

Synthesis and Photoluminescence Characterization of Polymeric Materials for Organic Light-Emitting Devices (OLEDs)

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Abstract

Organic light-emitting devices (OLEDs), which show promise to replace traditional liquid crystal displays, are capable of emitting light in all directions—even at low power—creating brilliant images even at wide viewing angles. The challenge today is to understand the underlying behavior well enough to synthesize polymers with long emission lifetimes in all necessary colors. However, as defects and other variations in chemical composition are common on polymer chains, oligomers (small polymers) can be more accurately synthesized and characterized. To characterize the behavior of a novel molecule R271, I synthesized symmetric three-unit oligomers. I used benzene, *t*-butyl benzene, naphthalene, and thiophene with R271 in our respective trimers and characterized them by UV-Visible Absorbance spectrophotometry and fluorescence spectrophotometry. I confirmed that increasing molecule length decreased the band gap, but electron-donating effects in thiophene also contributed to the effect. However, destruction of excited states in thiophene molecules limited the photoluminescence efficiency of the trimer.

1 Introduction

Polymer-based organic light-emitting devices (OLEDs) are poised to replace liquid crystal displays (LCDs) in the next generation of thin, lightweight screens for flat-panel televisions, notebook computers, mobile phones, and digital cameras. Operating on the principles of photo- and electroluminescence, OLED polymers emit light when stimulated by light or electricity. These polymers emit light in all directions and create brilliant images that are visible from wide viewing angles. Moreover, polymer-based OLEDs consume less power than LCDs and require less manufacturing complexity. The future holds the possibility of flexible, large-area displays created by inkjet printing of polymers from solution. Today, several companies market products made with OLED screens that range from digital cameras to mobile phones to high-end electric shavers. In fact, 40-inch flat-panel televisions created by inkjet printing of polymers onto electrically conducting glass exist as prototypes and should be marketed by 2007.¹ The OLED market is projected to reach \$0.5B in 2004 before ballooning to approximately \$4B by 2010.² In this industry, only obstacles of emission lifetime and blue-emitting material quality remain before ultrathin, lightweight, low power screens boasting wide viewing angles and unmatched brightness will be realized at a fraction of the cost of current technology.

Polymers are highly versatile materials whose properties can be tuned by subtle changes in chemical structure. Moreover advances in polymer chemistry knowledge over decades have brought forth reagents, catalysts, and polymerization reactions that allow researchers to synthesize novel polymers. Therefore, OLED polymers can be customized endlessly to achieve desired device behavior. Recent efforts in OLED polymer development focus on adding special monomers to the polymer chains that allow the device to take advantage of light emission modes previously thought impossible. Toward optimizing power efficiency and color tuning of already good polymers, some polymer engineers are focused on adding molecules like iridium and fluorine to the polymer chains. Standard spectroscopy methods facilitate comparison of behavior across synthesized polymers and across fabricated devices. However, statistically, any sample of polymer in solution contains chains of various lengths whose chemical compositions vary as a result of defects. Therefore it remains difficult to achieve the fundamental physical understanding of the phenomena occurring on a long polymer chain and between neighboring chains in solution. The problem is that researchers design monomers but evaluate large, dynamic polymers. One solution is to design short polymers, or oligomers, that can be accurately identified and evaluated after synthesis.

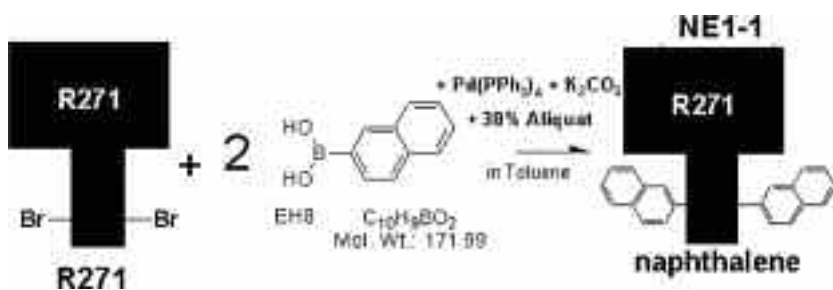


Figure 1. Suzuki Coupling Reaction to Create NE1-1.

