

Novel Organic Phosphorescent Crystals and Derivative Compounds of Interest

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Introduction

Organic Light Emitting Diodes (OLEDs) have demonstrated key advantages over current devices, which suggests their use is the next step in display technology^{1,2}. OLEDs offer improved contrast, better viewing angles, and markedly lower power consumption compared to current LCD technologies as well as the possibility of sturdier or flexible devices^{1,2}. Phosphorescent organic compounds are of interest for these devices as they can potentially improve the efficiency by a factor of four over analogous fluorescent compounds. The Phosphorescent Organic Crystals (POCs) explored in this paper represent novel, all-organic materials that currently exhibit phosphorescence in the solid state. The crystals represent unique materials in that current phosphorescent OLEDs necessitate the use of organo-metallic complexes to achieve the intersystem crossing necessary for phosphorescence¹. POCs instead utilize all organic compounds that take advantage of the Heavy Atom Effect (HAE), which is typically only seen at liquid nitrogen temperatures, to allow intersystem crossing³⁻⁷. These materials have also been shown to only phosphoresce in the crystalline state and have markedly increased quantum yields and brightness in certain mixed crystal configurations. A wide range of mixed crystal compositions and slight alterations to the chemistry of the materials are thoroughly investigated in this paper. The understanding gained by these studies is then used to pursue control of key properties of the POC materials, such as conductivity and emission wavelength.

Properties of Phosphorescent Organic Crystals

Myriad derivative POCs have been developed and investigated, however the most basic POCs are the di-ether bromo benzaldehydes (see figure 1). The typical composition of a POC is a mixed co-crystal with two molecular components: a major component, typically called the 'bulk' compound, and a minor component where one of the bromine atoms is replaced with an aldehyde functional group. Crystallographic data suggests that these molecules pack in such a manner that the aldehyde group of one molecule is adjacent to the bromine of another; this proximity of the bromine to the chromophore is a distinguishing feature of the heavy atom effect^{3,4}. While the aromatic rings stack in an off-center manner, the long alkane chains do not fill as much volume, leaving substantial void space in the crystal. This space forces the crystal to contract, leaving the aromatic rings and their functional groups extremely tightly packed. By forcing the bromine and aldehyde to be in extremely close proximity it is believed that the heavy atom effect is greatly enhanced and competing pathways for decay of the excited state are inhibited.

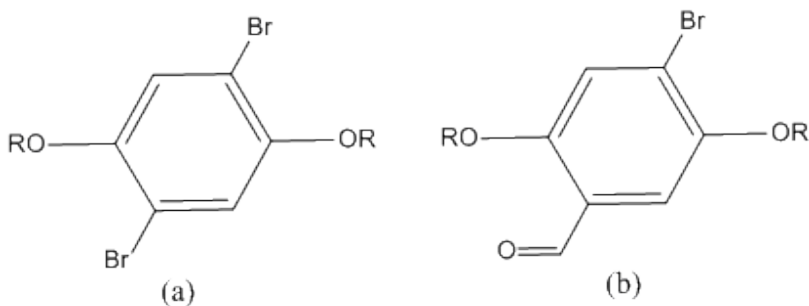


Figure 1 – Molecular components of a basic POC (a) “bulk” compound (b) aldehyde derivative

The POCs investigated here represent an extremely novel phenomenon for a number of reasons. These POCs have demonstrated an on/off mechanism whereby the phosphorescence is only observed in the solid state, and best observed in certain crystal

configurations. As previously stated, the phosphorescence observed is a phenomenon caused by the packing of the co-crystal and thus unique to the solid state. This is in contrast to many phosphorescent compounds which cannot luminesce in the solid state due to phonon quenching of the excited state before phosphorescent decay can occur. As will be discussed, the phosphorescent phenomenon generates its greatest quantum yield when the proportions of the co-crystal are approximately one aldehyde per 100 bulk molecules. The aldehyde appears to need to crystallize as an 'impurity' taking the place of a bulk molecule inside a crystal structure of almost entirely bulk molecules. The luminescence observed in the POCs is confirmed as phosphorescence via measurements of the decay lifetime.

Identification of Initial Crystals

The POC phenomenon was first observed during the synthesis of diether bromo benzaldehyde (see figure 2). Upon crystallization the reaction products showed bright green luminescence when irradiated with a handheld UV lamp. Even more surprising, the luminescence appeared to have a lifetime visible to the human eye – indicating a phosphorescent mechanism. However the intended product, called BrA6 due to the six carbon length alkane chains on the ether, when isolated via column chromatography showed no luminescence at all, while the collection of all reaction byproducts was only weakly luminescent and had a blue color. Only upon crystallizing BrA6 with the reaction byproducts was the strong green phosphorescence regained. Unfortunately, the identity of the byproduct causing the phosphorescent mechanism was not initially known due to the extremely small molar amount produced as a side reaction and the presence of numerous

other byproducts in the reaction mixture. Therefore, further separation of the reaction byproducts was undertaken via high pressure liquid chromatography (HPLC).

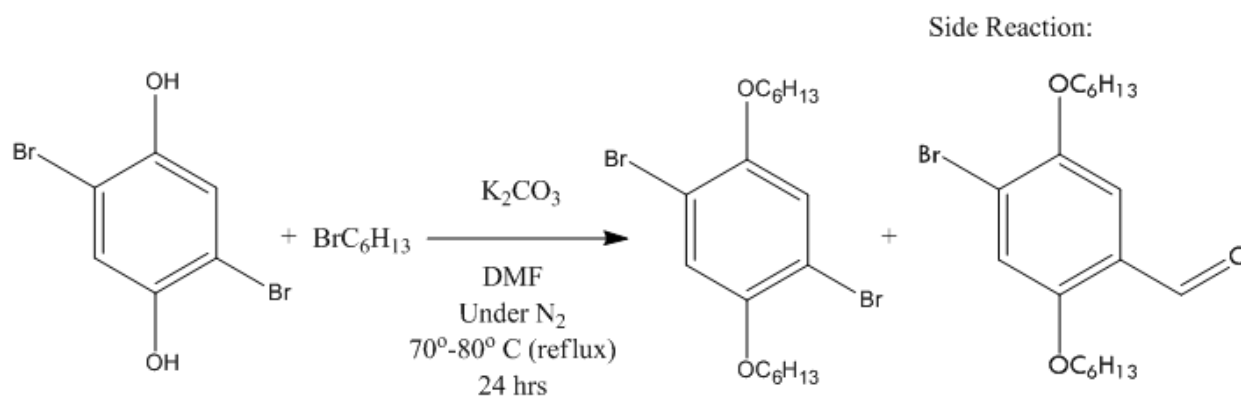


Figure 2 – Initial reaction scheme where the first set of POCs were discovered

HPLC is undertaken using a reverse phase column with an acetonitrile solvent system at a flow rate of 5 ml per minute and at a constant temperature of 45°C (see figure 3). Numerous major and minor byproducts were identified, collected, co-crystallized with bulk material, and analyzed via fluorometer (see figure 4). This process identifies a single byproduct causing the phosphorescence which exits the HPLC column at the 4 minute mark. A significant portion of this byproduct is collected via HPLC separation and analyzed using mass spectroscopy. Possible chemical structures are then identified and separately synthesized. However, the mass spectroscopy of this byproduct identified a large number of possible molecular structures. Thus, while the synthesis of these various possible structures was ongoing, a separate investigation into a molecular system with analogous behavior was undertaken in order to gain more insight into the chemical structure of the byproduct.

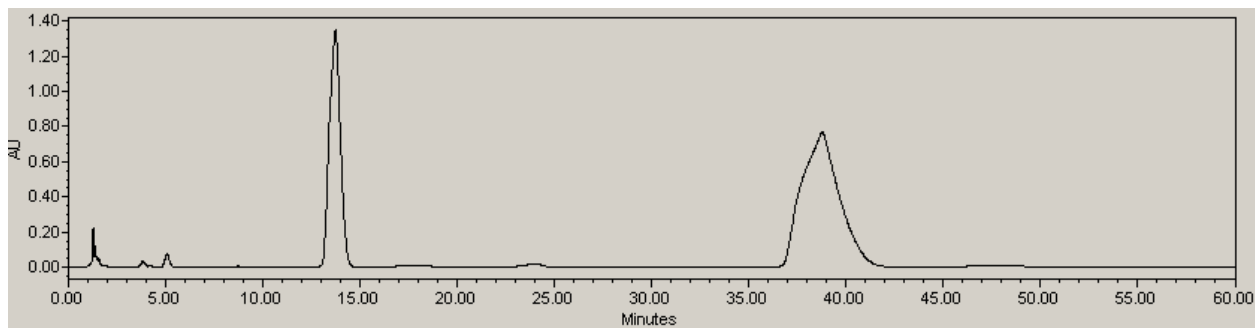


Figure 3 – Reverse phase HPLC separation of BrA6 synthesis byproducts used to identify the specific compound activating the phosphorescent phenomenon. Solvent system – Acetonitrile, Temperature - 45°C, and flow rate – 5 ml/min. Note that the peak at the four minute mark is found to be the aldehyde derivative of BrA6, the byproduct of interest.

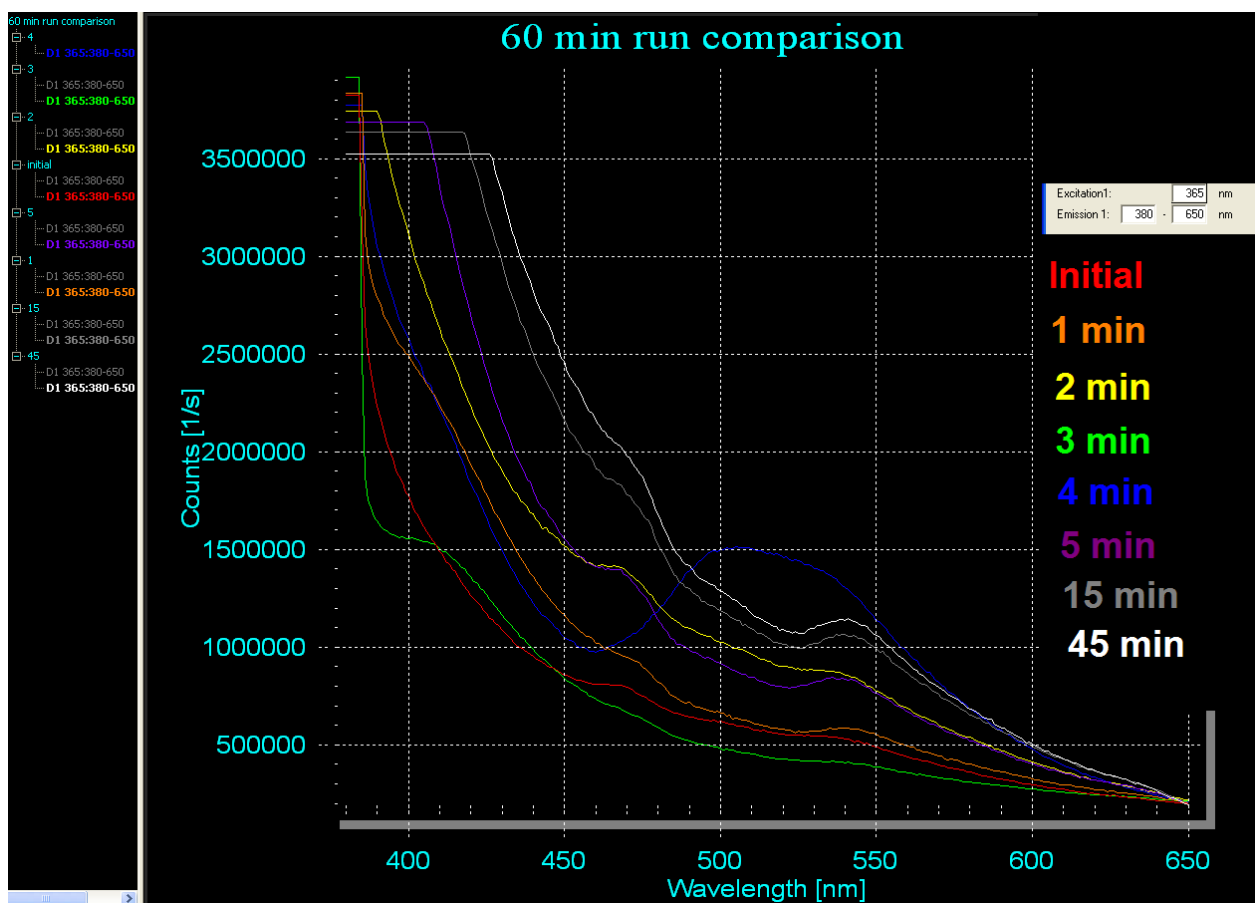


Figure 4 –Spectral analysis of the various byproduct of the synthesis of BrA6. The peaks isolated via HPLC are mixed with BrA6 and crystals formed via drop cast. These crystals are then analyzed via fluorometer. Note the phosphorescent behavior displayed by the 4 minute peak mix.

