

# Synthesis and Electro-optic Properties of Anthracene Derivatives for Blue Emitting OLED Devices.

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## Abstract

Anthracene derivatives, 9,10-trimethylsilylanthracene (SA) and bis(2-phenylethynyl)trimethylsilylanthracene (Si-BPEA) were synthesized and their emission properties were studied with UV and PL spectrometers. The PL maxima of anthracene, SA, bis(2-phenylethynyl)anthracene (BPEA), Si-BPEA were obtained at 401, 438, 475, 478nm, respectively. The electro-optical properties of OLED devices made with these anthracene derivatives were discussed.

were obtained to compare the corresponding anthracene derivatives. Anthracene derivatives have been reported to give blue emission, however, they are not easy to process in the OLED devices due to high sublimation property. We also fabricated flexible OLED based PES (polysulfone) film and their electro-optical properties made with these anthracene derivatives were evaluated.

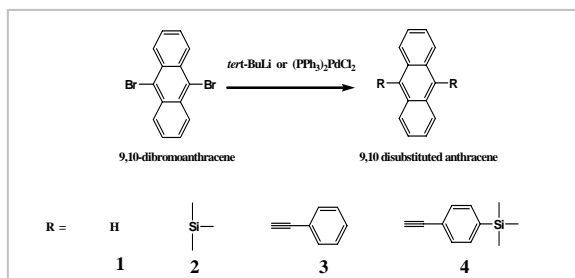
## 1. Introduction

Organic light-emitting diodes (OLEDs) based on organic molecules are currently the subject of an intense research effort due to their promise as devices for full-color large display applications [1-3], numerous conjugated organic molecules have been synthesized and reported to exhibit electroluminescence (EL), from red, to green, to blue. [4-5] Although considerable research efforts have been carried out to enhance the performance suitable for practical use, however, a lot of problems to solve still remain, for example blue emitting material, the device lifetime and the luminous efficiency, etc.

In this study, we synthesized anthracene derivatives such as 9,10-trimethylsilylanthracene and bis(2-phenylethynyl)trimethylsilylanthracene as blue emitting materials for OLED. These two materials were composed with anthracene and bis(2-phenylethynyl)anthracene from viewpoint of introduction of trimethylsilyl groups at both side of anthracene core. The UV and PL spectra

## 2. Experimental

The structure and synthetic scheme of the anthracene derivatives used in the OLED devices are shown in Fig. 1.

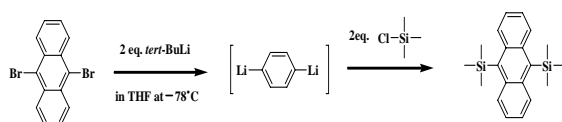


**Figure 1.** anthracene derivatives

As shown in Scheme 1, 9,10-bis(trimethylsilyl)anthracene (2) was synthesized as follows.

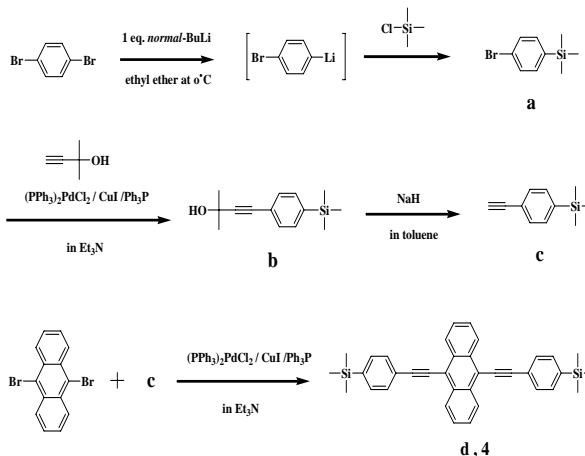
9,10-Dibromoanthracene (5.03g, 15mmol) and dry tetrahydrofuran (50ml) were placed in the flask, and the solution was cooled down to -78°C. *tert*-Butyllithium (36.71ml, 1.7M in pentane) was added dropwise and stirred for 1hr. And then chlorotrimethylsilane (4.18ml, 33.0mmol) was added dropwise to the solution. Then the mixture

was allowed to warm gradually to room temperature and was stirred for 2hr. At this time, the color of the mixture was changed clear yellow. The mixture was hydrolyzed with aqueous sodium hydrogen carbonate solution and was extracted with petroleum ether. The organic layer was washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was purified by a short column of silica gel (eluent: hexane). Recrystallization of eluted materials from ethanol gave 9,10-bis(trimethylsilyl) anthracene (1.5g) as yellow crystals in 31.04% yield.



