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Synthesis and Assembly of Dihydroindolizines on Gold Surfaces for Light Induced Work Function Alterations

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LOYOLA UNIVERSITY CHICAGO

SYNTHESIS AND ASSEMBLY OF DIHYDROINDOLIZINES ON GOLD SURFACES FOR LIGHT INDUCED WORK FUNCTION ALTERATIONS

A DISSERTATION SUBMITTED TO
THE FACULTY OF THE GRADUATE SCHOOL
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

PROGRAM IN CHEMISTRY

BY
MATTHEW A. BARTUCCI

CHICAGO, IL

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CHAPTER ONE

AN INTRODUCTION TO WORK FUNCTION MODULATION OF METAL ELECTRODES

Organic light emitting diodes (OLEDs) and organic field-effect transistors (OFETs) are remarkable devices that find application in modern day electronics.\textsuperscript{1-3} In an OFET, the metal source sends electrons through an organic pathway to the drain electrode. The organic channel then serves as the active material in the field effect transistor, i.e. the material that switches from resistive to conductive in response to an electric field from a nearby gate (Figure 1a). OLEDs are light emitting diodes where the luminescent layer is a film of organic material (Figure 1b), in contrast to traditional light emitting diodes which use inorganic semiconducting materials. These technologies are useful because of their flexibility, low weight, and facile processing. Additionally, both architectures are more cost efficient than traditional electronics which tend to be bulky and expensive to manufacture.\textsuperscript{2,4,5} While these technologies hold much promise, there are an array of challenges ranging from the lifetime of the devices, to their overall electrical efficiency.\textsuperscript{6,7} Our chemistry focuses on the metal/organic interface of these devices, where the metal electrode meets the organic channel.
A majority of these aforementioned devices are hindered by a relatively high contact resistance at the organic-metal interface and, as we shall see, this inefficient process can be corrected via self-assembled monolayers (SAMs).\textsuperscript{5,8,9} First, the source of this resistance is due to poor alignment of the Fermi level of the metal and the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) of the organic bulk material\textsuperscript{10} (Figure 2a). This energy difference is defined as the Schottky energy barrier ($\Phi$). This can also be described as the energy difference between the metal’s work function and the electron affinity of the organic material.\textsuperscript{11-14} The work function is the amount of energy needed to remove an electron from the Fermi level to the vacuum level, or to where that electron has no interaction with the respective material. The relative value of the work function, with respect to the HOMO or LUMO, has a direct correlation to device efficiency. The larger the gap or energy difference, the larger the external bias needed for the devices to work properly. To minimize misalignment, the metal’s Fermi level can be altered via SAMs.\textsuperscript{13-15} The dipoles of the
adsorbed SAMs “tune” the Fermi level (i.e. work function) of the metal with respect to either the HOMO or LUMO of the organic channel, allowing for improved hole or electron transport, thereby decreasing the Schottky energy barrier of the device and increasing its efficiency (Figure 2b, c).  

![Figure 2](image)

**Figure 2.** Electronic structure diagram for gold with an organic polymer interface. (a) Schottky energy barrier for hole ($\Phi_h$) and electron ($\Phi_e$) transport with no monolayer present. A monolayer present on the gold surface creates a dipole either decreasing the Schottky energy barrier for (b) hole transport, or (c) electron transport in organic bulk material. The direction of the dipole, determines the direction of the Fermi level shift.

Fermi level alterations of metal electrodes, when accomplished via organic monolayers, are dependent upon many factors; including charge transfer, packing density, etc. However, the primary contributing factor is the direction of the molecular dipole vector of the organic monolayers. The dipole vector of the monolayer, with respect to the surface normal, has a linear dependence on the change in the work function of the underlying metal.  

![Figure 3](image)

**Figure 3** illustrates this dependence of the work function of the metal surfaces on the identity of organic monolayers using data taken from Campbell$^{14}$ and Sita.  

Monolayers with a dipole vector pointing away from the surface decrease the work function, while dipoles towards the surface increase the work function.
Figure 3. The work function of metal electrodes as a function of the dipole of an applied monolayer. Fluorinated species that have a negative dipole (surface + -) increase the work function, while simple alkyl chains that have a positive dipole (surface - +) decrease the work function of bare gold.

With the ability to tune the work function of the underlying metal substrates, several researchers\textsuperscript{8,10,21-23} have utilized this phenomenon to enhance and alter device efficiency. One example by Lee and coworkers showed that OFET device efficiency is improved by applying pentafluorobenzendienethiol (PFTP) and 4-fluorothiophenol (4-TP) when compared to bare silver and silver modified with thiophenol.\textsuperscript{21} These monolayers altered the work function of the electrodes, aligning them with the HOMO level of the organic semiconductor (triisopropylsilylethynyl pentacene) allowing for improved hole transport. The current/voltage plot reflects this with an increased slope for the fluoro capped monolayers, which represents a smaller contact resistance between the metal drain and organic channel and in turn a more efficient device (Figure 4). These types of effects have been reported by other scientists. Kitamura and coworkers employ different thiophenol derivatives (nitro, methyl, amino, and amine substituents) to reduce the
electron energy barrier between gold electrodes and the C₆₀ semiconducting organic channel.²² Their current/voltage plots demonstrate that all functionalized monolayers decrease the resistance of the device when compared to bare gold. Furthermore, Gholamrezaie and coworkers show that regardless of the OFET device configuration, the performance was affected by the adsorbed monolayer on the metal electrode. They found that 1H,1H,2H,2H-perfluorodecanethiol decreased the resistance (increased device efficiency) while hexadecanethiol either increased or was similar to the resistance of bare silver.²³

Figure 4. A current/voltage plot shows that when fluorinated monolayers are applied to the metal, device efficiency improves by decreasing the total resistance of the device with respect to bare silver and silver modified with thiophenol. Data taken directly from reference 21.

Although it has been demonstrated that device efficiency can be controlled by a monolayer based dipole on the metal electrodes, it would be far more interesting if this phenomenon was controlled by means of a photosensitive monolayer. With a monolayer that is responsive towards external stimuli, one would create a ‘smart’ device that is controlled by a molecular trigger. To do this, a light sensitive organic monolayer (i.e. one containing a photochromophore) is first adsorbed to the source and/or drain electrodes. External stimuli, for instance light, causes an active change in that monolayer, either by changing conformation (e.g. E-Z isomerization) or the
rearrangement of bonds (e.g. electrocyclization), that alters its dipole orientation with respect to the surface normal, and thus directly changing the work function. As a result, this chemistry generates a light driven molecular switch or trigger for these organic based electronics.

Of the widespread list of photochromophores that are available, azobenzenes, stilbenes, and spiropyrans have been extensively studied in solution and the solid-state, allowing for simplistic surface interpretation. Azobenzenes and stilbenes are photochromophores that have two phenyl rings linked by an N=N (azo) or C=C (stil) double bond. When irradiated with select frequencies of light, these double bonds undergo a trans-cis (e.g. E-Z) isomerization (Figure 5a). Both of these systems are traditionally characterized by their n to π* and π to π* transitions. Spiropyrans, on the other hand, often have two heterocycles at their core which are joined by a shared sp³ carbon atom. When excited, this spiro bond, which is typically a C-O bond, breaks, allowing for a ring opening (Figure 5b). This open isomer is often referred to as a merocyanine, and depending on the structural motifs, the merocyanine can resonate between different stereoisomers.

![Figure 5. (a) Photoisomerization of azobenzenes, stilbenes and (b) spiropyrans. The merocyanine structure can exist in various different conformations (or hybrid resonance structures) and the local charges can resonate through the molecule depending on the electronic effect of the substituents.](image-url)
These molecules find use in a variety of non-electrical applications (e.g. transition lenses) and some of the examples discussed have recently been applied to surfaces. Garcia and coworkers alter the wettability of a glass surface by means of covalently bound spiropyrans. By using UV and visible light, the isomerization from the open to the closed forms was demonstrated via a change in the water contact angles on the surface. Using vibrational spectroscopy, Feringa and Darwish have further characterized spiropyran switching on surfaces. When the targeted spiropyran was adsorbed onto gold and irradiated with UV light, surface enhanced Raman spectroscopy shows a decrease at 1335 cm\(^{-1}\) (spiro band) and an increase at 1197 cm\(^{-1}\) (C-O band). This data mirrors their solid-state observations, confirming their switch on the surface (Figure 6). Furthermore, when they selectively excite parts of the surface via NIR irradiation, the authors create organized patterns on the surface via external stimuli as seen by the letters ‘MC’ in the image. Furthermore, not only can spiropyrans undergo their conformational change via light but the switch has also been observed via the tunneling current from the tip of an STM. However, attempts to trigger the back reaction with the current from the tip were unsuccessful.
Figure 6. Applications of Photoswitchable of spiropyrans on gold. When the monolayer is irradiated with UV light the spiro bond opens and affords the merocyanine conformer which is confirmed via Raman spectroscopy. The back reaction can occur with visible light or thermally. MC dots correspond to selective irradiated (785 nm) zones where the switch has occurred – note photograph of MC dots correspond to thin films (0.1-0.3 mm). After 12 hours the MC pattern disappears because of the relaxation back to the spiropyran conformer. Image taken directly from reference 27.

More towards the focus of our research, photo-reversible work function alterations have been observed based on a trans-cis conformation change of azobenzene monolayers. Here, incident light induces isomerization which alters the dipole of the monolayer, and in-turn, generates a measureable shift in the work function of the underlying metal (Figure 7). Building on this, Tamada and coworkers have altered the tail ends of the azobenzene monolayers with electron donating or withdrawing substituents (e.g. H, CN, and C\textsubscript{6}H\textsubscript{13}), demonstrating that the active control of the work function is responsive to those substituents. This switching system can occur when the tether chain is either six or twelve carbons in length. Saturated azobenzene monolayers did not switch; dilute monolayers were used due to the volume needed for the isomerization to occur. These examples represent the current state of this research.
This dissertation seeks to expand the field to a second class of photochromophores (dihydroindolizines, DHIs), which has obvious spectroscopic signatures and large persistent dipoles (ca. 3-5 Debye). If accomplished, a simple correlation between molecular change and substrate perturbation will be demonstrated. This work began with DHI-1\textsuperscript{33} (Figure 8a, left) which was adsorbed onto the surface to test this effect. However, the desired work function shift was only observed intermittently for this molecule. Our vibrational surface spectroscopy suggested that DHI-1 was consistently switching on the surface; however, the work function shifts were inconsistent and often did not follow the trend predicted from the dipole orientation with respect to the surface normal. We hypothesized this was due to the monolayer’s packing which restricted molecular motion and, in turn, forced the zwitterion moiety into an unexpected conformation (Figure 8b). If true, this would generate a dipole parallel to the surface, resulting in minimal and inconsistent changes to the work function. While this theory ignores other resonance forms of the zwitterion, it is consistent with the need for appreciative free volume as seen for azobenzene isomerizations (Figure 7).\textsuperscript{20,31,32}
To minimize steric effects, DHI-1 was co-adsorbed with thiophenol or hexanethiol to allow the zwitterion a larger volume to switch from the cis to the trans orientation on the surface. Unfortunately, the electronic shifts were still inconsistent, and often the dilution made it difficult to observe the vibrational changes, especially in the case of the thiophenol spacer. Our second hypothesis was that the inconsistent electronic data could be due to the conjugation of the oligo(phenylene ethynylene) (OPE) linker which mediates charge transfer with the surface. Under this scenario, the previous spectroscopic interpretation of the zwitterion would be incorrect, and in fact minimal switching had occurred. More definitive vibrational interpretation of the zwitterion species was impossible due to the interfering peaks from the OPE tether. At this point the OPE system appeared too complex to initiate my studies.

To simplify the system, two new alkyl tethered DHIs (5 and 6) which would facilitate spectroscopic interpretation. Chapter two of this work reports the success of this system: surface infrared signatures of DHI molecules are used in conjunction with Kelvin probe measurements of the surface potential to demonstrate light induced changes to the molecular monolayer and the resulting change in the substrate’s work function. DFT calculations of vibrational states allow for nuanced discussion of the molecular change as related to the spectroscopic measurements, the resulting molecular dipole, and its effect on the surface’s work function. This is accomplished via DHI-5 and -6 shown in Figure 8b.
Figure 8. (a) DHI-1 adsorbed onto a gold surface and irradiated to a possible conformer of the zwitterion on the surface. Due to the inconsistent electronic data, the dipole vector is unknown and could also be affected by a charge transfer with the surface. (b) DHIs 5 and 6 are used for our initial work function studies. The DHIs exists in a spiro conformer and when irradiated, the spiro bond breaks affording a zwitterion. This form is expected to generate a new dipole and in-turn a change in the work function. (c) Due to the reaction mechanism a mixture of the 6′ and 8′ isomers can be formed when generating DHIs from asymmetric pyridines.

With this spectroscopic evidence of the work function modulation in hand, it would be beneficial to investigate how the molecular dipole vector of the DHI can be oriented with respect to the surface normal, showing an effective correlation with the direction of the dipole and corresponding change in the work function. This could be accomplished by attaching the surface tether at different locations on the DHI moiety, namely at the 6′ or 8′ carbons on the DHI. However, these new substitution patterns come at a cost and lead to an interesting question. Chapter three focuses on the challenge of generating DHIs from asymmetric pyridines, specifically, how the substituent on the pyridine ring affects the ratio of the constitutional isomers (6′ or 8′) that were formed.
(Figure 8c). As we shall see, this isomer ratio loosely corresponds to the electron donating/withdrawing capacities of the R substituents and its corresponding stability of the zwitterion. Chapter four brings the results from chapters two and three together and explains the future goals with the project.