Along with the BrA6 system another system was shown to exhibit the POC phenomenon. Called the BrC6 system the molecular structure of the bulk molecule was nearly identical to the BrA6 system, with the exception that the six carbon alkane chain was terminated with an ethyl ester (see figure 5). The products of the reaction are separated using first a gravity column then HPLC in an analogous fashion to the BrA6 system. However, significant issues with the HPLC separation prevented the BrC6 system from being useful in determining the identity of the activating byproduct. After separation via gravity column the product mixture still exhibited phosphorescence as expected, but after HPLC no luminescence was observed in the products (see figure 6). Even recollecting all of the material exiting the HPLC column throughout the entire separation did not lead to a product mixture exhibiting luminescence. The activating byproduct was either lost or destroyed in the HPLC column, preventing the BrC6 system from being utilized in mass spectroscopy in order to elucidate further information on the chemical structure of the activating byproduct. Nevertheless, one of the separately synthesized possible structures for the activating byproduct identified via the BrA6 investigation led to the phosphorescent phenomenon upon mixing with the purified bulk sample. Thus the activating byproduct was identified as the BrA6 aldehyde derivative (see figure 1b).

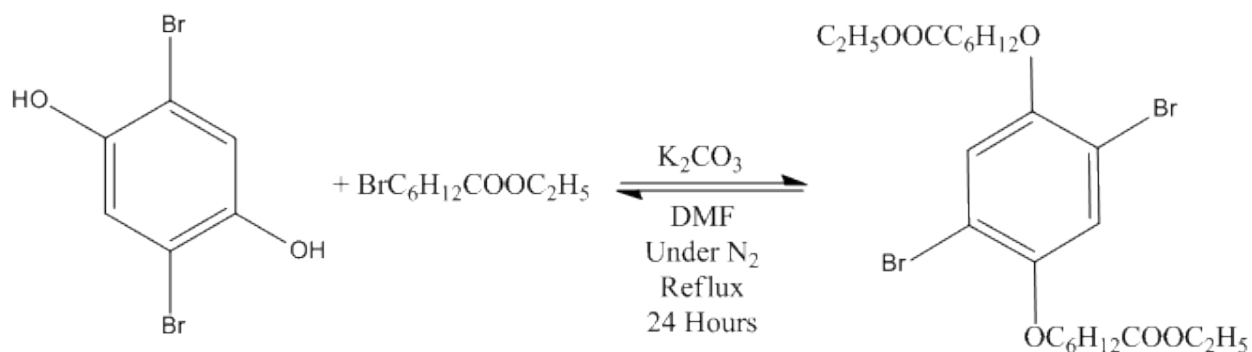


Figure 5 – Analogous ester reaction in which the POC phenomenon was also observed in the products. The products of this reaction were likewise studied in via HPLC and fluorescence spectroscopy in the pursuit of the identity of the activating byproduct.

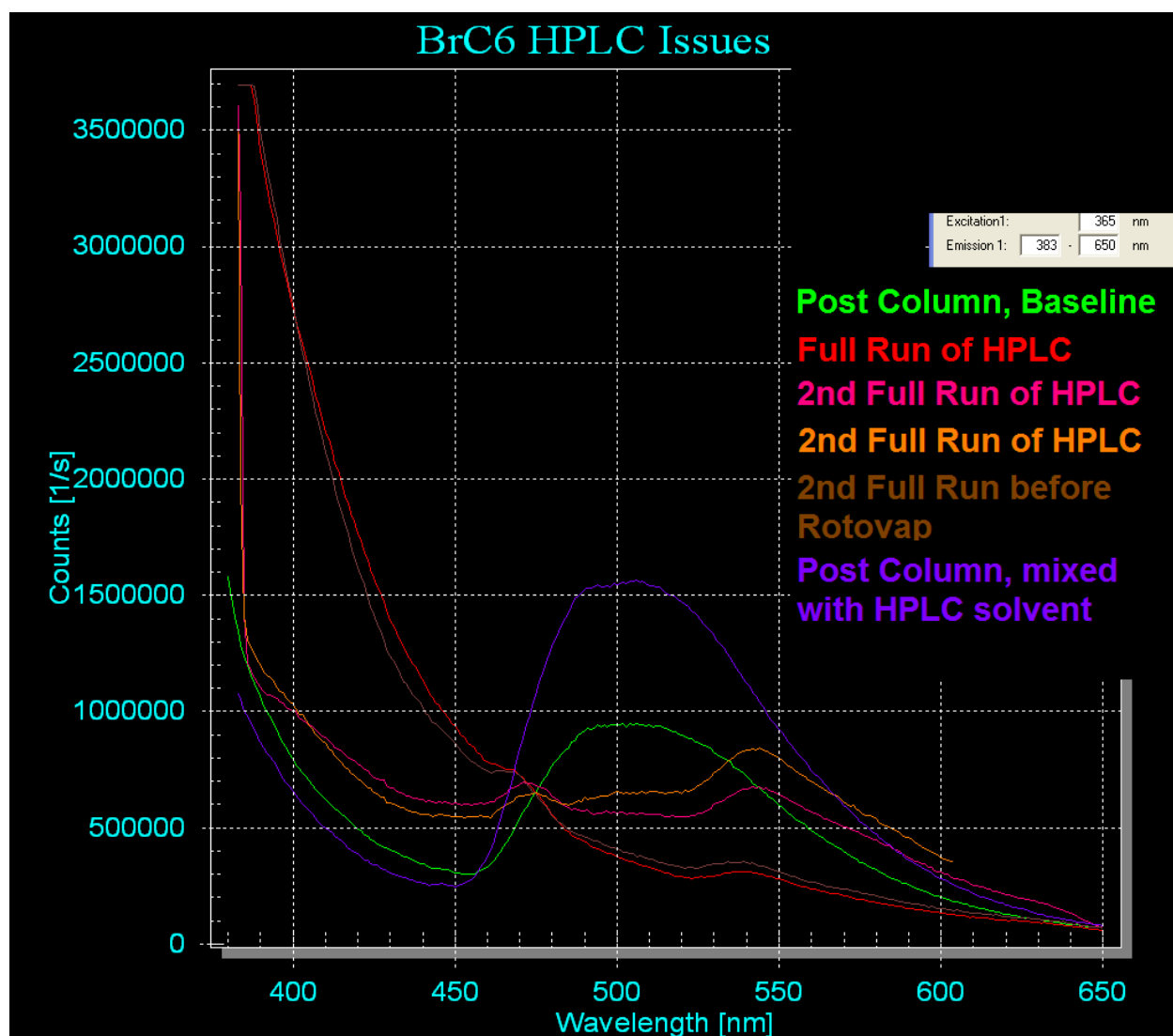


Figure 6 – Spectral analysis of the BrC6 system. Serious issues inhibited analysis of the BrC6 system as the byproduct was never recovered from the HPLC.

Phosphorescence Phenomenon and the Heavy Atom Effect

Luminescence: Fluorescence vs. Phosphorescence –

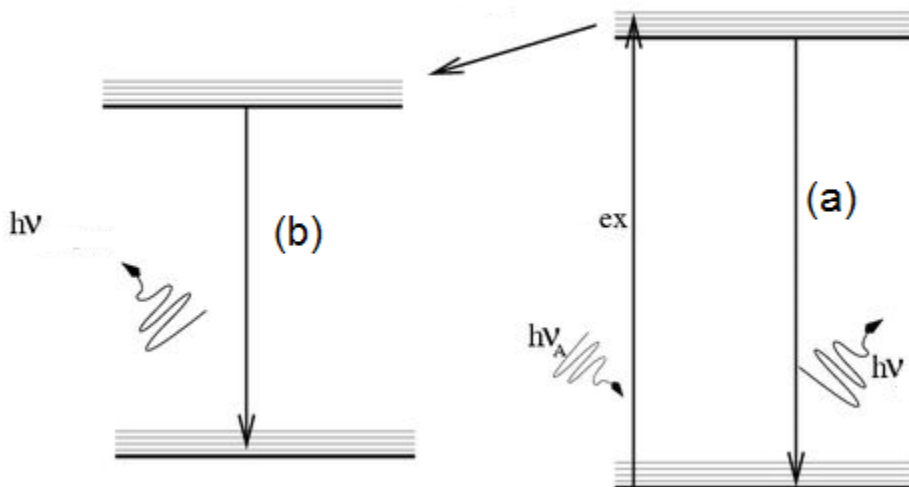


Figure 7 –Jablonski diagram detailing two different luminescent phenomena. (a) Fluorescence occurs when an electron is promoted to an excited state, undergoes radiationless decay, then emits a photon to decay back to the ground state. (b) Phosphorescence occurs when the excited state undergoes intersystem crossing to a 'spin forbidden' state before undergoing decay back to the ground state. Figure is courtesy: Wikipedia. Jablonski Diagram. <http://en.wikipedia.org/wiki/File:FRET-Jablonski-diagram.jpg> (accessed April 9, 2010)

Luminescent phenomena are best described with a Jablonski diagram detailing the electronic energy levels (see figure 7). In the fluorescence pathway, (a), a photon excites one of the highest energy ground state electrons to an excited state orbital. The excited state then undergoes radiationless decay, typically to the vibrational and rotational ground states, until it releases a photon to return to the ground electronic state. Due to the radiationless decay however the emitted photon is almost always of significantly lower wavelength. Thus a fluorescent molecule excited by ultraviolet light may emit in the visible range. In phosphorescence, (b), the excited state electron undergoes intersystem crossing and switches its spin state. This new state is called the triplet state. While intersystem

crossing can again allow the excited state to decay, releasing the phosphorescent photon, the 'forbidden' nature of the process causes the excited state to have a much longer lifetime than a corresponding fluorescent state.

Intersystem crossing and spin-orbit coupling –

Since a photon is a spin zero particle, electronic excitation/relaxation via photon absorption/emission alone cannot change the spin of the excited electron. While the spin of the excited electron pairs with its ground state electron 'partner' the state is called a singlet (see figure 8). If however the spin of the excited state electron is flipped the system is called a triplet, and relaxation to the ground state requires another spin flip during photon emission, a 'spin-forbidden' process. These spin flips, called intersystem crossing, typically take place in compounds with strong spin-orbit coupling such as metals and halogens. By exchanging the spin and orbit angular momentum a spin flip can occur without violating conservation of the total angular momentum.

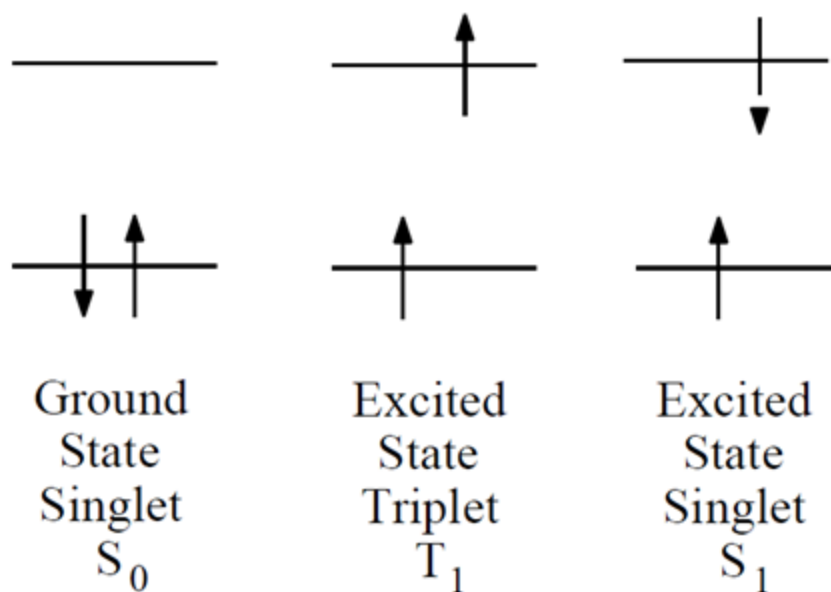


Figure 8 – Ground and excited singlet and triplet states of a simple two electron, two orbital system.

Halogen bonding and the heavy atom effect –

As stated previously the presence of halogens in a molecule can lead to the availability of intersystem crossing via spin-orbit coupling. Even the presence of nearby, non-bonded halogens can lead to intersystem crossing and have a significant effect on the photonic behavior of the molecule. Generally referred to as the heavy atom effect, the halogen quenches fluorescence^{4,5}, generates phosphorescence where previously unavailable, and decreases the phosphorescent lifetime⁶. All of these effects have also been shown to be extremely dependent on the distance between the halogen and the chromophore^{3,4}. Most commonly the effect is seen due to the presence of halogenated solvents⁵, and in the case where the halogen is not directly bonded to the chromophore the phenomenon is called the intermolecular heavy atom effect.