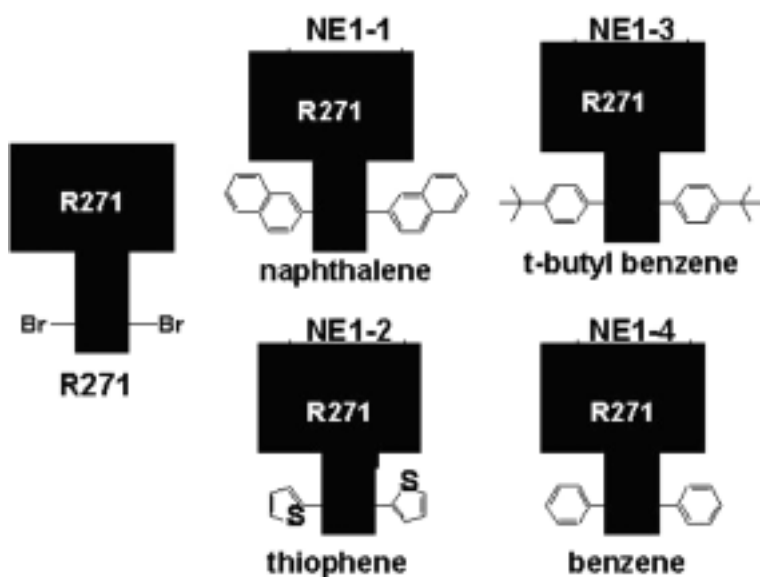


Figure 1. Suzuki Coupling Reaction to Create NE1-1.

At Hitachi Chemical, I measured strong emission of light from solutions of a long-chain polymer that contained a novel monomer R271 but no detectable emission from solutions of R271 alone. Therefore, I sought to understand the contribution of R271 in a polymer such that I could use it effectively in our syntheses.

The objective of this work is to synthesize and evaluate various R271-containing conjugated trimers in order to characterize the interactions between R271 and attached monomers. In this paper, I discuss the physics that underlies light-emitting polymer behavior and explain the techniques and experiments that I used to study our synthesized trimers.

2 Background

2.1 Photoluminescent Materials

Photoluminescence is emission of light from a material that has absorbed light energy. In this process, the material's electrons are promoted to excited states by absorption of photons of light energy. The emitted light is the result of those electrons which relax back to the ground state by emitting photons. Both the wavelength of light required to cause photoluminescence and the wavelength of light emitted depend on the

energy difference between the ground and excited electron states. That is, the band gap energy is a key parameter in photoluminescence.

The relationship between energy and wavelength is given by:

$$E = hc / \lambda \quad (1)$$

where h is Planck's constant, c is the speed of light, and λ is the wavelength of light.

Most organic photoluminescent materials are π -conjugated semiconducting materials. They are molecules that feature alternating single and double or single and triple bonds. The energies of electrons in the resulting π molecular orbitals are usually higher than in (σ) orbitals. Therefore, the energy gap between the highest occupied molecular (π bonding) orbital (HOMO) and the lowest unoccupied (π^* antibonding) orbital (LUMO) is small, making the materials semiconductors.³ Small band gap (1.3–3 eV) allows photoluminescence with small energy input (light of wavelengths in the near UV to near infrared range).

In the case of organic π -conjugated polymers, the π orbital is delocalized over the length of the chain. The overlap of neighboring atomic orbitals along the length of the molecule creates bonding and anti-bonding molecular orbitals that electrons could occupy. A molecule as large as a polymer will therefore have many closely spaced electron energy levels. The measurable result of this overlap is decreasing band gap with an increasing molecule length, and the length at which this effect stops is the effective conjugation length. Effective conjugation length is determined by factors that might disrupt the overlap of atomic orbitals along a polymer chain. These factors include experimentally controllable bonding geometry, defect concentration, and proximity of neighboring polymer chains. Conjugation involving an electron donor molecule might populate some antibonding energy levels and thereby raise the HOMO level, decreasing the energy required to excite an electron to the LUMO level. In summary, the size of the band gap can be controlled. Therefore, polymer engineers can chemically tune the wavelength of photoluminescence emission by adjusting the effective conjugation length.