Work within this thesis has been disseminated via three separate publications in Tetrahedron Letters,\textsuperscript{33} the Journal of Physical Chemistry C,\textsuperscript{34} and the Journal of Organic Chemistry.\textsuperscript{35} The response to this work at meetings and seminars has been well received, and not only can the DHI system be a candidate as a molecular switch towards a ‘smart’ device but this initial work also opens the door to other more advanced spiropyran systems (Figure 6). In time, I hope that this science is incorporated into thin film devices, whether by my hands or others.
CHAPTER TWO

SPECTROSCOPIC EVIDENCE OF WORK FUNCTION ALTERATIONS DUE TO PHOTOSWITCHABLE MONOLAYERS ON GOLD SURFACES

Work function (i.e. Fermi level) modulation of metal electrodes, due to an adsorbed organic monolayer, allows modern electronic devices such as OLEDs and OFETs to operate in a more efficient manner.\textsuperscript{1-5,18} The majority of devices are inherently hindered by a high contact resistance that is caused by the misalignment of the Fermi level of the metal and the HOMO or LUMO of the bulk organic.\textsuperscript{5,8,9} To minimize misalignment, the metal’s Fermi level can be altered via self-assembled monolayers (Figure 2).\textsuperscript{13-15} The molecular and interfacial dipoles of the adsorbed SAMs “tune” the Fermi level of the metal with respect to either the HOMO or LUMO of the organic channel allowing for improved hole or electron transport.\textsuperscript{10-12} For example, either straight chain hydrocarbons or fluorinated alkanes can respectively decrease\textsuperscript{14,16} or increase\textsuperscript{14,17} the work function of the substrate with a high degree of correlation to the aforementioned dipoles (Figure 9a).\textsuperscript{12}

As described in the introduction, this effect has been observed based on a \textit{trans-cis} conformation change of azobenzenes monolayers. We seek to build on these results with a second class of photochromophores (dihydroindolizines, DHIs), which has both obvious spectroscopic signatures and large persistent dipoles (ca. 3-5 Debye). For this study, characteristic vibrational modes of the spiro and zwitterion DHI provide
substantial evidence that the predicted conformational change has occurred on the surface which results in a measurable change in the surface potential of an underlying gold substrate, and these surface measurements will be correlated to powder and DFT calculated spectra for a further understanding of the molecular change. The DHI moiety has several structural parameters incorporated into it to aid us in this study.

The first is the DHI core (terminal end, Figure 9b) which has been incorporated into two molecules, DHI-5 and 6. The DHIs photochemical process uses visible light (ca. 400 nm) to break the spiro sigma bond in the 2,3-dihydropyrrole to generate the zwitterion. The lifetime of the electrocyclization back to the spiro conformer is largely dependent on the electronic capacities of the substituents which either stabilize or destabilize the zwitterion. The second half of the molecule, the aliphatic chain which links the DHI to the surface, is variable, and the aliphatic linker was chosen for these studies because of simpler vibrational interpretation of switched states, in contrast to conjugated systems. Furthermore, the extended alkyl system limits energy and electron transfer to surfaces which can complicate the photochemistry of surfaces.
Figure 9. (a) Energy diagram of bare gold and gold that has been modified with 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanethiol (FDT). The molecular dipole orientation of the FDT monolayer increases the work function with respect to bare gold. (b) The DHI adsorbed onto gold. (left) In the spiro state, the molecule has a small, non-zero, dipole perpendicular to the surface, and a corresponding initial work function that is similar to a straight chain alkane. (right) Zwitterionic DHI after being excited with 400 nm light which affords a similarly oriented dipole to the FDT monolayer. This results in an increase in the work function when compared to the spiro species. Dashed boxes in the energy diagram represent the dipole of the monolayer.

Synthesis of DHI-5 and 6

The project begins with the synthesis of the two target DHIs which are prepared via the same synthetic pathway (Scheme 1) with only slight differences in purification.

The synthesis of DHI-5 and DHI-6 start from their respective alcohols, 10-undecen-1-ol and 5-hexen-1-ol which were protected with trimethylsiloxane to afford 1. Following a procedure similar to de Lera and coworkers, a hybrid Suzuki coupling using 9-borabicyclo[3.3.1]nonane was employed with 4-iodopyridine to afford 2. The trimethylsilyl group was removed by heating 2 overnight, in dimethoxyethane with cesium fluoride generating 3, which was difficult to purify via column chromatography and was taken on as a crude mixture. The next two functional group transformations were facile. First triphenylphosphine dibromide was used to convert the alcohol to the bromide 4 and then potassium thioacetate displaced the bromide to form thioester 5. Potassium hydroxide was used to remove the acetyl group from 5 allowing for the air
oxidation to form disulfide 6. With the disulfides in hand, the target DHIs were generated by condensing 6 with dimethyl spiro[2]ene-1,9'-fluorene]-2,3-dicarboxylate in the dark.


Characterization of Photoswitch via UV-vis and IR Spectroscopies

DHIs, as a class, exist in two forms: the stable spiro form, and the zwitterion form which can be accessed via photoisomerization (Figure 9b). This transition is characterized by the molecules’ optical absorptions, particularly the π to π* transition (360-410 nm) in the spiro species and a presumed charge transfer transition (500-700 nm) for the photoisomerized, zwitterionic, species.

Both DHI-5 (Figure 10a) and 6 undergo the same optical transitions. In the spiro state, the π to π* transition for DHI-5 (386 nm) occurs well within the accepted range of established DHIs. When DHI-5 is irradiated with 400 nm light, the assumed charge transfer band appears at 583 nm (Figure 10a), confirming the generation of the stable, and persistent, zwitterion. Transitions differ by only ±3 nm for DHI-6. These measurements, performed in the solid state, mirror solution data.
Figure 10. Solid-state (KBr) correlation study of (a) UV-vis and (b) IR spectra of DHI-5. Yellow curves represent spiro DHI. Sample was irradiated for 1.5 minutes generating a persistent zwitterion conformer (green curves) in the solid-state. Additional irradiation yielded no further change in either spectra. The gray dashed arrows show an increase in the zwitterion character at 1645 cm\(^{-1}\) along with a decrease of the isolated olefins signal at 1559 cm\(^{-1}\).

As the optical properties change, accompanying vibrational differences are expected. Specifically, the stretches of double bonds in the dihydropyridine ring should diminish, while the frequencies corresponding to the pyridinium ion are expected to appear (Figure 10a, inset). It should be noted that the DHI moiety in the zwitterionic form could potentially exist in different conformers\(^{24,43,44}\) however; the formation of the aromatic pyridinium ion is consistent with all variations of the zwitterion and is an obvious spectroscopic signature for the IR data. Such signals are apparent in our experimental spectra (Figure 10b) and can be explained as follows.

For the spiro conformer, the characteristic vibrations of the C=C bonds in the dihydropyridine ring are typically observed near 1650 and 1580 cm\(^{-1}\), and appear at 1645 and 1559 cm\(^{-1}\) in DHI-5.\(^{45-47}\) In the scaled B3LYP/6-31G* vibrational spectrum (Figure 11, provided by Prof. Jan Florián), the corresponding normal modes lie at 1638 and 1547 cm\(^{-1}\) and the assignment can be confirmed (Appendix B: Figure S3-11 show atomic displacement vectors during normal vibrations for the major peaks, provided by Prof. Jan
Florián). In this instance, the calculations also show the 1547 cm\(^{-1}\) mode also contains significant contribution from the stretching vibration of the C=C bridge between the two ester groups. Readers curious about interpretation of other modes can find them in the Table S1.

When this sample is irradiated to promote formation of the zwitterion, the IR spectrum shows new stretches for the pyridinium ion in conjunction with the appearance of the charge transfer transition band in the visible spectrum. The two normal vibrations that are correlated to this appearance are observed near 1643 and 1506 cm\(^{-1}\). IR bands in these regions are commonly assigned to the stretching vibrations of the pyridinium ring.\(^ {48,49}\) Our calculations show that each of these two bands corresponds to the stretching vibrations of the pyridinium ring that are coupled to the C=O stretch of one of the two ester groups (Appendix B: Table S1). The appearance of the two bands at each location of the calculated spectrum (and shoulders in the experimental) is due to presence of two rotational conformers of the zwitterionic DHI. The contribution of the stretch of the polar C=O bond to these normal modes explains the large IR intensity increase in this spectral region upon DHI irradiation by the UV light (Figures 10b and 11). Both vibrations can be used diagnostically to discern the state of the DHI but, due to reasons discussed later, we focus on the peak at 1643 cm\(^{-1}\).

In addition to the intensity increase at 1643 cm\(^{-1}\), the spiro/zwitterion switch can be monitored via the decrease of the IR intensity of the dihydropyridine C=C bonds at 1559 cm\(^{-1}\). This spectral change is consistent with our calculations that show a strong IR band at 1547 cm\(^{-1}\) for the spiro DHI but no band for the zwitterionic DHI in this spectral region (Figure 11). As such, this spiro C=C stretch can be used to provide a
semiquantitative measure of the percentage of photochromophores which have switched. Implicit here is the fact that only about one third of photochromophores are in the zwitterionic form in the solid state (Figure 10b), even if irradiation is extended. This hypothesis is consistent with the presence of the shoulder in the UV-vis data (~390 nm). Both the peak at 1643 and 1559 cm\(^{-1}\) will provide a spectroscopic handle for subsequent identification of the molecular DHI on the surface for Kelvin probe measurements.

![Figure 11](image.png)

**Figure 11.** Calculated DFT vibrational spectra displays a new peak for the zwitterion at 1651 cm\(^{-1}\) and the disappearance of the stretch at 1547 cm\(^{-1}\) which are represented by the dashed arrows. Changes are consistent with the experimental solid-state switch.

**Photochemically Induced Work Function Shifts and Correlation with Spectroscopic Signatures**

To test the photochromophores’ ability to dynamically tune a metal’s work function, both DHI-5 and 6 were assembled onto freshly prepared gold, and were compared to freshly prepared ODT monolayers via Kelvin probe, which measures the surface potential difference between substrates. The spiro surface potential for DHI-5 and 6 were found to be at 27.8 ± 42.4 and 148.4 ± 83.9 mV respectively, relative to ODT
on gold. The higher standard deviation from the mean for the spiro DHI-6 is presumably related to less efficient packing and higher disorder often reported for shorter alkyl chains. Surface spectroscopy for both spiro DHIs correlates well with the solid-state data (vide infra), providing evidence for the integrity of the assembled material.

When the spiro DHI-5 and 6 were irradiated for thirteen minutes with 400 nm light, the surface potential increased by 178 mV and 164 mV from their respective initial values (Figure 12, circles and squares). These individual samples, which were correlated with their spectroscopy, are representative of a greater trend – on average, the shift for five DHI-5 samples at 13 minutes irradiation was 186 mV with a standard deviation of 23 mV. The direction of the work function shift is consistent with the orientation of the molecular dipole of the zwitterion with respect to the surface normal, suggesting that we are observing the effect of DHI switching from its spiro to zwitterionic form. The molecular origin of this effect can be supported by two additional observations. First, no/minimal absorption, and thus isomerization, is expected for 501 nm light (Figure 10a). As expected, DHI monolayers irradiated with this wavelength show an insignificant work function change (Figure 12). Second, a sample of 1-dodecanethiol assembled on gold was irradiated with 400 nm light and the measured work function shift from irradiation was negligible (21 mV) allowing us to rule out other effects such as photo-oxidation of the Au-S bond. This second data set can be found in Appendix B (Appendix B, Figure S12). Combined, the results show that it is possible to dynamically shift the work function of a material, based on molecular effects, by c.a. 170 meV.
Figure 12. Work function measurements of DHI-5 (*) and DHI-6 (■). The DHIs were irradiated with 400 nm light for 0, 2, 8 and 13 minutes, and an active shift in the surface potential was noted, corresponding to the zwitterion species. When DHI-6 was irradiated with 501 nm light (×), a negligible shift was observed.

The same DHI samples reported in Figure 3 were examined sequentially via polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) so that the electronic switch could be correlated with the vibrational signatures of the zwitterion. For the first two irradiation intervals, (0-2 and 2-8 minutes) the same increase (ca. 70 mV) was observed for each measurement. The substantial shift appears in conjunction with vibrational evidence for isomerization, with an increase in C=N (1644 cm\(^{-1}\)) pyridinium bond character and the decrease in the isolated dihydropyridine C=C bonds (1559 cm\(^{-1}\)) (Figure 13). For the final five minutes of irradiation (8-13 min) a smaller increase of 35 mV was observed, and as expected the difference in spectra are less pronounced suggesting minimal change in configuration. In fact, DHI-6 shows virtually no vibrational changes, while DHI-5 shows minor changes at 1559 cm\(^{-1}\). These have been omitted for clarity, but can be seen in the Appendix B (Appendix B, Figure S13).
The electronic and spectroscopic changes were consistent for all DHI samples that were subjected to the same experiment.

![Figure 13. PM-IRRAS of spiro (yellow) monolayers of (a) DHI-5 (b) DHI-6. Irradiation times of 2 (blue), and 8 (green) minutes support the formation of the zwitterion on the surface. Dashed arrows represent formation of the pyridinium ring (1645 cm$^{-1}$) and the decrease of the isolated olefins (1559 cm$^{-1}$).](image)

In the initial characterization of the photoswitch (as a KBr pellet, Figure 10b), three absorptions appear to be highly correlated with the change from the spiro form to zwitterion; only two are observed for the monolayer samples (1645 cm$^{-1}$, 1559 cm$^{-1}$). The stretch at 1506 cm$^{-1}$, which according to the DFT calculations corresponds to the C=C bond formed at the 9-position of the fluorene moiety (Figure 10), does not appear in the surface IR of the irradiated samples (Figure 13, 2 min, 8 min). A common explanation for these situations is the surface selection rule. The net dipole of the vibrations that are parallel to the surface are nullified by those from an image charge, and no absorption appears.$^{51}$ Naively, based off of the SAM tilt angles, as well as molecular geometry (Figure 9b), one might expect this to be case for the C=C bond at 1506 cm$^{-1}$.

To confirm this hypothesis, DHIs were spin coated onto the surface, rather than assembled, and non-oriented multilayers of varying thicknesses were formed as a result.
The randomly oriented multilayers display the missing stretch (Appendix B, Figure S14). As the layer thickness decreases (and a greater portion of the signal is from molecules bonded to the surface) the 1507 cm\(^{-1}\) peak decreases in intensity relative to the other signals.

