conversion of unproductive parallel form to productive anti-parallel form (Figure 2.2.1). This result from the thin film would restrict the further application in the practical use.
Figure 2.4.14 Changes in UV-Vis absorption and emission spectra of 2.14Zn in a) Film 1 (the irradiation with 365 nm light for absorption spectroscopy was carried out for 5 sec, 15 sec, 1 min, 2 min, 3 min and 4 min.), b) Film 3 (the irradiation with 365 nm light for emission spectroscopy was carried out for 2 min, 3 min and 4 min.), insert: Film 2 (modulated emission spectra during alternating irradiation with 365 nm light for 4 min and >525 nm for 5 min.) Emission spectra were obtained using excitation wavelength of 470 nm.
Table 2.4.1 Comparison of wavelengths of $2.14Zn$ in solutions and thin films

<table>
<thead>
<tr>
<th>wavelength</th>
<th>solution</th>
<th>film</th>
</tr>
</thead>
<tbody>
<tr>
<td>absorption of</td>
<td>280 nm, 343 nm, and 478 nm</td>
<td>281 nm, 343 nm,</td>
</tr>
<tr>
<td>ring-open</td>
<td></td>
<td>and 478 nm</td>
</tr>
<tr>
<td>absorption of</td>
<td>280 nm, 343 nm, 478 nm and 665 nm</td>
<td>281 nm, 343 nm,</td>
</tr>
<tr>
<td>ring-closed</td>
<td></td>
<td>478 nm and 665 nm</td>
</tr>
<tr>
<td>excitation</td>
<td>470 nm</td>
<td>470 nm</td>
</tr>
<tr>
<td>emission</td>
<td>502 nm</td>
<td>499 nm</td>
</tr>
</tbody>
</table>

Figure 2.4.15 Comparison of photochromic reactions of $2.14Zn$ in solution ($\lambda_{\text{max-closed}} = 665$ nm and $\lambda_{\text{max-open}} = 280$ nm) and thin film ($\lambda_{\text{max-closed}} = 665$ nm and $\lambda_{\text{max-open}} = 281$ nm). Y-axis is the ratio of the absorbance at $\lambda_{\text{max-closed}}$ and the absorbance at $\lambda_{\text{max-open}}$ for $2.14Zn$ in solution and thin film respectively. The comparison is based on the assumption that the molar extinction coefficients are the same in solution as in the film.
2.4.9.2 Measurement of thickness of thin films with ellipsometry

Many methods can be used to determine the thickness of thin films. Among those methods, ellipsometry and atomic force microscopy (AFM) are two attractive methods. In this thesis, ellipsometry has been used to measure the thickness of all thin films. The technique of ellipsometry relies on the fact that linearly polarized light becomes elliptically polarized on reflection from a metal or glass surface. The presence of a surface film alters the ratio, \( \Psi \), of the electric vectors vibrating in the plane of incidence and perpendicular to it, as well as their difference of phase \( \Delta \). Both \( \Delta \) and \( \psi \) can be measured as a function of wavelength in spectroscopic ellipsometry. This data then can be fit into an assumed model to extract information about the thickness and some other properties (e.g. refractive index) of the sample. This is achieved by using commercially available ellipsometry software. In this thesis, all the films were fitted to an amorphous model to determine the thickness. The thicknesses for film 1, film 2 and film 3 are 568 nm, 225 nm, and 166 nm respectively because of different concentration of PMMA solutions and different spin-coating rate. For film 1 and film 3, two spots were measured for each film. 568 nm and 166 nm were the average thicknesses of the two spots for each film. Other detailed data from the ellipsometry were shown in Experimental section of Chapter 2 and in the Appendices.

2.5 Conclusions

As described above, the UV-Vis absorption spectra and emission spectra showed the ring-open isomers have a strong fluorescence at 502 nm when excited at 470 nm while the ring-closed isomers have very weak fluorescence (1% of the ring-open isomer). The fluorescence switching process could be turned “on” and “off” for ten cycles without
formation of notable side products. This photochromic behaviour plus its thermal stability make it potentially possible to be used for the non-destructive readout application. However, it was found that the irradiation at 470 nm and 502 nm resulted in 1% ring-closing and ring-opening reactions. This would restrict this system to be used in this application. Although the system has no perfect performance for non-destructive readout application, a very large number of fluorescence readings can be performed before significant change takes place in principle.

Another goal of this project was to use the hybrid system $\text{2.14 Zn}$ as a fluorescent probe. The desired characteristics of a fluorescent probe for biological labelling are high molar extinction coefficient, high fluorescence quantum yield, and high photo stability in aqueous solution. Comparing to fluorescent dyes typically used in biological labelling (Table 2.5.1), values of molar extinction coefficient and fluorescence quantum yield are lower but close. However, our goal of this project was to use the fluorescence quenching property of this system for biological labelling where the high fluorescent intensity contrast ratio and thermal irreversibility are required. The high contrast ratio of 99:1 in solution comparing to the reported highest one of 58:1 in solution shows that it is a promising photochromic fluorescent dye that can be potentially used in biological labelling.
Table 2.5.1 Properties of 2.14Zn and fluorescent dyes typically used in biological labelling

<table>
<thead>
<tr>
<th>Property</th>
<th>2.14Zn</th>
<th>Fluorescent Dyes Typically Used in Biological Labelling</th>
</tr>
</thead>
<tbody>
<tr>
<td>molar extinction coefficient</td>
<td>6000 cm⁻¹M⁻¹ at λ = 470 nm</td>
<td>70,000 - 90,000 cm⁻¹M⁻¹ (e.g. BODIPY FL 91,000, Joe 71,000, Rox 82,000)</td>
</tr>
<tr>
<td>Fluorescence quantum yield</td>
<td>0.12</td>
<td>0.5 - 0.95 (e.g. BODIPY FL 0.9, Joe 0.6, Rox 0.7)</td>
</tr>
</tbody>
</table>

2.6 Future Work

To make this system useful in practical applications, the fast cyclization rate and high photostationary state are required in solid state. Increasing the weight ratio of the photochromic compound in PMMA film can be implemented in the future.

Although the hybrid system 2.14Zn is very stable in CH₂Cl₂ solutions, the high photo stability in aqueous solution is very important for practical use in biological labelling. Therefore a water-soluble version of this hybrid system is attempted by synthesizing a cobalt complex of the imidate using the procedures from R. Scheffol et al. Unfortunately due to the difficulties of recrystallization, the cobalt complex could not be purified. More work on the purification of the cobalt system can be tried in the future. Alternatively other water-soluble versions of this hybrid system can be designed.

2.7 Experimental

Materials. All solvents used for synthesis and spectroscopy were dried and degassed by passing through steel columns containing activated alumina under nitrogen using mBraun solvent purification system with the exception of the solvents used for NMR analysis (Cambridge Isotope Laboratories), which were used as received. Column
chromatography was performed using silica gel 60 (230-400 mesh) from Silicycle Inc. All other reagents and starting materials were purchased from Aldrich with the exception of the bis(amidine) 2.0, which was provided by Dr. R. Scheffold et al. 67

**Techniques.** $^1$H and $^{13}$C NMR characterizations were performed on a Bruker AMX 400 instrument working at 400.103 MHz for $^1$H NMR and 100.610 MHz for $^{13}$C NMR spectroscopy or a Varian Inova 500 instrument working at 499.77 MHz for $^1$H NMR and 125.68 MHz for $^{13}$C NMR spectroscopy. Chemical shifts $\delta$ were reported in parts per million relative to tetramethylsilane using the residual solvent peak as a reference standard. Coupling constants ($J$) are reported in Hertz. FT-IR measurements were performed using a Nicolet Nexus 670 instrument. Mass spectrometry were performed using a Waters matrix assisted laser desorption /ionisation (MALDI) or HP5985 mass spectrometer with isobutane as the chemical ionization source for Low Resolution Mass Spectrometry (LRMS). The Mass spectrometry by LRMS method was done by M. Simon Wong. Elemental analysis measurements were done by Mr. M. K. Yang using a Kratos Concept-H instrument with perfluorokerosene as the standard. Melting point measurements were performed using a Fisher-Johns Melting Point Apparatus.

**Semi-empirical Molecular Orbital Models Calculations** were performed using uprogram of Spartan\textsuperscript{TM} '02 for Macintosh in the following steps: 1) Click on New from the File Menu. The “entry” model kit appears. Click Expert from the “entry” model kit to bring up expert model kit. Click inside the box to the right of “Element” and select Zn from Periodic Table and the Octahedral from the list of atomic hybrids. Select O from the Periodic Table and click on one of the free valences of the Octahedral. Select
another \( O \) and two \( N \), one after the other, \textit{click} on three of the free valences in the same plane as the first one. Select Cl and \textit{click} on the last free valence perpendicular to the first four free valences. Build the rest of the molecule with sp, sp\(^2\), sp\(^3\) carbon and oxygen, nitrogen and thiophene.

2) Select \textbf{Calculations} from the \textbf{Setup} menu. Select \textbf{Equilibrium Geometry} and then \textbf{Ground} from the top menu under “Calculate”. This specifies optimisation of geometry. Select \textbf{Semi-empirical} and then \textbf{PM3} from the two bottom menu under “Calculate”. This specifies the calculation of equilibrium geometry using PM3 semi-empirical model. Set start from “Initial”, total charge “\textbf{Neutral or cation}”, multiplicity “\textbf{Singlet}”, subject to “\textbf{Symmetry}”, Print “\textbf{Orbitals & Energies}” and “\textbf{Thermodynamics}”. \textit{Click} “Apply Globally”. Then \textit{click} “\textbf{OK}”.

3) Select \textbf{Submit} from the \textbf{Setup} menu. A file browser appears. Provide a name in the box to the right of “Save As”, and then click on \textbf{Save}. You will be notified that the calculation has started.

4) You will be notified when the calculation has completed. \textit{Click} \textbf{OK} to remove the message from the screen. Select \textbf{Output} from the \textbf{Display} menu. A window containing “text output” for the job appears.

5) Select \textbf{Properties} from the \textbf{Display} menu. The \textbf{Molecule Properties} dialog appears. HOMO and LUMO energies are shown in this screen.

\textbf{UV-Vis absorption and fluorescence measurements} were performed using a Varian Cary 300 Bio spectrophotometer and a PTI QM-2000-4 scanning spectrofluorometer with a 2 nm slit-width, respectively. The ring-closing reactions of all compounds were carried out using the standard lamps whose light was passed through the solutions of the compounds inside a glass cuvette for absorption or a quartz cuvette for fluorescence and the ring-opening reactions were carried out using the light of a 150-W
tungsten source that was passed through the appropriate cut off filter to eliminate higher energy light.

**Time-resolved fluorescence measurements** were performed by Tamara C. S. Pace from Dr. Cornelia Bohne's research group of the University of Victoria with an Edinburgh Instruments OB 920 single-photon counting system with a hydrogen flash lamp excitation source. The excitation and emission wavelengths were set to 470 and 502 nm, respectively, and the band pass for the excitation and emission monochromators was ca. 16 nm (2 mm slits). An iris was employed to ensure that the frequency of the stop pulses was smaller than 2% of the start pulse frequency. The number of counts in the channel of maximum intensity was 2000. The instrument response function was collected using Ludox (Aldrich) to scatter light at the excitation wavelength. A Lauda RM6 bath was used to keep the sample at a constant temperature of 20°C. Data were analyzed using the Edinburgh software. The instrument response function was deconvoluted from the experimental data, and the data were fitted to monoexponential decays. The value of $\chi^2$ (0.9 to 1.1), and visual inspection of the residuals and the autocorrelation were used to determine the quality of the fit (1).