We discussed photoexcitation of electrons to excited states, but not all of those electrons relax luminescently and contribute to photoluminescence. This fact is important when considering the efficiency of OLEDs. An excited electron will have one of several possible fates that include relaxation to a ground state by releasing only heat. However, the dominant path in polymer photoluminescence involves an electron thermally dissipating some energy to settle into the lowest energy excited state before emitting a photon to relax to the ground state. This transition from a singlet excited state to a singlet ground state is called fluorescence and occurs in one-billionth of a second. Other excited electrons may jump to neighboring molecules or segments of the same molecule and thereby transfer charge. For instance, in what is called a well-barrier structure, there might be a large difference in the HOMO levels between adjacent molecules in a chain that electrons move to the lower

energy molecule. Otherwise, some electrons may jump from singlet excited states to low-energy triplet excited states before emitting photons in a 1-second process called phosphorescence. Electron spin restrictions allow only 25% of created excited states to be of the singlet type while all others are non-emissive triplet states. Therefore, at a maximum, only 1 in 4 excited electrons will contribute photoluminescence. Nevertheless, the photoluminescence quantum efficiency Φ_{PL} is defined as the percentage of singlet states that do indeed emit light,⁷ and is proportional to the intensity of fluorescence.

Experimentally, fluorescence quantum efficiency is given by:

$$\Phi_{PL} = \Phi_{ST} \left(\frac{Grad_{SA}}{Grad_{ST}} \right) \left(\frac{\eta_{SA}^2}{\eta_{ST}^2} \right) \quad (2)$$

where Φ_{ST} and η_{ST} are the fluorescence quantum efficiency and solvent index of refraction of a standard sample, respectively. The "SA" subscripts refer to the test sample. The $Grad_x$ parameter is the slope of a linear-regression line relating change in sample concentration to fluorescence intensity. The $Grad_x$ parameters are measured by fluorescence spectrophotometry by a technique in which error is normally ± 0.1 .⁸

2.2 Electroluminescence in OLEDs

Electroluminescence is emission of light by a photoluminescent material in response to an electric potential. This phenomenon drives OLED devices. In a typical polymer-based OLED, a thin film of photoluminescent polymer is sandwiched between two electrodes, with one being indium tin oxide (ITO)-coated conductive glass and the other being a metal cathode. When a voltage is applied across the device, with positive voltage applied to the ITO anode, electrons are injected from the cathode while the positive charge-carrying holes are injected from the anode. As the charge carriers drift through in the applied electric field, they may recombine to form neutral excited states called excitons. As in photoluminescence, if the excited states are singlets, they may relax to the ground state by emitting photons. The light escapes the device through the transparent anode.⁹

3 Experimental

Our experiment included synthesizing and purifying four conjugated trimers before evaluating their photoluminescence properties. I synthesized the trimers by Suzuki Coupling* reactions before identifying the trimers by Nuclear Magnetic Resonance and Mass Spectrometry and Elemental Analysis. Finally, I evaluated the trimers by collecting absorbance spectra and measuring photoluminescence intensity and color by spectrophotometry.

3.1 Polymer Synthesis by Suzuki Coupling

Our desired trimers would include an R271 molecule sandwiched between two identical conjugated molecules. The conjugated end-unit molecules would be a pair of benzene, t-Butyl benzene, naphthalene, or thiophene molecules. For each reaction, I obtained the following reagents: conjugated end-unit

molecule attached to a boron ester and R271 molecule with Bromine atoms attached on each end. I proposed Suzuki Coupling reactions in which two conjugated end-units would attach to an R271 molecule (Figure 1). In each case, Toluene served as the organic solvent, $^1Pd(PPh_3)_4$ as the metal catalyst, K_2CO_3 as the base, and 30% Aliquat as the phase transfer catalyst. Each synthesis is described below.

NE1-1

In a test tube, I combined 0.8 mmol of the R271 reagent with 1.6 mmol of the naphthalene reagent and a magnetic stirrer, and then vacuum dried the powder mixture for 30 minutes

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Imagination at work 

* See Appendix A.1 for diagram of Suzuki Coupling.

† Known industrially as Tetrakis Palladium.