It has been proposed that the phosphorescent phenomenon observed in the POCs is due to the intermolecular heavy atom effect between the bromine of the bulk molecule and the aldehyde functional group in the aldehyde derivative (see figure 9). The phosphorescence is 'turned on' through co-crystallization, and thus likely depends on an intermolecular interaction. Furthermore crystallographic data from parallel work in POCs has suggested a usually small spacing between these two functional groups, and given the sharp dependence on distance in the intermolecular heavy atom effect it is likely that the unusually close interaction is leading to a heavy atom effect of previously unseen strength. The distance between these two functional groups is likely to be so short for two reasons. First of all, the long alkane chains present in the molecules leave large void spaces which cause the crystal to contract. Secondly, halogen bonding between the oxygen and bromine likely leads to reduced spacing. Halogen bonding, analogous to hydrogen bonding, is a favorable interaction between electron deficient halogens and an electron rich atom, such as oxygen. The favorable interaction between their orbitals causes them to be spaced closer together than would be expected from their atomic radii. Thus, halogen bonding between the bromine of the bulk and the aldehyde functional group likely leads to an extremely strong intermolecular heavy atom effect, which in turn quenches the fluorescence of the POCs and generates their phosphorescence.

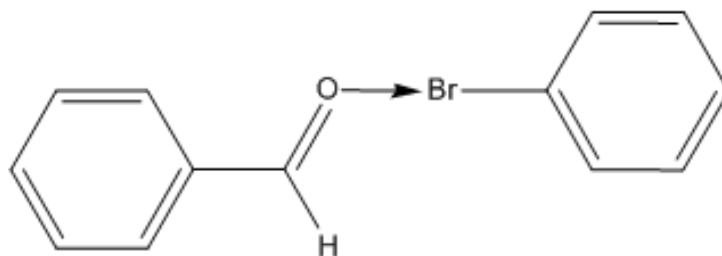


Figure 9 – Halogen bonding, favorable interaction between electron deficient halogens and nucleophilic atoms, allows for the unusually small spacing between the bromine and aldehyde seen the crystallographic data for POCs.

The importance of phosphorescence for LED devices -

Having phosphorescent, as oppose to simple fluorescent, materials for LED and OLED devices is critical to maximizing the efficiency of the device. In an LED device, current is run through a luminescent compound in order to trigger photon emission. Excited state electrons are injected into the molecule while holes remove electrons from the ground state. Charge recombination then leads to photon emission. Since the excited state electrons arrive from an external source however the resulting wavefunction may be any of the four spin states.

$$\left\{ \begin{array}{l} |1\ 1\rangle = \uparrow\uparrow \\ |1\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ |1\ -1\rangle = \downarrow\downarrow \end{array} \right\} s = 1 \text{ (triplet)}$$

$$\left\{ |0\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \right\} s = 0 \text{ (singlet)}$$

Without the ability to undergo intersystem crossing fluorescent compounds can only use a quarter of the injected electrons to decay via photon emission. Phosphorescent compounds however can use every injected electron to generate a photon. The vastly superior efficiency of phosphorescent compounds makes them extremely desirable for LED devices.

Synthetic and Analytic Techniques – Thin Layer Chromatography

Thin layer chromatography (TLC) is an extremely popular chemical technique used to monitor reaction progress and purity of products due to its speed, cost, and simplicity⁸. The technique involves using a silica gel covered plate along which solvent runs – which will lead to separation of the components of a sample by polarity. The plate itself is typically composed of a thin strip of metal support on which a layer of silica gel mixed with fluorescent powder is placed. The fluorescent powder emits a bright green light when exposed to 254 nm UV light, however most organic compounds will absorb this light allowing one to easily locate the sample on the plate. If the compound is not sufficiently quenching the luminescence of the plate, numerous staining techniques (such as Iodine powder) are available to help identify the position of the sample.

To run a TLC separation one ‘spots’ a small amount of sample liquid or solution towards the bottom of the plate using a thin capillary. The plate is then placed upright inside a beaker with a small amount of eluent such that the capillary force drags the eluent up the plate. The distance a given compound will travel up the plate will depend on the amount of time spent adsorbed to the surface versus the time spent in solution. Therefore, more polar compounds will travel less as they interact strongly with the silica gel, while more polar eluents cause all components to travel further as they strongly displace sample from the silica gel. As long as there is a significant difference in the polarity of different components, TLC is an ideal way of identifying the progress of a reaction – once the ‘reagent’ spot has disappeared the reaction is complete – and presence of reaction by

products. While TLC cannot chemically identify a component or distinguish compounds of very similar polarity, it is an extremely fast and simple first step for investigating a reaction.

Synthetic and Analytic Techniques – Extraction and Washing

Extraction is a critical synthetic technique for separating aqueous and organic components of a product mixture⁸. A typical extraction procedure consists of placing the sample in a separatory funnel along with an organic and an aqueous solvent. It is critical that the solvents are immiscible; that way two layers of solvent will be formed with the organic components of the sample dissolved in the organic layer and the aqueous components in the water layer. This technique is incredibly useful, and common, for removal of salts from an organic synthesis reaction.

A few considerations can greatly improve the effectiveness of extraction as a purification technique. First, any surfactant (a molecule with one polar side and one non-polar) will make extraction extremely difficult. At best the surfactant will clump up at the solvent border obscuring the differentiation of the two solvents. At worst the surfactant will form micelles, which will prevent the separation of aqueous and organic solvents completely. Secondly, the separation process can often be greatly sped up by adding a simple salt, such as NaCl, to the aqueous layer. The addition of electrolytes further polarizes the aqueous solvent and increases the driving force separating the two layers.

Synthetic and Analytic Techniques – Column Chromatography

Column chromatography is the workhorse separation technique of organic synthesis⁸. The technique shares many similarities with TLC, but is a separation technique,

not an analytic technique. Instead of having sample flow up a plate of silica, the sample is placed on top of a column of silica gel while eluent flows through due to gravity. Just as in TLC, a more polar compound will move more slowly through the column while a more polar solvent will cause all compounds to move through the column faster. The techniques are so complimentary that TLC is often used to determine the ideal eluent system for column chromatography and to monitor when and what components are exiting the column.

Synthetic and Analytic Techniques – Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) has rapidly become one of the most popular, and powerful, techniques in modern chemistry research⁹. The technique takes advantage of extremely powerful magnetic fields to probe the quantized spin state of atomic nuclei. Certain nuclei, such as hydrogen's, exist in either a spin up or a spin down state. Under normal conditions this has no observable effect on the atom; however the presence of a strong magnetic field causes spins aligned with the field to be of lower energy. Once a significant energy difference between the two spin states has been generated, the sample is bombarded with radio frequency (RF) photons to excite the system to a higher energy spin. The relaxation of the spin state causes emission of RF waves of characteristic frequency. These frequencies correspond to the energy gap between the two spins, which is in turn determined by the local magnetic environment of the nuclei. The local magnetic field however is dependent not only on the applied field, but also the local electronic, and thus local chemical, environment. In this way NMR can elucidate a great deal of information

about bonding and neighboring atoms. For example, a hydrogen in a very electron rich environment will be significantly shielded and 'feel' a reduced magnetic field.

NMR also provides information about nearby spin active atoms. Bonding interactions contain a certain amount of nuclear spin information, such that aligned nuclear spins are in a slightly lower energy state. Even if the nuclei are separated by four bonds, a significant splitting of the energy levels is observed. This splitting is characteristic of the number of nearby hydrogen atoms, and the local chemical environment of those atoms. This information allows for extremely accurate structural predictions of even quite complex molecules.

Finally, NMR spectra provide insight into the relative abundances of different hydrogen atoms via integration values. The signal response for each nuclei is quantitative to such an extent that by integrating the total signal received from a given peak and comparing this integrated value to that of other peaks one can obtain ratios of hydrogen atom populations. These ratios are useful for distinguishing the number of hydrogen atoms in chemically 'identical' environments that may be hidden within a single peak or for comparing the relative abundance of different compounds present in a sample, such as in a tautomerization equilibrium reaction. The technique can be used to characterize a number of different atoms, but most commonly the technique is used on hydrogen-1 and carbon-13 atoms to explore the structure of organic molecules and is used here throughout the synthesis of every POC (see figure 10).

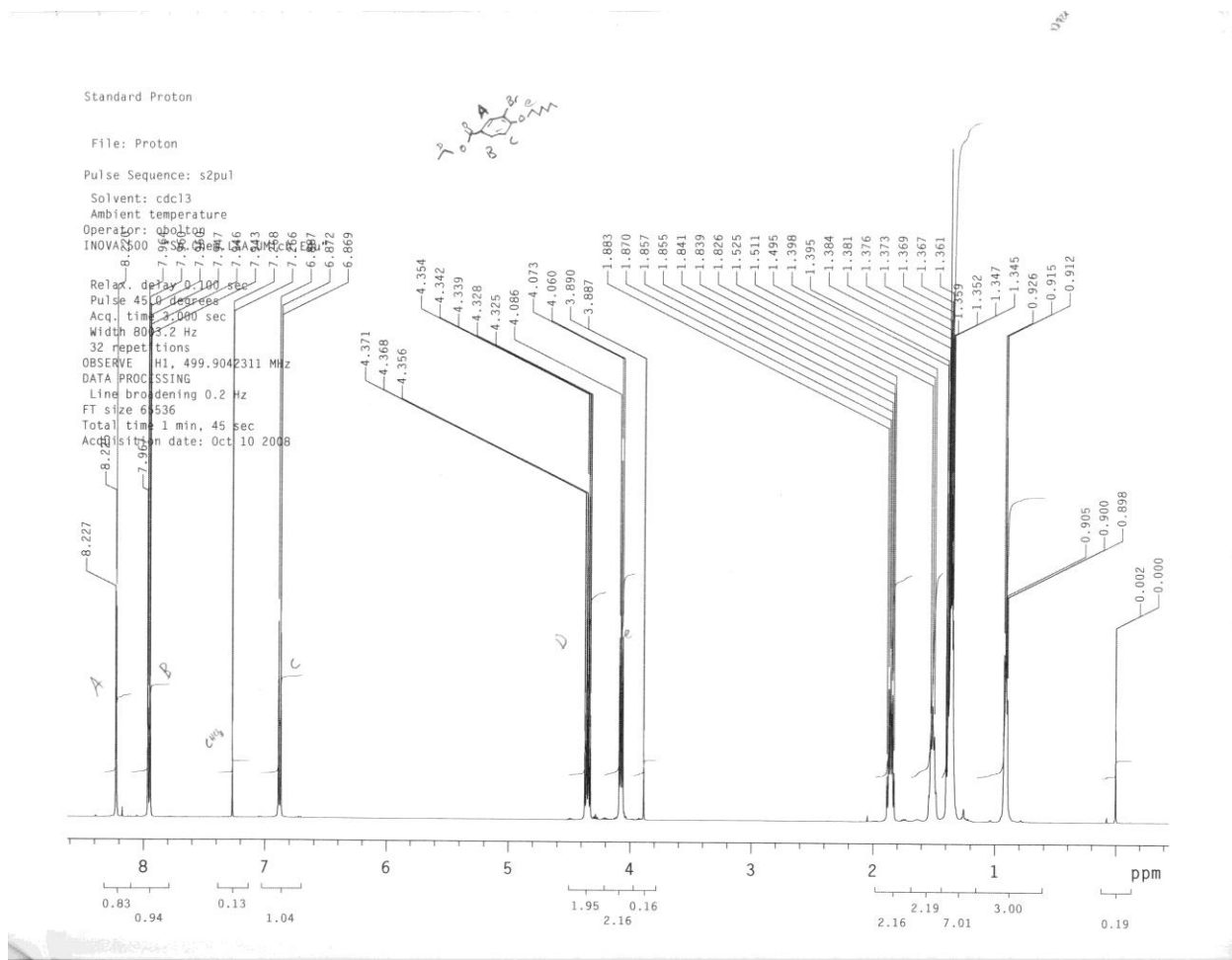


Figure 10 –Example H1-NMR spectrum

Synthetic and Analytic Techniques – Mass Spectroscopy

Molecular mass spectroscopy, while slow, expensive, and destructive towards the sample, allows the separation and identification of molecular species via mass – an extremely simple and powerful differentiating characteristic⁹. In molecular mass spectroscopy the sample is ionized and vaporized through a number of different means, such as electron impact, matrix-assisted desorption, or electrospray ionization. The ions are then focused into a beam and separated via their mass to charge ratio.