**Spin-coating.** Thin films of Zn imidate $\textbf{2.14Zn}$ were obtained by spin-coating solutions of the compound and PMMA onto quartz substrates using a Laurell WS-400A-6NPP/Lite spin coater. The quartz substrates were first cleaned by sequentially rinsing with acetone, ethanol and methanol and dried with clean air immediately before spin-coating. The thin films for UV-Vis absorption and fluorescence measurements were prepared by saturating the substrate with CHCl$_3$ solutions (film 1 - 16.5 mg of PMMA ($M_w = 120,000$) and 2.0 mg of $\textbf{2.14Zn}$ in 0.2 mL CHCl$_3$, film 2 - 8.8 mg of PMMA
(120,000) and 0.8 mg of 2.14Zn in 0.2 mL CHCl₃, film 3 - 5.6 mg of PMMA and 0.5 mg of 2.14Zn in 0.2 mL CHCl₃) and spinning (film 1, at 6000 rpm for 2 min, film 2 and film 3, at 3000rpm for 2 min). All solutions were passed through 0.2 μm PTFE filters (S&S Biopath) and added dropwise to the substrate using a syringe.

**Ellipsometry measurement.** The film thickness of each film was determined as 568 nm for film 1 (2.5 cm x 1.2 cm), 225 nm for film 2 (2.5 cm x 1.2 cm) and 166 nm for film 3 (2.5 cm x 1.2 cm) by spectroscopic ellipsometry using Jovin-Yvon UVISEL spectroscopic Ellipsometer. In this experiment, both Δ and ψ were measured as a function of wavelength in spectroscopic ellipsometry. These quantities were fitted to an amorphous model with the aid of computer modelling using commercially available ellipsometry software. The software compared the experimental data set and the calculated values using an iterative fitting algorithm and calculated "the goodness fit parameter $\chi^2$", which described how well the calculated date matched the experimental data. The software is designed to minimize the value of $\chi^2$. For all intents and purposes a $\chi^2 < 1$ indicates a good fit.

![Chemical structure](image)

**Synthesis of phenyl control 2.1** A solution of bis(amidine) 2.0 (300 mg, 1.04 mmol) and Et₃N (0.35 mL, 2.5 mmol) in anhydrous CH₂Cl₂ (25 mL) was treated dropwise over 5 min with a solution of benzoyl chloride (0.27 mL, 2.3 mmol) at 0°C under an N₂
atmosphere. After 30 min of stirring, the cooling bath was removed and the reaction was allowed to slowly warm to room temperature and stirred for 2 h. The solvent was evaporated to a slurry and the slurry was loaded onto a silica plug (25 g silica, 4 cm high, development solvent: CH₂Cl₂, 2.5 % CH₃OH, 1% Et₃N). The yellow solution was collected and evaporated to dryness resulting in a mixture of yellow solid and a viscous oil. The mixture was washed with ether and the yellow solid was collected after filtering. The resulted yellow solid was purified by recrystallization (CH₂Cl₂ and ether) to yield 2.1 (351 mg, 59%) as yellow crystals. Mp = 202 - 207 °C. ¹H NMR (CDCl₃, 500 MHz), δ 12.70 (br. s, 1 NH), 8.20 (d, J = 7.8 Hz, 2H), 7.50 (t, J = 7.8 Hz, 2H), 7.42 (t, J = 7.8 Hz, 4H), 5.32 (s, 1H), 1.22 (s, 12H), 1.16 (s, 12H). ¹³C NMR (CDCl₃, 125 MHz): δ 181.8, 179.1, 175.7, 135.7, 132.3, 130.2, 128.0, 89.6, 49.3, 47.8, 23.6, 22.8 (12 of 12 carbons found). FT-IR (KBr cast) 3433, 3263, 3067, 2973, 1662, 1622, 1658, 1497, 1379, 1317, 1281, 1245, 1142, 1112, 1075, 1058, 1025, 783, 721, 691 cm⁻¹. MALDI m/z = 497 [M+H]⁺. Anal. Calcd for C₆₁H₅₂N₄O₂S₄F₁₂: C, 74.97; H, 7.31; N, 11.28. Found: C, 74.67; H, 7.36; N, 11.56.

Synthesis of Zn-phenyl control 2.1Zn A solution of ligand 2.1 (100 mg, 0.2 mmol) and Et₃N (56 µL, 0.40 mmol) in anhydrous CH₂Cl₂ (25 mL) was treated with a solution of the anhydrous zinc chloride (137 mg, 1.01 mmol) in anhydrous CH₃CN (25 mL) under an N₂
atmosphere. The solution was stirred for 0.5 h. The solution was evaporated to a slurry and the slurry was loaded onto a silica plug (15 g silica, 2 cm high, development solvent: CH$_2$Cl$_2$, 5% CH$_3$OH). The yellow solution was collected and evaporated to dryness. The resulted yellow solid was redissolved in CH$_2$Cl$_2$ and any insoluble solids were filtered off. The solution was washed with water (5 mL) and the organic layer was separated and evaporated in vacuo. The crude product was purified by recrystallization twice (first time, CH$_2$Cl$_2$ and ether, second time, CHCl$_3$ and ether) to yield **2.1Zn** (83 mg, 69%) as bright yellow cotton like fine crystals. Mp = 265 - 270 °C. $^1$H NMR (CDCl$_3$, 500 MHz), $\delta$ 8.55 (d, $J$ = 7.8 Hz, 2H), 7.59 (t, $J$ = 7.8 Hz, 2H), 7.49 (t, $J$ = 7.8 Hz, 4H), 5.67 (s, 1H), 1.32 -1.17 (m, 24H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 196.1, 196.0, 180.8, 136.7, 133.7, 131.5, 128.3, 93.2, 51.2, 50.5, 25.3, 23.9, 23.2, 22.6 (14 of 21 carbons found). FT-IR (KBr cast) 3449, 2976, 1619, 1554, 1493, 1384, 1317, 1261, 1133, 1109, 1089, 1075, 1059, 1023, 778, 695 cm$^{-1}$. MALDI m/z = 596 [M+H]$^+$. Anal. Calcd for C$_{61}$H$_{52}$N$_4$O$_2$S$_4$F$_{12}$: C, 62.42; H, 5.91; N, 9.39. Found: C, 62.68; H, 5.98; N, 9.60.

**Synthesis of 2-bromo-5-methyl thiophene 2.2** A solution of N-bromosuccinimide (9.24 g, 51.9 mmol) in N,N-dimethylformamide (DMF) (75 mL) was treated with 2-methylthiophene in one portion via syringe. The resulting yellow solution was stirred at room temperature for 18 h. Distilled water (100 mL) was added to the solution and the aqueous layer was separated and extracted with Et$_2$O (3 x 100 mL). The combined organic layers were washed with distilled water (10 x 100 mL) and brine (100 mL), dried (Na$_2$SO$_4$), filtered, and evaporated to dryness in vacuo and dried under high vacuum (1 mmHg) for 20 min yielding **2.2** (8.37g, 91%) as a light yellow oil. $^1$H NMR (CDCl$_3$, 400
MHz), δ 6.83 (d, J = 3.4 Hz, 1H), 6.52 (d, J = 3.4 Hz, 1H), 2.42 (s, 3H). FT-IR (KBr cast) 3055, 2919, 2859, 1546, 1444, 1216, 1155, 1053, 993, 946, 788, 666 cm⁻¹. Low-resolution mass spectrometry (LRMS) [chemical ionization (CI) with isobutene] m/z = 179 [M+H]^+.

Synthesis of 5-methyl-2-thiophenecarboxylic acid 2.3 A solution of 2-bromo-5-methyl thiophene 2.2 (2 mL, 17.6 mmol) in anhydrous Et₂O (50 mL) was treated with n-butyllithium (10.4 mL, 2.5 M in hexane, 26.0 mmol) dropwise at −78 °C under N₂ atmosphere. The resulting yellow solution was stirred at this temperature for 20 min. The cooling bath was removed and the anhydrous CO₂ gas was bubbled through the reaction for 30 min and the reaction was quenched with aqueous HCl solution (100 mL, 1.7 M). The aqueous layer was separated and extracted with CH₂Cl₂ (2 x 50 mL). The combined organic layers were washed with brine (2 x 50 mL), dried (Na₂SO₄), filtered, and evaporated to dryness in vacuo. The crude product was purified by recrystallization (CH₂Cl₂) to yield 2.3 (1.12g, 45%) as a white powder. ¹H NMR (CDCl₃, 400 MHz), δ 7.71 (d, J = 3.8 Hz, 1H), 6.81 (d, J = 3.8 Hz, 1H), 2.55 (s, 3H). FT-IR (KBr cast) 3461, 3291, 2992, 2836, 1671, 1465, 1309, 1105, 751, 514 cm⁻¹. Low-resolution mass spectrometry (LRMS) [chemical ionization (CI) with isobutene] m/z = 143 [M+H]^+.

Synthesis of 5-methyl-2-thiophenecarboxylic acid chloride 2.4 A solution of 5-methyl-2-thiophenecarboxylic acid 2.3 (700 mg, 4.9 mmol) and anhydrous N,N-
dimethylformamide (DMF) (32 μL) in anhydrous CH₂Cl₂ (50 mL) was cooled to 0°C and treated dropwise over 5 min with oxalyl chloride (1.3 mL, 14.8 mmol) under an N₂ atmosphere. The cooling bath was removed and the reaction mixture was allowed to slowly warm to room temperature and stirred there for 18 h. The mixture was evaporated to dryness in vacuo and dried under high vacuum (1 mm Hg) for 20 min yielding 2.4 (0.73g, 92%) as a thick brown oil. \(^1\)H NMR (CDCl₃, 500 MHz), δ 7.81 (d, \(J = 3.7\) Hz, 1H), 6.87 (d, \(J = 3.7\) Hz, 1H), 2.57 (s, 3H).

**Synthesis of thienyl control 2.5** A solution of bis(amidine) 2.0 (341 mg, 1.18 mmol) and Et₃N (0.36 mL, 2.6 mmol) in anhydrous CH₂Cl₂ (25 mL) was treated with a 5-methyl-2-thiophenecarboxylic acid chloride 2.4 (0.42g, 2.60mmol) at 0°C under an N₂ atmosphere. After 30 min stirring, the cooling bath was removed and the reaction was allowed to slowly warm to room temperature and stirred for 2 h. The solution was evaporated to a slurry and the slurry was loaded to a silica plug (27 g silica, 4 cm high, development solvent: CH₂Cl₂, 2.5 % CH₃OH, 1% Et₃N). Yellow solution was collected and evaporated to dryness resulting in a mixture of a yellow solid and a viscous oil. The mixture was washed with ether and yellow solid was collected after filtering. The yellow solid was purified by recrystallization (CH₃OH) to yield brown crystals 2.5 (445 mg, 70%). Mp = 202 - 203 °C. \(^1\)H NMR (CDCl₃, 400 MHz), δ 12.73 (Br. s, 1 NH) 7.73 (d, \(J = 3.9\) Hz, 2H), 6.77 (d, \(J = 3.9\) Hz, 2H), 5.30 (s, 1H), 2.52 (s, 6H), 1.18 (s, 12H), 1.14 (s,
$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 181.8, 175.9, 173.3, 147.9, 138.7, 133.6, 126.5, 89.5, 49.3, 47.7, 23.5, 22.7, 16.1 (13 of 13 carbons found). FT-IR (KBr cast) 3435, 3210, 2971, 1686, 1644, 1611, 1589, 1494, 1456, 1281, 1249, 1141, 1058, 828, 796 cm$^{-1}$.

MALDI m/z = 536 [M+H]$^+$. Anal. Calcd for C$_{29}$H$_{36}$N$_4$O$_2$S$_2$: C, 64.89; H, 6.76; N, 10.44. Found: C, 65.21; H, 6.56; N, 10.72.