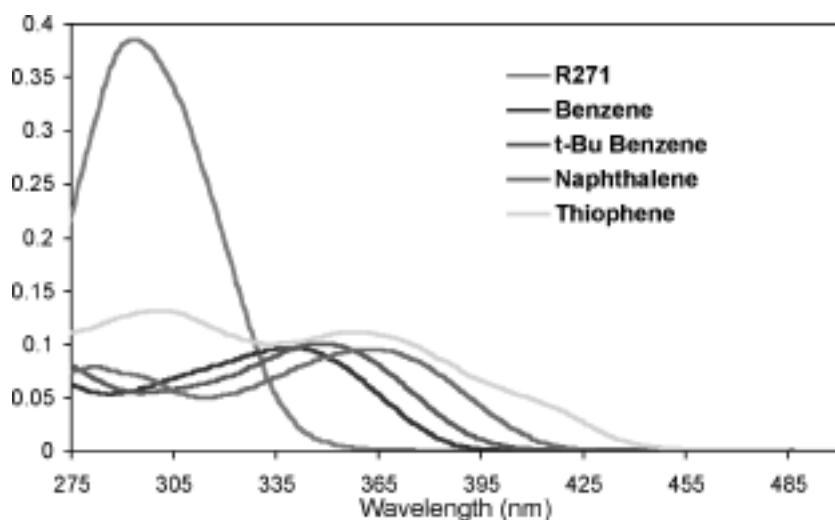


Figure 3. UV-Visible Spectra for synthesized trimers and R271.

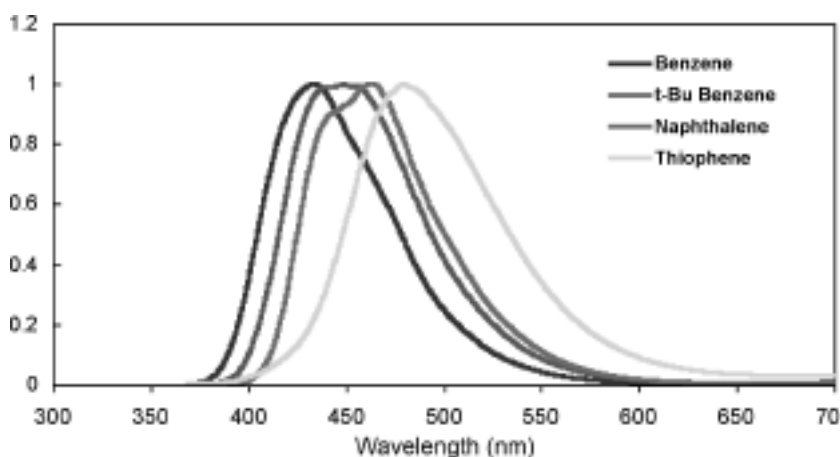


Figure 4. Fluorescence Emission Curves for the Synthesized Trimers at 0.1 Peak Absorbance.

using an oil rotary vacuum and a plastic tube. Next, I quickly added 0.016 mmol of the Tetrakis palladium catalyst powder. While I added the powder reagents, the liquid reagents had been bubbled with Nitrogen gas. I used metal syringes to add the liquid reagents to the test tube while N_2 gas flowed into the test tube to preserve an inert atmosphere. I added 5.8 mL of the Toluene solvent, 0.64 mL of the 30% Aliquat phase transfer catalyst and 4.2 mL of the 2M K_2CO_3 base, respectively. I initiated the reaction by mounting the test tube with its tip submerged in a 95°C oil bath while N_2 gas flowed into the top of the test tube through a plastic tube and the magnetic stirrer agitated the solution. I monitored the reaction by thin-layer chromatography* (TLC) and stopped the reaction after 19.5 hours when only one product was apparent. The post-reaction mixture was a green-yellow liquid phase above a clear liquid phase.

* Thin layer chromatography separates compounds in a mixture on the basis of chemical affinity. A solvent is selected for polarity and allowed to climb up a thin layer of alumina that had been blotted with a drop of reaction mixture. The compounds in the mixture having little affinity for alumina move far up the alumina surface while those with high affinity move less.