Depending on the molecule and the ionization technique the molecule will frequently break down into multiple fragments. While this can sometimes obscure the signal of the original analyte, more often the fragmentation is advantageous. The ionization, and proceeding fragmentation, will occur at the bond of shallowest potential; often this means that the molecule fragments into full functional groups which can either themselves be identified in the mass spectrum or be identified via the mass 'lost' from the analyte molecule. Identification of the different fragmentation occurring in the molecule allows for insight into the chemical structure of the analyte.

Mass spectroscopy is especially useful in identifying certain elements in the molecular composition of an analyte. Since the technique separates compounds via mass down to an individual atomic mass unit mass spectroscopy is able to identify the presence of certain elements via isotope populations. For example, bromine is composed of an almost 50/50 mix of Br^{79} and Br^{81} . Therefore any compound containing bromine will have its mass spectrum peak split into two even peaks separated by 2 atomic mass units.

While cost and speed have prevent mass spectroscopy from becoming a ubiquitous technique in chemical analysis the ability to separate and identify molecular masses of molecules, investigate chemical structure via fragmentation, and pursue elemental analysis via isotope splitting makes the technique incredibly powerful. The depth of analysis, despite the cost, makes mass spectroscopy an ideal technique when other techniques simply cannot give enough information.

Synthetic and Analytic Techniques – Fluorescence Spectroscopy

Fluorescence Spectroscopy utilizes electronic transitions in the ultraviolet to visible range of certain molecules to both explore the behavior of these transitions and analyze the molecules containing them⁹. The technique has received great interest in recent years due to its extremely low limits of detection and applications to biochemistry. However, in this study fluorescence spectroscopy is utilized to characterize the phosphorescent phenomenon in POCs. Fluorescence spectroscopy typically consists of a photon source which strikes the sample, followed by detection of emitted photons. Due to the radiationless decay in fluorescence and phosphorescence, the emitted photon is almost always of significantly lower wavelength, distinguishing the analyte signal from the photon source. Furthermore, since the luminescence is omnidirectional the detector is often placed perpendicular from the beam path, which reduces the background signal from the photon source. By scanning large ranges of wavelengths one can easily determine the wavelengths of maximum absorption and emission (see figure 11).

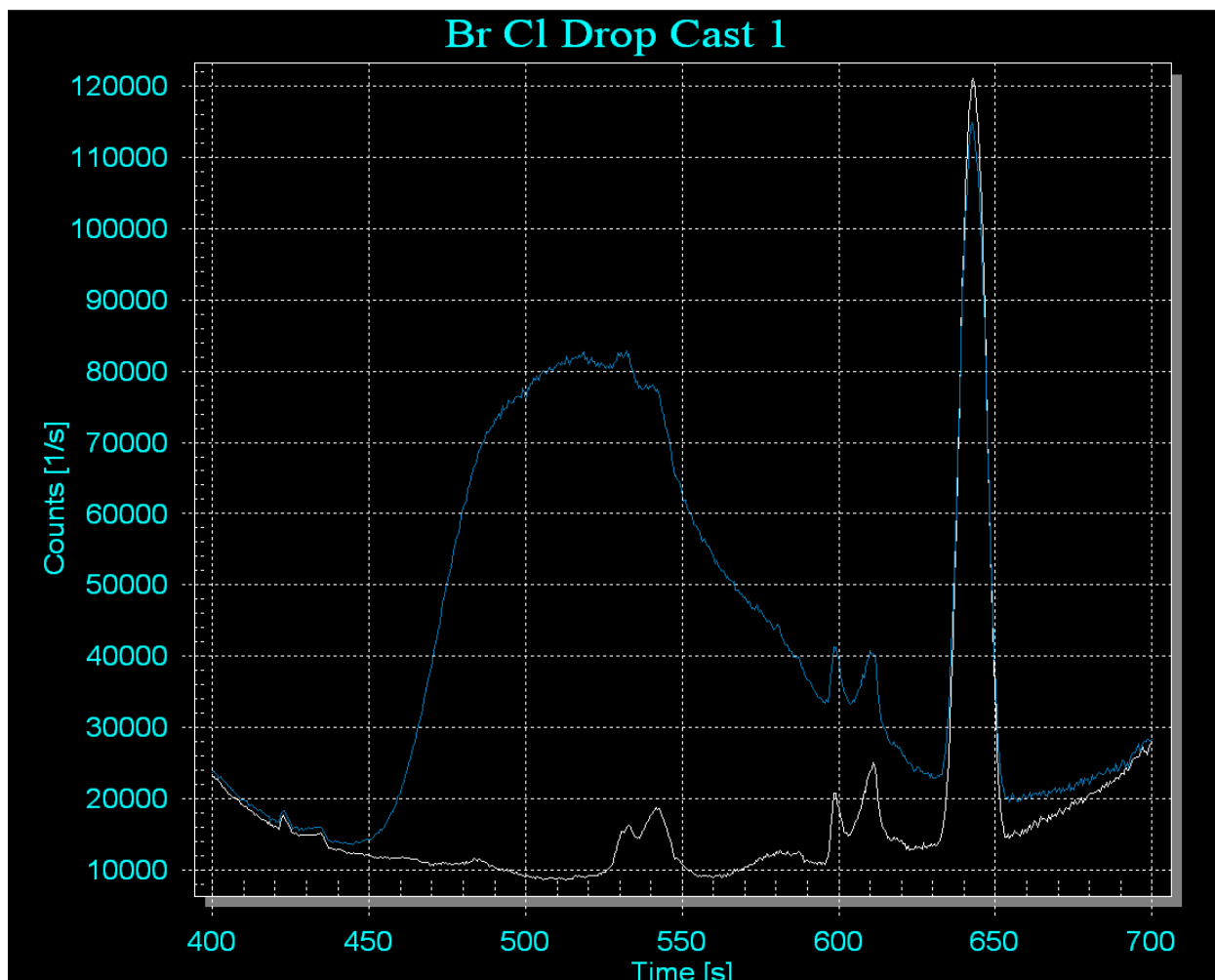


Figure 11 -Example fluorescence emission spectrum of a phosphorescent organic crystal

Using the emission and excitation wavelengths, one can determine the intensity of the beam lost through absorbance by the sample and the intensity of emission in order to determine the quantum yield, Φ , described by

$$\Phi = \frac{\text{Number of Photons Emitted}}{\text{Number of Photons Absorbed}}$$

This allows one to determine a quantitative figure of merit for the efficiency of the luminescent phenomenon. In order to obtain accurate numbers for these intensities an integrating sphere is used. The integrating sphere is a device which directs all of the light

from the sample and beam path to the detector – increasing the noise of the technique but allowing quantitative measurements of the omnidirectional emission.

Phosphorescence and fluorescence can be distinguished using fluorescence spectroscopy capable of measuring the lifetime of the excited state. Since phosphorescent emission requires a spin forbidden transition the lifetime of the excited state is significantly longer than the fluorescent lifetime. Therefore lifetime measurements are obtained by emission of a pulse of excitation photons followed by time resolved measurements of the emission. In this manner phosphorescent phenomenon, key to the novelty of the POCs, can be distinguished from simple fluorescence.

Synthesis of the Bulk Compound

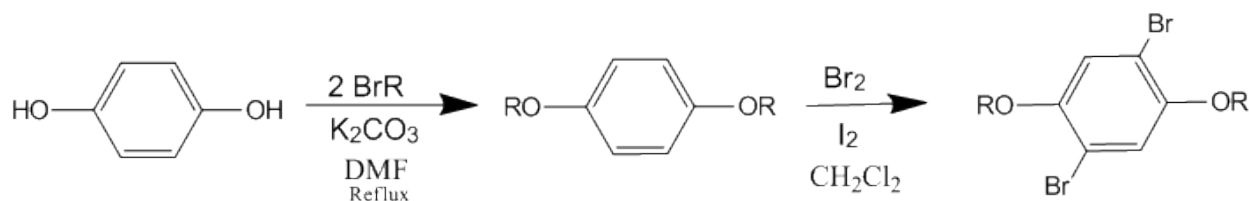


Figure 12 –Synthetic route for typical “bulk” compound.

The synthetic route for the basic diether POCs begins with a Williamson ether synthesis. The quinone is reacted with the bromo-alkane of interest in order to produce the ether of desired chain length (see figure 12). For example, the BrA6 compound is reacted with two equivalents of bromohexane. In the next step of the reaction, liquid bromine is added with a catalytic amount of iodine in order to brominate the aromatic ring. Initially all four aromatic sites are equivalent, however after the first bromination the bromine is

weakly para directing. Para bromination is thus observed for all symmetric POC compounds.

Synthesis of the Aldehyde

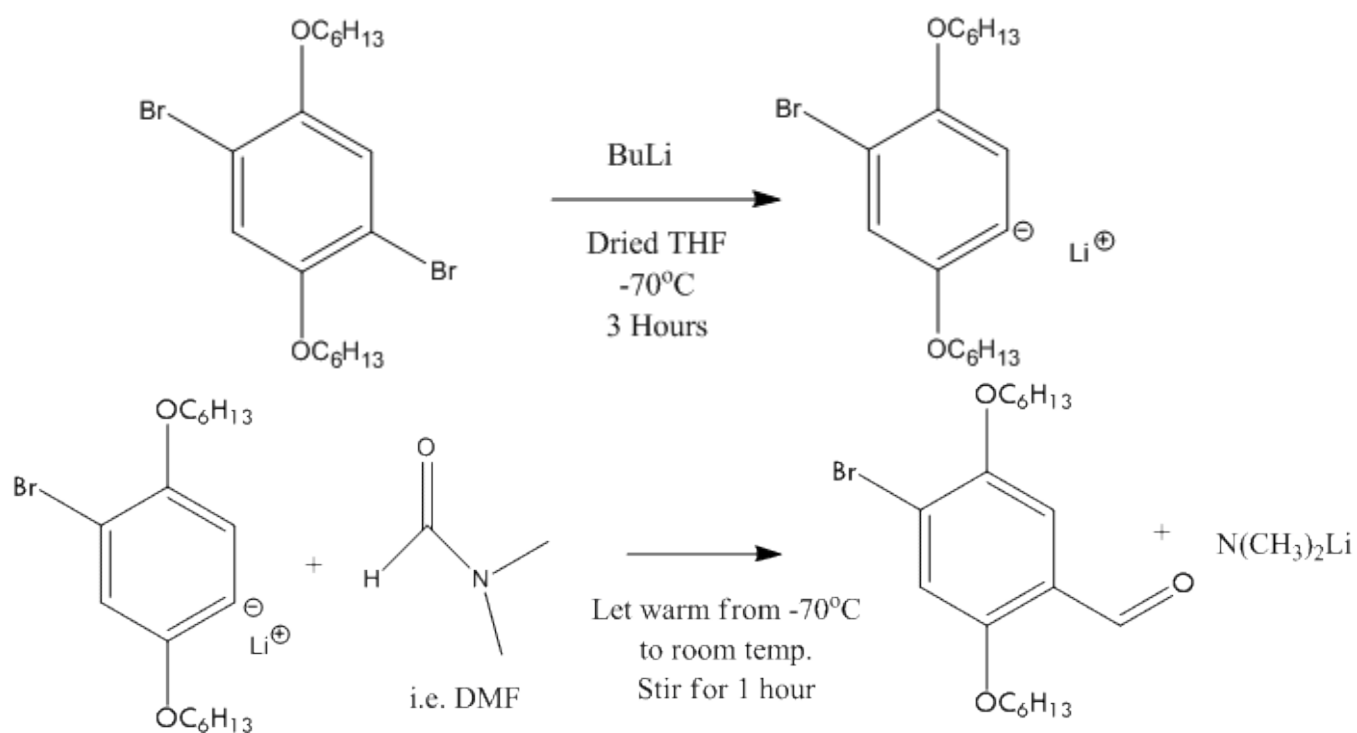


Figure 13 –Synthetic route for conversion of BrA6 “bulk” compound to the aldehyde derivative.

The primary reagent used in the synthesis of the aldehyde derivative is the “BrA6 Bulk” compound itself. Butyl lithium will attack the easiest source of hydrogen and is thus extremely water sensitive. Therefore the THF must be dried in order to remove any remnant water in the solvent. The THF solvent drying process involves sealing the THF under Nitrogen gas and adding solid Sodium. Solid sodium is extremely reactive with water, and converts any remnant water in the THF solvent to Sodium Hydroxide (which

crashes out of solution in THF) and Hydrogen gas. Furthermore, the reaction takes place under Nitrogen gas and is chilled to -70°C , due to the extremely exothermic reaction mechanism and in order to slow and stabilize the reaction to reduce byproducts. Stoichiometry considerations proved to be critical in reducing byproduct formation. The most common byproduct, the doubly Aldehyde substituted version of the compound, was suppressed by greatly diluting the BrA6 reagent in the THF solution and adding the Butyl Lithium drop wise. The second step of the reaction involved adding DMF and allowing the mixture to warm to room temperature while stirring. The result was then purified by column chromatography in order to remove the most common byproduct, the doubly aldehyde substituted compound.

