Synthesis and Study of Conjugated Carbazole Derivatives for Potential Use in Organic

Light Emitting Diodes (OLEDs).

Honors Thesis

Carroll College Natural Science Department
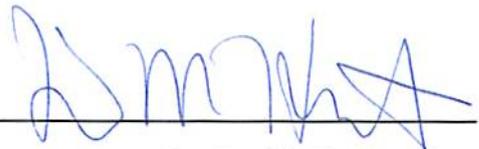
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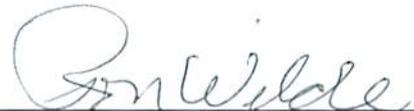
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Abstract

Organic light emitting diodes (OLEDs) are devices that use thin films of organic
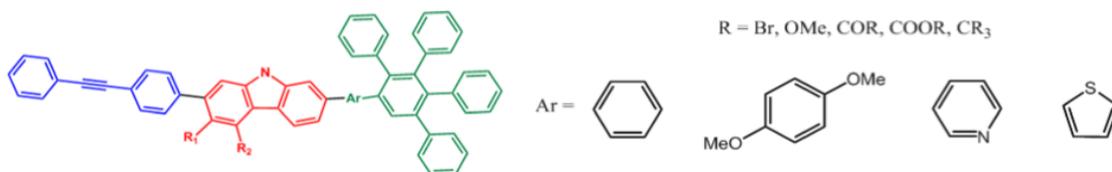
molecules to create light when electricity is applied. A full color display consists of red,

green, and blue light emissions. Stable, long lived, red and green light emitting molecules

have been successfully synthesized. Blue light emitting molecules have been synthesized,

but suffer shorter lifetimes and less stability than red and green light emitting molecules.

My research is currently focused on synthesizing conjugated carbazole centered

compounds with the hope of creating a stable blue light emitting molecule. The parent

molecule consists of 2,7-dibromocarbazole which will be coupled with two terminal

subunits, 1-(2',3',4',5'-tetraphenyl) phenyl-4-bromobenzene and 4-bromodiphenyl-

acetylene (DPA) (Figure 1). The DPA subunit was formed through a Sonogashira

coupling of a phenylacetylene with an aryl halide. DPA was then borylated via a

Lithium-Halogen Exchange in order to be coupled to the central carbazole moiety.

Current work involves producing diphenylacetylene, borylating it, and linking it to the

carbazole through a Suzuki coupling reaction.

Figure 1. Parent molecule.

Introduction

Organic light emitting diodes (OLEDs) are devices that use thin films of organic

molecules to create light when electricity is applied. OLEDs are becoming applicable in

many areas of technology. Some of the main uses of OLEDs include electronic displays and traffic lighting, as well as in televisions and other forms of general lighting[5]. OLEDs can consist of two or three layers of organic material[5]. The first two layers are the emissive layer and the conductive layer[5]. These two layers are set between the cathode and the anode, which are then placed on a substrate which is used to support the OLED[5]. The third layer of organic material may be present to transport electrons to the emissive layer from the cathode[5]. When an electrical charge is applied, electrons are transported from the cathode into the emissive layer, while the anode is removing electrons from the conductive layer[2]. These empty spaces, called holes, are filled with electrons from the emissive layer[2]. When holes and electrons combine, energy is lost and light is emitted through electrophosphorescence[2] (Figure 2).