I purified 0.280 g of pale-yellow powder, a 57% yield. I identified the trimer product by NMR, mass spectrometry, and elemental analysis.

NE1-2

Using the same techniques as in NE1-1 synthesis, I combined 0.8 mmol of R271 reagent with 1.6 mmol of thiophene reagent before adding 0.016 mol of $Pd(PPh_3)_4$, 5.8 mL of Toluene, 0.64 mL of 30% Aliquat, and 4.2 mL of 2M K_2CO_3 . After 19.5 hours the reaction was complete and the mixture was an orange-green liquid phase above a clear liquid phase.

Human error prevented complete purification of a solid product, so I repeated the synthesis to obtain a flaky orange powder. I then identified the trimer product in the mixture by mass spectrometry and NMR.

NE1-3

I combined 0.8 mmol of R271 with 1.6 mmol of the t-butylbenzene reagent before adding 0.016 mol of $Pd(PPh_3)_4$, 4.8 mL of Toluene, 0.64 mL of 30% Aliquat, and 4.2 mL of K_2CO_3 . After 19.5 hours, the reaction was complete and the mixture was a purple-brown liquid phase above a clear liquid phase.

I purified 0.396 g of light-green powder, a 79% yield. I then identified the trimer product in the mixture by mass spectrometry and NMR.

NE1-4

I combined 0.8 mmol of R271 with 1.6 mmol of benzene reagent before adding 0.016 mol of $Pd(PPh_3)_4$, 4.8 mL of Toluene, 0.64 mL of 30% Aliquat, and 4.2 mL of K_2CO_3 . After 19.5 hours, the reaction was complete and the mixture was a purple-brown liquid phase above a clear liquid phase.

I purified 0.203 g of colorless needle-shaped granules, a 49.1% yield. I identified the trimer product in the mixture by mass spectrometry, NMR, and elemental analysis.

3.2 UV-Visible Absorbance Spectrophotometry

To evaluate the light absorption characteristics of each trimer in solution, I used a Hitachi U-3310 spectrophotometer. I obtained curves of absorbance vs. wavelength at various concentrations of each trimer in solution. From the UV-Visible absorbance curves, I determined the optical band gap of each material.

3.2.1 Sample Preparation

Samples for the U-3310 spectrophotometer are 3 mL quartz vials of the material of interest dissolved in an organic solvent. Here I dissolved approximately 1 mg of a given trimer in 3 mL of Tetrahydrofuran (THF). Before collecting data on a sample, I bubbled N_2 gas through the sample for five minutes to displace oxygen.

3.2.2 Data Collection

As the quartz vials transmit only approximately 84% of light into the liquid sample, the first step was to evaluate the absorbance of two samples of pure THF simultaneously. In each test, the spectrophotometer irradiated a baseline sample and a

trimer sample simultaneously. Therefore, the absorbance data is relative to a baseline measurement of a pure THF sample.

We tested our trimer samples over the wavelength range from 800-200 nm and concerned ourselves with the location and height of the first absorbance peak. I diluted each sample to adjust the height of the first absorbance peak to 1 (arbitrary unit), and then recorded the absorbance vs. wavelength curve. Then I obtained curves for absorbance peaks of 0.1, 0.08, 0.06, and 0.04. Also, for each of these concentrations, I recorded the wavelength where the absorbance peaks occurred, λ_{pk} . Finally, I drew a straight line along the slope of the leading edge of the absorbance peak and designated the wavelength at which the line crosses the x-axis the λ_{ab} . I put λ_{ab} , the wavelength at which absorbance begins, into equation (1), I calculated the optical band gap E_g for each trimer.

3.3 Fluorescence Spectrophotometry

To evaluate the photoluminescent fluorescence characteristics of each trimer in solution, I used a Hitachi F-4500 fluorescence spectrophotometer. I obtained curves of fluorescence intensity vs. wavelength (nm) at various concentrations of each trimer in solution. These curves showed us the wavelength range and intensity of the light emitted by each trimer. In addition to learning the color and intensity of each trimer's emission, fluorescence data allowed us to calculate the photoluminescence quantum efficiencies, Φ_{PL} .