The directed synthesis of aldehyde derivatives helps to explain how the POCs were discovered in the first place. Once the bromine is removed from the aromatic ring, the position is open to attack from DMF. The original reaction conditions (see figure 2) include quite high temperatures, and DMF is plentiful as the solvent. Furthermore, even a one in one thousand or one in ten thousand concentration of aldehyde derivative is enough to achieve significant phosphorescence, as will be demonstrated in the mixing study. Thus, despite the fact that removal of a bromine atom purely via thermal interaction is quite unlikely, only an extremely small proportion of molecules needed to undergo this reaction route in the original synthesis for the POC phenomenon to be discovered.

Synthesis of Derivative Compounds – Mixing Studies

In order to pursue the intended application of POCs, OLED devices, and further investigate the heavy atom phenomenon numerous aspects of the composition of the POCs were adjusted to enact changes in quantum yield, absorption/emission wavelength, and conductivity. The first of these investigations involved exploration of the co-crystal phenomenon. The necessity of co-crystallization and the extremely small amount of aldehyde needed to trigger the phosphorescence mechanism indicated that the behavior of the phosphorescence was extremely sensitive to the relation between the bulk and aldehyde materials. Thus the mixing studies involved investigating the quantum yield of either mixes of different proportions of aldehyde and bulk, or extremely simple adjustments to the chemical formula of the bulk and aldehyde materials.

Given the extremely small amount of aldehyde necessary to trigger noticeable phosphorescence in the bulk, the first parameter of the POC system to be adjusted was the ratio of aldehyde to bulk present. The BrA6 system was utilized to measure the quantum yields of 0.0001% to 100% relative aldehyde compositions (see figure 14). The results of this mixing study supported the asserted co-crystallization intermolecular interaction as the cause of the phosphorescence. Since the aldehyde absorbs photons at 365 nm, at high concentrations of aldehyde the quantum yield rapidly decreases; as the aldehyde molecules begin to encounter more of each other than bulk molecules the probability of forming the necessary halogen bonding interaction greatly decreases. Furthermore, while the 10% and 20% aldehyde crystals were qualitatively the brightest, the most efficient mix was the 1% mix. At such a low proportion of aldehyde the vast majority of aldehyde molecules interact solely with bulk molecules. Thus, no aldehyde-aldehyde interactions block the formation of

the bulk-aldehyde intermolecular interaction proposed to generate the phosphorescence phenomenon.

There are two important additional observations to be discerned from the behavior of these mixed crystals at the two extremes of pure aldehyde and pure bulk. First, while quite small, the quantum yield of a pure aldehyde crystal is non-zero. This suggests that an aldehyde POC is able to halogen bond with a bromine atom from another aldehyde molecule in absence of a bulk molecule. Nevertheless factors such as crystal packing or electronegativity must severely inhibit the halogen bonding interaction to make the phosphorescence far less efficient. Second, the quantum yield does not continue to increase as the aldehyde concentration goes to zero, but rather steadily decreases. This runs against the previous assertion that as the aldehyde-aldehyde interactions decrease the quantum efficiency should increase. However, as the absolute strength of the phosphorescent emission decreases, other interfering factors (such as instrument loss, internal photon scattering, and weak bulk absorbance) will have a much stronger relative effect and could account for this trend.

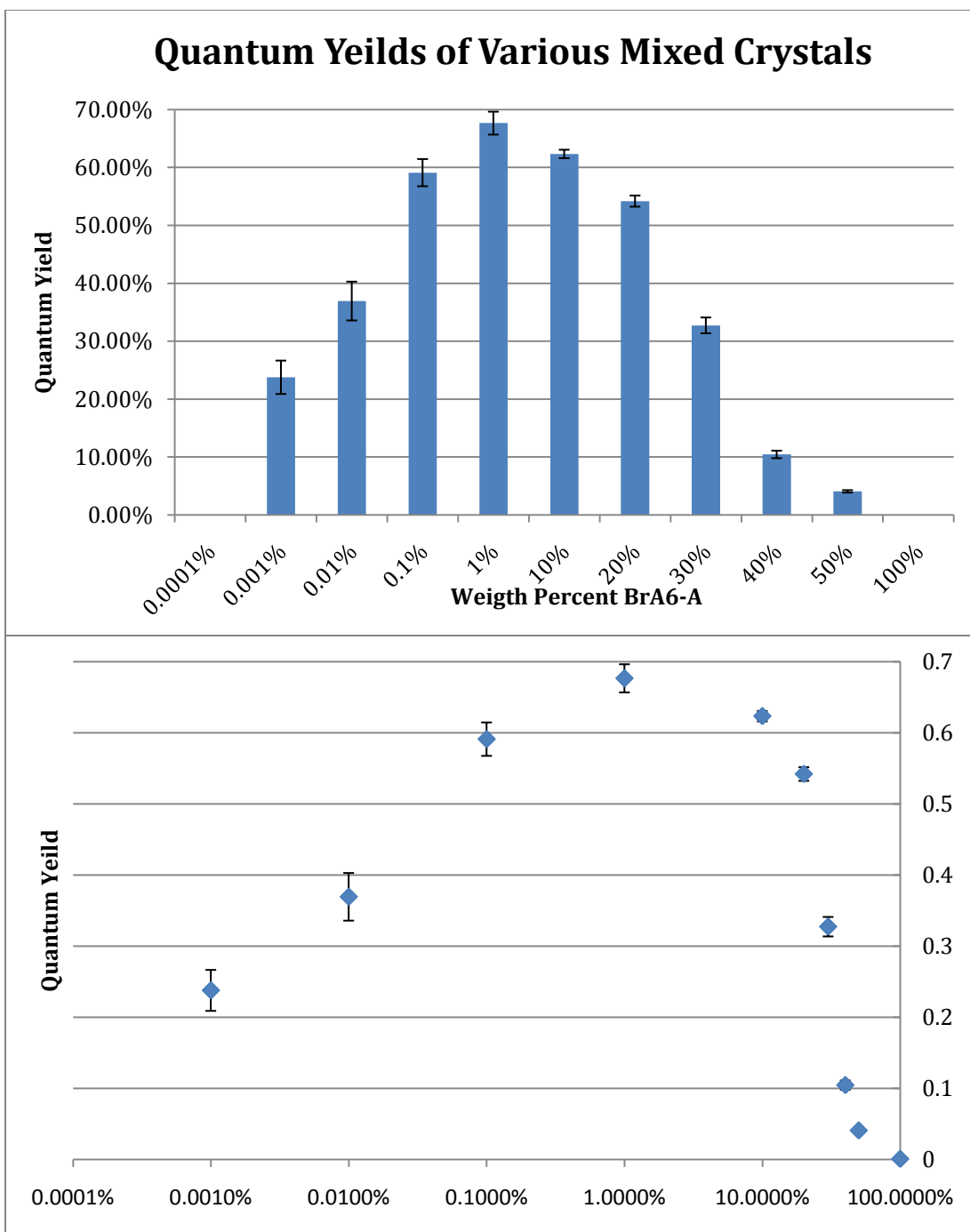
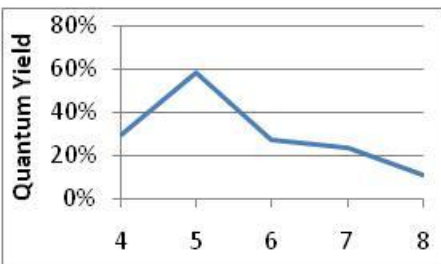


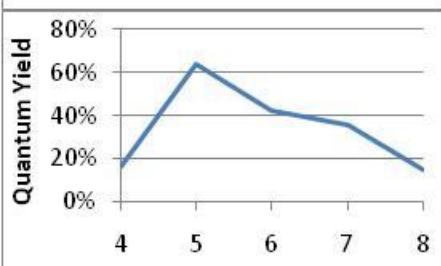
Figure 14 –Quantum yield measurements of various BrA6 bulk/aldehyde mixes, indicating a maximum quantum yield of 67% at a 1% aldehyde composition. Note that the pure aldehyde is still weakly phosphorescent

The next parameter to be investigated was how mixes of different alkane chain length POCs behaved. The extremely tight crystal packing due to the large void spaces left by the alkane chains causes the strong halogen bonding interaction suggested to be the source of the phosphorescence in the POC. Adjusting this void space should therefore have a significant impact on the quantum yield of the system. If the void space could be taken advantage of to alter the phosphorescence, then mixing smaller aldehyde molecules into bulk crystals should increase the quantum yield. The study involved determining the quantum yields of mixes of aldehyde and bulk molecules containing 4-8 carbon length alkane chains (see figure 15). The results of the study demonstrate that the system efficiency is dominated by co-crystallization considerations, not void space considerations. Every system except the smallest alkane chain achieves its greatest quantum yield when the aldehyde and bulk alkane chains are equivalent lengths. A mismatch in alkane chain length severely inhibits co-crystallization and leads to the formation of 'islands' of congregated aldehyde – which reduce the quantum yield significantly. The smallest system deviates from this behavior only due to the fact that at such a small alkane chain length the material does not have a strong driving force to crystallize and only very poor crystals can be collected. The results of this mixing study demonstrate the critical importance of crystallization considerations.

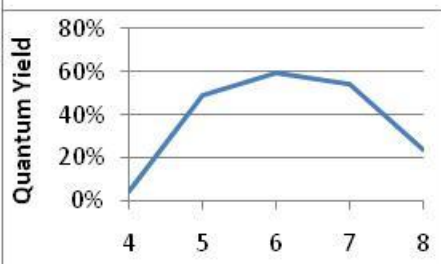
BrA4-A



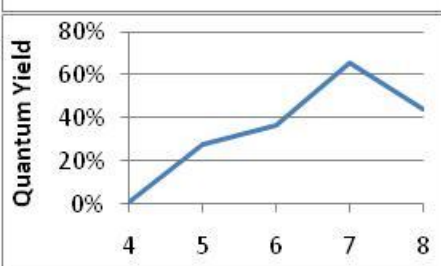
BrA5-A



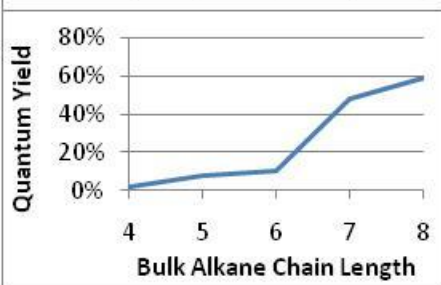
BrA6-A



BrA7-A



BrA8-A



Bulk Alkane Chain Length

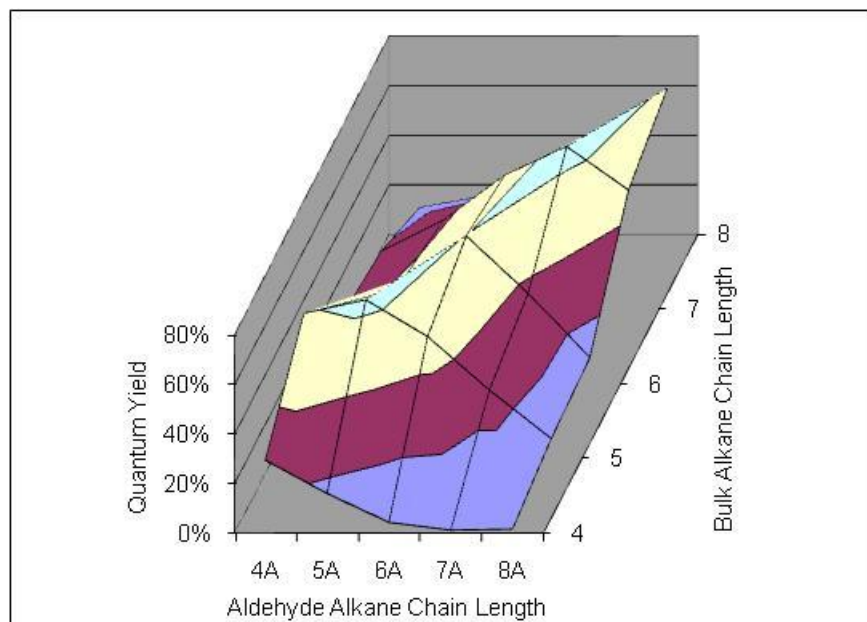


Figure 15 –Quantum yield measurements of mixes of BrA6 bulk/aldehyde alkane chain lengths. The results indicate that almost every bulk chain length obtains its best quantum yield when mixed with an alkane of equivalent chain length demonstrating the importance of good co-crystal inclusion

Synthesis of Derivative Compounds – Color Tuning

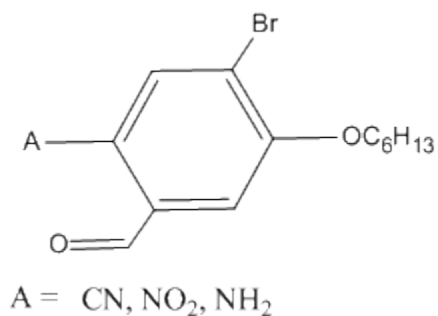


Figure 16 –Proposed POC derivative compounds of interest for color tuning capabilities.