**DHI-5** and **6** serve as effective model systems for this class of photochromophores. However, as we begin to analyze the relationship between DHIs and the work function change, it would be ideal if the dihydropyridine C=C bond stretch remains diagnostic for other molecules within this subclass. If true, substituents impacting optical absorption, stability, the dipole, and even molecular orientation could be appended to the molecule.\(^{24}\) Such flexibility would be extremely powerful for reconciling theoretical changes in the work function with experiment. Preliminary analysis indicates this to be true. The indicative C=C stretch is present in other DHIs we have synthesized, where the alkyl chain has been exchanged for various alkynyl, aryl, or oxy substituents. Stretches for the four compounds are reported at 1569, 1559, 1551, and 1547 cm\(^{-1}\).\(^{33}\) Of these, **DHI-1** (Figure 14) was examined both pre- and post-irradiation for vibrational changes. The C=C peak at 1547 cm\(^{-1}\) is highly correlated with the switching event. The above sequence of substitutions should allow for varying degrees of electron/energy transfer between the photochromophore and the surface, which inhibits switching.\(^{36}\) Combined work function/spectroscopic analysis can clarify some of these effects.
In sum, an active shift in the work function of a gold surface was generated by two photochromic DHI monolayers, and the surface IR suggests that the electronic alterations are caused by the light induced conformation change from the spiro to the zwitterionic species. Changes in the surface spectroscopy were confirmed via experimental solid-state spectroscopy and DFT vibrational calculations. The characteristic isolated olefin vibrational feature appears general across the class of molecules and can be used for analysis of dihydroindolizines designed with other work function applications. With this in mind, we were inspired to relocate the tether from the 7’ carbon to either the 6’ or 8’ positions in order to reorient the DHI’s core with respect to the surface normal. With this, a general correlation between the change in the work function and dipole orientation of the zwitterion could be reached. However, upon synthesis of the newly functionalized DHIs, additional parameters needed to be considered - namely selective isomer formation of the 6’ and 8’ DHIs. Chapter three will focus on the means of selectivity for 6’ and 8’ isomer population and the synthesis of these new molecules.
CHAPTER THREE
SYNTHESIS OF DHIs FROM ASYMMETRIC PYRIDINES AND SUBSTITUENT CONTROLLED ISOMER FORMATION

As discussed in chapter two, DHI-5 and 6 proved to be sound model systems for initial studies to investigate light induced changes in the work function due to a photochromic monolayer; one where the switch was confirmed via IR spectroscopy. Within our DHI light driven molecular switch system, a question of particular importance arises: what is the relationship between the dipole of the molecule and the surface’s work function change? From the work function modulation data in chapter two, it would be ideal to build DHIs that, when irradiated, have their respective dipoles aligned at varying angles to the surface normal. Such molecules would allow us to experimentally demonstrate the direct correlation between the normal component of the molecular dipole and the change in the work function.

Currently, DHIs 5 and 6 are substituted at the 7’ position. However, to change the molecular dipole orientation on the surface, it would be beneficial to have the surface tether attachment at other positions. Typically, monolayers on gold are oriented about 30 degrees with respect to the surface normal, and based on the alkyl tether of the 7’ substituted DHIs, a dipole ~ 28 degrees from surface normal was likely produced when irradiated with light. To alter this second angle, the tether location on the DHI can be relocated to the 6’ position which should generate a dipole nearly parallel to the surface.
(based off the most stable packing structures).\textsuperscript{53,54} Other substitutions such as 8’ would generate a similarly oriented dipole to 7’, and thus serve as an effective positive control molecule (R, Figure 15).

![Figure 15](image)

**Figure 15.** DHI orientation on a surface when tethered via 6’, 7’, and 8’, positions. As the location of the tether is moved so does the corresponding zwitterion dipole orientation with respect to the surface normal.

However, with these substitutions in mind, the synthetic pathway to generate the asymmetric DHIs leads to an interesting challenge: due to the reaction mechanism, a mixture of the spiro 6’ and 8’ isomers is often formed via synthesis from the asymmetric 3-substituted pyridines, but the rules determining the isomers formed are not clear. However, isomer control may be possible via the identity of the substituent at the 3-position. Moreover, the changes at the 3-position also impact the optical properties of these photochromophores which are strongly influenced by the electron donating or withdrawing capacities of these substituents, adding a second factor to the molecular design.\textsuperscript{24,25,55}
To elucidate the cause of selectivity between the constitutional isomers, we have synthesized a series of asymmetric DHIs and shown a relative trend towards formation of the 6′ isomer as the substituents become more electron withdrawing. In addition we gain insight to the control of the isomer formation and corroborate our results with the initial findings reported by Durr.

The target compounds are generated via a condensation reaction between dimethyl spiro[cycloprop[2]ene-1,9'-fluorene]-2,3-dicarboxylate and the appropriate 3-substituted pyridine (Scheme 2). The reaction mechanism begins via nucleophilic addition of the pyridine to the spiropcyclopropene generating a cyclopropyl anion. From there, the unstable three membered ring opens to afford the E-isomer of the zwitterion, and the local negative charge can resonate between the C₁ and C₃ atoms. The rate determining step occurs during the E to Z isomerization, and once the Z-isomer is reached, the formation of the 6′ or 8′ spiro species is rapid. However, if the substituents on the pyridinium ion actively donate or withdraw electron density to the positive reaction center, the speed of the electrocyclization is altered and has been correlated with their respective Hammett parameters, showing a linear tendency. More germane to the formed product(s), there is little within this mechanism to suggest selectivity of one constitutional isomer over the other as, for example, transition state stabilization ortho to the substituent rather than para is expected to be comparable. In fact, the only obvious means for selecting between 6′ and 8′ formation from this mechanism is steric effects.
Based off mechanistic arguments, we hypothesize that the pyridyl substituents (R) affect the ratio of the 6’ and 8’ isomers primarily by thermodynamic considerations. To test this, substituents that traditionally range in their electronic directing capabilities were incorporated at the 3-position, from the highly donating amino to the withdrawing acetyl. Furthermore, these pyridine derivatives were beneficial due to their commercial availability and/or ease of synthesis. As noted before, the formation of the DHIs is facile and the reaction progress is visually apparent. The separation of most isomers was possible via column chromatography except for the methoxy and methyl DHIs.

**Scheme 2.** Mechanism for general DHI condensation reaction of a 3-substituted pyridine with dimethyl spiro[cycloprop[2]ene-1,9'-fluorene]-2,3-dicarboxylate. Both the 6’ and 8’ isomers can form during the 1,5-electrocyclization attack to either carbon adjacent to the nitrogen.
From these syntheses, the formation of DHIs 7-13 follow a loose trend – as the R substituent becomes more electron withdrawing, the percentage of the 6’ spiro isomer increases (Table 1). Of these, only the aminopyridine forms exclusively one product (8’), and it was rare to form the 6’ in excess, even with acetyl substitution. We were slightly surprised at the different ratios for the iodo and chloro species, especially as the iodo prefers the sterically hindered 8’ to a greater extent than the chloro. The ratio of isomers was consistent when monitored as a function of time via NMR, in the dark, suggesting that reaction work ups or minute exposure to light have not impacted our results. Additionally the barrier to interconversion is sufficiently high: pure DHI-11 (either pure 6’ or 8’) conformers, heated to 50 ºC for 15 minutes, show no observable interconversion via 1H NMR.

<table>
<thead>
<tr>
<th>DHI</th>
<th>R</th>
<th>Isomer Ratio (6 : 8)</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>NH₂</td>
<td>0 : 100</td>
<td>86</td>
</tr>
<tr>
<td>8</td>
<td>MeO</td>
<td>7 : 93</td>
<td>83</td>
</tr>
<tr>
<td>9</td>
<td>Me</td>
<td>16 : 84</td>
<td>95</td>
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<tr>
<td>10</td>
<td>I</td>
<td>20 : 80</td>
<td>67</td>
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<td>11</td>
<td>Cl</td>
<td>30 : 70</td>
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<td>12</td>
<td>55 : 45</td>
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<td>92</td>
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<tr>
<td>13</td>
<td>COCH₃</td>
<td>63 : 37</td>
<td>79</td>
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</table>
While we can conclude little from our results outside of the general electron donation/withdrawal trend, the analysis becomes clearer once one examines the only other report of the 6′ and 8′ isomer formation in DHIs. We reexamined observations by Durr on the formation of the 6′ and 8′ isomers for DHIs where the ester groups in our molecules have been replaced by cyanides. Durr notes that isomer formation was regiospecific when the R₂ substituents are electron donating (Table 2). However, what becomes clear is that the 8′ conformer is driven by the strongly electron withdrawing cyanide substituents which have replaced the esters. Indeed, Durr notes selective formation of the 8′ isomer for the methoxy, methyl, and chloro species; however our DHIs show a mixture for these same substituents (7, 16, and 30 % respectively). Taken in the context of the electron donating groups effect on the pyridinium ring, we propose the formation of the 8′ conformer can be driven by substituents which stabilize either the pyridinium via electron donation or the anion via withdrawal of electrons. Such observations would seem to suggest that perhaps the mechanism steps from the cyclopropyl anion to the spiro species (Scheme 2) might be less distinct than initially assumed. Regardless of the cause, the zwitterion stabilization trend is distinct, allowing for other minor contributing factors such as sterics.
With this insight on the control of the isomer ratio, we can predict the viability of our typical surface tethers: thiolated alkyl and oligo(phenylene ethynylene) (OPE).

Based off the electronics of the alkyl and OPE surface tethers, it would be ideal to generate both 6’ and 8’ conformers for future dipole orientation surface studies. As our previous data has shown, selecting towards one alkyl or OPE isomer could prove to be difficult (though preparatory separation via HPLC is a possibility). How could we alter this isomer ratio to prefer one conformer over another? One way to accomplish this would be with the substitution of the methyl esters. When comparing our data to Durr’s, as the double bond substituent becomes less electron withdrawing, a change in the isomer formation was noted for DHIs-8, 9 and 10, with the population of the 6’ isomer increasing. If the esters were to be replaced by an acetyl or an aldehyde (weaker electron withdrawing groups), one would expect that the population of the 6’ conformer to
increase for **DHIs-7-13**. With our target OPE and alkyl linkers in mind, the weaker electron withdrawing groups should produce nearly selective formation the 6’ isomer. In the opposite direction, if the cyano functionality replaced the esters for **DHIs-10, 12, and 13**, the 8’ population would be heavily favored for **DHI-13**, if not completely selective for **DHIs-10 and 12**. Finally, if the substitution of the esters does not substantially shift the population of the isomers, more direct measures could be taken to modify the pyridyl derivatives to force the isomerization one direction. If substitutions were placed on the carbons alpha to the pyridyl nitrogen, the electrocyclization to the spiro could be forced in one direction due to sterics, resulting in one isomer. Results from Durr show this to be true. When attaching a single methyl substituent alpha to the pyridine, the electrocyclization is forced to the opposite side.\(^{24,55}\)

Chapter three has provided us with a good outline on the electronic effects on isomer ratios via the condensation with 3-substituted pyridines. Regardless of the location of the substitutions, either on the heterocyclic pentene or on the pyridine, their electronic donating/withdrawing abilities can either stabilize the positive pyridinium ion or the negative anion of the zwitterion. When combining Durr’s results to our own, we find that these electronic trends are essential to isomer population. With this newfound control of isomer selectivity, one could build future DHIs with specific functions in mind.
CHAPTER FOUR

CONCLUSION

In sum, this thesis has demonstrated that DHIs are a viable system for smart organic based electronics. Our light induced work function modulation data has been supported via spectroscopic evidence on the surface, in the solid-state, and by DFT calculations. These spectroscopic identifiers have proven to extend to more complex DHIs that have been reported in Tetrahedron Letters, with other work function applications in mind. Furthermore, when generating DHIs with various tether locations, we show that isomer ratio (and the tether location) can be controlled via the electronic abilities of the substituents on the DHI core, allowing future research to build specific structural motifs into future molecules.

The field of surface science and nanotechnology as a whole has been of major focus of modern chemical research over the past twenty years and has been expanding rapidly. Towards our end in this field, much has been done in the last five years, but this prior work has been dominated by the simplistic azobenzene system. This thesis has shown that the DHI system is applicable towards these smart devices, which opens the door not only for our research but other complex systems as well. In the short term, I will be looking investigate the change in the work function with the targeted OPE-DHIs from our first publication in Tetrahedron Letters to gain insight on the charge transfer effect on the work function with the conjugated tethers. I also seek to continue the work of chapter
three by investigating the stability of the zwitterions via optical properties and show how they are directly related to the electronics of the substituents. Furthermore, since the research group has recently moved into device testing and fabrication, it will be ideal to put our original motivation for this research into motion by testing the DHI in an OFET device. As a final point, we hope that this data inspires others to investigate photochromic molecules on surfaces with expectations of applying this science in modern electronic devices, towards a greater goal of smart devices and better technology for the future.
CHAPTER FIVE
EXPERIMENTAL METHODS

All NMR spectra were taken on a Varian 500 or 300 MHz spectrometer. $^1$H chemical shifts ($\delta$) were referenced to tetramethylsilane dissolved in CDCl$_3$. The $^1$H NMR exceptions to this were DHI-7 which was referenced to CD$_2$Cl$_2$ at 5.32 ppm, DHI-10, DHI-11, DHI-12, and 6'-DHI-13 were referenced to CD$_3$CN at 1.94 ppm. $^{13}$C NMR were referenced to tetramethylsilane or CDCl$_3$ at 77.23 ppm. Reactions were run under a nitrogen atmosphere unless otherwise noted. All plug purifications and column chromatography separations were carried out on silica gel 60 (40-63 $\mu$m from BDH). Thin layer chromatography (TLC) was performed on silica gel 60 (F$_{254}$) with glass support.

Metal evaporations were performed in a Kurt J. Lesker NANO 38 thermal evaporator. The thickness of monolayers on gold were determined with a Gaertner stokes ellipsometer LSE. Solution and solid-state UV-vis spectra were acquired on a Shimadzu UV-2550 spectrometer. IR spectra of solid-state KBr samples were obtained with a Tensor 37 FT-IR from Bruker Optics with MCT detector. Surface IR spectra were acquired on a Tensor 37 FT-IR from Bruker Optics with polarization modulation accessory (PMA 50) and MCT detector. DHI irradiations utilized a 400 or 501 nm LED (12 mW/cm$^2$), and all surface potential data was attained via a Kelvin probe from KP.
Technologies. With the exception of ellipsometry and UV-vis, all measurements were made under nitrogen.