**Synthesis of Thiophenyl control 2.5Zn**

A solution of ligand 2.5 (100 mg, 0.19 mmol) and Et$_3$N (52 µL) in anhydrous CH$_2$Cl$_2$ (25 mL) was treated with a solution of the anhydrous zinc chloride (127 mg, 0.93 mmol) in anhydrous CH$_3$CN (25 mL) under an N$_2$ atmosphere. The solution was stirred for 2 h. The solution was evaporated to a slurry and the slurry was loaded onto a silica plug (20 g silica, 3 cm high, development solvent: CH$_2$Cl$_2$, 5 µL CH$_3$OH). Yellow solution was collected and evaporated to dryness. The resulted yellow solid was redissolved in CH$_2$Cl$_2$ and any insoluble solids were filtered off. The solution was washed with water (5 ml) and the organic layer was separated and evaporated in vacuo. The crude product was purified by recrystallization (CH$_3$CN and ether) to yield bright orange crystals 2.5Zn (27 mg, 23%). Mp = 247 - 248 °C. $^1$H NMR (CDCl$_3$, 500 MHz), $\delta$ 8.00 (d, $J = 3.9$ Hz, 2H), 6.84 (d, $J = 3.9$ Hz, 2H), 5.58 (s, 1H), 2.55 (s, 6H), 1.32 - 1.12 (m, 24H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 195.3, 190.0, 175.0, 151.5, 140.3, 136.2, 127.5, 92.7, 50.7, 50.4, 24.5, 24.4, 23.0, 21.9, 16.3 (15 of 22 carbons}
found. FT-IR (KBr cast) 3435, 3210, 2971, 1686, 1644, 1589, 1494, 1456, 1281, 1249, 1141, 1058, 828, 796 cm\(^{-1}\). MALDI m/z = 634 [M+H]\(^+\). Anal. Calcd for C\(_{29}\)H\(_{33}\)ClN\(_4\)O\(_2\)S\(_2\)Zn: C, 54.72; H, 5.54; N, 8.80. Found: C, 54.20; H, 6.61; N, 6.48 (this compound failed elemental analysis might be because that water was trapped inside the complex and could not be evaporated).

![Structure of 2-chloro-5-methyl thiophene]

**Synthesis of 2-chloro-5-methyl thiophene 2.6**\(^{78}\) N-chlorosuccinimide (6.90 g, 51.7 mmol) was added to solution of 2-methyl thiophene (5 mL, 51.7 mmol) in benzene (80 mL) and Ac(OH) (20 mL). The mixture was heated at reflux for 18 h. The heat source was removed and the solution was allowed slowly warm to room temperature. The solution was neutralized with saturated Na\(_2\)CO\(_3\) (150 mL) and diluted with distilled water. The aqueous layer was separated and extracted with Et\(_2\)O (3 x 50 mL). The combined organic layers were washed with brine (3 x 50 mL), dried (Na\(_2\)SO\(_4\)), filtered, solvent was removed under reduced pressure in a cool water bath to avoid loss of the volatile product. The resulted yellow oil was purified by distillation (bp. 75 °C at 20 mm Hg) to yield 2.6 (4.10 g, 60%) as a colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz), \(\delta\) 6.69 (d, \(J = 3.7\) Hz, 1H), 6.52 (d, \(J = 3.7\) Hz, 1H), 2.41 (s, 3H).

![Structure of 3-bromo-5-chloro-2-methyl thiophene]

**Synthesis of 3-bromo-5-chloro-2-methyl thiophene 2.7**\(^{79}\) A solution of 2-chloro-5-methyl thiophene 2.6 (4.10 g, 30.9 mmol) in CHCl\(_3\) (40 mL) was treated with Br\(_2\) (1.60 mL, 30.9 mmol) in CHCl\(_3\) (10 mL) dropwise via additional funnel over 30 min at 0°C. The cooling bath was removed and the solution was stirred there for 1 hour. The reaction
was quenched by pouring the solution into ice water (50 mL). The aqueous layer was separated and extracted with CHCl₃ (2 x 50 ml). The combined organic layers were washed with distilled water (2 x 50 mL), dried (Na₂SO₄), filtered, and concentrated to a viscous yellow oil. The oil was purified by distillation (bp. 54 °C at 1 mm Hg) to yield 2.7 (3.98 g, 61%) as a colorless oil. ¹H NMR (CDCl₃, 400 MHz), δ 6.73 (s, 1H), 2.32 (s, 3H). FT-IR (KBr cast) 3100, 2920, 2855, 1536, 1460, 1311, 1038, 973, 815, 785, 646 cm⁻¹. Low-resolution mass spectrometry (LRMS) [chemical ionization (CI) with isobutene] m/z = 213 [M+H]⁺.

![Image](image.png)

**Synthesis of 3, 5-dibromo-2-methylthiophene 2.8** A solution of 2-methyl thiophene (5 mL, 56.2 mmol) in AcOH (20 mL) was treated with Br₂ (5.8 mL, 112.5 mmol) in AcOH (10 mL) dropwise via additional funnel over 1 h. The solution was stirred for 18 h with condenser. The reaction was quenched by pouring the solution to an Erlenmyer flask with ice inside. The aqueous layer was separated and extracted with Et₂O (75 mL). The combined organic layers were washed with NaOH solution (2 x 50 mL, 2M), brine (2 x 50 mL), dried (Na₂SO₄), filtered, and concentrated to a viscous black oil. The oil was purified by distillation (bp. 55 °C at 1 mm Hg) to yield 2.7 (5.06 g, 35%) as a colorless oil. ¹H NMR (CDCl₃, 400 MHz), δ 6.86 (s, 1H), 2.34 (s, 3H). FT-IR (KBr cast) 3097, 2919, 2853, 1534, 1449, 1304, 1143, 1023, 952, 816, 784, 692 cm⁻¹. Low-resolution mass spectrometry (LRMS) [chemical ionization (CI) with isobutene] m/z = 257 [M+H]⁺.
Synthesis of 3-bromo-2-methyl-5-phenylthiophene 2.9

A mixture of toluene (50 mL) and an aqueous Na₂CO₃ solution (40 mL, 2M) was deoxygenated by bubbling N₂ for 30 min. A solution of phenyl boronic acid (3.16 g, 25.9 mmol) in ethanol (10 mL) was added to the mixture in one portion via syringe. A 3, 5-dibromo-2-methylthiophene 2.8 (6.04 g, 23.6 mmol) was added to the above solution in one portion via syringe. Tetrakis (triphenyl phosphine) palladium (0) was added to the above solution under an N₂ atmosphere. The solution was heated at reflux for 18 hours under an N₂ atmosphere. The heat source was removed and the resulted yellow solution was allowed to slowly cool to room temperature. The aqueous layer was separated and extracted with Et₂O (2 x 30 mL). The combined organic layers were washed with distilled water (2 x 50 mL), brine (50 mL), dried (Na₂SO₄), filtered, and evaporated to dryness in vacuo. The resulted thick yellow oil was purified by column chromatography using silica (hexane) to yield 2.9 (3.65 g, 61%) as white crystals. Mp = 65 - 67 °C. ¹H NMR (CDCl₃, 400 MHz), δ 7.51 (d, J = 7.3 Hz, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 7.11 (s, 1H), 2.42 (s, 3H). FT-IR (KBr cast) 3282, 2921, 2863, 1499, 1443, 1423, 1311, 830, 757, 689 cm⁻¹. Low-resolution mass spectrometry (LRMS) [chemical ionization (CI) with isobutene] m/z = 255 [M+H]^+. 
Synthesis of 1-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopent-1-ene 2.10

A solution of 3-bromo-2-methyl-5-phenylthiophene 2.9 (1 g, 4.0 mmol) in anhydrous Et$_2$O (50 mL) was treated with $n$-butyllithium (1.8 mL, 2.5 M in hexane, 4.5 mmol) dropwise at -78 °C under N$_2$ atmosphere. The resulting suspension was stirred at this temperature for 15 min and treated with octofluorocyclopentene (0.59 mL, 4.4 mmol) in one portion using a cooled gas tight syringe. After stirring at this temperature for 1 h, the cooling bath was removed and the solution was allowed slowly warm to room temperature and stirred there for 30 min. The solution was quenched with 50 mL saturated NH$_4$Cl solution (50 mL) and the aqueous layer was separated and extracted with Et$_2$O (2 x 50 mL). The combined organic layers were washed with brine (2 x 50 mL), dried (Na$_2$SO$_4$), filtered, and evaporated to dryness in vacuo. The crude product was purified by column chromatography using silica (hexane) to yield 2.10 (1.14 g, 79%) as a cream solid. $^1$H NMR (CDCl$_3$, 400 MHz), δ 7.55 (d, $J = 7.9$ Hz, 2H), 7.40 (t, $J = 7.9$ Hz, 2H), 7.32 (t, $J = 7.9$ Hz, 1H), 7.25 (s, 1H), 2.48 (d, $J = 2.9$ Hz, 3H).

Synthesis of 1-(2-methyl-4-chlorothiophen-3-yl)-2-(2-methyl-4-phenylthiophen-3-yl)hexafluorocyclopent-1-ene 2.11

A solution of 3-bromo-5-chloro-2-methyl thiophene 2.7 (1.03 g, 4.86 mmol) in a mixture of anhydrous Et$_2$O (40 mL) and
anhydrous THF (40 mL) was treated with \(n\)-butyllithium (1.9 mL, 2.5 M in hexane, 4.9 mmol) dropwise at \(-78\) °C under \(N_2\) atmosphere. The solution was stirred at this temperature for 15 min, treated with a solution of 1-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopent-1-ene 2.10 (1.6 g, 4.4 mmol) in hexane (20 mL) in one portion. After stirring at this temperature for 30 min, the cooling bath was removed and the solution was allowed to slowly warm to room temperature and stirred there for 30 min. The solution was quenched with saturated \(NH_4\)Cl solution (50 mL) and the aqueous layer was separated and extracted with \(Et_2O\) (2 x 50 mL). The combined organic layers were washed with brine (2 x 50 mL), dried (\(Na_2SO_4\)), filtered, and evaporated to dryness in \(vacuo\). The crude product was purified by column chromatography using silica (hexane) to yield 2.11 (1.04 g, 50%) as a viscous yellow oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz), \(\delta\) 7.54 (d, \(J = 7.3\) Hz, 2H), 7.39 (t, \(J = 7.3\) Hz, 2H), 7.31 (t, \(J = 7.3\) Hz, 1H), 7.24 (s, 1H), 6.93 (s, 1H), 1.97(s, 3H), 1.88 (s, 3H).

![Chemical structure](image)

**Synthesis of 4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-4-phenylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophene-2-carboxylic acid 2.12**\(^{69}\) A solution of 1-(2-methyl-4-chlorothiophen-3-yl)-2-(2-methyl-4-phenylthiophen-3-yl)hexafluorocyclopent-1-ene 2.11 (0.53 g, 1.1 mmol) in anhydrous \(Et_2O\) (50 mL) was treated with \(t\)-butyllithium (1.0 mL, 1.7 M solution in pentane, 1.7 mmol) dropwise at \(-78\) °C under \(N_2\) atmosphere. The resulting yellow solution was stirred at this temperature for 20 min. The cooling bath was removed and the anhydrous \(CO_2\) gas was bubbled through the reaction for 1 h. After
quenching with aqueous HCl solution (25 mL, 1.7 M), the aqueous layer was separated and extracted with CH2Cl2 (2 x 50 mL). The combined organic layers were washed with Brine (2 x 50 mL), dried (Na2SO4), filtered, and evaporated to dryness in vacuo. The crude product was purified by column chromatography using silica (CHCl3 and 5% MeOH) to yield 2.12 (0.29 g, 54%) as a cream powder. Mp = 190 - 192 °C (literature 189 - 191 °C).

1H NMR (CDCl3, 500 MHz), δ 7.87 (s, 1H), 7.53 (d, J = 7.3 Hz, 2H), 7.39 (t, J = 7.3 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 7.24 (s, 1H), 2.02 (s, 3H), 1.94 (s, 3H).

