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Position Effect Based on Anthracene Core for OLED Emitters

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Green-orange emitters based on anthracene core have been successfully synthesized by substitution with triphenylamine side group in the 9,10 or 2,6 positions. There are larger blue shifts in the UV-visible absorption and PL spectra of the synthesized 2,6-substituted derivative compared to the 9,10-substituted derivative. When the synthesized compounds were used as emitting layers in non-doped OLED devices, a related trend was observed in their optical properties. In particular, the OLED device containing the 2,6-substituted derivative was found to exhibit excellent characteristics, with maximum EL emission at 518 nm, pure green emission with CIE coordinates of (0.334, 0.604), and external quantum efficiency of 2.83%.

Keywords: OLED, Anthracene, Green-Orange Emission, Link-Position, Density Functional Calculation.

1. INTRODUCTION

The interest in organic functional materials based on π-conjugated molecules has been rapidly growing in diverse fields. Many remarkable results have been reported, especially in the field of optoelectronics (organic light-emitting diodes [OLEDs], solar cells, and organic thin-film transistors [OTFTs].[1–8] Many researchers are engaged in ongoing efforts to systematically elucidate the correlation between their molecular structures and properties, with the aim of developing materials with good performance and stability for particular optoelectronic applications. Most existing studies of emitters use molecules with excellent fluorescence characteristics such as anthracene, pyrene, and fluorene as core or side moieties. Many studies have investigated the use of anthracene as the core of emitting materials since they have high PL efficiencies.

Anthracene derivatives synthesized as emitting materials mainly substituted the side group in the 9,10 positions of anthracene. This is because substitution of 9,10 positions is relatively easy due to higher reactivity. However, many interests have been recently focused on link position of emitters inside.[9] In this study, position effect of anthracene was examined by substituting the same side group in other positions of anthracene. If emission wavelength and efficiency can be expected according to link position between core and side groups, it would be helpful in case of molecule design for OLED emitter.

Although varying the substitution positions of side groups on emitting cores offers important information about the intrinsic properties of the molecules, it is difficult to change substitution positions of the side group for most emitting cores (e.g., fluorene, bifluorene and anthracene).[10–19] In this study, bromoanthracenes for which Br is substituted into the 9,10 or 2,6 positions were synthesized and used as precursors of two derivatives. This process allowed for synthesis of two compounds with different link-position of side group by substituting triphenylamine as an electron donating group with vinyl group in the 9,10 and 2,6 positions of anthracene (Scheme 1). And the synthesis method is shown in Scheme 2.

2. EXPERIMENTAL DETAILS

2.1. Synthesis

2.1.1. Synthesis of DPAS

4.66 g of diphenylamine (27.5 mmol), 11.6 g of sodium-tert-butoxide and 0.84 g of $Pd_2(dba)_3$ (0.46 mmol) were dissolved in 130 ml of anhydrous toluene in a round flask with nitrogen substitution. 3 ml of 4-bromosyrene (22.9 mmol) and 0.2 ml of tri-tert-butylphosphine were added before reacting the solution for 1 hour at room temperature. 2 ml of HCl was added after the reaction. The solution was extracted using dichloromethane and moisture was removed by $MgSO_4$. The product was refined

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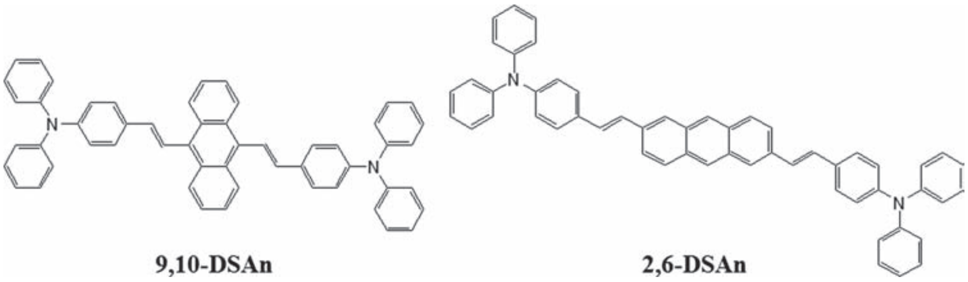
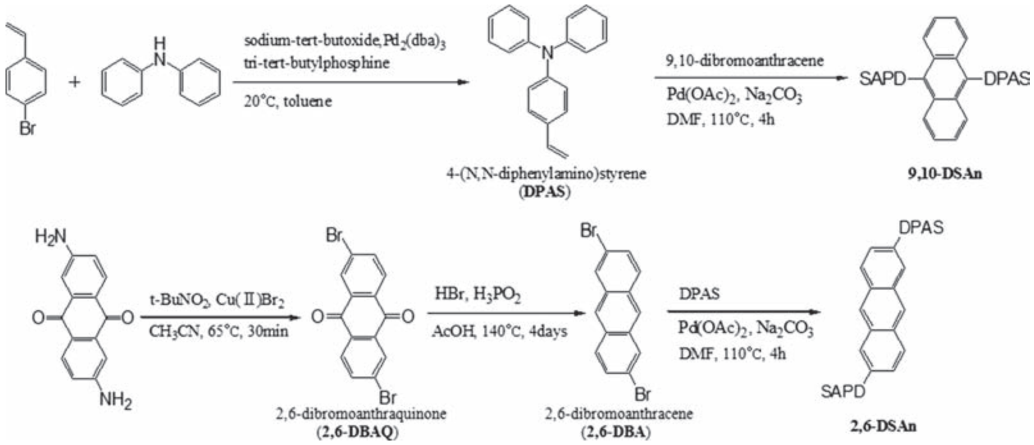