Figure 2. OLED structure.[2]
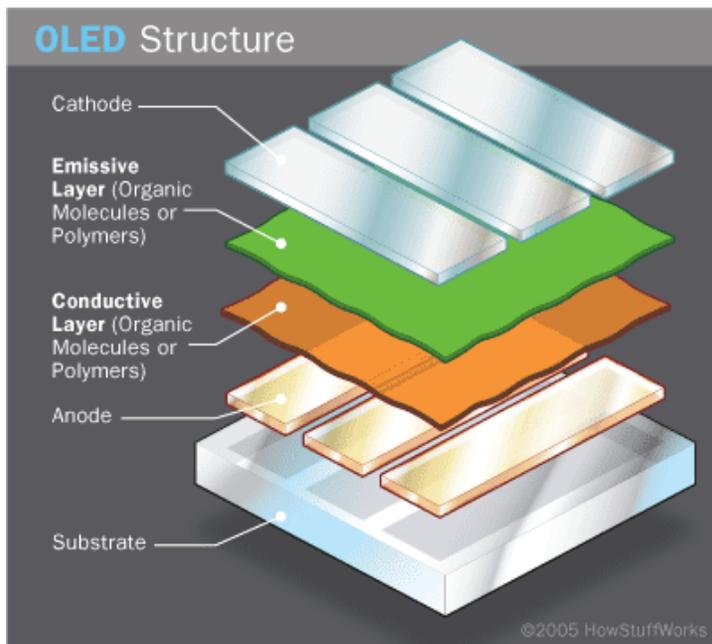
OLEDs have numerous advantages over light emitting diodes (LEDs) and liquid crystal displays (LCDs). The first advantage is OLEDs are much thinner and more flexible[5]. Because the organic layers of OLEDs are only 100-500 nanometers thick and can be fabricated on a plastic substrate, they are much more flexible and lighter than the crystalline layers of LCDs[5]. The thinness of OLEDs compared to the inorganic crystal layers of LEDs also makes them produce brighter images than LEDs[5]. Another advantage of OLEDs is that they produce their own light, not requiring backlighting, whereas LCDs do[5]. This results in much less power being consumed by OLEDs, thus making them more efficient[5]. OLEDs are also more efficient in that they are easier to produce in large quantities[5]. Because the substrate can be plastic, they can be made in large sheets[5]. Finally, OLEDs are advantageous because they have large fields of view: a field of view of about 170 degrees[5]. This is because they produce their own light unlike LCDs which block light. LCDs block light selectively, thus producing the images you see by blocking specific areas of the backlight[5].

While there are many advantages to OLEDs, there are also challenges that limit their use in technology. One disadvantage is that blue light emitting molecules for use in OLEDs have a shorter lifetime than red and green light emitting molecules[5]. A full color display consists of red, green, and blue light emissions[5]. Stable, long lived, red and green light emitting molecules have been successfully synthesized[5]. Blue light emitting molecules have been synthesized, but suffer shorter lifetimes and less stability than red and green light emitting molecules[1]. It is hypothesized that the synthesis of a molecule

with a central carbazole moiety and dendron and DPA moieties coupled together via a
Suzuki coupling reaction will create a stable blue light-emitting molecule.

To produce stable emission, the films used in OLEDs must contain molecules that
are asymmetric as well as nonplanar in structure[7]. The subunit that aids in forming this
nonplanar structure is the dendron. The dendron is essential to the overall parent
molecule because it is effective in blocking the formation of molecular aggregation, also
known as pi-pi stacking in the solid state[7] (Figure 3). Pi-pi stacking is a problem due to
its suppression of light emission[7]. This nonplanar polyphenylphenyl dendron increases
the stability of the molecule, thus allowing amorphous films to be readily processed and
used in OLEDs[7].

Figure 3. Pi-pi stacking.
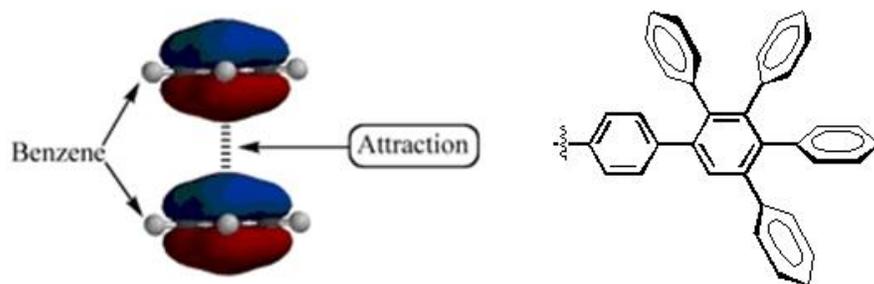
The central subunit of the parent molecule consists of a carbazole moiety.
Carbazoles are commonly used as blue light emitters because of their well-known
luminescence[1]. Besides their luminescence which makes them an attractive compound for
OLEDs, they also have hole transporting properties[1]. Carbazoles undergo a reversible
oxidation process, which makes them capable of being hole carriers[1]. The final subunit in

the parent compound is diphenylacetylene, which elongates the conjugation of the pi system and resonance throughout the molecule, thus increasing its overall stability.