13C NMR (CDCl3, 100 MHz): δ 167.0, 150.7, 143.0, 141.4, 135.2, 133.3, 130.7, 129.2, 128.2, 126.5, 125.8, 125.5, 122.2, 15.2, 14.7 (15 of 20 carbons found). FT-IR (KBr cast) 3423, 2926, 1679, 1624, 1551, 1462, 1436, 1380, 1319, 1273, 1194, 1122, 1098, 1049, 985, 902, 801, 756, 692, 617 cm⁻¹. Low-resolution mass spectrometry (LRMS) [chemical ionization (CI) with isobutene] m/z = 489 [M+H]+.

Synthesis of 4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-4-phenylthiophen-3-yl)cyclopent-1-enyl)-5-methyliophene-2-carboxylic acid chloride 2.13 A solution of 4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-4-phenylthiophen-3-yl)cyclopent-1-enyl)-5-methyliophene-2-carboxylic acid chloride 2.12 (0.29 g, 0.59 mmol) and anhydrous N,N-dimethylformamide (DMF) (33 μL) in anhydrous CH2Cl2 (50 mL) was cooled to 0°C and treated dropwise over 5 min with oxalyl chloride (0.37 mL, 4.2 mmol) under an N2 atmosphere. The cooling bath was removed and the reaction mixture was allowed to slowly warm to room temperature and stirred there for 4 h. The mixture was evaporated...
to dryness in vacuo and dried under high vacuum (1 mm Hg) for 18 h to yield 2.13 (0.26 g, 87\%) as a yellow solid. $^1$H NMR (CDCl$_3$, 500 MHz), $\delta$ 7.96 (s, 1H), 7.53 (d, $J = 7.3$ Hz, 2H), 7.40 (t, $J = 7.3$ Hz, 2H), 7.32 (t, $J = 7.3$ Hz, 1H), 7.22 (s, 1H), 2.05 (s, 3H), 1.96 (s, 3H).

**Synthesis of imidate 2.14** A solution of bis(amidine) 2.0 (0.04 g, 0.14 mmol) and Et$_3$N (43 µL) in anhydrous CH$_2$Cl$_2$ (25 mL) was treated dropwise over 5 min with a solution of 4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-4-phenylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophene-2-carboxylic acid chloride 2.13 (157 mg, 0.31 mmol) in anhydrous CH$_2$Cl$_2$ (2 mL) at 0°C under an N$_2$ atmosphere. After 30 min stirring, the cooling bath was removed and the reaction was allowed to slowly warm to room temperature and stirred for 5 h. The solvent was evaporated to a slurry and the slurry was loaded to a silica plug (25 g silica, 4 cm high, development solvent: CH$_2$Cl$_2$, 2.5 % CH$_3$OH, 1% Et$_3$N). Green solution was collected and evaporated to dryness. The crude product was purified by recrystallization (CH$_3$OH and CH$_2$Cl$_2$) to yield 2.14 (122 mg, 71\%) as green powders. Mp = 176 - 177 °C. $^1$H NMR (CDCl$_3$, 500 MHz), $\delta$ 12.95 (Br. s, 1 NH) 7.74 (s,
2H), 7.49 (d, J = 7.8 Hz, 4H), 7.36 (t, J = 7.8 Hz, 4H), 7.28 (t, J = 7.8 Hz, 2H), 7.23 (s, 2H), 5.36 (s, 1H), 1.96 (s, 6H), 1.82 (s, 6H), 1.17 (s, 12H), 1.15 (s, 12H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz), \(\delta\) 182.2, 177.1, 172.6, 149.2, 142.5, 141.7, 139.3, 133.4, 132.8, 129.1, 128.1, 125.7, 122.3, 90.40, 49.4, 47.9, 23.6, 22.8, 15.2, 14.6 (20 of 27 carbons found). FT-IR (KBr cast) 3435, 2978, 1685, 1654, 1624, 1590, 1549, 1499, 1458, 1380, 1338, 1276, 1191, 1137, 1107, 1058, 985, 756 cm\(^{-1}\). MALDI m/z = 1228 [M+H]+. Anal. Calcd for C\(_{61}\)H\(_{52}\)N\(_4\)O\(_2\)S\(_4\)F\(_{12}\): C, 59.60; H, 4.26; N, 4.56. Found: C, 59.90; H, 4.26; N, 4.66.

**Synthesis of Zn imidate 2.14Zn** A solution of bis(amidine) imidate 2.14 (50 m g, 0.04 mmol) and Et\(_3\)N (6.2 \(\mu\)L, 0.04 mmol) in anhydrous CH\(_2\)Cl\(_2\) (25 mL) was treated with a solution of the anhydrous zinc chloride (44 mg, 0.32 mmol) in anhydrous CH\(_3\)CN (25 mL) under an N\(_2\) atmosphere. The solution was stirred for 5 h. The solution was evaporated to dryness *in vacuo* and under high vacuum for 10 min and redissolved in CH\(_2\)Cl\(_2\). The cloudy solution was centrifuged and green clear solution was collected and evaporated to dryness. The resulted green solid was purified by recrystallization twice
(ethyl acetate) to yield $\text{2.14Zn}$ (31 mg, 57%) as green fine powders. $\text{Mp} = 247 - 248 ^\circ \text{C}$.

$^1\text{H NMR} \ (\text{CDCl}_3, 400 \text{ MHz}), \delta 8.19 \ (s, 2\text{H}), 7.55 \ (d, J = 7.3 \text{ Hz}, 4\text{H}), 7.39 \ (t, J = 7.3 \text{ Hz}, 4\text{H}), 7.32 - 7.28 \ (m, 4\text{H}), 5.66 \ (s, 1\text{H}), 2.00 \ (s, 6\text{H}), 1.95 \ (s, 6\text{H}), 1.28 \ (s, 6\text{H}), 1.25 \ (s, 6\text{H}), 1.19 \ (s, 6\text{H}), 1.17 \ (s, 6\text{H})$. 

$^{13}\text{C NMR} \ (\text{CDCl}_3, 125 \text{ MHz}), \delta 196.1, 191.3, 174.2, 151.8, 142.7, 141.7, 140.2, 135.2, 133.4, 129.1, 128.1, 127.0, 125.7, 122.2, 93.60, 51.0, 50.7, 25.0, 23.4, 22.7, 15.5, 15.4, 15.0, 14.9 \ (24 \text{ of } 36 \text{ carbons found})$. 

FT-IR (KBr cast) 3433, 2980, 1599, 1499, 1451, 1365, 1336, 1270, 1231, 1192, 1105, 1056, 1031, 988, 893, 751 \text{ cm}^{-1}$. MALDI $m/z = 1327 \ [\text{M+H}]^+$. 

Anal. Calcd for $\text{C}_6\text{H}_{52}\text{N}_4\text{O}_4\text{S}_4\text{F}_{12}$: C, 55.12; H, 3.87; N, 4.22. Found: C, 54.80; H, 4.05; N, 3.95.

**Photochemical synthesis of the ring-closed isomer of Zn imidate 2.14Zn**

A solution of the Zn imidate $\text{2.14Zn}$ (1.7 mg) in $\text{CD}_2\text{Cl}_2$ (0.55 mL) in an NMR tube was irradiated with 365 nm light using a hand held TLC lamp and monitored by $^1\text{H NMR}$ spectrum of the ring-open and ring-closed isomers levelled off indicating that the photostationary state (PSS) was reached (30 min) and yielded a solution containing 99% of $\text{2.14Zn ring-closed}$ isomer at the PSS. The remaining 1% was assigned to $\text{2.14Zn ring-open isomer}$. Photobleaching of the ring-closed isomer with $> 525$ nm light regenerated the original $^1\text{H NMR}$ spectrum. 

$\text{2.14Zn ring-open isomer} \ ^1\text{H NMR} \ (\text{CD}_2\text{Cl}_2, 500 \text{ MHz}), \delta 8.18 \ (s, 2\text{H}), 7.56 \ (d, J = 7.8 \text{ Hz}, 4\text{H}), 7.39 \ (t, J = 7.8 \text{ Hz}, 4\text{H}), 7.32 - 7.29 \ (m, 4\text{H}), 5.73 \ (s, 1\text{H}), 2.04 \ (s, 6\text{H}), 1.99 \ (s, 6\text{H}), 1.28 \ (s, 6\text{H}), 1.23 \ (s, 6\text{H}), 1.20 \ (s, 6\text{H}), 1.17 \ (s, 6\text{H})$. 

$\text{2.14Zn ring-closed isomer} \ ^1\text{H NMR} \ (\text{CD}_2\text{Cl}_2, 500 \text{ MHz}), \delta 8.16 \ (s, 1\text{H}), 7.62 \ (d, J = 7.8 \text{ Hz}, 2\text{H}), 7.56 \ (d, J = 7.8 \text{ Hz}, 2\text{H}), 7.48 - 7.43 \ (m, 3\text{H}), 7.39 \ (t, J = 7.8 \text{ Hz}, 2\text{H}), 7.32 - 7.29 \ (m, 3\text{H}), 6.74 \ (s, 1\text{H}), 5.76 \ (s, 1\text{H}), 2.30 \ (s, 1.5\text{H}), 2.28 \ (s, 1.5\text{H}), 2.26 \ (s,
1.5 H), 2.24 (s, 1.5H), 2.05 (s, 3H), 1.99 (s, 3H), 1.29 (s, 6H), 1.23 (s, 6H), 1.21 - 1.18 (m, 12H).
3 Photoregulating Self-Assembly in Thin Films

3.1 Approaches to Photoregulate Self-Assembly of Amphiphiles

3.1.1 Amphiphilic Systems

Amphiphiles are molecules with a polar hydrophilic “head” group and a non-polar hydrophobic “tail” group. Typical amphiphiles are long chain fatty acids, which are organic compounds consisting of a hydrocarbon chain (more than 8 - 10 carbon atoms) and a terminal carboxylic acid, and phospholipid, which is one of a group of lipids having both a phosphate group and one or more fatty acids. An example of a typical fatty acid and a phospholipid is shown in Figure 3.1.1. Phospholipids readily form membrane-like bilayer structures in water with their hydrophobic hydrocarbon “tails” clustering together. They are a major component of biology cell membrane. Photoregulation of this membrane-like bilayer structure can be used to control encapsulating a drug and releasing a drug. When the structure is closely packed, the drug can be encapsulated inside the membrane. When the closely packed structure is weakened by external stimuli such as heat or light, the structure becomes loosely packed and the drug can be released from the membrane. Therefore photoregulation of an amphiphilic system can be potentially used in drug delivery.
Figure 3.1.1 A typical fatty acid (stearic acid) and a phospholipid (distearoylphosphatidylcholine).

3.1.2 Three Approaches to Photoregulate Self-Assembly of Amphiphiles

Self-assembly is a spontaneous order arising in a system when certain parameters of the system reach critical values. The geometrical structures of the amphiphilic molecule, the polarity of the “head” group and the size of the long chain non-polar “tail” group will determine the self-assembly of an amphiphilic system. Correspondingly, three approaches can be used to photoregulate self-assembly of amphiphilic structures: changing the geometrical structure of the molecule, changing the charge of the “head” group, and cutting the “tail” group from the “head” group (Figure 3.1.2).
In the latter two approaches, changing the charge of the “head” group from the positive or negative charge to the neutral decreases the strength of the polar “head” and cutting the “tail” from the “head” results in the size of the non-polar long chain changing to zero. In this thesis, the first approach was implemented because simply the ring-closing and ring-opening reactions of the DTEs can result in the geometrical structure change in the two isomers. Two photoresponsive DTE derivatives were decorated with fatty acids to investigate whether the changes in the geometrical structure of the two isomers of the DTE fatty acid can affect the packing of the molecule on an air/water surface. The differences in the packing of this DTE molecule between its ring-open and ring-closed isomers on air/water surface were measured by Langmuir technique.
3.2 Langmuir Technique for Self-Assembly of Amphiphiles

3.2.1 Introduction to the Langmuir Technique

When amphiphiles, dissolved in a non-aqueous volatile solvent, are introduced onto a polar liquid (e.g. water) surface, the volatile solvent will evaporate leaving the amphiphiles at the liquid-gas interface with the hydrophilic groups directed towards the bulk water phase and the hydrophobic groups directed towards the air. Sweeping two barriers over the water surface causes the molecules to come closer together and eventually to form a compressed, ordered monolayer. The film produced by such a method is known as a Langmuir film. This monolayer film bears a resemblance to the naturally occurring biological membrane.