**Scheme 1. The structure of 9,10 bis(trimethylsilyl)anthracene**

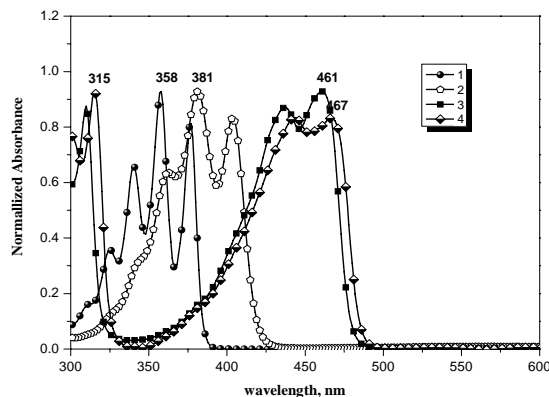
9,10-bis(2-(4-(trimethylsilyl)phenyl)ethynyl)anthracene(**4**) was synthesized by Sonogashira reaction as see the Scheme 2. A Schlenk tube was equipped with a reflux condenser and was then flushed with dry nitrogen. Triethylamine (40ml), triphenylphosphine (0.060g, 0.23mmol), copper(I) iodide (0.066g, 0.34mmol), bis(triphenylphosphine)palladium(II) chloride (0.040g, 0.06 mmol) and 4-trimethylsilyl phenylacetylene (3g, 17mmol) were placed in the tube, and the mixture was stirred for 1hr. Then, a solution of 9,10-dibromoanthracene (1.9g, 5.7mmol) in triethylamine (40ml) was added and stirring was continued for 24hr at refluxed temperature. The reaction of the mixture is filtered and the triethylamine was evaporated. For the extraction of the reaction product, diethyl ether (ca. 200ml) was added, and then the solution was washed with 1N hydrochloric acid and water. The organic phase was dried over anhydrous magnesium sulfate overnight. The solvent was evaporated, and the residue was passed through a short column of silica gel (eluent: hexane: Ethyl acetate =9:1). Recrystallization of eluted materials with hexane gave 9,10-bis(2-(4-(trimethylsilyl)phenyl)ethynyl)anthracene (0.3g) as a orange needle crystals in 10% yield.



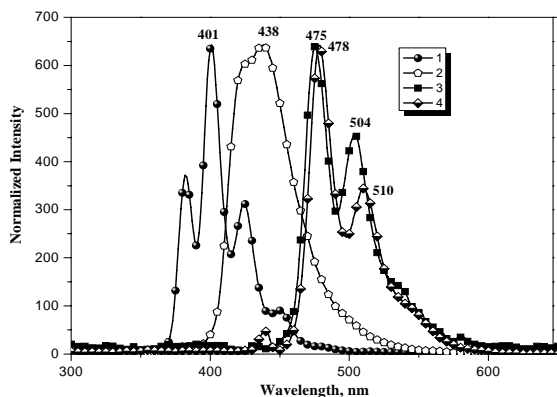
**Scheme 2. The structure of 9,10-bis(2-(4-(trimethylsilyl)phenyl)ethynyl)anthracene**

### 3. Results and discussion

Figure 2. and 3. exhibit the UV-visible absorption and fluorescence spectra of anthracene derivatives 1-4 shown in Fig.1 in the dilute THF solution. It was measured at the concentration in which UV absorbance is under 1.0. The absorption maxima ( $\lambda_{max,abs}$ ) wavelength of the derivatives 1-4 is appeared at 358, 381, 461, and 467nm, respectively. The derivative 3, 4 exhibited two absorption maxima at (437,461) and (444, 467) nm. The front absorption may be caused by  $\pi$ - $\pi^*$  transitions in the anthracene backbone and the rear peak caused by  $\pi$ - $\pi^*$  and  $\sigma^*$ - $\pi^*$  transition of Si- $\pi$  interaction in the side chain. Their cutoff wavelengths of 1-4 were 392, 430, 491 and 496nm. When the derivatives 1-4 were excited at the  $\lambda_{max}$  (abs), they showed the fluorescence peaks ( $\lambda_{max,em}$ ) in the blue or greenish blue region of 401, 438, 475, 478nm, respectively.