Scheme 1. Chemical structures of 9,10-DSAn and 2,6-DSAn.



Scheme 2. Synthetic routes for 9,10-DSAn and 2,6-DSAn.

by column chromatography to obtain 5.3 g of white solid (yield: 71%).

^{1}H-NMR (300 MHz, DMSO, δ): 7.35 (d, 2H), 7.31 (t, 4H), 7.04 (m, 6H), 6.93 (d, 2H), 6.67 (q, 1H), 5.70 (d, 1H), 5.16 (d, 1H).

2.1.2. Synthesis of 2,6-DBAQ

Solution made by dissolving 3.44 g of 2,6-diaminoanthraquinone (14 mmol) in 50 ml of anhydrous acetonitrile was dropped to the mixture of 7.76 g of $CuBr_2$ (35 mmol) and 5.16 ml of t-$BuNO_2$ at 65 °C. 200 ml of HCl was added after the reaction. The solution was washed sufficiently and filtered using ethanol and water. The precipitate was dissolved in chloroform and re-filtered after adding $MgSO_4$. The solvent was removed by evaporation and the product was re-precipitated with chloroform and MeOH to obtain 3.1 g of brown solid (yield: 58%).

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.43 (s, 2H), 8.17 (d, 2H), 7.95 (d, 2H).

2.1.3. Synthesis of 2,6-DBA

3 g of 2,6-DBAQ (8.2 mmol), 170 ml of AcOH, 20 ml of HBr and 15 ml of H_3PO_2 were sequentially added to a round flask and refluxed at 140 °C. After 5 days of reaction, the solution was washed and filtered using ice water and ethanol to obtain 1.46 g of solid (yield: 53%).

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.31 (s, 2H), 8.18 (s, 2H), 7.90 (d, 2H), 7.56 (d, 2H).

2.1.4. Synthesis of 9,10-DSAn

1.5 g of 9,10-dibromoanthracene (4.5 mmol), 2.85 g of DPAS (10.7 mmol), 0.9 g of Na_2CO_3 and 0.2 g of $Pd(OAc)_2$ were added to a round flask for nitrogen substitution. After adding 150 ml of DMF, the solution was allowed to react for 3 hours at 90 °C. The solution was extracted using chloroform and water, and moisture was removed using $MgSO_4$. The product was refined by column chromatography to obtain 1.73 g of yellow solid (yield: 53%).

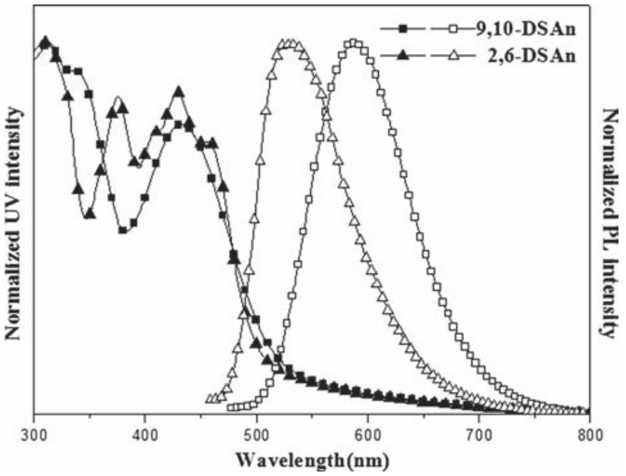


Figure 1. Normalized UV-Vis. and PL spectra of 9,10-DSAn and 2,6-DSAn in film state.

Table I. Optical, electrical and thermal properties of the synthesized compounds.