A trough used for all Langmuir experiments is shown in Figure 3.2.1. The trough holding the subphase (water) is made of Teflon®, a hydrophobic material to make the subphase easily to be cleaned during the experiments. Sweeping movable barriers over the surface of the trough can vary the surface area of the trough. The barrier is made of Delrin®, a hydrophilic material that is heavy enough to prevent any leakage of the monolayer beneath the barrier.

The subphase used in Langmuir trough should be as pure as possible. Distilled water was used for all Langmuir experiments in this thesis. ZnSO₄ was added into distilled water (1.0 x 10⁻⁴M) to get a more condensed film. The purpose of deliberately adding the divalent ions to the subphase is to form a mixture of fatty acid and fatty acid salt, which provides long-range attractive forces between the polar groups. The solvent chosen for the experiments is critical and will affect the film forming properties of the solute. Two major factors must be considered: (1) the volatility-evaporation time must be
short but not so short that the concentration of the solution cannot be determined due to evaporation; (2) the solubility of both amphiphile and solvent in water must be minimal.

Figure 3.2.1 The trough used for the Langmuir experiments and a schematic illustration of a Langmuir film balance.

3.2.2 Isotherm of Surface Pressure Versus Area per Molecule

The single most important indicator of the monolayer properties of a material is given by a plot of surface pressure as a function of the area of water surface available to
each molecule. This is carried out at constant temperature and is accordingly known as a (surface pressure / area per molecule) isotherm, and is often abbreviated to "isotherm".

The presence of amphiphilic molecules on a water-air interface has a marked effect on the surface tension of the water. Surface tension can be defined as the force required to increase the surface area isothermally by a unit amount. The surface tension of the aqueous phase ($\gamma'$) will be lowered by a value $\pi$ (the surface pressure of the adsorbed layer of surfactant) to a new value $\gamma$ according to the following equation:

$$\gamma = \gamma' - \pi$$

Continually compressing the monolayer will change the surface pressure. A simple terminology used to classify different monolayer phases of fatty acids was proposed by W.D. Harkins as early as 1952. At large area, the monolayer exists in the gaseous state (G) and can on compression undergo a phase transition to the liquid-expanded state (L$_1$). Upon further compression, the L$_1$ phase undergoes a transition to the liquid-condensed state (L$_2$), and at even higher densities, the monolayer finally reaches the solid state (S). If the monolayer is further compressed after reaching the S state, the monolayer will collapse into a three-dimensional structure. Typical isotherms of a fatty acid with a single hydrocarbon chain (left) and a phospholipid with two hydrocarbon chains (right) are illustrated in Figure 3.2.2.
3.2.3 Surface Pressure Measurements

The surface pressure is measured by the Wilhelmy plate-method in which a plate is suspended and partially immersed in the subphase (Figure 3.2.3). The plate is very thin and, in this thesis, a strip of chromatography paper was used. This plate is pulled down into the bulk of the subphase due to the surface tension of the water. When a contaminant is spread on the water surface, the surface tension will decrease to minimise the free energy of the surface. The force acting on the paper is measured by means of an electric balance.
The forces acting upon the plate are gravity and surface tension acting downwards into the subphase, and buoyancy due to displaced water acting upwards. If the plate has dimension \( l \times w \times t \) (length \( l \) \) width \( w \) \( t \) thickness) and a density \( \rho \) and is immersed in water to a depth \( h \), then the net force downwards, \( F \), can be described by the following equation:\(^{83}\)

\[
F = \rho g l w t - \rho' g h w t + 2 \gamma (t + w) \cos \theta
\]

Equation 3.2.1  Equation used to calculate the force for Wilhelmy Plate.

Where \( \gamma \) is the surface tension of the liquid, \( \theta \) is the contact angle of plate to liquid (0° for a completely wetted filter paper), \( g \) is a constant due to gravity at the earth (9.81 m/s\(^2\)) and \( \rho' \) is the density of the subphase. If the plate is completely wetted by the liquid (i.e. \( \cos \theta = 1 \)) the surface pressure is then obtained form the following equation:

\[
\pi = \gamma' - \gamma = \frac{\Delta F}{2(t + w)} = \frac{\Delta F}{2w}, \text{ if } w >> t
\]

Equation 3.2.2  Equation used to calculate the surface pressure of the air water interface.
\( \gamma' \) being the surface tension of pure, clean water (72.8 mN/m). The sensitivity can thus be increased by using a very thin plate. The change in force \( \Delta F \) is then related to the surface pressure.

3.2.4 Molecular Structure of Langmuir Films

Chemists have been concerned with the spatial or steric arrangement of amphiphiles in Langmuir films. The information about the way in which the molecules packs at the interface and the information about the stability of the compressed layer at high pressure can be obtained from the surface / area isotherms. In general, a fatty acid containing more than 13 carbon atoms can be spread to form a monolayer and increasing the chain length and decreasing the temperature will condense the film. Less steric hindered molecules will form more condensed film. For the same molecule, improved quality can be obtained by compressing (never going above collapse pressure) and expanding a number of times. Such a procedure encourages more efficient packing and often a shift to lower molecular areas is observed.

3.2.5 Photochromic Langmuir Films

Since the first study of Blair et al. dealing with the photoresponse of mixed monolayer of polymers with photochromic spiropyran and azo polymer, a lot of work on monolayers containing different photochromic systems has been done. However most of the work has been done using the spiropyran and azobenzene derivatives, while only a few examples were reported with diarylethene-based langmuir films. In general, in diarylethene-based Langmuir systems, the ring-open isomer has a relatively loose twisted conformation, whereas the ring-closed isomer has a rigid, planar structure. Although
comparing to azobenzene and spiropyran, the geometrical structure change is relatively small, the difference in rigidity and conjugation associated with photochromism in DTE derivatives is anticipated to induce the change in the formation/dissociation of the self-assembled structure.\textsuperscript{97}

3.3 \textbf{Synthesis and Photochromic Reactions of a Dithienylethene Fatty Acid}

3.3.1 \textbf{Synthesis}

The DTE carboxylic diacid 3.2 was prepared as shown in Scheme 3.3.1. This diacid 3.2 and two equivalents of hexadecanol were heated at reflux with one equivalent of diphenylphosphorazine (DPPA) and one equivalent of Et\textsubscript{3}N base in toluene to afford a carbamate linked DTE fatty acid 3.3. In this reaction, the diacid 3.2 was first converted to an isocyanate by Curtius Rearrangement and then the isocyanate was treated with the hexadecanol to afford the carbamate 3.3.\textsuperscript{99} 3.3 was purified by column chromatography using CHCl\textsubscript{3} and 0-5\% MeOH and 0.25\% AcOH.
3.3.2 UV-Vis Absorption Spectroscopy and Photochemical Cycling

The UV-Vis absorption measurements of the DTE fatty acid 3.3 were carried out using different solvents. For solutions using CH$_2$Cl$_2$, THF, hexane, cyclohexane, benzene and ether (Figure 3.3.1, Figure 3.3.2 and Figure 3.3.3), irradiation with 312 nm light induced immediate decreases in the high-energy absorptions and corresponding appearances of absorptions in the visible regions of the spectra as solutions of the ring-open DTEs are converted from clear to their blue ring-closed forms. The irradiation cycles were repeatedly carried out for 10 cycles and the decreasing of the intensity was observed for solutions of all the above solvents. This indicated the degradation during cycling. Among these solvents, CH$_2$Cl$_2$ and THF are the best two solvents in which the compound 3.3 has got least degradation during cycling (Figure 3.3.1). For solutions using CH$_3$CN and CH$_2$ClCH$_2$Cl (Figure 3.3.2), after irradiation with 312 nm light, the
absorbance in visible regions are very low (the maximum absorbance in visible region of the closed form is about 6% of the maximum absorbance in UV region of the open form for CH$_3$CN and CH$_2$ClCH$_2$Cl solutions, while for CH$_2$Cl$_2$, THF, hexane, cyclohexane, benzene and ether solutions, the percentage is about 30%). Therefore CH$_3$CN and CH$_2$ClCH$_2$Cl are not good solvents for photoreactions of the compound 3.3.
Figure 3.3.1 Changes in the UV-Vis absorption spectra of 3.3 with irradiation of 312 nm in a) CH$_2$Cl$_2$ (the irradiation for absorption spectroscopy was carried out for 5 sec, 15 sec, 30 sec, 1 min) with modulated absorptions at 257 nm (open circles) and 582 nm (black squares) during alternating irradiation at 312 nm (1 min) and > 490 nm (1 min). b) THF (the irradiation for absorption spectroscopy was carried out for 5 sec, 15 sec, 30 sec, 1 min, and 1.5 min in THF solution with modulated absorptions at 259 nm (open circles) and 582 nm (black squares) during alternating irradiation at 312 nm (1.5 min) and > 490 nm (1 min). Concentrations are $\sim 10^{-5}$ M.
Figure 3.3.2 Changes in the UV-Vis absorption spectra of 3.3 with irradiation of 312 nm light in a) CH$_3$CN (total irradiation periods are 10 sec, 20 sec, 30 sec, 1 min, 1.5 min, 2.5 min and 5.5 min.), b) CH$_2$ClCH$_2$Cl (total irradiation periods are 5 sec, 15 sec, 30 sec, and 1 min.), c) hexane (total irradiation periods are 5 sec, 15 sec, 30 sec, 1 min, 1.5 min, 2 min, and 2.5 min.), d) hexane with modulated absorptions at 255 nm and 567 nm during alternating irradiation at 312 nm (1.5 min) and >490 nm (1 min), e) cyclohexane (total irradiation periods are 5 sec, 15 sec, 30 sec, 1 min, 1.5 min, and 2 min.), f) cyclohexane with modulated absorptions at 255 nm and 575 nm during alternating irradiation at 312 nm (1 min) and >490 nm (1 min). Concentrations are ~10$^{-5}$ M.
Figure 3.3.3  Changes in the UV-Vis absorption spectra of 3.3 with irradiation of 312 nm light in a) benzene (total irradiation periods are 5 sec, 15 sec, 30 sec, 1 min, and 1.5 min.), b) benzene with modulated absorptions at 587 nm during alternating irradiation at 312 nm (1 min) and > 490 nm (1 min), c) ether (total irradiation periods are 5 sec, 15 sec, 30 sec, 1 min, and 1.5 min.), d) ether with modulated absorptions at 257 nm and 574 nm during alternating irradiation at 312 nm (1.5 min) and > 490 nm (1 min).
Concentrations are \( \sim 10^{-5} \) M.

3.3.3 Thermal Stability Study on CH\(_2\)Cl\(_2\) and THF solutions

Thermal stability study by UV-Vis spectroscopy was carried out on both CH\(_2\)Cl\(_2\) and THF solutions for the ring-closed isomer of the DTE fatty acid 3.3. The UV-Vis
spectra of the ring-closed isomer did not change in CH$_2$Cl$_2$ solutions after 3 days in the dark. This showed the excellent thermal irreversibility of the compound 3.3 in CH$_2$Cl$_2$ solutions. However, it was not thermally stable in THF solutions as the ring-closed isomer converted back to the ring-open isomer in THF solutions. After 16 h in the dark, the intensity of the closed peak dropped 60% of that of the photostationary state and after 41 h it dropped 70% of that of the photostationary state.