Assembly substrates were prepared as follows. Glass slides were cleaned in a piranha solution (3:1 H$_2$SO$_4$:H$_2$O$_2$) for 30 minutes at ca. 100º C and washed copiously with 18 MΩ water. The glass samples were dried extensively with nitrogen before being placed in the thermal evaporator. Gold (125 nm) was thermally evaporated onto the freshly cleaned slides with a 5 nm chromium adhesion layer at a base pressure of $< 1 \times 10^{-6}$ Torr and a deposition rate of 1 Å/s.

The disulfide functionality of DHI-5 and 6 allows for facile self-assembly of organized monolayers onto gold surfaces from solution.$^{52,56}$ Both thiol (FDT, ODT, dodecanethiol) and disulfide assemblies were performed in high purity ethanol which was degassed for 30 min with nitrogen prior to use. Assembly concentrations ranged from 0.1-0.5 mM, and times were 14-20 hours. After assembly, samples were rinsed with ethanol and dried with nitrogen. For the DHIs, all assembly procedures were performed in the dark. During assembly solution preparation, the DHIs were sonicated to mediate dissolution. After assembly, the substrates containing the DHI monolayer were placed in fresh ethanol, sonicated to remove excess DHI, before drying with nitrogen.

Ellipsometry was used to confirm monolayer coverage. Measured thicknesses match theoretical$^{50}$ within ± 2 Å.

All Kelvin probe measurements of surface potential were referenced to an ODT monolayer ($\Delta \Phi = \Phi_{\text{SAM}} - \Phi_{\text{ODT}}$). The standard deviation was less than 5 mV per sample.
ODT-gold serves as a consistent, reproducible, reference and its work function is reported to be 1.2 eV smaller than bare gold (3.9 eV for ODT-gold and 5.1 eV for bare gold).\textsuperscript{17,57}

**Theoretical Methods**

Quantum-mechanical calculations of the structure and vibrational spectra of the cyclic and zwitterionic forms of DHI were carried out using the B3LYP/6-31G* hybrid density functional theory (DFT) method implemented in the Gaussian 03 program.\textsuperscript{58} In these calculations, the alkane chain (Figure 1b) was replaced by hydrogen atom. The IR spectrum of the zwitterionic form of DHI was modeled as arithmetic average of its two major conformers. The calculated frequencies were scaled by a factor of 0.96 that was determined by comparing B3LYP/6-31G* and experimental frequencies of CN, CC and CO stretching vibrational modes of cytosine.\textsuperscript{59}

**General Procedures for Sonogashira Couplings**

All Sonogashira couplings were performed in sealed tubes containing Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, CuI, and their respective aryl halides and alkynes. Sealed tubes were evacuated and filled with nitrogen 3-5 times. The exceptions were reactions containing trimethylsilylacetylene (TMSA) which was added after solvents and not degassed. Base (triethylamine) and THF were added via a syringe while stirring. Reactions lasted from 13-48 h at 40 °C. Reaction mixtures were poured into water or NH\textsubscript{4}Cl and extracted with CH\textsubscript{2}Cl\textsubscript{2} (×3). The collected organic layers were dried with MgSO\textsubscript{4} (aq) and filtered. Solvent was removed via rotary evaporation, and the reaction was purified by column chromatography.
**General Procedures for DHI Condensations**

For the DHI condensations, dimethyl spiro[cycloprop[2]ene-1,9'-fluorene]-2,3-dicarboxylate and its respective pyridial derivative were added to an oven dried round bottom flask in a 1:1 mole ratio. The exceptions to this were the bis-DHIs 5 and 6 which used two equivalents of dimethyl spiro[cycloprop[2]ene-1,9'-fluorene]-2,3-dicarboxylate for one mole of disulfide tether. The round bottoms were purged with nitrogen for 30 minutes, in the dark, at room temperature before the addition of chloroform, THF, or dichloromethane. Reaction mixtures were allowed to stir for 2-24 h and the solvent was removed by rotary evaporation. All reactions were purified via column chromatography. The 6' and 8' isomer ratios were obtained by comparing the $^1$H NMR signals on dihydropyridine ring.

**Synthetic Procedures**

Trimethyl(undec-10-enyloxy)silane (1a). Pyridine (12 mL) and hexamethyldisilazane (2.33 mL, 11.1 mmol) were added to 10-undecen-1-ol (0.944 g, 5.54 mmol) in a round bottom flask. Chlorotrimethylsilane (0.77 mL, 6.07 mmol) was then added dropwise to the reaction and the resulting mixture was allowed to stir for 30 min at room temperature. The reaction was quenched with water and extracted with CH$_2$Cl$_2$ ($\times$3). The combined organic layers were dried with MgSO$_4$ and filtered. The CH$_2$Cl$_2$ was removed via rotary evaporation and the product was separated from the excess pyridine via a silica plug (4:1 hexanes : EtOAc) to afford 1a (1.302 g, 5.370 mmol) as a clear oil in 97% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.85-5.77 (m, 1 H), 5.01-4.96 (m, 1 H), 4.94-4.91 (m, 1 H),
3.57 (t, \(J = 6.8\) Hz, 2 H), 2.06-2.01 (m, 2 H), 1.54-1.49 (m, 2 H), 1.37 (p, \(J = 7.3\) Hz 2 H), 1.28 (s, 10 H), 0.11 (s, 9 H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 139.3, 114.1, 62.8, 33.8, 32.8, 29.6, 29.5 (2), 29.1, 29.0, 25.9, -0.4. IR (liquid film, cm\(^{-1}\)): 2920, 2856, 1641, 1465, 1439, 1387, 1250, 1098.

4-(11-(Trimethylsilyloxy)undecyl)pyridine (2a). At 0 °C, 9-borabicyclo[3.3.1]nonane (0.5 M in THF, 20.2 mL, 10.1 mmol) was added to 1a (0.816 g, 3.37 mmol). The mixture was brought room temperature for 2 h and transferred via syringe to a sealed tube that contained 4-iodopyridine (0.761 g, 3.71 mmol), Pd(PPh\(_3\))\(_4\) (0.389 g, 0.337 mmol), DMF (10 mL) and aqueous K\(_2\)CO\(_3\) (16.9 mmol, 3 M). The resulting mixture was allowed to stir for 2 h at 70°C. After cooling to room temperature, the mixture was diluted with water and extracted with diethyl ether (×3). The combined ether layers were then washed with water (×5), dried with MgSO\(_4\), filtered, and the solvent was removed via rotary evaporation. The crude mixture was then passed through a silica plug (1:1 hexanes : EtOAc, +10% triethylamine) to remove excess salts and further purified via column chromatography (1:1 hexanes : EtOAc, \(R_t = 0.42\)) to afford 2a (0.434 g, 1.35 mmol) as a clear oil in 40% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.48 (dd, \(J = 4.4, 1.5\) Hz, 2 H), 7.10 (dd, \(J = 4.4, 1.5\) Hz, 2 H), 3.56 (t, \(J = 6.8\) Hz, 2 H), 2.59 (t, \(J = 7.8\) Hz, 2 H), 1.65-1.59 (m, 2 H), 1.55-1.49 (m, 2 H), 1.37-1.24 (m, 14 H), 0.11 (s, 9 H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 151.9, 149.5, 123.9, 62.8, 35.3, 32.8, 30.3, 29.60, 29.56, 29.51, 29.44, 29.40, 29.2, 25.8, -0.4. IR (liquid film, cm\(^{-1}\)): 2926, 2855, 1602, 1465, 1415, 1250, 1095.
11-(Pyridin-4-yl)undecan-1-ol (3a). In a sealed tube, cesium fluoride (2.05 g, 13.5 mmol) was added to 2b (0.434 g, 1.35 mmol) and the mixture dissolved in 1,2-dimethoxyethane (20 mL). The reaction was heated to 70 °C for 14 h. After the reaction was cooled to room temperature, the mixture was poured into water and extracted with CH₂Cl₂ (×3). The combined organic layers were dried with MgSO₄, filtered, and the solvent was removed off via rotary evaporation to afford the crude alcohol which was taken on to the next step without purification.

4-(11-Bromoundecyl)pyridine (4a). In a round bottom flask open to the atmosphere, triphenylphosphate (0.737 g, 2.81 mmol) was dissolved in CH₂Cl₂ (6 mL). The solution was cooled to 0 °C and bromine (0.14 mL, 2.8 mmol) was then added dropwise generating a dark orange mixture. Excess triphenylphosphate was then added until the solution appeared clear and then the crude alcohol (0.463 g, 1.87 mmol), dissolved in CH₂Cl₂ (1 mL), was added. The reaction was allowed to stir for 15 min at 0 °C and then at room temperature for 1.5 h. The reaction was quenched with water and extracted with ether (×3). The combined organic layers were dried with MgSO₄, filtered, and the solvent was removed via rotary evaporation. The product was isolated via column chromatography (1:1 hexanes : EtOAc, +10% triethylamine, Rf = 0.42) to afford pure 4a (0.280 g, 0.897 mmol) as a yellow oil in 66% yield (over two steps). ¹H NMR (500 MHz, CDCl₃) δ 8.48 (dd, J = 4.4, 1.7 Hz, 2 H), 7.10 (dd, J = 4.4, 1.7 Hz, 2 H), 3.41 (t, J
= 7.0 Hz, 2 H), 2.59 (t, \( J = 7.8 \) Hz, 2 H), 1.88-1.82 (m, 2 H), 1.62 (p, \( J = 7.3 \) Hz, 2 H), 1.42 (p, \( J = 7.1 \) Hz 2 H), 1.35-1.24 (m, 12 H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 151.7, 149.7, 123.9, 35.2, 34.0, 32.8, 30.3, 29.47, 29.45, 29.40, 29.37, 29.2, 28.7, 28.2 IR (liquid film, cm\(^{-1}\)): 2927, 2854, 1602, 1558, 1464, 1415, 1232, 1219. HRMS calcd for C\(_{16}\)H\(_{26}\)BrNH\(^+\) [M + H]\(^+\): 312.1321, found: 312.1331.

\[ \text{S-11-(pyridin-4-yl)undecyl ethanethioate (5a).} \]

Potassium thioacetate (0.275 g, 2.41 mmol) was dissolved in dry DMF (8 mL) and added to 4a (0.251 g, 0.804 mmol) at 0 \(^{\circ}\)C. The mixture was brought to room temperature and stirred for 3 h. The mixture was poured into water and extracted with ether (\( \times 3 \)). The combined organic layers were then washed with water (\( \times 5 \)) and ether layer was dried with MgSO\(_4\), filtered, and the solvent was removed via rotary evaporation to afford 5a (0.244 g, 0.794 mmol) as a brown oil in 99% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.48 (dd, \( J = 4.6, 1.5 \) Hz, 2 H), 7.10 (dd, \( J = 4.6, 1.5 \) Hz, 2 H), 2.86 (t, \( J = 7.3 \) Hz, 2 H), 2.59 (t, \( J = 7.8 \) Hz, 2 H), 2.32 (s, 3 H), 1.65-1.59 (m, 2 H), 1.56 (p, \( J = 7.1 \) Hz, 2 H) 1.36-1.24 (m, 14 H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 196.1, 151.7, 149.7, 123.9, 35.2, 30.6, 30.3, 29.5, 29.46, 29.43, 29.37, 29.17, 29.15, 29.09, 28.8 (2). IR (liquid film, cm\(^{-1}\)): 2926, 2854, 1692, 1602, 1464, 1415, 1353, 1134, 1109. HRMS calcd for C\(_{18}\)H\(_{29}\)NOS\(^+\) [M + H]\(^+\): 308.2043, found: 308.2062.
1,2-Bis(11-(pyridin-4-yl)undecyl)disulfide (6a). Compound 5a (0.124 g, 0.403 mmol) was dissolved in a mixture of THF (5 mL), methanol (5 mL), and water (5 mL). Potassium hydroxide (0.068 g, 1.21 mmol) was added and the reaction was allowed to stir overnight open to the atmosphere. The pH of the reaction was adjusted to ~6-7 with 1 M HCl and extracted with CH₂Cl₂ (×3). The combined organic layers were then dried with MgSO₄, filtered, and the solvent was removed via rotary evaporation to afford 6a (0.102 g, 0.193 mmol) as a yellow oil in 96% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.48 (dd, J = 4.4, 1.5 Hz, 4 H, ArH), 7.10 (dd, J = 4.4, 1.5 Hz, 4 H), 2.68 (t, J = 7.4 Hz, 4 H), 2.59 (t, J = 7.8 Hz, 4 H), 1.70-1.58 (m, 8 H), 1.40-1.24 (m, 28 H). ¹³C NMR (125 MHz, CDCl₃) δ 151.7, 149.6, 123.9, 39.2, 35.2, 30.3, 29.53, 29.48, 29.47, 29.39, 29.22, 29.21, 29.18, 28.5. IR (liquid film, cm⁻¹): 2925, 2853, 1602, 1558, 1463, 1415, 1265, 1219. HRMS calcd for C₃₂H₅₂N₂S₂H⁺ [M + H]⁺: 529.3645, found: 529.3659.
Dimethyl 7′-(4-undecyl)-8a′H-spiro[fluorene-9,1′-indolizine]-2′,3′-dicarboxylate disulfide (DHI-5). Linker 5a (0.010 g, 0.019 mmol) and dimethyl spiro[cycloprop[2]ene-1,9′-fluorene]-2,3-dicarboxylate (0.012 g, 0.038 mmol) were dissolved in CH₂Cl₂ (10 mL) in the dark at room temperature. After 3 h, the solvent was removed via rotary evaporation and the crude mixtures was purified via column chromatography (3:1 hexanes : EtOAc, Rᵣ = 0.34) affording DHI-5 (0.015 g, 0.013 mmol) as a yellow oil in 68% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.76-7.70 (m, 4 H), 7.57 (d, J = 7.3 Hz, 2 H), 7.46 (d, J = 7.6 Hz, 2 H), 7.40-7.29 (m, 6 H), 7.20 (dt, J = 7.6, 1.1 Hz, 2 H) 6.40 (d, J = 7.6 Hz, 2 H), 5.45 (s, 2 H), 5.08 (dd, J = 7.6, 1.5 Hz, 2 H), 4.14-4.13 (m, 2 H), 3.99 (s, 6 H), 3.26 (s, 6 H), 2.67 (t, J = 7.4 Hz, 4 H), 1.82-1.63 (m, 8 H), 1.40-0.94 (m, 32 H). ¹³C NMR (125 MHz, CDCl₃) δ 163.9, 162.3, 147.5, 146.9, 142.8, 141.8, 140.3, 136.0, 128.2, 128.0, 127.5, 127.0, 124.8, 124.0, 123.5, 119.9, 119.6, 112.5, 108.5, 107.5, 70.0, 64.4, 53.2, 50.9, 39.2, 34.7, 29.6, 29.51, 29.48, 29.37, 29.26, 29.24, 28.7, 28.6, 28.1. IR (KBr, cm⁻¹): 3017, 2926, 2853, 1742, 1700, 1645, 1598, 1559, 1436,
1399, 1267, 1227, 1191, 1137, 1092. HRMS calcd for C_{70}H_{80}N_{2}O_{8}S_{2}Na^+ [M + Na]^+:
1163.5248, found: 1163.5265.