3.3.1 Data Collection

Using the same samples used in absorbance evaluation, I characterized each trimer's fluorescence while it was irradiated by light of λ_{pk} . I thus obtained curves of fluorescence intensity vs. wavelength of emission (nm).

To calculate photoluminescence quantum yield, I analyzed the effects of sample concentration upon fluorescence intensity. For each trimer at each concentration, I first graphed fluorescence intensity vs. wavelength in Kcm-1 units and calculated the area under the curve. Next, I graphed the resulting values against concentration (peak absorbance) and determined the slope of the least squares regression line. Finally, putting the slope into equation (2), I calculated the photoluminescence quantum yield for each trimer.

3.4 Expectations

As for band gap energies, I expected that attaching thiophene, an electron-donating molecule, to R271 in NE1-2 would populate additional energy levels and decrease the gap between HOMO and LUMO. I expected this effect to be in addition to the band gap decrease that results from increasing the total length of the molecule. I also thought the t-butyl groups on NE1-3 would provide electron donation that would make its emission redder than NE1-4, which has plain phenyl rings. Similarly, I expected that the length of the double-phenyl rings of naphthalene in NE1-1 would redden its emission versus NE1-4.

As for photoluminescent fluorescence efficiency, I believed that the t-butyl group on NE1-3 might provide a non-emissive vibrational or rotational route for energy dissipation. Therefore, I expected fluorescence quantum yield to be lowest for NE1-3.

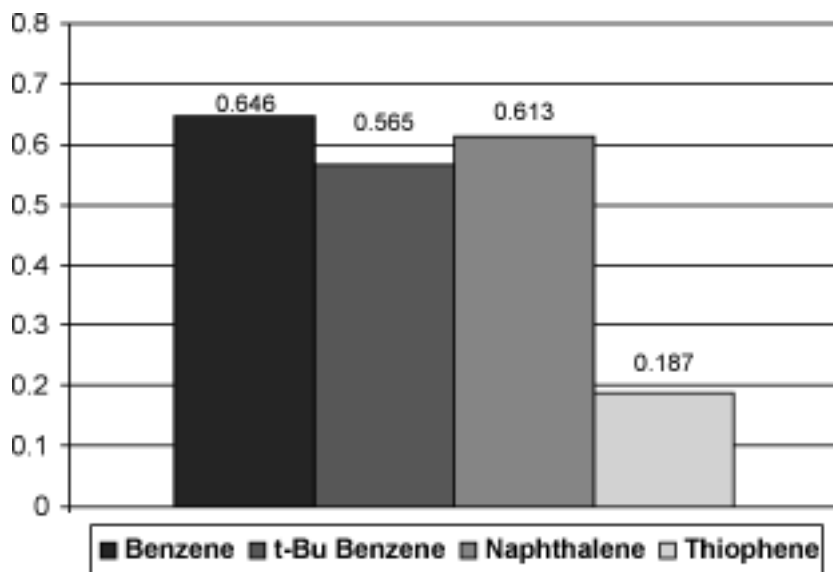


Figure 5. Photoluminescence Quantum Efficiency for Synthesized Trimers.

4 Results and Discussion

In this section and onward, I will refer to the oligomers by the conjugated end-unit molecule. For example, I will refer to NE1-4 as "the Benzene oligomer".

4.1 UV-Visible Absorbance Spectrophotometry

In Figure 1, I compare the absorbance vs. wavelength curves for the synthesized trimers against a curve for R271 from reference data. The onset for R271 is at 340 nm while for all of the trimers, the value of λ_{ab} is greater than 387 nm. Therefore, I can confirm overlap between R271 and each of the conjugated end-unit molecules.

Comparing across trimers, the Thiophene oligomer's λ_{ab} was longest at 440 nm, corresponding to a band gap of 2.82 eV. All the others had larger band gap energies: Benzene oligomer at 3.21, t-Butyl Benzene oligomer at 3.13 eV, and Naphthalene oligomer at 2.99 eV. The results meet expectations, as increasing molecule length decreased band gaps relative to the Benzene oligomer, and the additional electron-donating effects in the Thiophene oligomer caused an even greater band gap decrease.