3.3.4 NMR Study on CD$_2$Cl$_2$ and THF solutions

The DTE fatty acid 3.3 was characterized by $^1$H NMR spectroscopy of a CDCl$_3$ solution. The photostationary state was identified by irradiating a CD$_2$Cl$_2$ solution and a THF-d$_4$ solution with 312 nm light in a quartz NMR tube. After 8 min of irradiation, the photostationary state was reached and was identified by $^1$H NMR spectroscopy (3.9 x 10$^{-3}$ M, CD$_2$Cl$_2$) as consisting of 91% of the ring-closed isomer for the CD$_2$Cl$_2$ solution. While for the THF-d$_4$ solution, it took 40 min to reach the photostationary state. Much longer time is needed to reach photostationary state for the THF-d$_4$ solution probably because that the ring-closed isomer in THF-d$_4$ solution was not thermally stable and the ring opening reactions were competing with the ring closing reactions during the irradiation periods. After 1 hour of irradiation, the THF-d$_4$ solution was irradiated with visible light at wavelength greater than 434 nm and it regenerated the original ring-open isomer spectra with small trace of one extra peak arising and the color of the solution stayed in blue instead of changed back to original color green. This revealed that side products were created after long exposure to UV light.
3.4 Isotherms of the Dithienylethene Fatty Acid

3.4.1 Isomers of Compound 3.3 Prepared from CH$_2$Cl$_2$ Solutions

Thin films of the DTE fatty acid 3.3 were prepared as Langmuir layers. To investigate the different steric structures between the ring-open isomer and the ring-closed isomer of this fatty acid, the “surface pressure / area per molecule” isotherm were obtained by spreading the CH$_2$Cl$_2$ solutions of compound 3.3 and compressing the area between the two barriers after 15 min of waiting periods (Figure 3.4.1). The closed isomer solution was obtained by irradiating solutions of the 3.3 in a vial with 312 nm light for 11.5 min and the change in their UV-Vis absorption spectra was monitored. The isotherms for the ring-closed isomer were produced in the dark.
As shown in Figure 3.4.1, the horizontal sections of the isotherms showed the coexistence of both liquid-expanded and liquid-condensed phases in the monolayer of DTE fatty acid 3.3. From this plot, two parameters can be used to identify an isotherm different from others: the area per molecule of the transition point where the coexistence
of the two phases starts and the slope of the curve at this point. As shown in Figure 3.4.1, the significant difference between the ring-open isomer and ring-closed isomer for both area per molecule at transition points (45.07 and 62.37 with the average of 53.72 \( \pm \) 8.65 for the ring-open isomer while 54.48, 45.61, 48.83 and 52.87 with the average of 50.45 \( \pm \) 3.47 for the ring-closed isomer) and the difference between the slopes of the curve at the transition points (the slopes of the three blue lines are bigger than those of the two red lines but the slope of the other blue line is similar to the slopes of the two red lines) were not observed.

The isotherms were also obtained for the compound irradiated by UV light directly on the film itself. This experiment was performed in the dark condition. The CH\(_2\)Cl\(_2\) solution of the compound 3.3 was spread on the interface and the isotherm was produced during the first compression. After the barriers expanding to the maximum, the film was irradiated with 312 nm light for 1 min and the isotherm was produced during the second compression. The barriers were expanded to maximum again and the film was irradiated for another 1 min and the isotherm was produced again during the third compression. The plots for this experiment were shown in Figure 3.4.2.
The trend of the isotherm did not show much difference between the films, before and after irradiation. The transition point where the coexistence of the two phases - condensed and expanded phases - starts was not obtained for the films before irradiation and after irradiation for 1 min. In order to obtain the transition point for these two conditions, the barriers might need to be compressed further. The reason that it wasn’t
compressed further was to avoid reaching the collapsing point. No significant difference between the slopes of each film was observed.

3.4.2 Isotherms of Compound 3.3 Prepared from THF Solutions

The same experiments were carried out for the compound 3.3 from THF solutions. The closed isomers were obtained by irradiating the THF solution of 3.3 in a vial with 312 nm light for 10 min. The irradiation periods for irradiating on the film itself were same as those in CH$_2$Cl$_2$ solutions. The plots for the ring-open and ring-closed isomers and for the irradiation on the film itself are shown in Figure 3.4.3 and Figure 3.4.4 respectively.
Figure 3.4.3 Isotherms of the ring-open isomer (black lines, each line represented one sample) and the ring-closed isomer (dashed lines, each line represented one sample) of the DTE fatty acid 3.3 prepared from THF solution (1 mg/mL). The plots were stacked from the bottom to the top by adding 0, 5, 10, 15, 20, 25, and 30 mN/m to the value of the surface pressure respectively. The solution of the ring-closed isomer was generated by irradiation with 312 nm light for 10 min. The value of area per molecule at transition points (O₁, O₂, O₃, C₁, C₂, and C₃) where the coexistence of the liquid-expanded state and the liquid- condensed state started were shown on upper right of the figure. The dashed line in red and blue showed the slope of the curve at the transition point.
Figure 3.4.4 Isotherms of the DTE fatty acid 3.3 prepared from THF solution (1 mg/mL) (three samples) with different irradiation (312 nm) periods on the film for each sample: no irradiation (thick line), 1 min irradiation (thin line) and 2 min irradiation (dashed line). The plots were stacked from the bottom to the top by adding 0, 5, 10, 15, 20, 25 and 30 mN/m to the value of the surface pressure respectively.

The values of the area per molecule at the transition points of ring-closed isomers (23.71, 21.19, 23.57 with the average of 22.82 ± 1.16) are slightly bigger than those of the ring-open isomers (19.07, 21.15, 21.76 with the average of 20.66 ± 1.15) as shown in Figure 3.4.3. However, this difference is not significant. Comparing to the isotherms prepared from CH2Cl2 solutions, these values is much smaller those shown on Figure 3.4.1. This might be because multilayers formed during the spreading procedure
due to the higher miscibility of the THF with water. No significant difference between the slopes of films was observed for the isotherms from THF solutions as shown in Figure 3.4.4.

3.5 Synthesis and Photochromic Reactions of a Bulkier Dithienylethene Fatty Acid

3.5.1 Synthesis

No significant change between the structures of the ring-open and ring-closed isomers of the DTE fatty acid 3.3 was observed according to the isotherms from the previous section, therefore a sterically bulkier DTE substituent 3.6 with the internal positions replaced by phenyl groups was prepared. Molecular models (Figure 3.5.1) of a DTE derivative with phenyl groups at internal positions suggest that this compound will undergo a significant change in geometrical structure when it is isomerised to the ring-closed form.
In analogy to the compound 3.3, the bulkier DTE fatty acid 3.6 was prepared as shown in Scheme 3.5.1 by Curtius Rearrangement and then by linking isocyanate to the hexadecanol with carbamate linkage. The compound 3.4 was provided by Dr. Tony Wigglesworth from Branda’s group at Simon Fraser University.
Scheme 3.5.1 Synthesis of a bulkier DTE fatty acid 3.6

3.5.2 UV-Vis Absorption and Photochemical Cycling

The UV-Vis absorption measurement of the bulkier DTE fatty acid 3.6 was carried out using different solvents. For solutions using THF, ether, and ethyl acetate (Figure 3.5.2 and Figure 3.5.3), irradiation with 312 nm light induced immediate decreases in the high-energy absorptions and corresponding appearances of absorptions in the visible regions of the spectra as solutions of the ring-open DTEs are converted from clear to their blue ring-closed forms. The irradiation cycles were repeatedly carried out for 10 cycles for THF solution and the decreasing of the intensity was observed in the solutions. Also the ring-closed isomer was not stable in the dark (details see the next section). The cycling study was not carried out on ether and ethyl acetate solutions because the ring-closed isomer was not stable in either of these solvents. For solutions
using CH$_3$CN, CH$_2$Cl$_2$, CHCl$_3$, benzene, acetone, and hexane (Figure 3.5.3 and Figure 3.5.4), after irradiation with 312 nm light, the absorbance in visible regions are very low (the maximum absorbance in visible region of the closed form is less than 8% of the maximum absorbance in UV region of the open form, while for THF, ether and ethyl acetate solutions, the percentage is about 30%). Therefore CH$_3$CN, CH$_2$Cl$_2$, CHCl$_3$, benzene, acetone, and hexane are not good solvents for photoreactions of the compound 3.6.

![Figure 3.5.2](image)

**Figure 3.5.2** Changes in the UV-Vis absorption spectra of a THF solution (~ 10$^{-5}$ M) of 3.6 during irradiation at 312 nm. The irradiation for absorption spectroscopy was carried out for 5 sec, 15 sec, 30 sec, 1min. Insert: modulated absorptions at 272 nm (open circles) and 598 nm (black squares) during alternating irradiation at 312 nm (1min) and > 490 nm (1 min).
Figure 3.5.3 Changes in the UV-Vis absorption spectra of 3.6 with irradiation of 312 nm light in a) CH$_3$CN (total irradiation periods are 5 sec, 15 sec, 30 sec, 1 min, and 2 min.), b) ether (total irradiation periods are 5 sec, 15 sec, 30 sec, 1 min, and 1.5 min.), c) ethyl acetate (total irradiation periods are 5 sec, 15 sec, 30 sec, and 1 min.), d) CH$_2$Cl$_2$ (total irradiation periods are 5 sec, 15 sec, 30 sec, 1 min and 1.5 min.). Concentrations are $\sim 10^{-3}$ M.
Figure 3.5.4 Changes in the UV-Vis absorption spectra of 3.6 with irradiation of 312 nm light in a) CHCl$_3$. (total irradiation periods are 5 sec, 15 sec, 30 sec, 1 min, and 2 min.), b) benzene (total irradiation periods are 5 sec, 15 sec, 30 sec, 1 min, and 1.5 min.). c) acetone (total irradiation periods are 5 sec, 15 sec, 30 sec, 1 min, and 2 min.), d) hexane (total irradiation periods are 5 sec, 15 sec, 30 sec, 1 min, and 2 min.). Concentrations are ~ $10^{-5}$ M.

3.5.3 Thermal Stability Study on THF solutions

Thermal stability study by UV-Vis spectroscopy was carried out using THF solutions for the ring-closed isomer of the DTE fatty acid 3.6. It was not thermally stable
in THF solutions. After 10 min in the dark, the intensity of closed peak dropped 59% of that of the photostationary state and after 40 min it dropped 92% as the ring-closed isomer converted back to ring-open isomer in THF solutions. The conversion speed of the phenyl fatty acid 3.6 is faster than the methyl fatty acid 3.3. The thermal stability study was also carried out on ether and ethyl acetate solutions and the similar phenomenon was observed. The conversion rate of the ring-closed isomer to ring-open isomer in ethyl acetate is much faster than in THF and ether. After 1 min in the dark, the intensity of closed peak dropped 40% of that of the photostationary state for ethyl acetate solutions.