The goal of this research is to form a stable blue light-emitting molecule, which will be accomplished by the synthesis of the parent molecule (Figure 1). The three subunit molecules will be synthesized individually and then coupled together (Figure 1). A central carbazole moiety (red) will be coupled with terminal dendron (green) and diphenylacetylene (blue) subunits. Specifically, 2,7-dibromocarbazole will be coupled with the remaining two subunits 1-(2',3',4',5'-tetraphenyl) phenyl-4-bromobenzene and 4-bromodiphenyl-acetylene. A Suzuki coupling reaction will be used to join the three subunits together. Once the final molecule has been successfully synthesized, its properties will be studied. Derivatives of the parent molecule will be synthesized and their properties will be tested as well, allowing for a large family of molecules to be studied. The properties of this final molecule and its derivatives could allow for an important contribution to OLED technology.

Results and Discussion

The Sonogashira coupling reaction was successfully performed using a modified procedure by the author to make 4-bromodiphenylacetylene[4] (Scheme 1). A palladium catalyst, a copper co-catalyst, and an amine base were used to couple the alkyne and aryl or vinyl halide together in this reaction[3]. Specifically in my research, 1-bromo-4-iodobenzene was coupled to phenyl acetylene to synthesize 4-bromodiphenylacetylene. The GC-MS characterization verifies the successful formation of 4-

bromodiphenylacetylene (Figure 4). Because ^{79}Br and ^{81}Br are two isotopes of equal abundance, the presence of two peaks of equal height in the GC-MS indicates a successful reaction. The most common fragmentation of 4-bromodiphenylacetlyene, occurring at 176, is the loss of the bromine. The conditions described in the experimental section for this synthesis provided 4-bromodiphenylacetylene with no byproducts for this reaction.
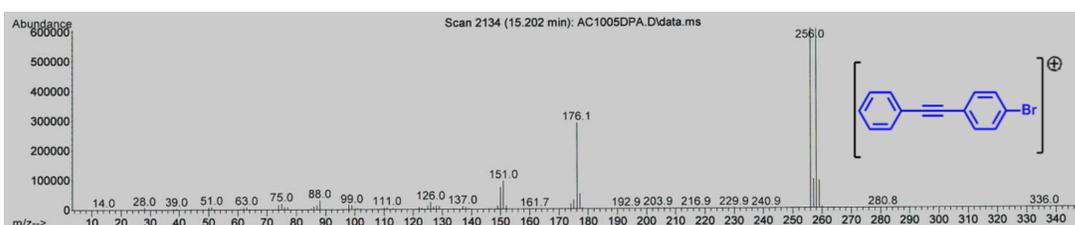
Scheme 1. Sonogashira Coupling Reaction
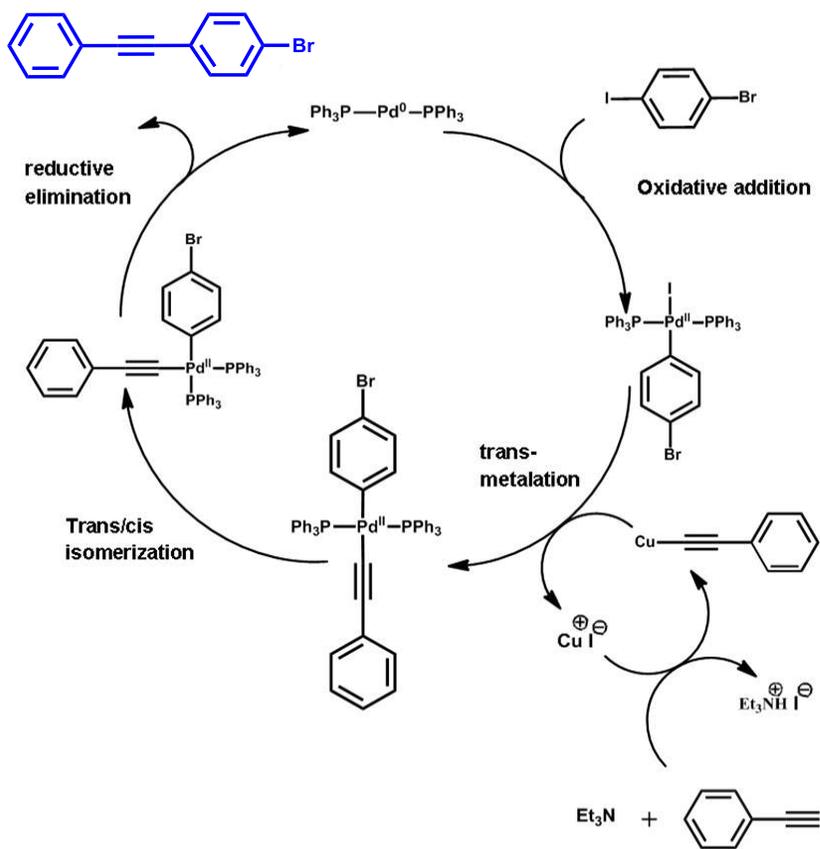
Figure 4. (a) Gas chromatogram spectrum for 4-bromodiphenylacetylene. (b) Mass spectrum for 4-bromodiphenylacetylene.