4.2 Fluorescence Spectrophotometry

In figure 3 I compare the normalized fluorescence intensity vs. wavelength curves for the oligomers and note that the R271 does not emit light. Therefore, I can conclude that the conjugated end-units in each oligomer serve as the emission sources. Otherwise, the increased conjugation length, in increasing available energy levels, might increase the occurrence of emissive excited states.

As for comparison across trimers, the color of emission varied with the size of the band gap. The spectrum began with the Benzene oligomer emitting a deep blue at 434 nm, and red-shifted through t-Butyl Benzene and Naphthalene to the Thiophene oligomer emitting greenish-blue at 479 nm.

In comparing the photoluminescence quantum efficiency across the oligomers in Figure 4, I see that fluorescence inten-

sity did not follow the trend of band gap energy. As I expected, the t-Butyl Benzene oligomer had lower quantum efficiency than the Benzene oligomer. However, the quantum efficiency values for the Benzene, t-Bu Benzene, and Naphthalene oligomers all fell within the measurement error and render the comparisons inconclusive. However, the efficiency of the Thiophene oligomer was 3 times less than the efficiency of any other oligomer. The Thiophene result is consistent with a published finding that the chain ends of thiophene oligomers act as non-radiative exciton recombination centers.¹⁰

5 Conclusions and Recommendations

We desired an in-depth study of observed behavior in organic light-emitting polymers that contain molecule R271. Therefore, I synthesized and purified symmetric trimers using molecule R271 with conjugated molecules as end-units. The results depended upon the choice of Benzene, t-Butyl Benzene, Naphthalene, or Thiophene that I used as the end-unit molecule.

UV-Visible absorbance spectrophotometry allowed us to calculate optical band gap for each trimer and make statements about the structural factors like conjugation length. I observed decreased band gaps that confirm overlap of molecular orbitals between R271 and the end-units. In the case of the thiophene-substituted oligomer, I observed additional band gap shrinkage due to electron donation.

Fluorescence spectrophotometry showed that fluorescence efficiency is related to several structural and electronic factors. I confirmed that thiophene end-units are sites for non-radiative exciton destruction that limits photoluminescence efficiency.

For future development, I recommend further experiments to explore the contributions of R271 to photoluminescence. First, it would be helpful to conduct photoelectron spectroscopy in air (PESA) to determine the exact energy of the HOMO levels of R271 and each end-unit molecule. With such data, I could learn more about the distribution of excited electrons across the oligomer. Meanwhile, toward the same end, I should compare the data of this experiment with data from characterization of oligomers that exclude R271, made only of the conjugated molecules that I used here. Also, I recommend that I reconfigure the fluorescence quantum efficiency measurement technique so that the error would be reduced. With a more robust technique I could confidently draw conclusions

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about the impacts of subtle structural variations like t-Butyl addition upon fluorescence efficiency.

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7 Appendix

Suzuki Coupling



Figure 6. Generic Suzuki Coupling Reaction.

Suzuki Coupling is Palladium-catalyzed cross coupling reaction that usually involves organic halides and organoboron compounds and proceeds with high stereo- and regioselectivity. Also needed for the reaction are a base and a phase-transfer catalyst. The mechanism is shown below.

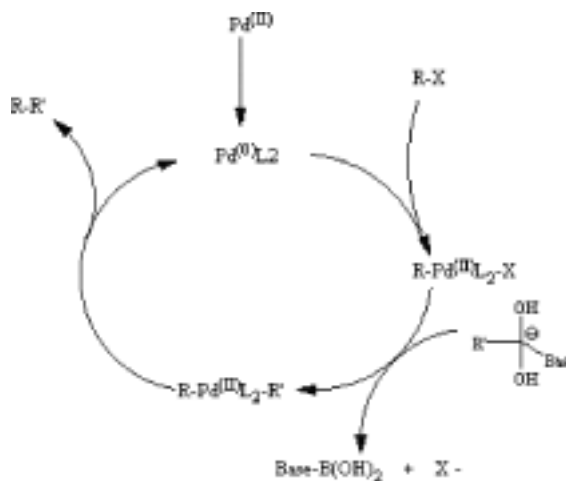


Figure 7. Detailed Suzuki Coupling Reaction Mechanism.