(Hex-5-enyloxy)trimethylsilane (1b). Pyridine (2 mL) and hexamethyldisilazane (0.42 mL, 2.0 mmol) were added to 5-hexen-1-ol (0.050 g, 0.50 mmol) in a round bottom flask. Chlorotrimethylsilane (0.07 mL, 0.55 mmol) was then added dropwise to the reaction and the resulting mixture was allowed to stir for 30 min at room temperature. The reaction was quenched with water and extracted with CH_2Cl_2 (×3). The combined organic layers were dried with MgSO_4 and filtered. The CH_2Cl_2 was removed via rotary evaporation and the product was separated from the excess pyridine with a silica plug (4:1 hexanes : EtOAc) to afforded 1b (0.077 g, 0.45 mmol) as a clear oil in 90% yield. 

\[ \text{^{1}H NMR (500 MHz, CDCl}_3 \delta 5.85-5.77 (m, 1 H), 5.03-4.98 (m, 1 H), 4.96-4.93 (m, 1 H) 3.58 (t, J = 6.7 Hz, 2 H), 2.09-2.04 (m, 2 H), 1.58-1.51 (m, 2 H), 1.46-1.39 (m, 2 H), 0.11 (s, 9 H).} \]

\[ \text{^{13}C NMR (125 MHz, CDCl}_3 \delta 138.9, 114.4, 62.5, 33.5, 32.2, 25.2, -0.5. IR (liquid film, cm}^{-1})): 3079, 2956, 2937, 2862, 1733, 1642, 1457, 1442, 1416, 1387, 1251, 1100.} \]

4-(6-(Trimethylsilyloxy)hexyl)pyridine (2b). At 0 °C, 9-borabicyclo[3.3.1]nonane (0.5 M in THF, 20.8 mL, 10.4 mmol) was added to 1b (0.595 g, 3.45 mmol). The mixture was brought to room temperature for 2 h and was transferred via a sealed syringe to a sealed tube that contained 4-iodopyridine (0.779 g, 3.80 mmol), Pd(PPh_3)_4 (0.399 g, 0.345 mmol), DMF (10 mL) and K_2CO_3 (3 M in H_2O, 5.75 mL). The resulting mixture
was allowed to stir for 2 h at 70 °C. After cooling to room temperature, the mixture was diluted with water and extracted with diethyl ether (×3). The ether layer was then washed with water (×5), the combined organic layers were dried with MgSO₄, filtered, and the solvent was removed via rotary evaporation. The crude mixture was then purified via a silica plug (1:1 hexanes : EtOAc, + 10% triethylamine) to remove excess salts and further purified via column chromatography (1:1 hexanes : EtOAc, Rᵣ = 0.42) to afford 2b (0.272 g, 1.08 mmol) as a yellow oil in 31% yield. 

**1H NMR (500 MHz, CDCl₃)** δ 8.48 (dd, J = 4.4, 1.5 Hz, 2 H), 7.10 (dd, J = 4.4, 1.5 Hz, 2 H), 3.56 (t, J = 6.6 Hz, 2 H), 2.60 (t, J = 7.8 Hz, 2 H), 1.68-1.60 (m, 2 H), 1.56-1.50 (m, 2 H), 1.38-1.32 (m, 2 H), 0.10 (s, 9 H).

**13C NMR (125 MHz, CDCl₃)** δ 151.6, 149.7, 123.9, 62.5, 35.2, 32.6, 30.3, 29.0, 25.6, -0.5. IR (liquid film, cm⁻¹): 3069, 3026, 2935, 2860, 1603, 1558, 1496, 1436, 1415, 1388, 1250, 1219, 1097, 1034. HRMS calcd for C₁₄H₂₅NOSiH⁺ [M + H]⁺: 252.1778, found: 252.1783.

**6-(Pyridin-4-yl)hexan-1-ol (3b).** In a sealed tube, cesium fluoride (0.677 g, 4.46 mmol) was added to 2b (0.224 g, 0.891 mmol) and mixture was dissolved in 1,2-dimethoxyethane (10 mL). The reaction was heated to 70 °C and while stirring for 16 h. After the reaction was cooled to room temperature, the mixture was poured into water and extracted with CH₂Cl₂ (×3). The combined organic layers were dried with MgSO₄, filtered, and the solvent was removed via rotary evaporation to afford the crude alcohol which was taken on to the next step without purification.
**4-(6-Bromohexyl)pyridine (4b).** In a round bottom flask open to the atmosphere, triphenylphosphine (0.435 g, 1.66 mmol) was dissolved in CH$_2$Cl$_2$ (5 mL). The solution was brought to 0 °C and bromine (0.09 mL, 1.66 mmol) was then added dropwise generating a dark orange mixture. Excess triphenylphosphine was then added until the color of the solution changed to a light yellow. The crude alcohol (0.198 g, 1.11 mmol), dissolved in CH$_2$Cl$_2$ (1 mL), was then added at 0 °C. The reaction was allowed to stir for 15 min at 0 °C, and then at room temperature for 1 h. After an hour, the reaction was diluted with diethyl ether (20 mL), extracted with water (×2), and with 1 M HCl (×2). The combined aqueous extracts were washed with ether (×2) and then the aqueous layer was made basic (pH 13-14) with 5 M NaOH. The basified aqueous layer was then extracted with ether (×5). These ether layers were dried with MgSO$_4$, filtered, and the solvent was removed via rotary evaporation to afford pure 4b (0.202 g, 0.834 mmol) as a yellow oil in 94% yield (over two steps). $^{1}$H NMR (500 MHz, CDCl$_3$) δ 8.49 (d, $J = 5.6$ Hz, 2 H), 7.10 (d, $J = 5.6$ Hz, 2 H), 3.40 (t, $J = 6.8$ Hz, 2 H), 2.61 (t, $J = 7.7$ Hz, 2 H), 1.89-1.83 (m, 2 H), 1.65 (p, $J = 7.6$ Hz, 2 H), 1.51-1.43 (m, 2 H), 1.40-1.33 (m, 2 H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 151.5, 149.6, 123.9, 35.1, 33.8, 32.6, 30.1, 28.3, 27.9. IR (liquid film, cm$^{-1}$): 3419, 3025, 2934, 2858, 1640, 1602, 1596, 1558, 1516, 1466, 1438, 1416, 1257, 1220, 1173, 1119, 1069. HRMS calcd for C$_{11}$H$_{16}$BrNH$^+$ [M + H]$^+$: 242.0539, found: 242.0541.
**S-6-(pyridine-4-yl)hexyl ethanethioate (5b).** Potassium thioacetate (0.024 g, 0.21 mmol) was dissolved in dry DMF (2 mL) and added to 4b (0.017 g, 0.070 mmol) at 0 °C. The mixture was brought to room temperature and stirred for an additional 3 h. The reaction was diluted with water, extracted with ether (×3), and the ether layers were washed with water (×5). The combined organic layers were dried with MgSO\(_4\), filtered, and the solvent was removed via rotary evaporation to afford 5b (0.015 g, 0.063 mmol) as a yellow oil in 90% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 8.48 (d, \(J = 5.6\) Hz, 2 H), 7.09 (d, \(J = 5.6\) Hz, 2 H), 2.86 (t, \(J = 7.3\) Hz, 2 H), 2.59 (t, \(J = 7.8\) Hz, 2 H), 2.32 (s, 3 H), 1.66-1.54 (m, 4 H), 1.57 (p, \(J = 7.8\) Hz, 2 H) 1.43-1.31 (m, 4 H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 195.9, 151.5, 149.7, 123.9, 35.1, 30.6, 30.1, 29.4, 29.0, 28.6, 28.5, IR (liquid film, cm\(^{-1}\)): 2930, 2857, 1691, 1602, 1558, 1462, 1415, 1354, 1135, 1070.

**1,2-Bis(6-(pyridine-4-yl)hexyl)disulfide (6b).** Compound 5b (0.032 g, 0.13 mmol) was dissolved in a mixture of THF (2 mL), methanol (2 mL), and water (2 mL). Potassium hydroxide (0.022 g, 0.39 mmol) was added and the reaction was allowed to stir overnight, open to the atmosphere. The following day, the pH of the reaction was adjusted to ~6-7 with 1 M HCl (aq) and extracted with CH\(_2\)Cl\(_2\) (×3). The combined organic layers were
then washed with water (20 mL) once that contained triethylamine (2 mL), dried with MgSO₄, and filtered. The solvent was removed via rotary evaporation to afford 6b (0.023 g, 0.059 mmol) as a yellow oil in 92% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.48 (d, J = 6.1 Hz, 4 H), 7.09 (d, J = 6.1 Hz, 4 H), 2.66 (t, J = 7.3 Hz, 4 H), 2.60 (t, J = 7.8 Hz, 4 H), 1.70-1.61 (m, 8 H), 1.45-1.32 (m, 8 H). ¹³C NMR (125 MHz, CDCl₃) δ 151.5, 149.7, 123.9, 38.9, 35.1, 30.1, 29.0, 28.7, 28.2. IR (liquid film, cm⁻¹): 2920, 2855, 1602, 1558, 1462, 1438, 1415, 1219. HRMS calcd for C₂₂H₃₂N₂S₂H⁺ [M + H]⁺: 389.2080, found: 389.2092.

Dimethyl 7′-(4-hexyl)-8a'H-spiro[fluorene-9,1′-indolizine]-2′,3′-dicarboxylate disulfide (DHI-6). Linker 6b (0.075 g, 0.193 mmol) and dimethyl spiro[cycloprop[2]ene-1,9′-fluorene]-2,3-dicarboxylate (0.118 g, 0.386 mmol) were dissolved in CH₂Cl₂ (5 mL) in the dark at room temperature. After allowing the reaction to proceed for 4 h, the solvent was removed by rotary evaporation and the reaction mixture was purified via column chromatography (3:2 hexanes : EtOAc, Rᵣ = 0.43) affording DHI-6 (0.123 g, 0.123 mmol) as a yellow oil in 64% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.73-7.70 (m, 4 H), 7.57 (d, J = 7.3 Hz, 2 H), 7.45 (d, J = 7.3 Hz, 2 H),
7.39-7.29 (m, 6 H), 7.21(dt, J = 7.7, 0.5 Hz, 2 H), 6.40 (d, J = 7.6 Hz, 2 H), 5.45 (s, 2 H), 5.06 (dd, J = 7.4, 1.3 Hz, 2 H), 4.13 (s, 2 H), 3.99 (s, 6 H) 3.26 (s, 6 H), 2.59 (t, J = 7.3 Hz, 4 H), 1.82-1.68 (m, 4 H), 1.58-1.51 (m, 4 H), 1.23-1.12 (m, 8 H), 1.08-0.96 (m, 4 H).

13C NMR (125 MHz, CDCl3) δ 163.9, 162.3, 147.4, 146.8, 142.7, 141.7, 140.3, 135.7, 128.2, 128.0, 127.5, 127.0, 124.7, 124.1, 123.5, 119.9, 119.6, 112.5, 108.6, 107.3, 69.9, 64.4, 53.2, 51.0, 39.0, 34.5, 29.0, 28.2, 28.1, 27.8. IR (KBr, cm⁻¹): 3017, 2927, 2854, 1743, 1699, 1645, 1598, 1559, 1435, 1397, 1266, 1227, 1189, 1137, 1087. HRMS calcd for C₆₀H₆₀N₂O₈S₂Na⁺ [M + Na⁺]: 1023.3683, found: 1023.3697.

DHI 1 (Dimethyl 7′-((4-(acetylthio)phenyl)ethynyl)-8a'H-spiro[fluorene-9,1′-indolizine]-2',3'-dicarboxylate). Compounds dimethyl spiro[cycloprop[2]ene-1,9′-fluorene]-2,3-dicarboxylate (0.200 g, 0.652 mmol), 11 (0.165 g, 0.652 mmol), and THF (40 mL) were added to a flask according to the general DHI procedure. The product was isolated via column chromatography (3:2 hexanes : EtOAc, Rf = 0.51) to afford DHI-1 (0.247 g, 0.441 mmol) in 68 % yield as a yellow oil. 1H NMR (300 MHz, CDCl3) δ 7.74 (d, J = 7.5 Hz, 1 H, ArH), 7.72 (d, J = 6.9 Hz, 1 H, ArH), 7.56 (d, J = 7.5 Hz, 1 H, ArH), 7.51 (d, J = 7.5 Hz, 1 H, ArH), 7.39 (t, J = 6.9 Hz, 2 H, ArH) 7.35-7.27 (m, 6 H, ArH), 6.51 (d, J = 7.5 Hz, 1 H, -CH=CH-NR₂), 5.54 (d, J = 2.7 Hz, 1 H, -C=CH-), 5.27 (dd, J = 7.5, 1.5 Hz, 1 H, -CH=CH-NR₂), 4.83-4.80 (m, 1 H, CHR₂(NR₂)), 4.00 (s, 3 H -CO₂CH₃), 3.27 (s, 3 H, -CO₂CH₃), 2.38 (s, 3 H, -SC(=O)CH₃). 13C NMR (75 MHz,
CDCl$_3$ δ 193.6 (-SC(=O)CH$_3$), 163.8 (-CO$_2$CH$_3$), 162.1 (-CO$_2$CH$_3$), 146.9, 146.5, 142.0, 141.9, 140.6, 134.3, 132.3, 128.8, 128.5, 128.3, 127.9, 127.6, 125.2, 124.7, 124.1, 123.7, 121.9, 120.3, 120.0, 119.3, 110.1, 106.2, 89.3, 88.3, 69.9, 64.1, 53.6 (-CO$_2$CH$_3$), 51.3 (-CO$_2$CH$_3$), 30.5 (-SC(=O)CH$_3$).