	$\mathrm{UV}^{a}_{\max}$ (nm)	$\mathrm{PL}^{a}_{\max}$ (nm)	$\mathrm{UV}^{b}_{\max}$ (nm)	$\mathrm{PL}^{b}_{\max}$ (nm)	FWHM^{b} (nm)	HOMO (eV)	LUMO (eV)	$\Delta E^{c}_{\mathrm{exp}}$ (eV)	T_m (°C)	T_d (°C)
9,10-DSAn	426	552	432	589	102.4	5.46	3.04	2.42	262.7	406
2,6-DSAn	421 443	503	426 459	530	91.7	5.45	2.94	2.51	265.7	430

Notes: [a]Solution in THF (1.00×10^{-5} M). [b]Film on glass. [c]Experimental band gaps.

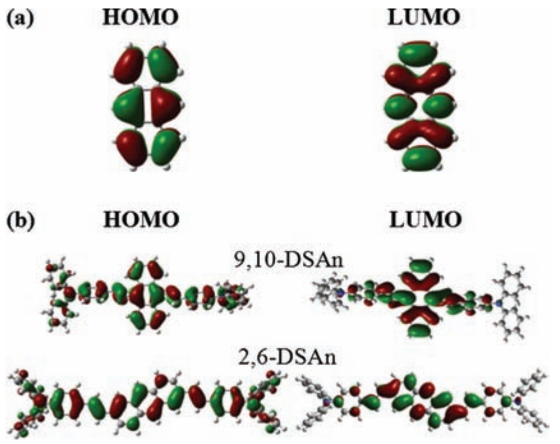


Figure 2. Electronic density distributions of the frontier molecular orbitals of the anthracene core (a) and of 9,10-DSAn and 2,6-DSAn (b).

^{1}H-NMR (300 MHz, THF-d_8, δ): 8.42 (*q*, 4H) 8.95 (*d*, 2H), 7.64 (*d*, 4H), 7.46 (*q*, 4H), 7.27 (*t*, 8H), 7.12 (*d*, 12H), 7.02 (*t*, 4H), 6.89 (*d*, 2H).

2.1.5. Synthesis of 2,6-DSAn

0.5 g of 2,6-dibromoanthracene (1.49 mmol), 0.95 g of DPAS (3.5 mmol), 0.3 g of Na_2CO_3 and 0.04 g of $Pd(OAc)_2$ were added to a round flask for nitrogen substitution. After adding 50 ml of DMF, the solution was allowed to react for 2 hours at 130 °C. The solution was extracted using chloroform and water, and moisture was removed using $MgSO_4$. The product was refined by column chromatography to obtain 0.53 g of yellow solid (yield: 50%).

^{1}H-NMR (300 MHz, THF-d_8, δ): 8.35 (*s*, 2H), 7.96 (*m*, 4H), 7.82 (*d*, 2H), 7.51 (*d*, 4H), 7.27 (*m*, 12H), 7.06 (*m*, 16H).

2.2. Measurements

The ^{1}H-NMR spectra were recorded on Bruker Avance 300 spectrometers. The optical absorption spectra were obtained by HP 8453 UV-VIS-NIR spectrometer. Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photo-luminescence (PL) spectroscopy. Thermal degradation temperature (T_d) of the compounds was measured by thermo-gravimetric analysis (TGA) using SDP-TGA2960 (TA instrument). The HOMO energy levels were determined with ultraviolet photoelectron yield spectroscopy (Riken Keiki AC-2). The LUMO energy levels were derived from the HOMO energy levels and the band gaps. All DFT calculations (B3LYP/6-311G(d)) were performed with the Gaussian09 program.

3. RESULTS AND DISCUSSION

The UV-Visible absorption spectra and photoluminescence (PL) spectra are shown in Figure 1, and the spectral features are summarized in Table I. In the PL spectra, maximum peak of 2,6-DSAn and 9,10-DSAn was 530 nm and 589 nm, showing maximum difference of about 59 nm. As a result, the emission spectrum of 2,6-DSAn showed green color and 9,10-DSAn exhibited orange color. These findings suggest that changing the substitution position alters the intrinsic optical properties of the molecule. Figure 2 shows HOMO and LUMO orbitals of 9,10-DSAn and 2,6-DSAn based on calculation of DFT. While 9,10-DSAn has HOMO and LUMO electron distributions similar to anthracene, 2,6-DSAn shows electron distributions different from electron density distributions of anthracene. 2,6-DSAn has relatively shorter conjugation length compared to 9,10-DSAn due to relatively low electron distribution at carbon atom of 2,6-DSAn. This makes 2,6-DSAn to possess emission with shorter wavelength than 9,10-DSAn. Such result agrees with the larger band gap shown by 2,6-DSAn compared to 9,10-DSAn, as shown in Table I.