(a)
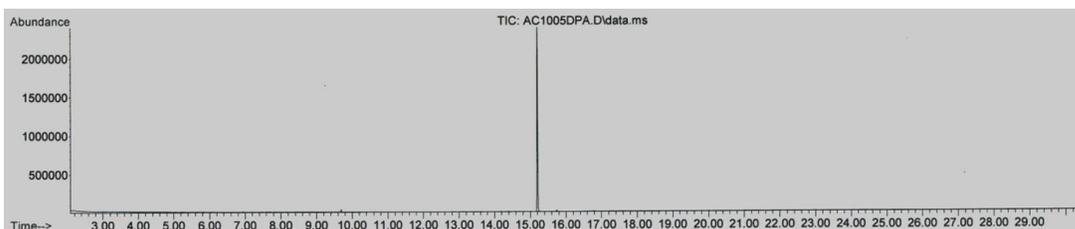
(b)

Following the synthesis of 4-bromodiphenylacetylene, diphenylacetylene was able to be successfully borylated reproducibly and on a larger scale via a lithium halogen exchange borylation reaction (Scheme 2). Initially, difficulties were experienced in obtaining a dry enough solvent throughout these experiments. Through troubleshooting, it was discovered that the drier the solvent, the less byproduct (biphenylacetylene) was observed. To ensure that the solvent was dry enough, dry THF in a SureSeal bottle was purchased and dried over 4 Å molecular sieves that were heated in the oven for a minimum of 24 hours. In some trials, the desired product was not obtained, only unreacted starting material was resulting. This was likely due to the degradation of the n-butyllithium. To account for this, the amount of n-butyllithium was increased by four times what the procedure suggested. After increasing the amount of n-butyllithium as

well as using a drier solvent, the desired borylated subunit was able to be successfully synthesized in addition to biphenyl byproducts. The borylated product was separated from any byproduct present via column chromatography using 2:1 hexanes/ethyl acetate as a solvent system. A GC-MS characterization of the borylated product, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) diphenylacetylene, was taken to verify the success of this reaction (Figure 5). The peak at 304 was the indicator that the product was obtained, as this is the mass of the parent ion.