IR (KBr, cm$^{-1}$): 2950, 2925, 2852, 1742, 1704, 1623, 1595, 1547, 1449, 1436, 1384, 1355, 1328, 1306, 1258, 1227. HRMS calcd for C$_{34}$H$_{25}$NO$_5$S: 560.1526, found: 560.1525.

Dimethyl 8'-amino-8a'H-spiro[fluorene-9,1'-indolizine]-2',3'-dicarboxylate (8'-DHI-7). Dimethyl spiro[cycloprop[2]ene-1,9'-fluorene]-2,3-dicarboxylate (0.043 g, 0.14 mmol), 3-aminopyridine (0.13 g, 0.14 mmol), and CH$_2$Cl$_2$ (5 mL) were added to a round bottom flask according to the general DHI procedure and stirred for 5 h. 8'-DHI-7 (0.050 g, 0.12 mmol) was generated in 86 % yield as an orange oil. $^1$H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.78-7.75 (m, 2 H), 7.66 (d, $J = 7.6$ Hz, 1 H), 7.52 (d, $J = 7.6$ Hz, 1 H), 7.46-7.37 (m, 3 H), 7.27 (dt, $J = 7.4$, 1.1 Hz, 1 H), 6.09 (d, $J = 7.5$ Hz, 1 H), 5.58 (s, 1 H), 5.23 (t, $J = 6.8$ Hz, 1 H), 4.73 (dd, $J = 6.4$, 2.0 Hz, 1 H), 3.95 (s, 3 H), 3.27 (s, 3 H), 2.33 (s, 2 H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 164.0, 162.7, 148.2, 147.6, 143.9, 141.2, 139.7, 136.9, 128.8, 128.5, 128.1, 127.8, 124.2, 124.1, 120.4, 120.3, 115.6, 107.2, 95.12, 95.10, 70.1, 64.2, 53.4, 51.0. IR (liquid film, cm$^{-1}$): 3361, 2952, 1742, 1691, 1642, 1575, 1438, 1390, 1348, 1301, 1242, 1191, 1147, 1127, 1105.
**DHI-8s.** Dimethyl spiro[cycloprop[2]ene-1,9′-fluorene]-2,3-dicarboxylate (0.254 g, 0.83 mmol), 3-methoxypyridine (0.091 g, 0.83 mmol), and CHCl₃ (40 mL) were added to a round bottom flask according to the general DHI procedure and stirred for 5 h. The product, 8′-DHI-8 (0.285 g, 0.69 mmol) was isolated via column chromatography (100 % CH₂Cl₂, Rf = 0.53) in 83% yield as a yellow oil.

**6′-Isomer:** Dimethyl 6′-methoxy-8a'H-spiro[fluorene-9,1′-indolizine]-2′,3′-dicarboxylate (6′-DHI-8) could not be isolated via column chromatography. Indicative 6′-isomer peaks allowing for quantification assigned from crude mixture; ¹H NMR (500 MHz, CDCl₃) δ 5.93 (s, 1 H), 5.69-5.65 (m, 1 H), 5.38-5.36 (m, 1 H), 4.66-4.63 (m, 1 H), 4.01 (s, 3 H), 3.56 (s, 3 H).

**8′-Isomer:** Dimethyl 8′-methoxy-8a'H-spiro[fluorene-9,1′-indolizine]-2′,3′-dicarboxylate (8′-DHI-8) ¹H NMR (500 MHz, CDCl₃) δ 7.72-7.69 (m, 2 H), 7.55 (d, J = 7.3 Hz, 1 H), 7.44 (d, J = 7.3 Hz, 1 H), 7.36 (dt, J = 7.4, 1.1 Hz, 1 H), 7.34-7.29 (m, 2 H), 7.18 (dt, J = 7.4, 1.0 Hz, 1 H), 6.14 (d, J = 7.3 Hz, 1 H), 5.58 (s, 1 H), 5.20 (t, J = 6.8 Hz, 1 H), 4.77 (dd, J = 6.6, 2.0 Hz, 1 H), 3.98 (s, 3 H), 3.25 (s, 3 H), 2.75 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃) δ 164.1, 162.6, 150.6, 149.0, 147.8, 144.2, 142.1, 140.8, 128.1, 127.7, 127.4, 126.8, 123.20, 123.15, 119.8, 119.7, 117.7, 108.6, 104.9, 93.5, 70.0, 64.8, 54.5, 53.4, 51.1. IR (liquid film, cm⁻¹): 3015, 2952, 2929, 2852, 1745, 1706, 1692, 1643, 1579,
DHI-9s. Dimethyl spiro[cycloprop[2]ene-1,9'-fluorene]-2,3-dicarboxylate (0.062 g, 0.20 mmol), 3-picoline (0.019 g, 0.20 mmol), and CHCl₃ (10 mL) were added to a round bottom flask according to the general DHI procedure and stirred for 4 h. Reactants and side products were removed via column chromatography but the 6' and 8' isomers were inseparable (1:1 hexanes : EtOAc, Rₚ = 0.72). The mixture of the 6' (16%) and 8' (84%) isomers of DHI-9s (0.077 g, 0.19 mmol) was analyzed via NMR and isolated in 95% combined yield, as a yellow oil.

Selective indicative ¹H NMR (500 MHz, CDCl₃) peaks for 6'-isomer: Dimethyl 6'-methyl-8a'H-spiro[fluorene-9,1'-indolizine]-2',3'-dicarboxylate (6'-DHI-9). δ 6.21-6.19 (m, 1 H, -C=CH-NR₂), 5.40-5.38 (m, 1 H, CHR₂(NR₂)), 4.52 (d, J = 10.0 Hz, 1 H, -C=CH), 4.01 (s, 3 H, CO₂CH₃), 3.26 (s, 3 H, CO₂CH₃), 1.73 (s, 3 H, -CH=CHCH₃).

Selective definitive ¹H NMR (500 MHz, CDCl₃) peaks for 8'-isomer: Dimethyl 8'-methyl-8a'H-spiro[fluorene-9,1'-indolizine]-2',3'-dicarboxylate (8'-DHI-9). 6.32 (d, J = 7.3 Hz, 1 H, -C=CH-NR₂), 5.45-5.41 (m, 1 H, -CH=CH-CH=C(CH₃)-), 5.16-5.12 (m, 1 H, -CH=CH-CH=C(CH₃)-), 3.98 (s, 3 H, CO₂CH₃), 3.24 (s, 3 H, CO₂CH₃), 0.63 (s, 3 H, HC=CHCH₃). IR for mixture (liquid film, cm⁻¹): 3063, 3040, 3016, 2951, 2926, 2853,
1743, 1703, 1649, 1598, 1571, 1448, 1437, 1428, 1391, 1344, 1302, 1260, 1227, 1193, 1147, 1106.

**DHI-10s.** Dimethyl spiro[cycloprop[2]ene-1,9'-fluorene]-2,3-dicarboxylate (0.064 g, 0.21 mmol), 3-iodopyridine (0.043 g, 0.21 mmol), and CH$_2$Cl$_2$ (10.5 mL) were added to a round bottom flask according to the general DHI procedure and stirred for 14 h. The 8'-isomer was isolated via column chromatography (3:1 hexanes : EtOAc). The 6'-isomer was then separated from the reagents and side products via a second column (100 % CH$_2$Cl$_2$). **DHI-10** (0.070 g, 0.14 mmol) was obtained in 67 % combined yield, as a yellow oil.

**6'-Isomer:** Dimethyl 6'-iodo-8a'H-spiro[fluorene-9,1'-indolizine]-2',3'-dicarboxylate (**6'-DHI-10**). (0.008 g, 100 % CH$_2$Cl$_2$, R$_f$ = 0.63). $^1$H NMR (500 MHz, CD$_3$CN) δ 7.82-7.78 (m, 2 H), 7.59 (d, $J$ = 7.3 Hz, 1 H), 7.44-7.40 (m, 3 H), 7.35 (dt, $J$ = 7.5, 1.1 Hz, 1 H), 7.30-7.27 (m, 1 H), 6.94-6.93 (m, 1 H), 5.66 (ddd, $J$ = 10.0, 2.6, 1.0 Hz, 1 H), 5.54-5.52 (m, 1 H), 4.28 (ddd, $J$ = 10.1, 2.0, 1.0 Hz, 1 H), 3.96 (s, 3 H), 3.28 (s, 3 H), $^{13}$C NMR (125 MHz, CDCl$_3$) δ 163.7, 161.9, 146.9, 145.6, 141.91, 141.87, 140.6, 131.0, 129.97, 129.95, 128.8, 128.5, 128.0, 127.4, 124.9, 123.7, 120.3, 120.0, 119.0, 109.8, 68.2, 65.1, 64.3, 51.4. IR (liquid film, cm$^{-1}$): 2951, 2925, 2854, 1743, 1703, 1596, 1546, 1438, 1416, 1369, 1324, 1306, 1262, 1229, 1189, 1166, 1131, 1107, 1074, 1047.
**8'-Isomer:** Dimethyl 8'-iodo-8a'H-spiro[fluorene-9,1'-indolizine]-2',3'-dicarboxylate (8'-DHI-10) (0.062 g, 3:1 hexanes : EtOAc, Rf = 0.68). $^1$H NMR (500 MHz, CD$_3$CN) δ 7.79-7.75 (m, 2 H), 7.58 (d, J = 7.6 Hz, 1 H), 7.49 (d, J = 7.6 Hz, 1 H), 7.46-7.41 (m, 2 H), 7.36 (dt, J = 7.5, 1.1 Hz, 1 H), 7.29 (dt, J = 7.4, 1.0 Hz, 1 H), 6.62 (d, J = 7.3 Hz, 1 H), 6.48 (dd, J = 6.2, 2.3 Hz, 1 H), 5.89 (d, J = 2.5 Hz, 1 H), 4.97-4.94 (m, 1 H), 3.93 (s, 3 H), 3.25 (s, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 163.5, 161.9, 147.3, 145.7, 143.4, 142.3, 142.0, 135.8, 128.8, 128.2, 127.4, 127.2, 125.2, 124.2, 123.5, 120.01, 119.98, 111.2, 103.5, 83.5, 72.2, 66.2, 53.3, 51.1. IR (liquid film, cm$^{-1}$): 2952, 2925, 2854, 1743, 1710, 1598, 1543, 1448, 1436, 1427, 1384, 1356, 1295, 1254, 1227, 1191, 1147, 1125, 1106.

![8'-DHI-11](image)

**DHI-11s.** Dimethyl spiro[cycloprop[2]ene-1,9'-fluorene]-2,3-dicarboxylate (0.150 g, 0.49 mmol), 3-chloropyridine (0.056 g, 0.49 mmol), and CHCl$_3$ (22 mL) were added to a round bottom flask according to the general DHI procedure and stirred for 9 h. The crude mixture was first passed through a silica plug (CH$_2$Cl$_2$) and then the two eluted isomers were separated via column chromatography (3:1 hexanes : EtOAc) to afford DHI-10s (0.116 g, 0.28 mmol) in 57 % combined yield, as a yellow oil.

**6'-Isomer:** Dimethyl 6'-chloro-8a'H-spiro[fluorene-9,1'-indolizine]-2',3'-dicarboxylate (6'-DHI-10). (0.026 g, Rf = 0.40). $^1$H NMR (500 MHz, CD$_3$CN) δ 7.82-
7.79 (m, 2 H), 7.60 (d, J = 7.6 Hz, 1 H), 7.44-7.40 (m, 3 H), 7.36 (t, J = 7.4 Hz, 1 H),
7.28 (t, J = 7.4 Hz, 1 H), 6.76 (s, 1 H), 5.69 (d, J = 10.0 Hz, 1 H), 5.52-5.50 (m, 1 H),
4.43 (d, J = 10.3 Hz, 1 H), 3.96 (s, 3 H), 3.28 (s, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$
163.7, 161.9, 146.9, 146.2, 142.0, 141.8, 140.6, 128.8, 128.5, 128.0, 127.4, 126.2, 124.8,
123.7, 122.3, 120.3, 120.0, 118.9, 112.2, 109.6, 69.1, 64.2, 53.6, 51.3. IR (liquid film,
$cmt^{-1}$): 2952, 2925, 2854, 1743, 1705, 1596, 1558, 1439, 1421, 1392, 1369, 1324, 1303,
1262, 1228, 1131, 1108, 1069.