Three derivatives (and their corresponding bulk compounds) of interest for novel expected properties and synthetic ease were identified (see figure 16). The compounds are essentially equivalent to the initial BrA6 phosphorescent compound but with one of the ether groups replaced with one of three new functional groups – a cyano, a nitro, or an amino functional group. These groups were chosen to explore the optical tunability of the

phosphorescent mechanism. By changing the charge density on the aromatic ring, corresponding changes in wavelength of phosphorescent emission are expected. Therefore the electron withdrawing nitro and cyano groups would blue-shift the emission, and the electron donating amino group would red-shift the emission. Spectra demonstrating these shifts in emission would constitute solid evidence for the viability of color tuning in these organic phosphorescent compounds, an extremely desirable feature if the system is to be applied to commercial products.

These compounds were also chosen for the simplicity of their intended synthetic route. Previous synthetic work with POCs had led to the development of a straight forward synthetic preparation from relatively simple reactants (see figures 12, 13). Nitro, amino, and cyano phenols are commercially available replacements for the hydroquinone starting material. Thus it was purposed that the same, known synthetic route be used for the new derivative compounds.

Unfortunately, numerous difficulties were encountered that prevented the synthesis of the derivative compounds. The nitro and cyano containing derivatives were the first attempted syntheses, however the strongly electron withdrawing behavior of these functional groups deactivate the bromination of the aromatic ring (see figure 17). The bromination reaction is an aromatic electrophilic substitution reaction requiring an electron rich site on the aromatic ring to attract an electron deficient site, in this case bromine. The electron withdrawing functional groups greatly decrease the electron density, making the reaction far less favorable.

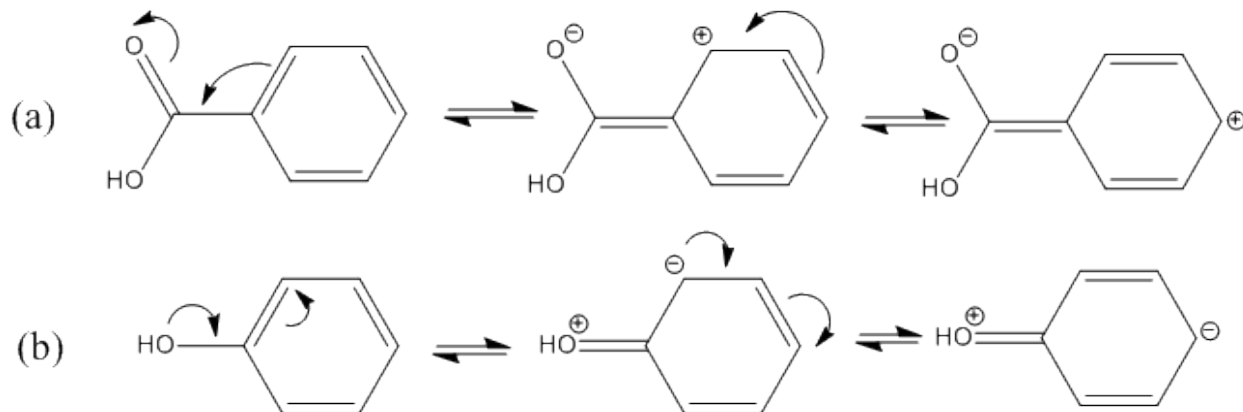


Figure 17 - Arrow mechanisms describing how different functional groups affect the electron density of an aromatic system and thus the reactivity of different sites for bromination. (a) Electron withdrawing groups deactivate ortho and para positions on the ring (b) Electron donating groups activate ortho and para positions

In order to try to drive the reaction to completion, the reaction container was heated, and iron flakes were added as a catalyst. Iron is known to catalyze the reaction by improving the electrophilicity of the bromine (see figure 18). It was also hoped that the electron deficiency of the aromatic ring was primarily an effect on activation energy and could be overcome by rigorous heating. Nevertheless, even under these harsh conditions, only monobromination could be achieved.

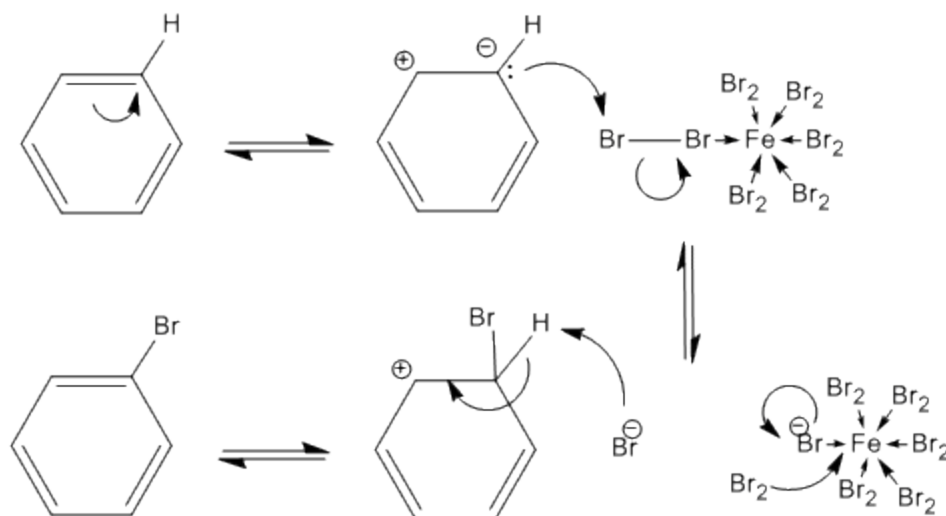


Figure 18 – Arrow mechanisms describing the catalytic effect of iron flakes on the bromination of an aromatic ring. The iron catalyst lowers the activation energy of the bromination reaction by producing semi-positive bromine in a recyclable manner.

The amino containing derivative was next pursued. Since the amino functional group is electron donating to the aromatic system, the synthetic problems previously encountered during the bromination reaction should not affect the amino synthetic route. Different problems, however, occurred during the first reaction to produce the amino ether. The amino ether compound is an extremely good surfactant – with polar, hydrogen bonding amine and an oily, non-polar ether side – which makes purification of the reaction products extremely difficult. Furthermore, a significant amount of secondary amine, a result of substitution of an amino hydrogen instead of a hydroxyl hydrogen, is produced. This byproduct behaves quite similarly to the desired amino ether and is difficult to separate. Finally, parallel work on POCs produced a different BrA6 derivative with red-shifted emission – the thioether derivative (see figure 19).

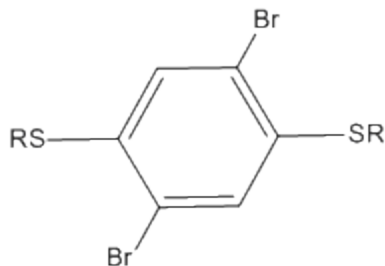


Figure 19 – The thioether bulk derivative synthesized during parallel work on POCs. The compound demonstrated significantly red-shifted emission, eliminating the need for the proposed amino derivative.

Synthesis of Derivative Compounds – Improved Conductivity

In order to apply POCs to a working OLED device the crystals must be able to conduct charge. Without significant conductivity current cannot reach the phosphorescent sites to allow the charge recombination necessary for luminescence. The POCs synthesized so far, however, have been quite unconductive. In order to address this issue, the carboxylic acid functional group was chosen as an ideal candidate for a far more conductive phosphorescent compound. The carboxylic acid functional group is known to strongly interact with other carboxylic acid groups, in our case interlocking with other molecules driving the side to side crystal packing (see figure 20a), and thus hopefully improving charge mobility amongst the molecules. Parallel work on POCs has shown a top-down crystal packing of flat, offset aromatic rings. The closely stacked carboxylic acid groups, with their large electron density, are suggested to act as a pathway for charge mobility through the crystal (see figure 20b). It has been shown previously in other carboxylic acid containing crystals that this property can be further improved via deprotonation and doping with a metal ion (see figure 20c). Improved conductivity would be a large step

towards the fabrication of a working diode as a proof of concept of an OLED using these organic phosphorescent compounds.

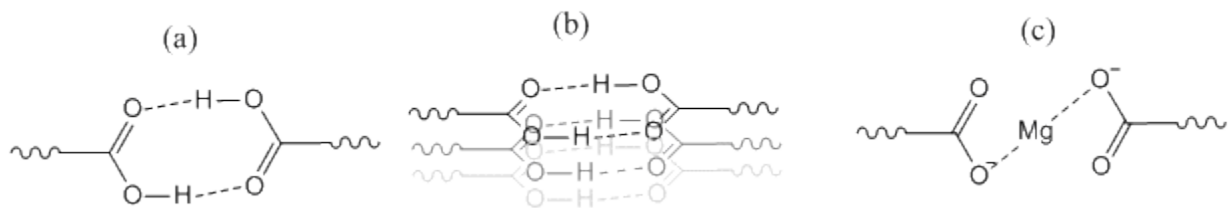


Figure 20 – (a) - Intermolecular carboxylic acid interactions driving side to side packing
(b) - Crystal 'stacking' of carboxylic acid functional groups based on currently observed top and bottom offset crystal packing

In order to overcome the difficulties that the electron withdrawing properties of the carboxylic acid functional group presented to bromination, the bromination of phenols containing functional groups known to be convertible to carboxylic acid was attempted. First, a primary alcohol containing phenol (easily convertible to carboxylic acid via oxidation) was brominated. The same reaction was attempted replacing the phenol alcohol group with an ether group (see figure 21). While both of these reactions lead to dibromination, the bromines atoms were not in the necessary para orientation to each other. In the synthesis of symmetric POCs there is no differentiation between all of the aromatic ring reaction sites, and the first bromine to be substituted weakly directs the second bromine to a para position. However, once the symmetry of the ether groups is broken, the differences in electron donating behavior between the two functional groups causes strong differentiation between the meta and ortho reaction sites on the aromatic ring. This leads both of the bromines to react at the sites ortho to the phenol.

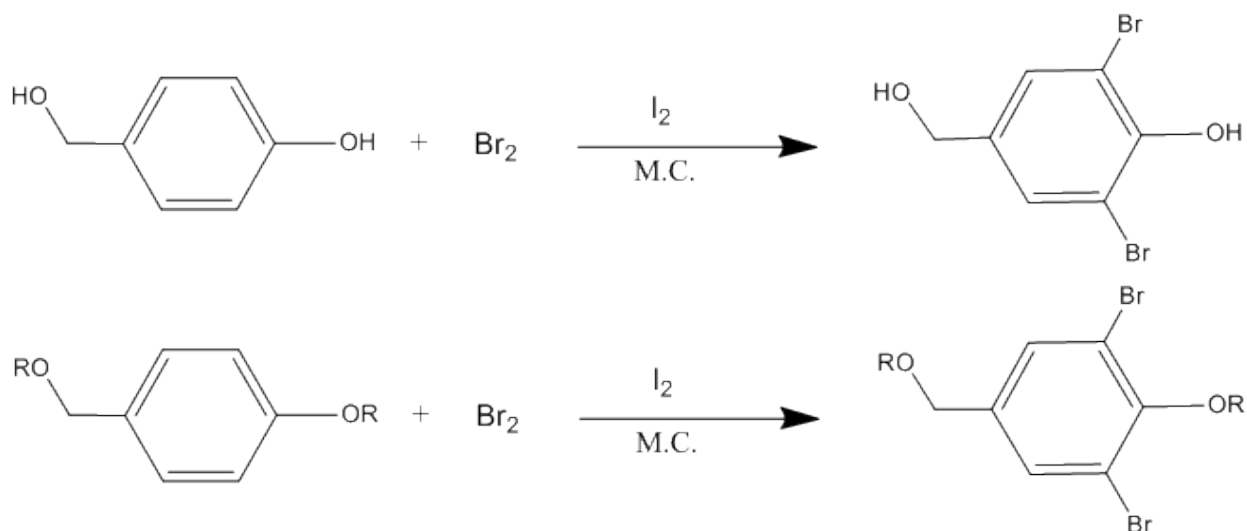


Figure 21 – Bromination products of secondary alcohol and ether derivatives. Since the strong electronegativity of the carboxylic acid group deactivated the molecule to bromination, functional groups convertible to carboxylic acid were pursued. These unfortunately did not lead to the desired para-bromination.