Scheme 2. Lithium Halogen Exchange Borylation Reaction
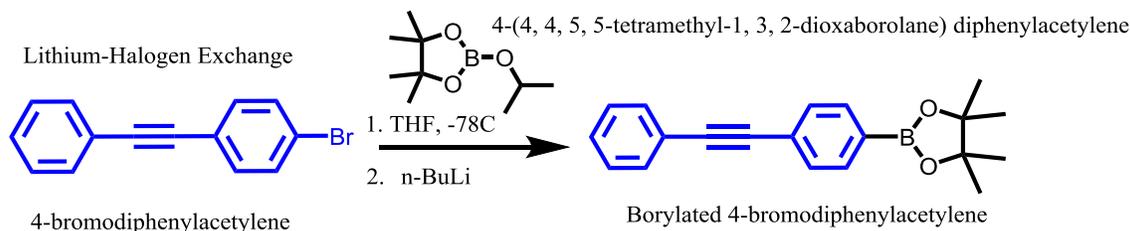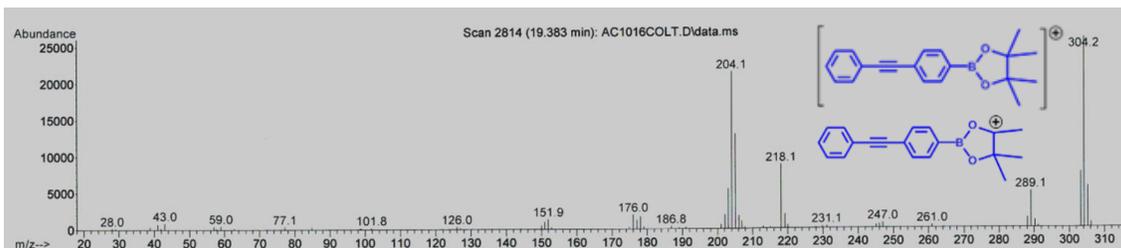

Figure 5. (a) Gas chromatogram spectrum for 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) diphenylacetylene. (b) Mass spectrum for 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) diphenylacetylene.

(a)
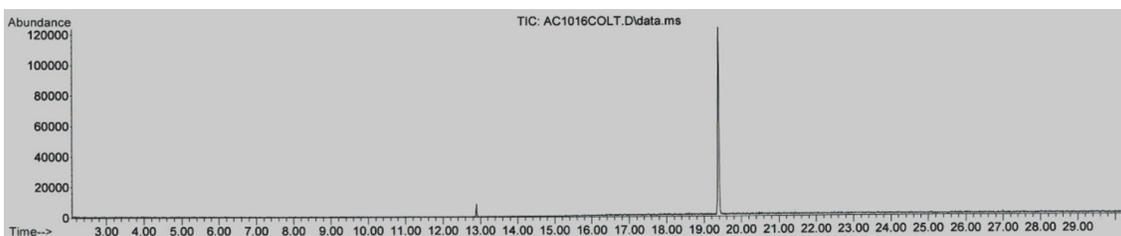
(b)

Experimental

Synthesis of 4-Bromodiphenylacetylene.[4]

1-bromo-4-iodobenzene (13.852 g, 48.964 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.354 g, 0.504 mmol), Copper(I) Iodide (0.096 g, 0.504 mmol), triethylamine (10.2 mL, 0.0732 mmol), and 50 mL of tetrahydrofuran dried over 4 Å molecular sieves were added to a 100 mL three-neck flask under nitrogen. Phenyl acetylene (5.3766 mL, 48.9595 mmol) was then added drop wise, and the mixture was then allowed to stir at room temperature for 1 h and 45 min. A TLC test was done to monitor when the reaction had gone to completion. Once the TLC indicated that there was no more starting material present, 25 mL of tetrahydrofuran and 15 mL of brine was added. Tetrahydrofuran was added as needed to increase the organic phase, whereas brine was added to allow the mixture to separate easier. The product was then washed with 2 M hydrochloric acid (2 x 25 mL), dried with magnesium sulfate, and gravity filtered. A GC-MS was taken of the crude product before being purified by multiple recrystallizations in methanol.

Borylation of Diphenylacetylene.[6]

4-Bromodiphenylacetylene (0.1 g, 0.30769 mmol) and tetrahydrofuran (10 mL) ordered and dried over molecular sieves were added to a 20 mL three-neck flask while stirring under a nitrogen atmosphere for 15 min. After being charged with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.1 mL, 0.49016 mmol), the reaction was cooled to -70 degrees Celsius using a dry ice and acetone bath. N-Butyl-lithium (0.64 mL, 6.9235 mmol) was added drop wise using a syringe over 15 min. The reaction mixture was then allowed to warm to room temperature while stirring overnight. Once the reaction mixture was at room temperature, distilled water (20 mL) was added to the product mixture. The organic phase was extracted with CH_2Cl_2 (3 x 15mL) washed with brine and dried over magnesium sulfate. The product was left to sit overnight to allow the solvent to evaporate. A GC-MS was taken of the resulting product.

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