8'-Isomer: Dimethyl 8'-chloro-8a'H-spiro[fluorene-9,1'-indolizine]-2',3'-
dicarboxylate (8'-DHI-10). (0.090 g, $R_f$ = 0.22): $^1$H NMR (500 MHz, CD$_3$CN) $\delta$
7.79-7.76 (m, 2 H), 7.60 (d, J = 7.3 Hz, 1 H), 7.48 (d, J = 7.3 Hz, 1 H), 7.44-7.39 (m, 2 H),
7.35 (dt, J = 7.4, 1.1 Hz, 1 H), 7.28 (dt, J = 7.4, 1.0 Hz, 1 H), 6.55 (d, J = 7.3 Hz, 1 H),
5.90-5.84 (m, 2 H), 5.17 (t, J = 7.0 Hz, 1 H), 3.94 (s, 3 H), 3.26 (s, 3 H). $^{13}$C NMR (125
MHz, CDCl$_3$) $\delta$ 163.7, 161.1, 147.7, 146.2, 142.8, 142.5, 141.4, 128.8, 128.2, 127.5,
127.3, 124.0, 123.8, 123.4, 123.2, 123.1, 120.2, 120.1, 111.1, 102.5, 71.7, 65.5, 53.5,
51.3. IR (liquid film, $cm^{-1}$): 2953, 2925, 2854, 1743, 1711, 1637, 1600, 1560, 1448, 1437,
1361, 1340, 1294, 1256, 1227, 1192, 1148, 1127, 1107, 1086.

DHI-12s. Dimethyl spiro[cycloprop[2]ene-1,9'-fluorene]-2,3-dicarboxylate (0.038 g,
0.12 mmol), (4-thioacetylphenyl)(3-pyridyl)acetylene (0.030 g, 0.12 mmol), and THF (0
mL) were added to a round bottom flask according to the general DHI procedure and stirred for 15 h. The two isomers were isolated via column chromatography (2:1 hexanes : EtOAc) to afford DHI-12 (0.062 g, 0.11 mmol) in 92% combined yield, as a yellow oil.

**6’-Isomer:** Dimethyl 6’-((4-(acetylthio)phenyl)ethynyl)-8a’H-spiro[fluorene-9,1’-indolizine]-2’,3’-dicarboxylate (6’-DHI-12) (0.034 g, Rf = 0.53). ¹H NMR (500 MHz, CD₃CN) δ 7.84-7.81 (m, 2 H), 7.62 (d, J = 7.8 Hz, 1 H), 7.46-7.41 (m, 5 H), 7.39-7.35 (m, 3 H), 7.30 (dt, J = 7.6, 1.0 Hz, 1 H), 7.05 (d, J = 1.0 Hz, 1 H), 5.78 (dd, J = 10.0, 2.6, 1.0 Hz, 1 H), 5.58-5.56 (m, 1 H), 4.45-4.42 (m, 1 H), 3.99 (s, 3 H), 3.31 (s, 3 H), 2.39 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃) δ 193.8, 163.7, 161.8, 146.6, 145.6, 141.9, 141.8, 140.6, 134.4, 131.8, 130.0, 128.8, 128.6, 128.0, 127.5, 127.4, 125.6, 125.0, 124.8, 123.7, 120.4, 120.1, 117.0, 112.2, 99.9, 89.8, 88.8, 69.1, 64.4, 53.7, 51.5, 30.4. IR (liquid film, cm⁻¹): 2952, 2924, 2853, 1742, 1707, 1632, 1559, 1551, 1488, 1438, 1421, 1373, 1309, 1264, 1191, 1121, 1105.

**8’-Isomer:** Dimethyl 8’-((4-(acetylthio)phenyl)ethynyl)-8a’H-spiro[fluorene-9,1’-indolizine]-2’,3’-dicarboxylate (8’-DHI-12) (0.028 g, Rf = 0.40). ¹H NMR (500 MHz, CD₃CN) δ 7.76 (d, J = 7.1 Hz, 1 H), 7.69 (d, J = 7.3 Hz, 1 H), 7.64 (d, J = 7.1 Hz, 1 H), 7.49 (d, J = 7.6 Hz, 1 H), 7.40 (dt, J = 7.4, 1.1 Hz, 1 H), 7.36 (dt, J = 7.5, 1.2 Hz, 1 H), 7.32 (dt, J = 7.4, 1.1 Hz, 1 H), 7.27-7.24 (m, 3 H), 6.83 (dd, J = 6.5, 1.8 Hz, 2 H), 6.70 (d, J = 7.3 Hz, 1 H), 6.19 (dd, J = 6.1, 2.2 Hz, 1 H), 5.77-5.74 (m, 1 H), 5.34 (dd, J = 7.3, 6.3 Hz, 1 H), 3.96 (s, 3 H), 3.26 (s, 3 H), 2.39 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃) δ 193.8, 163.7, 162.2, 147.7, 145.8, 142.84, 142.77, 141.7, 133.7, 132.0, 131.3, 128.6, 128.1, 127.58, 127.55, 127.3, 126.3, 124.2, 124.1, 123.6, 120.17, 120.15, 111.8, 110.9,
104.1, 92.7, 87.9, 69.1, 64.7, 53.6, 51.3, 30.5. IR (liquid film, cm$^{-1}$): 2952, 2925, 2854, 1744, 1708, 1595, 1529, 1487, 1450, 1432, 1408, 1352, 1301, 1256, 1228, 1191, 1150, 1124, 1091, 1016.

DHI-13s. Dimethyl spiro[cycloprop[2]ene-1,9'-fluorene]-2,3-dicarboxylate (0.058 g, 0.19 mmol), 3-acetylpyridine (0.023 g, 0.19 mmol), and CHCl$_3$ (9.5 mL) were added to a round bottom flask according to the general DHI procedure and stirred for 2 h. The product was isolated via column chromatography (1:1 hexanes : EtOAc) to afford the two isomers of DHI-13 (0.064 g, 0.15 mmol) in 79 % combined yield, as a yellow oil.

6'-Isomer: Dimethyl 6'-acetyl-8a'H-spiro[fluorene-9,1'-indolizine]-2',3'-dicarboxylate (6'-DHI-13). (0.039 g, $R_f = 0.50$). $^1$H NMR (500 MHz, CD$_3$CN) $\delta$ 7.84-7.81 (m, 2 H), 7.61 (d, $J = 7.6$ Hz, 1 H), 7.57 (s, 1 H), 7.47-7.41 (m, 2 H), 7.40-7.35 (m, 2 H), 7.28 (t, $J = 7.6$ Hz, 1 H), 6.26 (dd, $J = 10.3$, 2.4 Hz, 1 H), 5.61-5.59 (m, 1 H), 4.35 (d, $J = 10.0$ Hz, 1 H), 4.00 (s, 3 H), 3.34 (s, 3 H), 2.20 (s, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 192.9, 163.1, 161.1, 145.6, 144.3, 141.8, 141.0, 140.5, 134.2, 128.9, 128.6, 127.9, 127.3, 124.5, 123.4, 121.9, 120.3, 120.1, 117.5, 116.8, 115.1, 69.4, 64.4, 53.6, 51.6, 25.1. IR (liquid film, cm$^{-1}$): 2953, 2927, 1741, 1731, 1650, 1630, 1611, 1556, 1535, 1438, 1376, 1315, 1287, 1259, 1212, 1184, 1132, 1109, 1066, 1037.
**8'-Isomer:** Dimethyl 8'-acetyl-8a'H-spiro[fluorene-9,1'-indolizine]-2',3'-dicarboxylate (8'-DHI-13). (0.025 g, R<sub>f</sub> = 0.55) ¹H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.70 (d, J = 7.6 Hz, 1 H), 7.67 (d, J = 7.6 Hz, 1 H), 7.55 (d, J = 7.1 Hz, 1 H), 7.50 (d, J = 7.3 Hz, 1 H), 7.40 (dt, J = 7.3, 1.2 Hz, 1 H) 7.37-7.30 (m, 2 H), 7.16 (dt, J = 7.3, 1.0 Hz, 1 H), 6.68 (d, J = 7.3 Hz, 1 H), 6.52-6.50 (m, 1 H), 6.01-5.99 (m, 1 H), 5.28-5.24 (m, 1 H) 3.97 (s, 3 H), 3.24 (s, 3 H), 1.48 (s, 3 H). ¹³C NMR (125 MHz, CDCl<sub>3</sub>) δ 193.9, 163.5, 161.9, 148.6, 144.9, 141.9, 141.8, 141.5, 131.6, 131.0, 129.3, 128.3, 127.5, 127.4, 126.1, 123.9, 122.1, 120.3, 119.5, 113.7, 101.7, 69.2, 65.7, 53.3, 51.2, 24.4. IR (liquid film, cm<sup>-1</sup>): 2953, 2925, 2853, 1743, 1714, 1665, 1610, 1535, 1449, 1439, 1383, 1354, 1295, 1271, 1227, 1149, 1127, 1105, 1042, 1004.

**3-Iodopyridine.** To a round bottom flask open to the atmosphere, paratoluene sulfonic acid (9.393 g, 49.38 mmol) was mixed with acetonitrile (60 mL) and was added to 3-aminopyridine (1.500 g, 16.46 mmol). The mixture was cooled to 10 ºC and an aqueous solution (10 mL) containing NaNO₂ (2.27 g, 32.92 mmol) and KI (6.831 g, 40.15 mmol) was added dropwise. The slurry was stirred for 10 min at 10 ºC and then brought to room temperature for 1 h. The reaction was brought to a pH (9-10) via 1 M NaHCO₃ (aq) and then decolorized from a dark brown to a light orange with 2 M Na₂S₂O₃ (aq). The reaction was then diluted and extracted (×3) with ethyl acetate. The combined organic layers were dried with MgSO₄, filtered, and the solvent was removed via rotary evaporation and column chromatography (2:1 hexanes : EtOAc, R<sub>f</sub> = 0.53) was used to isolate 3-iodopyridine (1.675 g, 8.171 mmol) in 48 % yield as an off white solid. MP 52-
53 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.85 (d, $J = 1.5$ Hz, 1 H), 8.56 (dd, $J = 4.9, 1.5$ Hz, 1 H), 8.03-8.00 (m, 1 H), 7.11 (ddd, $J = 8.1, 4.8, 0.9$ Hz, 1 H).$^{60}$

### 3-(Trimethylsilylethynyl)pyridine.

Pd(PPh$_3$)$_2$Cl$_2$ (0.086 g, 0.123 mmol), 3-iodopyridine (1.258 g, 6.137 mmol), CuI (0.047 g, 0.245 mmol), THF (12 mL), triethylamine (1.7 mL, 12.27 mmol), and TMSA (0.96 mL, 6.751 mmol) were subject to the general Sonogashira coupling procedure. The dark brown mixture was stirred for 12 h. The product was isolated by column chromatography (3:1 hexanes : EtOAc, $R_f = 0.45$) which afforded 3-(trimethylsilylethynyl)pyridine (0.872 g, 4.97 mmol) as a dark oil in 81% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.69 (d, $J = 1.2$ Hz, 1 H), 8.53 (dd, $J = 4.9, 1.7$ Hz, 1 H), 7.74 (dt, $J = 7.9, 1.8$ Hz, 1 H), 7.23 (ddd, $J = 7.9, 4.9, 0.9$ Hz, 1 H), 0.27 (s, 9 H).$^{61}$

### 3-Ethynylpyridine.

To a round bottom flask 3-(trimethylsilylethynyl)pyridine (1.000 g, 5.701 mmol) was dissolved in MeOH (9 mL) and CH$_2$Cl$_2$ (18 mL). Anhydrous KOH (0.640 g, 11.4 mmol) was added to the mixture which was then stirred for 1.5 h. The reaction was partitioned between CH$_2$Cl$_2$ and water, and the aqueous layer was further extracted two times (CH$_2$Cl$_2$). The combined organic solutions were then dried with MgSO$_4$, and the solvent was removed by rotary evaporation which afforded 3-ethynylpyridine (0.581 g, 5.63 mmol) as an off-white solid in 99% yield. $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) $\delta$ 8.68 (d, $J = 1.2$ Hz, 1 H), 8.58 (dd, $J = 4.8, 1.3$ Hz, 1 H), 7.89-7.86 (m, 1 H), 7.40 (ddd, $J = 7.8, 4.9, 1.0$ Hz, 1 H), 3.88 (s, 1 H).$^{62}$
Compound 4-iodophenyl thioacetate (0.167 g, 0.600 mmol), 3-ethynylpyridine (0.068 g, 0.660 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.013 g, 0.018 mmol), CuI (0.007 g, 0.036 mmol), THF (15 mL), and triethylamine (0.48 mL, 3.42 mmol) were subject to the general the Sonogashira coupling procedure. The dark brown mixture was stirred for 18.5 h. The product was isolated by column chromatography (1:2 hexanes : EtOAc, R$_f$ = 0.56) which afforded (4-thioacetylphenyl)(3-pyridyl)acetylene (0.030 g, 0.12 mmol) as an off white solid in 70% yield from recovered starting material. MP 95-98 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.77 (d, $J$ = 2.0 Hz, 1 H), 8.57 (dd, $J$ = 4.9, 1.5 Hz, 1 H), 7.82, (dt, $J$ = 7.9, 1.9 Hz, 1 H), 7.57 (dd, $J$ = 6.5, 1.8 Hz, 2 H), 7.42 (dd, $J$ = 6.5, 1.8 Hz, 2 H), 7.30 (dd, $J$ = 7.8, 4.9 Hz, 1 H), 2.45 (s, 3 H).

4-Iodopyridine. In a round bottom flask open to the atmosphere, 4-aminopyridine (6.00 g, 63.8 mmol) was dissolved in concentrated HBF$_4$ (50 mL). The mixture was then cooled to -10 °C. While maintaining this temperature, NaNO$_2$ (4.80 g, 69.6 mmol) was added (SLOWLY) to the mixture so that no nitric oxide (brown gas) could be seen. Previous reports state that the intermediate, 4-pyridyldiazonium tetrafluoroborate, decomposes at warmer temperatures (0 to 10 °C), hence, it is essential to keep the mixture at -10 °C when the sodium nitrite is added. The resulting solid was filtered (CAUTION! Do not let dry, reported to be explosive$^{64}$ and immediately transferred, scoop wise, to a solution containing 17.00 g (102.4 mmol) of KI dissolved in acetone (40 mL) and H$_2$O (60 mL). Note: if the precipitate was added too quickly the solution
bubbled over. The dark brown slurry was then decolorized to a lemon yellow with aqueous Na$_2$S$_2$O$_3$, and neutralized with aqueous Na$_2$CO$_3$. The resulting mixture was extracted with diethyl ether (4 × 100 mL), and the combined organics were washed once with Na$_2$S$_2$O$_3$. The organic layer was then dried with MgSO$_4$, and the diethyl ether was removed via rotary evaporation to afford an off white solid, 4-iodopyridine (8.45 g, 41.2 mmol) in 65 % yield. MP 98-99 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.28 (dd, $J = 4.8$, 1.5 Hz, 2 H), 7.69 (dd, $J = 4.5$, 1.5 Hz, 2 H).