In order to combat this issue, another synthetic route would be needed. Successful para dibromination of cresol, a methyl phenol, and that bromination reaction has been found in the literature and was thus also undertaken. The literature described different reaction conditions from those normally used; therefore a reaction using these conditions was also run (see figure 22). Like the primary alcohol, the methyl group of the cresol has a known synthetic route for conversion to carboxylic acid. But like the primary alcohol, the cresol reactions lead to non para orientation dibromination. While parallel work on POCs has shown a few asymmetric reactions that brominate as desired, these examples were only asymmetric past the oxygen on the ether functional group (see figure 23). Thus only very limited asymmetry viability has been demonstrated previously.

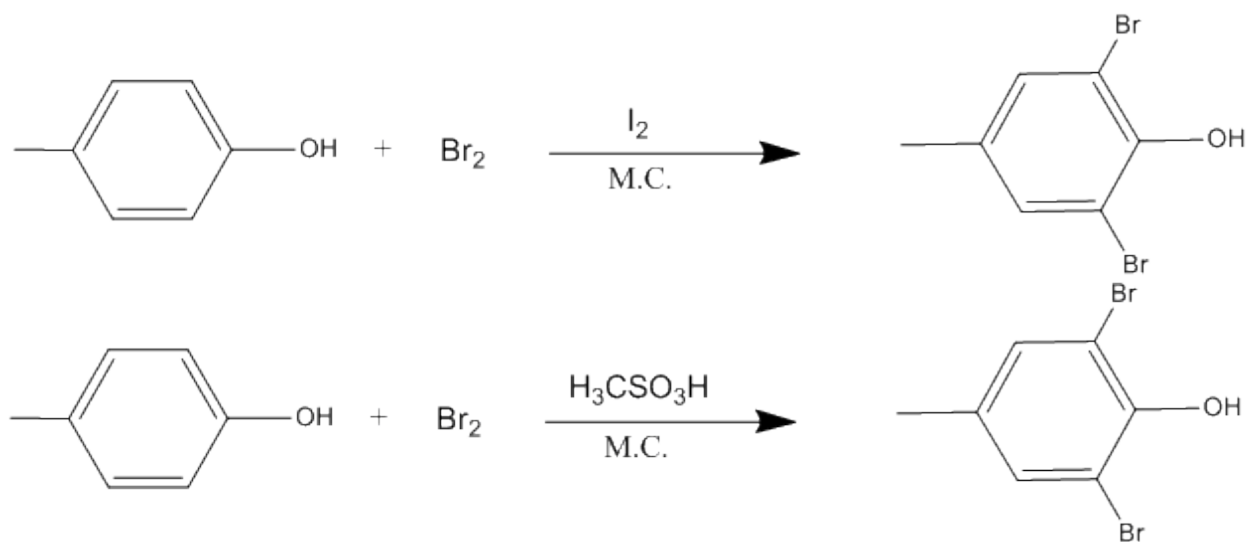


Figure 22 - Bromination products of cresol. As with the secondary alcohol and ether compounds the methyl group in cresol is convertible to carboxylic acid. Despite literature references to the contrary however, bromination of cresol did not lead to para-bromination.

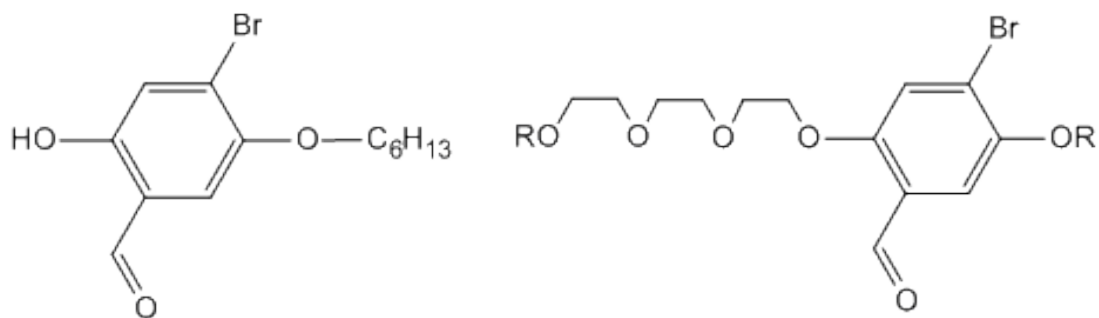


Figure 23 - Asymmetric POC derivatives that have been shown to be synthetically viable in parallel work on POCs.

Continued Work on POC Derivatives

While the initial, simplest synthetic routes to both the color tuning derivatives and improved conductivity derivative POCs proved unworkable, these properties were still extremely desirable and worth continued pursuit. While parallel work on POCs was able to produce both an orange and a blue color POC, an improved range of colors is still desirable in demonstration of applicability of POCs towards OLED technologies. Likewise an electrically conductive POC continued to prove elusive. Therefore a new synthetic route was undertaken which proposed to make the amino, cyano, and carboxyl acid derivatives (see figure 24).

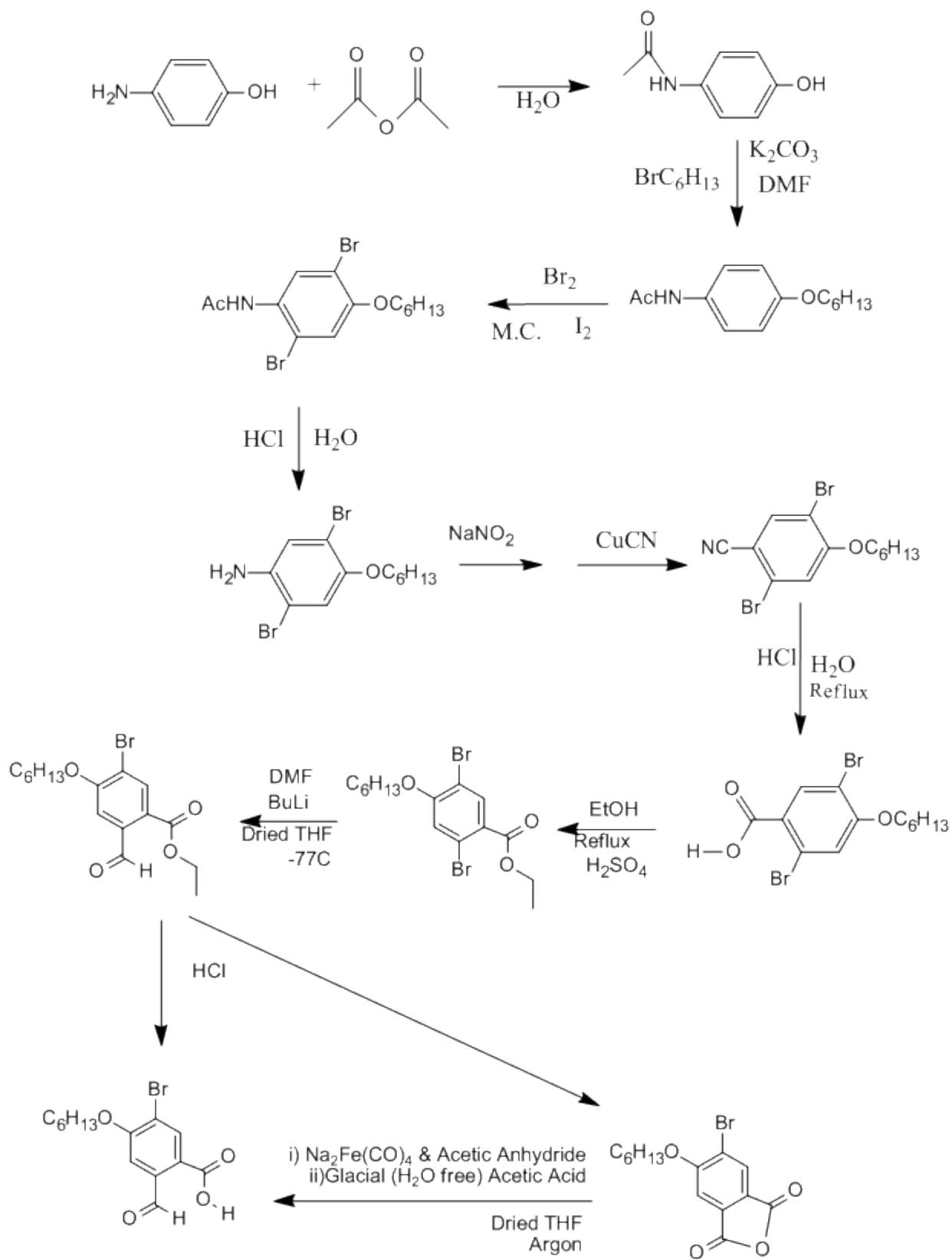


Figure 24 – Proposed synthetic route for the synthesis of cyano and carboxylic acid derivative compounds for color tuning and conductivity studies. The route uses an amide to avoid the electron withdrawing deactivation of bromination reactions and then converts the amine group to the desired functional groups.

The biggest impediment to the synthesis of the color tuning compounds was the bromination of an electron deficient aromatic system. In order to remedy this issue the synthetic route proposed converting an amine functional group into cyano and carboxylic acid groups after bromination had occurred. Thus the difficulties of the amine derivative synthesis needed to be addressed. By converting the amine group to an amide the functional group is protected from reactions with the bromoalkane while the surfactant nature of the compound is functionally removed. Through the use of the amide protecting group both of the synthetic difficulties are avoided. Once the protecting group was returned to an amine, the amine derivative would be complete. Unfortunately an amine containing aldehyde compound could not be obtained from this synthetic route. In order to synthesize aldehyde derivative compounds reactions with butyl-lithium are undertaken. However, as previously mentioned, butyl-lithium will react vigorously with the most available hydrogen source, and in the case of the amine derivative would react with the amine hydrogen atoms before the aromatic ones. Since the color tuning is expected to be due to electronic effects on the aldehyde functional group, not the bulk molecule, a red-shifted POC could not be synthesized simply from this synthetic route.

The next step of the synthetic route involved converting the amine to a cyano group and then converting that to a carboxylic acid. The addition of the aldehyde functional group is saved for last for numerous reasons. As described above the butyl-lithium reaction cannot take place in the presence of any hydrogen source, and thus cannot be

undertaken before the amine functional group is converted. Secondly, due to the similarities between the carboxylic acid and the aldehyde, most reaction conditions that would generate a carboxylic acid functional group would likewise convert the aldehyde to a carboxylic acid. Finally, synthesizing the bulk compound, then converting some of the bulk compound to aldehyde derivative is synthetically simpler than attempting parallel synthesis of the bulk and aldehyde compounds. While it is possible that the color tuning aldehyde derivatives would achieve their intended effect in a basic, dibromo-ether bulk compound, the extreme sensitivity to crystal mismatch demonstrated in the mixing studies suggests that mixing of molecules with these different functional groups would lead to severely inhibited co-crystallization.

In order to successfully synthesize the aldehyde derivative of the carboxylic acid bulk compound, the carboxylic group is protected via conversion to an ester. With the reactive hydrogen site protected the aldehyde is synthesized and the protective group is then removed. Unfortunately, it could not be determined if deprotection of the ester would lead to a ring closing mechanism with the aldehyde. Therefore, a ring opening reaction scheme is included in the overall synthetic route.

While this synthetic route avoided the past synthetic impediments, numerous new issues prevented successful synthesis of either the cyano or carboxylic derivative compounds. While using the amide as a protecting group greatly reduced the synthetic difficulty, surfactant issues lingered and the overall yield after deprotection was poor. Nevertheless the amine derivative was successfully synthesized. Despite numerous attempts, however, the amine could not be converted to a cyano functional group. Infrared

spectroscopy and mass spectroscopy both confirmed that no detectable amount of cyano functional group was synthesized using the given reaction scheme. Furthermore, due to the presence of reactive hydrogen atoms present in the amine group, an amine containing aldehyde derivative could likewise not be synthesized.

Proposed Derivatives of Interest – Liquid Crystal

While the mixing studies and crystallographic data strongly suggest the heavy atom effect as a means of explaining the phosphorescence of POCs, demonstrating an on-off behavior of the phenomenon based on physical distance between molecules in the crystal would exhibit definitive proof of the heavy atom effect mechanism. Parallel work on the POCs proposed using a soapy POC derivative in a Langmuir-Blodgett trough to physically compress the molecules together. Unfortunately, difficulties in asymmetric synthesis and layering of the molecules prevented this scheme from demonstrating an on-off behavior. Liquid crystals represent a unique opportunity to continue pursuit of dynamic control of the crystal packing.

Liquid crystals are composed of a liquid compound with a strong internal dipole. By applying an external electric field the dipoles cause the molecules to tend to align (see figure 25). In this fashion an external macroscopic property, the electric field, is able to change the microscopic orientation of the molecules. Therefore the liquid crystals are an ideal candidate for pursuing an on-off behavior in POCs in order to definitively prove the proposed heavy atom effect mechanism. If the phosphorescent phenomenon is critically dependent on the intermolecular bromine-aldehyde distance, then there should be no observed phosphorescence if the proper crystal packing is not present. Therefore, by

synthesizing a liquid crystal POC one should be able to 'turn on' the phosphorescence through application of an electric field.