**Figure 2. The UV-visible Spectra of 1-4.**



**Figure 3. The Fluorescence Spectra of 1-4.**

Table 1. shows the quantum yield of the anthracene derivatives 1-4. The quantum yield was measured in dilute THF solution under the condition that UV/vis absorbance was below 0.1 using the following equation.

$$\Phi_s = \Phi_r (A_r F_s / A_s F_r) (n_s^2 / n_r^2)$$

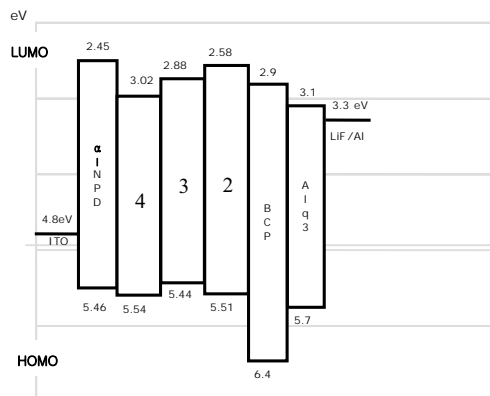
As shown in Table 1, compound 2 showed about 4% increase as compared to anthracene but 4 showed about 10% improvement than derivative 3. This may be due to extension of conjugated structure and increase of electron density by the electron donating trimethylsilyl group, especially in compound 4.

Product	Tm(K)	A <sub>max</sub> .asb.	PL/A <sub>max</sub> (nm).	Φ <sub>s</sub>
Anthracene	217	358	401	0.19
Si-anthracene	115-117	381	438	0.22
BPEA	248-50	461	475	0.68
Si-BPEA	274	467	478	0.77

**Table 1 Properties of anthracene derivatives as blue emitting material**

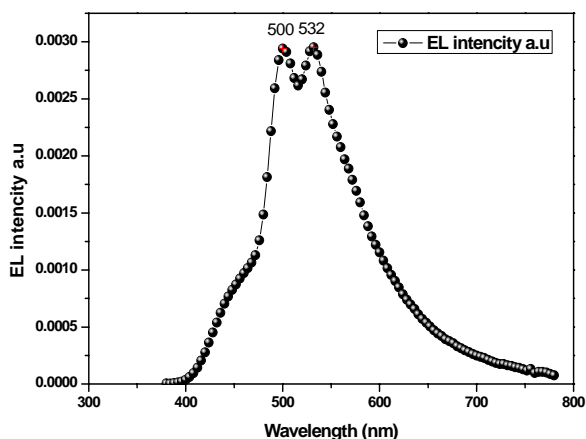
All of the three compounds give bright blue fluorescence with high quantum yields, and have thermal stable properties with high melting point that was obtained DSC measurement. This property is beneficial for its application as a non-doping emitter or a host in OLEDs. The energy band diagrams, as shown in Figure 4, of the compounds were determined from the absorption edges, and the HOMO energy levels which were

estimated from the photoelectrometer AC-2 measurement. The HOMO energy levels of compound 2, 3 and 4 were estimated to be 5.54-5.44 and also LUMO energy levels were determined to be 2.58 to 3.02 eV. As a consequence, the optical band gap of compound 4 is decrease compared with other derivatives. These results are well matched with those obtained from UV/Vis spectrometer measurements.



**Figure 4. The band diagram of compound.**

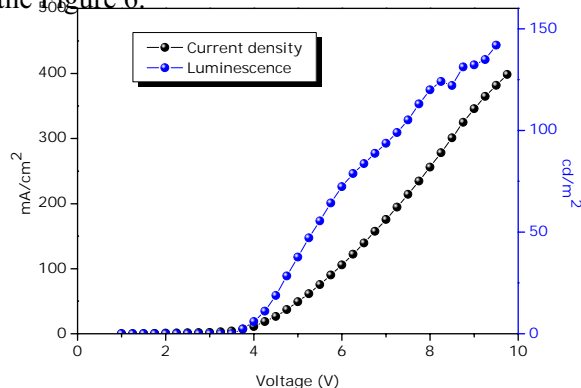
Figure 5 shows the EL spectra of compound 4 based device was fabricated with flexible film PES (polyethersulfone). EL peak appeared nearly 500 nm, but it has additional at around 530 nm by Alq3 as an electron transporting material.



**Figure 5. The EL spectra of flexible device based on compound 4.**

The flexible EL device showed a little good performance compared to other emitting materials, it was obtained the brightness of 142 cd/m<sup>2</sup> at

9.5V with lower turn-on voltage at 3.75V as see the Figure 6.



**Figure 5. IVL characteristic of flexible OLED**

#### 4. Summary

Anthracene derivatives have been known to give blue emission. In this study, compound **4** exhibited greenish blue color with high quantum yield (0.77) due to increased conjugation length and electron density. The combination of greenish blue emission of **4** with organic emission material may give highly efficient white OLED devices. Since the compound synthesized has trimethylsilyl groups, it could be fabricated high efficient flexible OLED devices based on flexible substrate.

#### Acknowledgements

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#### 5. Reference

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