4-(Trimethylsilylethynyl)pyridine. Compound 4-iodopyridine (2.00 g, 9.75 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.062 g, 0.088 mmol), CuI (0.200 g, 1.05 mmol), THF (20 mL), diisopropylamine (7.1 mL, 50.6 mmol), and TMSA (1.5 mL, 11 mmol) were subject to the general the Sonogashira coupling procedure. The dark brown mixture was stirred for 18 h. The product was isolated by column chromatography (1:1 hexanes : EtOAc, R$_f$ = 0.65) which afforded 4-(trimethylsilylethynyl)pyridine (1.32 g  7.53 mmol) as a dark oil in 77 % yield. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.56 (dd, $J = 4.5$, 1.5 Hz, 2 H), 7.31 (dd, $J = 4.5$, 1.5 Hz, 2 H), 0.27 (s, 9 H).

4-Ethynylpyridine. 4-(trimethylsilylethynyl)pyridine (0.750 g, 4.28 mmol) was dissolved in MeOH (10 mL) and CH$_2$Cl$_2$ (5 mL) in a round bottom flask. Anhydrous KOH (0.480 g, 8.56 mmol) was added to the mixture which was then stirred for 2.5 h. The reaction was partitioned between CH$_2$Cl$_2$ and water, and the aqueous layer was
further extracted two times (CH$_2$Cl$_2$). The combined organic solution was then dried with MgSO$_4$, and the solvent was removed by rotary evaporation which afforded 4-ethynylpyridine (0.296 g, 2.87 mmol) as an off-white solid in 67% yield. MP 92-94 °C. 

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.60 (dd, $J$ = 4.4, 1.7 Hz, 2 H), 7.35 (dd, $J$ = 4.4, 1.7 Hz, 2 H), 3.30 (s, 1 H).^66

(4-Thioacetylphenyl)(4-pyridyl)acetylene. 4-Iodophenyl thioacetate (0.464 g, 1.70 mmol), 4-ethynylpyridine (0.193 g, 1.87 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.048 g, 0.068 mmol), CuI (0.026 g, 0.14 mmol), THF (30 mL), and triethylamine (1.35 mL, 9.69 mmol) were added to a sealed tube as described by the general Sonogashira procedure. The reaction was stirred for 21 h. The crude mixture was isolated by column chromatography (1:2 hexanes:EtOAc, $R_f$ = 0.64) which afforded (4-thioacetylphenyl)(4-pyridyl)acetylene (0.165 g, 0.651 mmol) as an off-white solid in 42% yield. MP 85-86 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.62 (dd, $J$ = 4.7, 1.4 Hz, 2 H), 7.58 (dd, $J$ = 6.6, 1.7 Hz, 2 H), 7.43 (dd, $J$ = 6.6, 1.7 Hz, 2 H), 7.39 (dd, $J$ = 4.7, 1.4 Hz, 2 H), 2.45 (s, 3 H).^66

9-Fluorenone hydrazone. In a round bottom flask, 9-fluorenone (5.00 g, 27.7 mmol) was dissolved in 1-butanol (30 mL). 85% aqueous N$_2$H$_4$ (3.5 mL) was added to the solution which was refluxed for 4 h open to the atmosphere. The solution (still hot) was poured into methanol (72 mL), which immediately caused precipitation of a yellow solid.
The solution was cooled and vacuum filtered to give 9-fluorenone hydrazone (5.03 g, 25.9 mmol) in 93% yield as a pure yellow solid. MP 152-153 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.92 (d, $J = 7.2$ Hz, 1 H), 7.78 (d, $J = 7.5$ Hz, 1 H), 7.74, (d, $J = 7.8$ Hz, 1 H), 7.66 (d, $J = 7.1$ Hz, 1 H), 7.45 (td, $J = 7.5$, 1.2 Hz, 1 H), 7.39-7.29 (m, 3 H), 6.42 (s, br, 2 H).67

9-Diazofluorene. In a round bottom flask open to the atmosphere, 9-fluorenone hydrazone (10.00 g, 51.48 mmol) was dissolved in diethyl ether (770 mL). Potassium hydroxide (0.750 g, 13.4 mmol) and yellow mercuric oxide (11.15 g, 51.48 mmol) were added. The solution immediately turned orange and the mixture was sonicated three times during first 3 h of the reaction. The reaction was stirred vigorously overnight. The mixture was passed through a celite plug which removed the mercuric sludge from the blood red solution. Solvent was removed by rotary evaporation affording 9-diazofluorene (8.83 g, 45.9 mmol) as a red solid in 89% yield. MP 95-96 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.96 (d, $J = 7.8$ Hz, 2 H), 7.53 (d, $J = 7.2$ Hz, 2 H), 7.40 (td, $J = 7.5$, 1.2 Hz, 2 H), 7.33 (td, $J = 7.5$, 1.2 Hz, 2 H).67

Dimethyl spiro[cycloprop[2]ene-1,9'-fluorene]-2,3-dicarboxylate. In a round bottom flask, 9-diazofluorene (2.00 g, 10.4 mmol) was dissolved in benzene (100 mL) followed by the addition of dimethyl acetylenedicarboxylate (1.27 mL, 10.4 mmol). The reaction
was stirred in the dark for 13 h, until the formation of the pyrazole intermediate was complete. The solution was then refluxed for 1 h to generate the cyclopropene. Solvent was removed by rotary evaporation and column chromatography (4:1 CH$_2$Cl$_2$ : hexanes, $R_f = 0.54$) was used to isolate dimethyl spiro[cycloprop[2]ene-1,9'-fluorene]-2,3-dicarboxylate (2.40 g, 7.84 mmol) as a yellow solid in 75% yield. MP 147-149°C. $^1$H NMR (300 MHz, CD$_3$CN) $\delta$ 7.92 (d, $J = 7.5$ Hz, 2 H), 7.47 (dt, $J = 7.2$, 1.2 Hz, 2 H), 7.37 (dt, $J = 7.5$, 0.9 Hz, 2 H), 7.29 (d, $J = 7.5$ Hz, 2 H), 3.79 (s, 6 H).
APPENDIX A

$^1H$, $^{13}C$ NMR, AND IR SPECTROSCOPY OF SYNTHESIZED MOLECULES
APPENDIX B

SUPPLEMENTAL DATA FOR CHAPTER TWO
IR and UV-vis correlation study for DHI-6

Figure S1. DHI-6 spectroscopy in the solid-state (KBr pellet) (a) UV-vis and (b) IR of spiro (yellow curves) and zwitterion (green curves), after irradiation with 400 nm light for 1.5 minutes. The spectra in (a) and (b) are the same sample run consecutively.

Solution UV-vis of DHI-5 and 6 half-life data

Figure S2. Optical properties of (a) DHI-5 (9.2 × 10⁻⁵ M) and DHI-6 (9.9 × 10⁻⁵ M) were investigated via solution (dichloromethane) UV-vis. Spiro absorptions, that correspond to the π to π* transition, of DHI-5 and DHI-6 are observed at 385 nm and 386 nm respectively (yellow curves). When irradiated with 400 nm light for two minutes, both solutions generate new, zwitterionic, absorptions with a λ_max of 583 nm for DHI-5 and 589 nm for DHI-6. Inset is the natural log of the decay of the zwitterion absorption which follows the predicted first order rate. Solution half-lives are 52.9 and 58.7 seconds for DHI-5 and 6 respectively.
Table S1: Assignment of vibrations of spiro and zwitterionic forms of DHI.

<table>
<thead>
<tr>
<th>Observed&lt;sup&gt;a&lt;/sup&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Calculated&lt;sup&gt;b&lt;/sup&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spiro-DHI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1742</td>
<td>1742</td>
<td>C=O stretch</td>
</tr>
<tr>
<td>1700</td>
<td>1695</td>
<td>C=O stretch</td>
</tr>
<tr>
<td>1645br</td>
<td>1638</td>
<td>C=C stretch of dihydropyridine ring</td>
</tr>
<tr>
<td>1599</td>
<td>1574</td>
<td>in-phase stretch of C=C bonds in the dihydropyridine ring and the C=C bridge between ester groups</td>
</tr>
<tr>
<td>1559</td>
<td>1547</td>
<td>out-of-phase stretch of C=C bonds in the dihydropyridine ring and the C=C bond between ester groups</td>
</tr>
<tr>
<td>1448</td>
<td>1460</td>
<td>coupled C-N stretch and CH bend in the pyridine ring</td>
</tr>
<tr>
<td>1436</td>
<td>1445</td>
<td>CH bending - overlap of several bands</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td>DHI-zwitterion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1740</td>
<td>1728</td>
<td>pure C=O stretch of conformer 1</td>
</tr>
<tr>
<td>1718br</td>
<td>1710</td>
<td>pure C=O stretch of conformer 2</td>
</tr>
<tr>
<td>1643br</td>
<td>1651</td>
<td>coupled C=O stretch and C=C stretch of pyridine ring of conformer 1</td>
</tr>
<tr>
<td>1643br</td>
<td>1641</td>
<td>coupled C=O stretch and C=C stretch of pyridine ring of conformer 2</td>
</tr>
<tr>
<td>1603</td>
<td>1612</td>
<td>coupled C=O stretch and C=C stretch of pyridine ring</td>
</tr>
<tr>
<td>1559</td>
<td></td>
<td>IR band from the spiro-DHI molecules that were not converted to their zwitterionic form by the UV irradiation</td>
</tr>
<tr>
<td>1516sh</td>
<td>1528</td>
<td>coupled stretch of C=C bond to the fluorene and pyridinium ring</td>
</tr>
<tr>
<td>1506br</td>
<td>1519</td>
<td>coupled stretch of C=C bond to the fluorene and pyridinium ring stretch</td>
</tr>
<tr>
<td>1448sh</td>
<td>1467</td>
<td>coupled C-N stretch and CH bend of the pyridine ring</td>
</tr>
<tr>
<td>1448</td>
<td>1464</td>
<td>coupled C-N stretch and CH bend of the pyridine ring</td>
</tr>
<tr>
<td>1433</td>
<td>1430</td>
<td>CH bending - overlap of several bands</td>
</tr>
</tbody>
</table>

a: KBr pellet for DHI-5; br and sh suffixes denote broad and shoulder bands, respectively.
b: B3LYP/6-31G* wavenumbers that were scaled by a factor of 0.96.
c: These interpretations are based on the movies of the normal mode vibrations generated by the program Gaussview version 3.0.
Figure S3: Atom displacement in the spiro 1547 cm$^{-1}$ vibration. Yellow arrow denotes molecular dipole.
Figure S4: Atom displacement in the spiro 1574 cm$^{-1}$ vibration. Yellow arrow denotes molecular dipole
Figure S5: Atom displacement in the spiro 1638 cm$^{-1}$ vibration. Yellow arrow denotes molecular dipole.
Figure S6: Atom displacement in the zwitterion 1467 cm$^{-1}$ vibration. Yellow arrow denotes molecular dipole.
Figure S7: Atom displacement in the zwitterion 1519 cm$^{-1}$ vibration. Yellow arrow denotes molecular dipole.
Figure S8: Atom displacement in the zwitterion 1528 cm$^{-1}$ vibration. Yellow arrow denotes molecular dipole.
Figure S9: Atom displacement in the zwitterion 1612 cm$^{-1}$ vibration. Yellow arrow denotes molecular dipole
Figure S10: Atom displacement in the zwitterion 1641 cm$^{-1}$ vibration. Yellow arrow denotes molecular dipole.
Figure S11: Atom displacement in the zwitterion 1651 cm$^{-1}$ vibration. Yellow arrow denotes molecular dipole.
Kelvin probe work function data for 1-dodecanethiol overlaid on DHI data

Figure S12. Light (400 nm) induced work function shifts from Figure 3 (501 nm data omitted for clarity) for DHI-5 (circles) and DHI-6 (squares). 1-Dodecanethiol monolayer on gold (triangles) irradiated with 400 nm light for 8 and 13 minutes has a minimal change on the work function from its initial point.

PM-IRRAS of DHI-5 and 6 with 13 minute data

Figure S13. Reproduced Figure 4 from manuscript showing (a) DHI-5 and (b) DHI-6, but with 13 minute irradiation spectra (dashed curve) overlaid on the spiro, 2 min (blue) and 8 min (green) spectra.
Figure S14. PM-IRRAS of spiro (yellow) and zwitterion (green) DHI-6 spin coated onto gold slides with corresponding thicknesses of (a) 27 nm (b) 13 nm and (c) 6 nm. (d) The 2.4 nm sample was subjected to the DHI assembly procedures except it was not washed or sonicated after the assembly time was complete, resulting in multilayer formation. The zwitterion absorption at 1507 cm$^{-1}$ decreases with the thinner films, relative to other absorptions.
REFERENCE LIST


(50) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. Spontaneously Organized Molecular Assemblies. 4. Structural Characterization of n-Alkyl Thiol


VITA

Matthew A. Bartucci was born in Chicago, Illinois and was raised just outside of the city in Oak Brook. Before attending Loyola University Chicago for his graduate studies, he attended the University of Iowa and received a B.S. in Chemistry with a focus on solid-state and materials chemistry in 2008.

While at Loyola University Chicago, Bartucci was awarded the Graduate Award in Chemistry from the Illinois State Academy of Science (ISAS) in 2009. In 2010, he won the Department of Chemistry and Biochemistry Denkewalter Lecture Poster Award for graduate students. For demonstrating an excellence in all aspects of graduate study, Bartucci received Advanced Doctoral Fellowship from Loyola University Chicago for the 2011-2012 academic year, and the Arthur J. Schmitt Fellowship from 2012-2013, which is intended to provide support to PhD students in the final year of their dissertations at Catholic Universities.

Currently, Bartucci hopes to continue the goals of the Schmitt fellowship to advance the field of chemistry and science as a whole to better humanity and society.