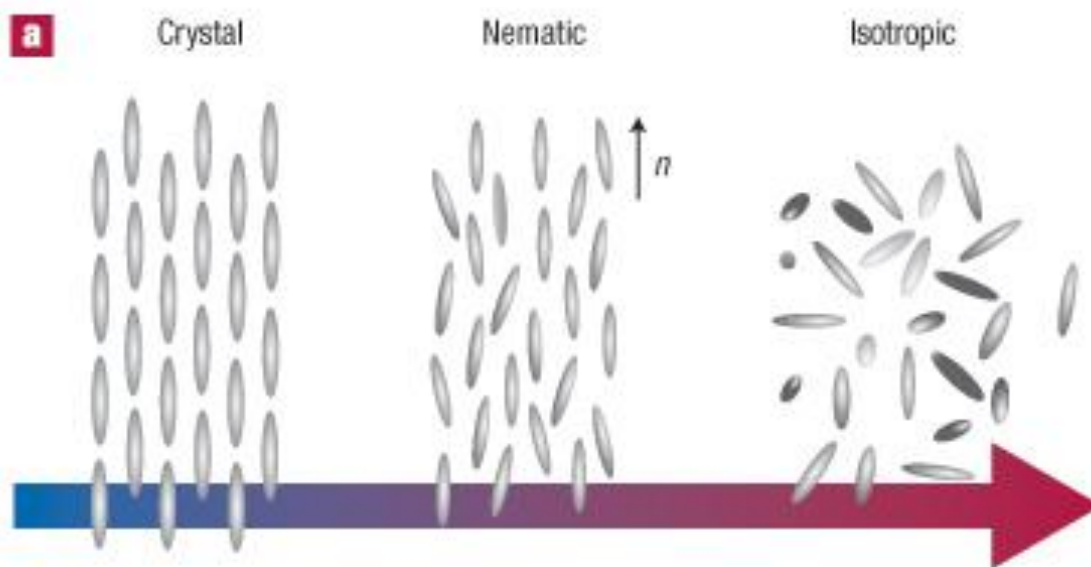


Figure 25 – Comparison of crystal structure to nematic and isotropic phases of liquid crystals. Liquid crystals randomly orient in the absence of an electric field (the isotropic phase). In an electric field however the strong dipole in the molecules causes them to tend to align (the nematic phase). Figure is courtesy: Woltman, S. J.; Jay, G. D.; Crawford, G. P. *Nature Materials*, **2007**, 929-938

In order to achieve a liquid crystal POC derivative the synthetic route pursues known liquid crystal molecular architecture¹⁰ and adds the bromo-aldehyde functional groups (see figure 26). Typical liquid crystals use a strongly electron withdrawing group next to an extended aromatic system to achieve a large dipole moment. In the proposed liquid crystal compounds this is achieved through the use of an ester group adjacent to a bithiophene. Then, in order to ensure that the material is liquid at room temperature despite the strong dipole moment, a phenyl group with a long chain ether is attached to the bithiophene adjacent to the ester group. While this project is currently in an ongoing state,

it is hoped that the products of this synthetic route will demonstrate phosphorescence only when aligned in the presence of an external electric field. Such on-off behavior would constitute extremely strong evidence that the intermolecular heavy atom effect is the cause of the POC phenomenon.

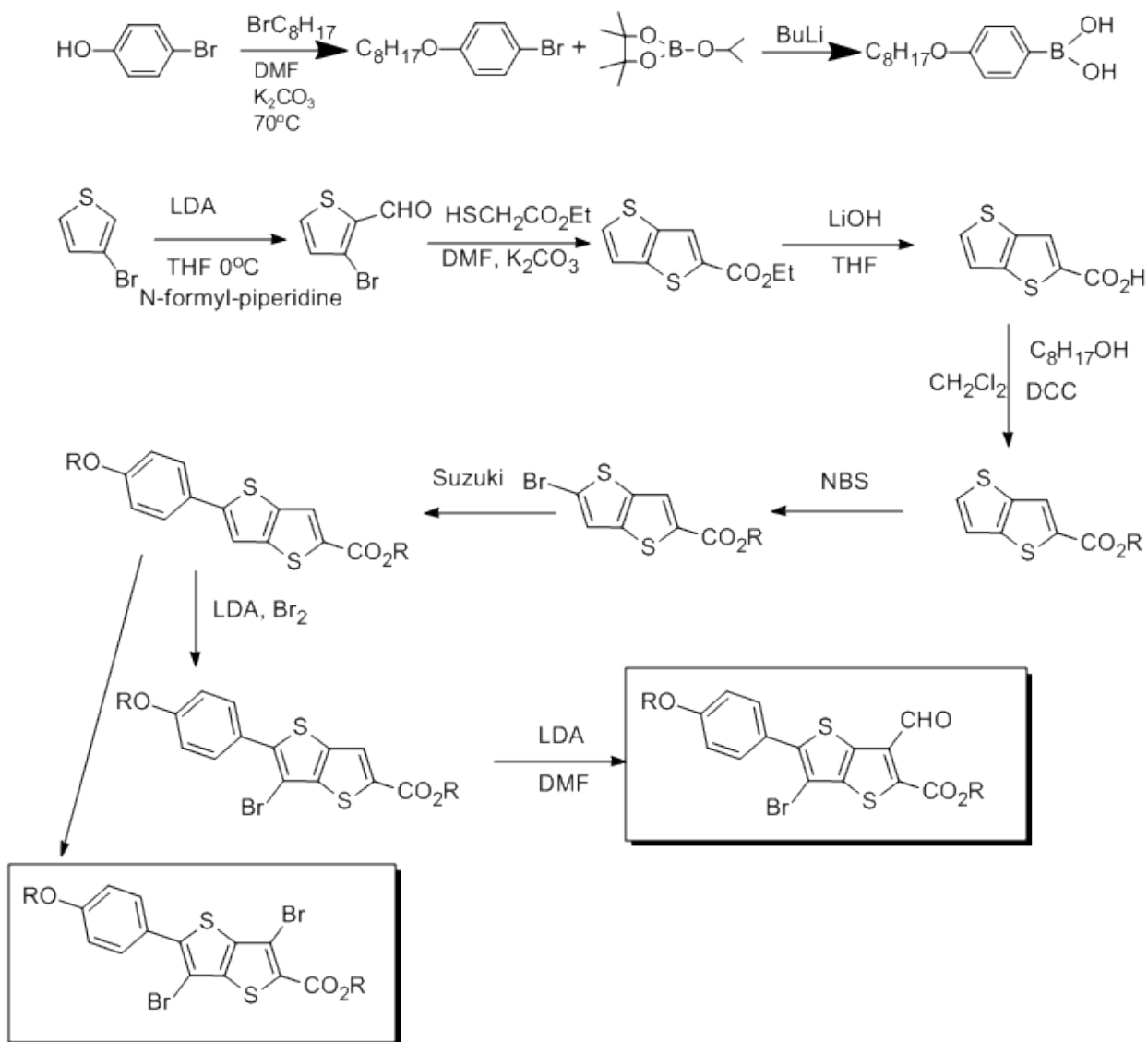


Figure 26 - Synthetic route for liquid crystal POC derivative. The liquid crystal is first synthesized in two parts, the bithiophene and the phenyl ether, which are coupled together using Suzuki coupling. The liquid crystal is then brominated and an aldehyde derivative generated in order to obtain the desired POC behavior.

Conclusion and Future Work

Myriad phosphorescent organic crystals and their properties have been investigated. It has been determined that good cocrystallization of two different molecules – the ‘bulk’ molecule and its aldehyde containing derivative – is critical to the presence and efficiency

of the phosphorescent phenomenon. Studies into the mixing of bulk and aldehyde crystal composition ratios and mixing of different sized bulk and aldehyde molecules have strongly suggested that a specific intermolecular interaction between the bromine atom of the 'bulk' molecule and the aldehyde functional group causes the observed phosphorescence. This interaction has not been previously observed at room temperature but is likely to be derived from a combination of halogen bonding and the intermolecular heavy atom effect.

The difficulties encountered in the synthesis of the derivative compounds have prevented a conclusion of the tunability study and the development of an improved conductivity derivative. The strong electron withdrawing effects of the desired functional groups may prevent the possibility of both the groups necessary for phosphorescence and the groups desired for tunability/conductivity being present on the same aromatic ring. Directed synthesis of multiple functional groups on a single aromatic ring is a difficult task in organic chemistry, and multiple new approaches have been proposed. Alternative compounds, ranging from polymers and extended aromatic systems and synthesis techniques such as ring closing and ring coupling, have been proposed to improve the conductivity of the organic phosphorescent materials, but these do have drawbacks (see figure 27). The ring binding route would utilize a Suzuki coupling scheme to couple a phosphorescent active ring to an electrically conductive ring. However both of these proposed routes involve difficult synthetic techniques, and much like the synthetic routes previously explored, it is unknown whether these techniques will be viable.

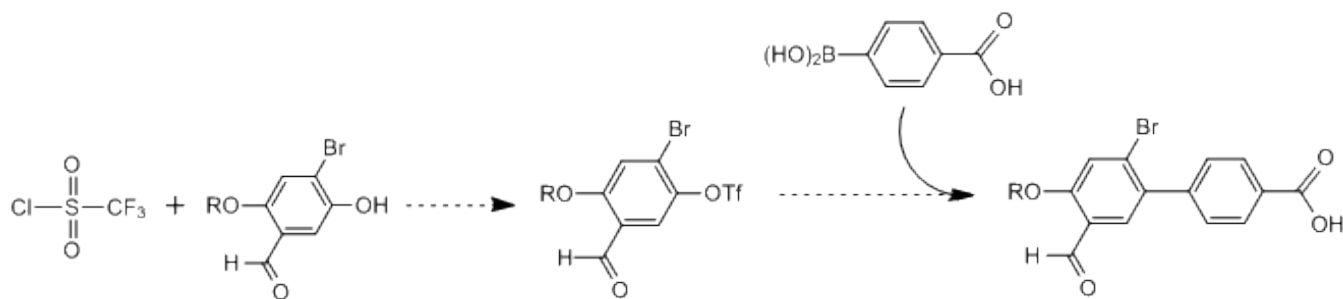


Figure 27 – Synthetic route for proposed ring binding mechanism for synthesizing a conductive POC derivative through a two ring system.

Nevertheless, in order to demonstrate the important application of POCs to OLED devices, a conductive derivative is necessary. Still, having the conductive functional group on the same aromatic ring as the phosphorescent groups ensures that the conducting charge gets to where it needs to be in order to trigger the phosphorescence. Likewise, having a highly electron withdrawing functional group on a single aromatic ring with all the other functional groups should greatly blue-shift the phosphorescent emission. Such high energy phosphorescence would be of extreme interest commercially and scientifically.

In order to continue pursuing the conductivity goal, multiple avenues have been proposed. For example, ring closing reactions and other unexplored methods of synthesis of the proposed carboxylic acid derivative can be explored. It has also been suggested that an aromatic ring containing the phosphorescent groups be bonded to an aromatic ring containing the conducting functional groups in hopes of improving the conductivity while preserving the phosphorescence. Other compounds with similarly small halogen-halogen spacing in the crystal packing are being explored for possible analogous systems where the intermolecular heavy atom effect could be triggered. It is thought that materials

with these similar interactions may likewise exhibit the phosphorescence seen in the currently known phosphorescent cocrystals. If this is the case, then more conductive materials with similar interactions will be investigated in order to pursue a working device from these materials.

One of the most promising leads in the search for new POC derivatives are the intramolecular heavy atom effect compounds. The goal of these compounds is to force the tight bromine-aldehyde intermolecular interactions to occur within a single molecule (see figure 28). These intramolecular derivatives would have a number of novel properties and uses. Since co-crystallization would not be necessary for the phosphorescent phenomenon these compound could potentially phosphoresce in solution (in the absence of solvent quenching). Furthermore they could be used in the development of an OLED device: though the compound itself would not be conductive it could be used as a phosphorescent dopant within a conductive material, as is done for many LED devices.

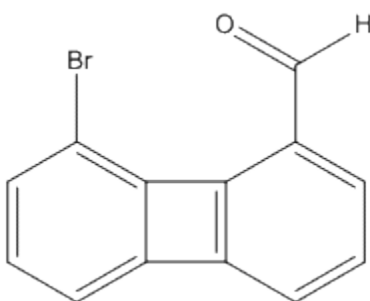


Figure 28 - Possible molecular structure for an intramolecular heavy atom effect phosphorescent compound. If the proper interaction distance between the aldehyde and bromine can be obtained within a single molecule many old problems and new applications of the POC phenomenon would be addressed.

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