3.5.4 NMR Study on CD$_2$Cl$_2$ and THF-d$_4$ solutions

The bulkier DTE fatty acid 3.6 was characterized by $^1$H NMR spectroscopy of a CDCl$_3$ solution. The content of the ring-closed isomer at photostationary states was measured by irradiating a CD$_2$Cl$_2$ solution and a THF-d$_4$ solution with 312nm light in quartz NMR tubes. After 2 h of irradiation on both solutions, the photostationary states were not reached according to $^1$H NMR spectroscopy (3.3 x 10$^{-3}$ M) and the color changed from light green to dark green. The ring-closed isomer was not observed in THF-d$_4$ solution from $^1$H NMR spectra but it was observed from UV-Vis absorption spectra probably because that the ring-opening reaction occurred so fast that the concentration of the ring-closed isomer was too low to be measured.
3.6 Isotherms of the Bulkier Dithienylethene Fatty Acid

3.6.1 Isotherms of Compound 3.6 Prepared from THF Solutions

Although according to previous sections, the compound 3.6 is photochromic in ether, ethyl acetate and THF, THF was chosen as the spreading solvent for all isotherms of compound 3.6 in this thesis because the ring-closed isomer was too unstable in ethyl acetate and the concentration of the ether solutions was too hard to maintain due to its fast evaporation. Isotherms of the compound 3.6 prepared from THF solutions were produced in the same way as for the 3.3 prepared from THF solutions. Because the ring-closed isomer of the compound 3.6 was not stable in THF solution as mentioned in thermal stability study of section 3.5.3, the solution of the ring-open isomer was irradiated for 10 min and right after the irradiation the isotherm was produced for the isotherms of the ring-closed isomer as shown in Figure 3.6.1. 10 min of irradiation on
the solutions to get the ring-closed isomers is determined by the UV-Vis absorption spectra for the same concentration of THF solutions of the compound 3.6. The irradiation periods for irradiating on the film itself were no irradiation, 1 min, 2 min and 5.5 min as shown in Figure 3.6.2.

![Figure 3.6.1](image)

**Figure 3.6.1** Isotherm of the ring-open isomer (black lines, each line represented one sample) and the ring-closed isomer (dashed lines, each line represented one sample) of the DTE fatty acid 3.6 prepared from THF solution (1 mg/mL). The plots were stacked from the bottom to the top by adding 0, 5, 10, 15, 20, and 25 mN/m to the value of the surface pressure respectively. The solution of the ring-closed isomer was generated by irradiation with 312 nm light for 10 min. The value of area per molecule at transition points (C1 and C2) where the coexistence of the liquid-expanded state and the liquid-condensed state started were shown in the figure.
The transition point of the ring-closed isomer was not obtained while that of the ring-closed isomer was shown in Figure 3.6.1. This implies that the value of the area per molecule at transition point of the ring-closed isomer is much bigger than the ring-open isomer. Similar to the isotherms of the compound 3.3 from both CH₂Cl₂ and THF solutions, the significant difference between the slopes of each films are not observed for
the isotherms of the compound 3.6 from THF solutions as shown in Figure 3.6.2. However the value of the area per molecule at the point where the surface pressure started to increase from zero shifted to smaller value by $3 - 9 \text{ Å}^2$ after the film was irradiated. The reason for that the difference between the films of the ring-open isomer and ring-closed isomer was observed in compound 3.6 but not in 3.3 is probably because of the significant change in geometrical structure between the two isomers with the bulkier internal phenyl group.

3.7 Conclusions

Although the DTE fatty acid 3.3 has excellent photochromic properties in CH$_2$Cl$_2$, the difference between the structures of the ring-open and the ring-closed isomers of the DTE fatty acid 3.3 was not observed by Langmuir technique. The slightly difference between the two isomers of the bulkier DTE fatty acid 3.6 was observed but the problem with this compound was the thermal stability of ring-closed isomer since it can convert back to ring-open isomer in the dark very quickly. Therefore the photoregulation of the membrane-like structure fabricated by these DTE fatty acids could not be implemented.

3.8 Future Work

Since only one of these two DTE fatty acids has excellent photochromic properties, synthesis of other amphiphilic DTE system with better photochromic properties would be one of the solutions to measure the changes. On the other hand, although the Langmuir trough technique presents a method of constructing simple artificial systems of cooperating molecules on a substrate, the conditions such as temperature, the compression speed of the barriers and the cleanness of the subphase, etc.
are critical for obtaining an accurate result. Also the isotherms do not provide sufficient information about molecular orientation in the DTE fatty acid monolayer. Other techniques such as reflection spectroscopy and Brewster angle microscopy can be used to detect the geometrical difference between the two isomers of the DTE fatty acid 3.3.\textsuperscript{100} Alternatively, transferring the floating monolayer of the 3.3 to a solid substrate to measure the structure change in solid state can be another method stimulated by Irie et al\textsuperscript{95-97} and Shimomura’s work\textsuperscript{98}

Using Langmuir technique to evaluate the difference in packing of the two isomers of the DTE amphiphilic system due to the geometrical structure change in the two isomers is a promising start for applying the systems in drug delivery application. However to apply this system \textit{in vivo} application, more work needs to be done including finding a water soluble photochromic amphiphilic system, testing the possibility of forming a vesicle or bilayer structure in water phase and eventually using the light to control the structure change to encapsulate a drug and release a drug.

\section*{3.9 Experimental}

\textbf{Materials.} All solvents used for synthesis and spectroscopy were dried and degassed by passing through steel columns containing activated alumina under nitrogen using mBraun solvent purification system with the exception of the solvents used for NMR analysis (Cambridge Isotope Laboratories), which were used as received. Column chromatography was performed using silica gel 60 (230-400 mesh) from Silicycle Inc. All other reagents and starting materials were purchased from Aldrich with the exception of the compound 3.4, which was provided by Dr. Tony Wigglesworth from Branda’s group at Simon Fraser University.
Techniques. \( ^1 \)H and \( ^{13} \)C NMR characterizations were performed on a Bruker AMX 400 instrument working at 400.103 MHz for \(^1\)H NMR and 100.610 MHz for \(^{13}\)C NMR spectroscopy or a Varian Inova 500 instrument working at 499.77 MHz for \(^1\)H NMR and 125.68 MHz for \(^{13}\)C NMR spectroscopy. Chemical shifts \( \delta \) were reported in parts per million relative to tetramethylsilane using the residual solvent peak as a reference standard. Coupling constants \( (J) \) are reported in Hertz. FT-IR measurements were performed using a Nicolet Nexus 670 instrument. Mass spectrometry were performed using a Waters matrix assisted laser desorption /ionisation (MALDI) or HP5985 mass spectrometer with isobutane as the chemical ionisation source for Low Resolution Mass Spectrometry (LRMS). The Mass spectrometry by LRMS method was done by M. Simon Wong. Elemental analysis measurements were done by Mr. M. K. Yang using a Kratos Concept-H instrument with perfluorokerosene as the standard. Melting point measurement were performed using a Fisher-Johns Melting Point Apparatus.

UV-Vis absorption and fluorescence measurements were performed using a Varian Cary 300 Bio spectrophotometer and a PTI QM-2000-4 scanning spectrofluorometer with a 2 nm slit-width, respectively. The ring-closing reactions of all compounds were carried out using the standard lamps whose light was passed through the solutions of the compounds inside a glass cuvette for absorption or a quartz cuvette for fluorescence and the ring-opening reactions were carried out using the light of a 150-W tungsten source that was passed through the appropriate cut off filter to eliminate higher energy light.
Langmuir experiment were performed using a Nima trough Model 622D2 with outer size of 37.1 cm x 17.2 cm x 0.7 cm and inner trough size 30.0 cm x 10.0 cm x 0.5 cm to monitor the surface pressure as a function of area per molecule and to produce the isothermal plots.

In such a plot, area per molecule $a$ is obtained by dividing the film area $A$ by the total number of molecules on the water surface:\(^8\)

$$a = \frac{AM}{(CN_AV)} = \frac{A}{(cN_AV)}$$

Where $M$ is the molecular weight of the monolayer material, $C$ is the concentration of the spreading solution in mass per unit volume, $c$ is the specific molar concentration of the solution and $V$ is its volume. All experiments were carried out under room temperature and the compression speed of 25 cm$^2$/min and expanding speed of 500 cm$^2$/min were used for each run. The isotherms for closed isomer were produced in the dark. Anhydrous CH$_2$Cl$_2$ and THF were the chosen spreading solvents. Waiting period for the solvents evaporation was 15 min. All solutions were 1 mg/mL. The composition of the subphase consisted of 1.0 x 10$^{-4}$ M of ZnSO$_4$ in Millipore water. Spreading volume was 20 μL to 30 μL.

Take an example from Figure 3.4.2. The trough was filled with water with 1.0 x 10$^{-4}$ M of ZnSO$_4$. The area between the two barriers was reduced to the minimum and the surface in this area was cleaned with a glass capillary tube attached to a vacuum line. The success of the cleaning operation can be determined by monitoring the surface pressure as the area is reduced. The cleaning operation was repeated several times until the surface pressure was reduced to an acceptable value. Then the barriers were expanded to the distance equal to 24.7 cm ($A = 247$ cm$^2$). A 20 μL CH$_2$Cl$_2$ solution of
compound 3.3 was spread onto the surface dropwise. After 15 min of waiting period, the surface pressure was set to zero and the barriers were compressed to the distance where the isotherm has not reached the collapsing point. So at the beginning of the isotherm, surface pressure is 0 and the corresponding *area per molecule* $a$ was calculated as following:

$$a = \frac{AM}{(CN_AV)} = \frac{247 \text{ cm}^2 \times 10^{-4} \text{ m}^2 / \text{ cm}^2 \times 695.82 \text{ g / mol} / (1 \text{ mg / mL} \times 10^{-3} \text{ g / mg} \times 20 \mu \text{L} \times 10^{-3} \text{ mL / } \mu \text{L} \times 6.02 \times 10^{23} / \text{ mol})}{1.43 \times 10^{-18} \text{ m}^2 = 143 \text{ Å}^2}$$

The barriers were compressed to stop at the distance equal to 8.4 cm ($A = 84 \text{ cm}^2$) where the isotherm has not reached the collapsing point, and then expanded to distance equal to 24.7 cm ($A = 247 \text{ cm}^2$). Then the surface was irradiated by the 312 nm UV lamp for 1 min. The barriers were compressed to stop at $A = 93 \text{ cm}^2$ and then expanded to $A = 247 \text{ cm}^2$ again. Then the surface was irradiated by the 312 nm UV lamp for 1 min again. The barriers were compressed to the minimum distance of 2.9 cm ($A = 29 \text{ cm}^2$) when the screen said that the barriers were too close.

![Chemical Structure](image)

**Synthesis of 1,2-bis(4-chloro-2-methylthien-3-yl)-hexafluorocyclopentene-1-ene 3.1**

A solution of 3-bromo-5-chloro-2-methylthiophene 2.7 (1.19 g, 5.64 mmol) in anhydrous Et$_2$O (50 mL) was treated with $n$-butyllithium (2.5 mL, 2.5 M in hexane, 6.21 mmol) dropwise at -78 °C under an N$_2$ atmosphere. The resulting suspension was stirred at this temperature for 15 min and treated with octofluorocyclopentene (0.38 mL, 2.8 mmol) dropwise via cooled gas tight syringe. After stirring at this temperature for 1 h, the
cooling bath was removed and the solution was allowed to slowly warm to room
temperature and stirred there for 5 h. The solution was quenched with 50 ml saturated
NH₄Cl solution (50 mL). The aqueous layer was separated and extracted with Et₂O (2 x
50 mL). The combined organic layers were washed with brine (2 x 100 mL), dried
(Na₂SO₄), filtered, and evaporated to dryness *in vacuo*. The crude product was purified
by flash chromatography using silica (hexane) to yield 3.1 (0.54g, 44%) as white crystals.

$$^1$$H NMR (CDCl₃, 400 MHz), δ 6.88 (s, 2H), 1.55 (s, 6H).

**Synthesis of DTE dicarboxylic acid 3.2** A solution of 1,2-bis(4-chloro-2-methylthien-
3-yl)hexafluorocyclopent-ene 3.1 (0.38 g, 0.89 mmol) in anhydrous Et₂O (80 mL) was
treated with t-butyllithium (1.8 mL, 1.7 M solution in pentane, 3.1 mmol) dropwise at -78
°C under N₂ atmosphere. The resulting yellow solution was stirred at this temperature for
20 min. The cooling bath was removed and the anhydrous CO₂ gas was bubbled through
the reaction for 1 h. The reaction was quenched with aqueous HCl solution (14 mL, 1.7
M) and the aqueous layer was separated and extracted with CH₂Cl₂ (2 x 30 mL). The
combined organic layers were washed with brine (2 x 50 ml), dried (Na₂SO₄), filtered,
and evaporated to dryness *in vacuo*. The crude product was purified by recrystallization
(hexane and ethanol) to yield 3.2 (0.23 g, 58%) as a white powder. Mp = 238 - 242 °C
(literature 227 - 229 °C).$$^1$$H NMR (CD₃OD, 400 MHz), δ 7.71 (s, 2H), 1.98 (s, 6H).