Comparing the full widths at half maximum (FWHM) of 9,10-DSAn and 2,6-DSAn in film state, FWHM of 2,6-DSAn is smaller than 9,10-DSAn by more than 10 nm. The sharper spectrum of 2,6-DSAn is probably because 2,6-DSAn has fewer electron transition states than 9,10-DSAn.[10]

To determine whether the changes with substitution position in the intrinsic molecular properties are reflected in OLED performance, non-doped OLED devices were

Table II. EL performances of multi-layered devices. Device: ITO/2-TNATA (60 nm)/NPB (15 nm)/9,10-DSAn or 2,6-DSAn (35 nm)/Alq_3 (20 nm)/LiF (1 nm)/Al (200 nm) at 10 mA/cm^2.

Compounds	Volt (V)	L.E. (cd/A)	P.E. (lm/W)	E.Q.E. (%)	$\mathrm{El}_{\max}$ (nm)	CIE (*x*, *y*)
9,10-DSAn	5.92	2.68	1.61	1.50	600	(0.540, 0.452)
2,6-DSAn	6.12	8.71	4.95	2.83	518	(0.334, 0.604)

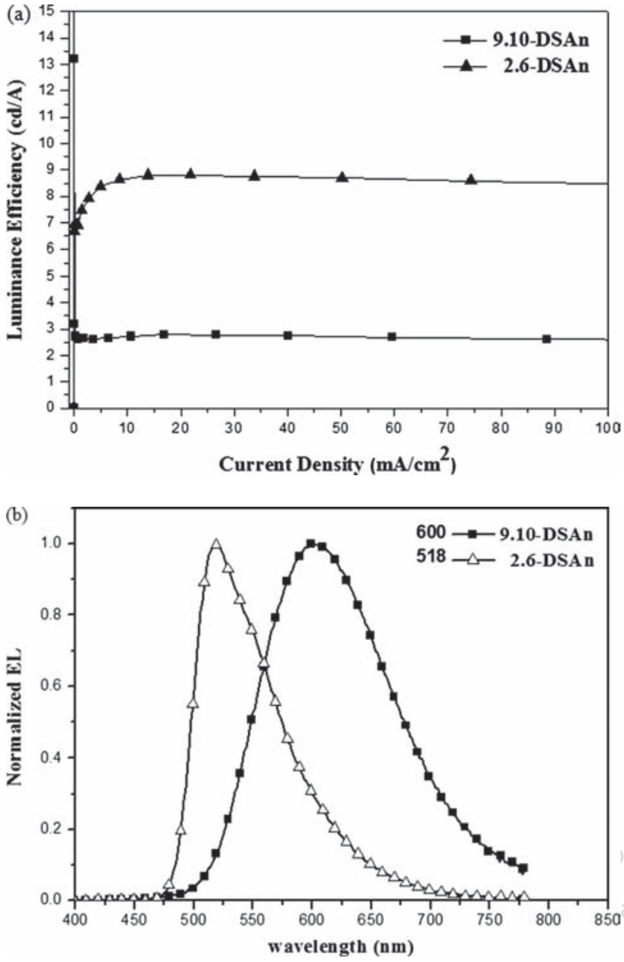


Figure 3. EL characteristics of devices using the synthetic materials as EML: (a) luminance efficiency against current density (b) EL spectra.

fabricated with the synthesized compounds as the emitting material layer (EML). The results are summarized in Table II and Figure 3.

Important observation is that maximum peak of the electroluminescence (EL) spectrum in 2,6-DSAn is blue-shifted by about 80 nm compared to the EL spectrum of 9,10-DSAn. This trend in the EL spectra is in good agreement with the shifts from the orange region to the green region observed in the PL spectra of the thin films. Furthermore, the EL spectrum of 2,6-DSAn has FWHM of 77 nm, which is much narrower than 12 nm of 9,10-DSAn. Such narrow emission spectrum can emit pure color, which becomes an advantage for emitting materials.

In EL devices, luminescence efficiency and external quantum efficiency is 2.68 cd/A and 1.50% for 9,10-DSAn, and 8.71 cd/A and 2.83% for 2,6-DSAn. Especially, luminescence efficiency of 2,6-DSAn is about 3 times as high as 9,10-DSAn. Though they have same core and side group, large change in efficiency and wavelength of EL device was made from changes in molecular properties caused by the difference in link-position.

4. CONCLUSION

Two new anthracene derivatives were successfully synthesized by substituting triphenylamine and vinyl group with anthracene core in different positions. Despite the same core and side group, 2,6-DSAn showed greater blue shift of the PL spectra compared to 9,10-DSAn in thin film state by different link-position. 9,10-DSAn showed orange emission and 2,6-DSAn showed green emission. Conjugation length was shortened when the side group is substituted in the 2,6 positions compared to 9,10 positions. In particular, luminescence efficiency was greatly improved from 2.68 cd/A in 9,10-DSAn to 8.71 cd/A in 2,6-DSAn, and the EL spectrum was blue-shifted by about 80 nm.

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