FT-IR (KBr cast) 3436, 2925, 2861, 1686, 1551, 1473, 1340, 1274, 1190, 1140, 1034,
980, 869, 653 cm\(^{-1}\). Low-resolution mass spectrometry (LRMS) [chemical ionization (CI) with isobutene] \(m/z = 458 [M+H]^+\).

**Synthesis of DTE fatty acid 3.3** A DTE carboxylic diacid 3.2 (100 mg, 0.2 mmol), Et\(_3\)N (33 \(\mu\)L, 0.24 mmol) and hexadecanol (106 mg, 0.44 mmol) were mixed in distilled toluene (20mL) under an N\(_2\) atmosphere. Diphenylphosphorazine (DPPA) (52 \(\mu\)L, 0.24 mmol) was added and the reaction mixture was heated at reflux for 5 h. The heat source was removed and the reaction was allowed to cool to room temperature and quenched with saturated NH\(_4\)Cl (20 mL). The aqueous layer was separated and extracted with Et\(_2\)O (2 x 25 mL). The combined organic layers were washed with distilled water (2 x 50 mL) and brine (50 mL), dried (Na\(_2\)SO\(_4\)), filtered, and evaporated to dryness *in vacuo*. The crude product was purified by flash chromatography using silica (0 - 5% MeOH and 0.25% AcOH in CHCl\(_3\)) to yield 3.3 (65 mg, 43%). as a green sticky solid. Mp = 50 - 51 °C. \(^1\)H NMR (CDCl\(_3\), 500 MHz), \(\delta\) 7.86 (s, 1H), 7.06 (s, 1 NH), 6.47 (s, 1H), 4.18 (t, \(J = 6.6\) Hz, 2H), 1.99 (s, 3H), 1.82 (s, 3H), 1.68-1.64 (m, 2H), 1.36 - 1.20 (m, 28H), 0.88 (t, \(J = 6.7\) Hz, 3H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) 150.5, 138.3, 135.1, 126.5, 116.0, 110.0, 80.3, 66.7, 32.1, 29.8, 29.8, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.4, 29.0, 26.0, 22.8, 15.2, 14.3, 14.1 (22 of 31 carbons found). FT-IR(KBr cast) 3448, 3294, 2925, 2854, 1693, 1580, 1548, 1466, 1338, 1274, 1193, 1120, 1074, 1043, 986, 900, 724, 541 cm\(^{-1}\). MALDI \(m/z = 696 [M+H]^+\). Anal. Calcd for C\(_{33}\)H\(_{43}\)NO\(_4\)S\(_2\)F\(_6\): C, 59.96; H, 6.23; N, 2.01. Found: C, 56.68; H, 5.91; N, 2.26.
Synthesis of DTE internal phenyl dicarboxylic acid 3.5 A solution of 1,2-bis(2-phenylthien-3-yl)hexafluorocyclopent-ene (0.15 g, 0.30 mmol) 3.4 in anhydrous Et₂O (25 mL was treated with t-butyllithium (0.6 mL, 1.7 M solution in pentane, 0.9 mmol) dropwise ) at -40 °C under an N₂ atmosphere. The resulting yellow solution was stirred at this temperature for 20 min. The cooling bath was removed and the anhydrous CO₂ gas was bubbled through the reaction for 1 hour. The reaction was quenched with aqueous HCl solution (20 mL, 2.4 M) and the aqueous layer was separated and extracted with CH₂Cl₂ (2 x 30 mL). The combined organic layers were washed with brine (2 x 50 mL) and dried (Na₂SO₄) filtered, and evaporated to dryness in vacuo. The crude product was purified by flash chromatography (silica, 0 – 10% MeOH and 0.1% AcOH in CH₂Cl₂) to yield 3.4 (0.11 g, 65%) as grey powders. Mp = 285 - 290 °C. ¹H NMR (CD₃OD, 500 MHz), δ 7.34 (t, J = 7.2 Hz, 2H), 7.26 (t, J = 8.0 Hz, 4H), 7.00 (d, J = 7.5 Hz, 4H), 6.66 (s, 2H). FT-IR(KBr cast) 3445, 3065, 1680, 1548, 1465, 1339, 1279, 1135, 1092, 946, 760, 692, 668, 611 cm⁻¹. Low-resolution mass spectrometry (LRMS) [chemical ionization (CI) with isobutene] m/z = 583 [M+H]⁺.
Synthesis of bulkier DTE fatty acid 3.6 A DTE internal phenyl carboxylic diacid 3.5 (0.11 g, 0.20 mmol), Et₃N (30 μL, 0.22 mmol) and hexadecanol (96 mg, 0.40 mmol) were mixed in distilled toluene (25 ml) under an N₂ atmosphere. Diphenylphosphorazine (DPPA) (47 μL, 0.22 mmol) was added and the reaction mixture was heated at reflux for 3.5 h. The heat source was removed and the reaction was allowed to cool to room temperature and quenched with saturated NH₄Cl (30 mL). The aqueous layer was separated and extracted with Et₂O (2 x 45 ml). The combined organic layers were washed with distilled water (2 x 80 mL) and brine (50 mL), dried over Na₂SO₄, filtered, and evaporated to dryness in vacuo. The crude product was purified by flash chromatography (silica, 0 – 10% MeOH and 0.1% AcOH in CHCl₃) to yield 3.6 (78 mg, 48%) as a green sticky solid. Mp = 78 - 80 °C. ¹H NMR (CDCl₃, 500 MHz), δ 7.30 - 7.32 (m, 2H), 7.19 - 7.25 (m, 4H), 7.02 (d, J = 6.6 Hz, 2H), 6.92 (d, J = 7.3 Hz, 2H), 6.80 (s, 1H), 6.76 (s, 1 NH), 5.48 (s, 1H), 4.22 (t, 7.0 Hz, 2H), 1.72 - 1.67 (m, 2H), 1.39 - 1.21 (m, 28H), 0.88 (t, J = 6.6 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ 166.5, 146.7, 131.9, 128.9, 127.9, 124.9, 32.1, 29.8, 29.8, 29.7, 29.7, 29.5, 29.4, 29.0, 25.9, 22.8, 16.7 (17 of 38 carbons found). FT-IR (KBr cast) 3461, 3060, 2926, 2856, 1734, 1717, 1700, 1684, 1653, 1635, 1577, 1558, 1539, 1522, 1506, 1457, 1434, 1228, 1090, 1031 cm⁻¹. MALDI m/z = 820 [M+H]⁺. Anal. Calcd for C₄₃H₄₇NO₄S₂F₆: C, 62.99; H, 5.78; N, 1.71. Found: C, 62.68; H, 5.54; N, 1.90.
Photochemical synthesis of the ring-closed isomer of DTE fatty acid 3.3 in 
$\text{CD}_2\text{Cl}_2$. A solution of the 3.3 (1.5 mg) in $\text{CD}_2\text{Cl}_2$ (0.55 mL) in an NMR tube was irradiated with 312 nm light using a hand held TLC lamp and monitored by $^1\text{H}$ NMR spectrum of the ring-open and ring-closed isomers levelled off indicating that the photostationary state (PSS) was reached (8 min) and yielded a solution containing 91% of 3.3 ring-closed isomer at the PSS. The remaining 9% was assigned to 3.3 ring-open isomer: $^1\text{H}$ NMR ($\text{CD}_2\text{Cl}_2$, 500 MHz), $\delta$ 7.82 (s, 1H), 7.16 (s, 1 NH), 6.47 (s, 1H), 4.15 (t, $J = 6.5$ Hz, 2H), 2.00 (s, 3H), 1.83 (s, 3H), 1.66 - 1.64 (m, 2H), 1.40 - 1.26 (m, 28H), 0.87 (t, $J = 7.0$ Hz, 3H). 3.3 ring-closed isomer: $^1\text{H}$ NMR ($\text{CD}_2\text{Cl}_2$, 500 MHz), $\delta$ 7.62 (s, 1H), 6.95 (s, 1 NH), 5.94 (s, 1H), 4.19 (t, $J = 6.5$ Hz, 2H), 2.16 (s, 3H), 2.10 (s, 3H), 1.68 - 1.64 (m, 2H), 1.40 - 1.26 (m, 28H), 0.87 (t, $J = 6.5$ Hz, 3H).

Photochemical synthesis of the ring-closed isomer of DTE fatty acid 3.3 in 
$\text{THF-}d_4$. A solution of the 3.3 (1.5 mg) in THF-$_d_4$ (0.55 mL) in an NMR tube was irradiated with 312 nm light using a hand held TLC lamp and monitored by $^1\text{H}$ NMR spectrum of the ring-open and ring-closed isomers levelled off indicating that the photostationary state (PSS) was reached (40 min) and yielded a solution containing 91% of 3.3 ring-closed isomer at the PSS. The remaining 9% was assigned to 3.3 ring-open isomer. Photobleaching of the ring-closed isomer with >434 nm light regenerated the original $^1\text{H}$ NMR spectrum. 3.3 ring-open isomer: $^1\text{H}$ NMR (THF-$_d_4$, 500 MHz), $\delta$ 7.62 (s, 1H), 6.32 (s, 1H), 4.01 (t, $J = 6.7$ Hz, 2H), 1.88 (s, 3H), 1.75 (s, 3H), 1.55 - 1.52 (m, 2H), 1.32 - 1.18 (m, 28H), 0.78 (t, $J = 6.8$ Hz, 3H). 3.3 ring-closed isomer: $^1\text{H}$ NMR (THF-$_d_4$, 500 MHz), $\delta$ 6.69 (s, 1H), 5.87 (s, 1H), 4.06 (t, $J = 6.8$ Hz, 2H), 2.03 (s, 3H), 1.97 (s, 3H), 1.58 - 1.55 (m, 2H), 1.32 - 1.19 (m, 28H), 0.78 (t, $J = 6.8$ Hz, 3H).
4 Appendices

4.1 Supplementary Ellipsometry Data for Chapter 2

a) film 1, first spot, thickness = 571 nm
   $\chi^2 = 0.155$

![Ellipsometry data for film 1, first spot](image)

b) film 1, second spot, thickness = 565 nm
   $\chi^2 = 0.153$

![Ellipsometry data for film 1, second spot](image)

c) film 2, thickness = 225 nm,
   $\chi^2 = 0.162$

![Ellipsometry data for film 2](image)

d) film 3, spot 1, thickness = 167 nm,
   $\chi^2 = 0.176$

![Ellipsometry data for film 3, spot 1](image)

e) film 3, second spot, thickness = 164 nm
   $\chi^2 = 0.155$

![Ellipsometry data for film 3, second spot](image)

Figure 4.1.1 Ellipsometry fits for three films of 2.14Zn spin-coated on quartz substrates. The film thicknesses were determined by fitting the ellipsometry data to an amorphous model. The spectra in dotted thick blue line describe $ls (= \sin(2\psi) \times \sin(\Delta))$ as a function of wavelength and the spectra in dotted thick red line describe $lc (= \sin(2\psi) \times \cos(\Delta))$ as a function of wavelength. The thin blue line and thin red line describe the fitting data.
5 Reference List


(19) Wigglesworth, T. J.; Sud, D.; Norsten, T. B.; Lekhi, V. S.; Branda, N. R. 


(21) McNaught, A. D.; Wilkinson, A. *IUPAC Compendium of Chemical 


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