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Bifunctional anthracene derivatives as non-doped blue emitters and hole-transporters for electroluminescent devices†

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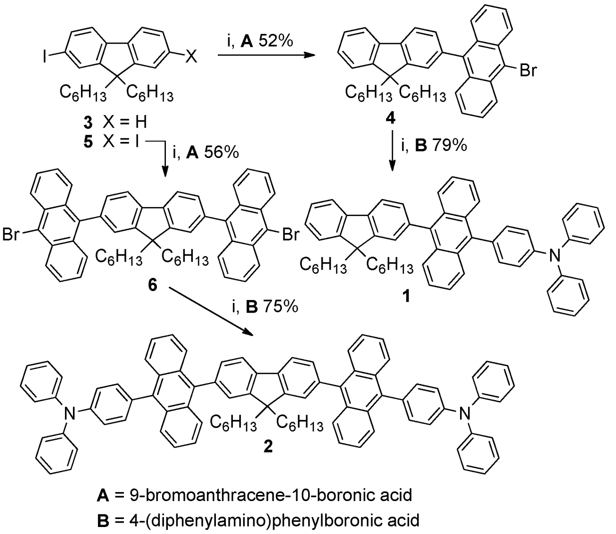
New highly fluorescent bifunctional anthracenes showed high thermal and electrochemical stability, and great potential as both blue emitters and hole-transporters for OLEDs. Deep-blue and Alq3-based green devices with maximum efficiencies and CIE coordinates of 1.65 and 6.25 cd A^{-1}, and (0.15, 0.16) and (0.26, 0.49) were achieved, respectively.

The use of π-conjugated organic compounds as electroluminescent materials in organic light-emitting diodes (OLEDs) was introduced by Tang and van Slyke over two decades ago.[1] Since then, extensive academic and industrial research has been carried out to bring OLEDs into the display markets.[2] OLEDs for full colour displays are showing great promise, and are required for red, green and blue-emitting materials. Although many blue light-emitting materials have been reported, such as pyrene, fluorene, and triarylamine derivatives,[3] materials emitting in the deep-blue colour (CIE coordinates of (0.15, 0.15)) with high efficiency are still rare.[4] Thus, there is still a clear need for further improvement for blue OLED compared to red and green devices.

Anthracene is a thermally and electronically stable rigid aromatic and its derivatives have been widely used as blue chromophores for many applications.[5] A number of anthracene derivatives have also been developed as blue emitters for OLEDs, but the factors of colour purity and efficiency continue to require improvement.[6] To this end, we report the new anthracene-based blue emitters. Our design involved an introduction of the bulky triphenylamine and 9,9-bis-*n*-hexylfluorene as 9,10-disubstituents. The former can suppress aggregation of the planar anthracene ring as well as increase the hole-transporting capability and thermal stability, while the latter also has a number of advantages including its ability to emit in the blue region and increase solubility.[7] This would result in new bifunctional anthracenes with combined blue emitting and hole-transporting properties. Herein, we report a detailed synthesis of compounds **1** and **2** (Scheme 1), physical and photophysical properties. Investigation on OLED device fabrication and characterization is also reported. We began with Suzuki coupling of readily obtained 2-iodo-9,9-bis-*n*-hexylfluorene **3**[8] in excess amounts with 9-bromoanthracene-10-boronic acid to give intermediate **4** in a fair yield of 52%. Anthracene **1** was obtained as light yellow solids in a good yield of 79% by Suzuki coupling of **4** with 4-(diphenylamino)-phenyl boronic acid.[9] Anthracene **2**, a dimer of **1**, was successfully synthesized by carrying out firstly Suzuki coupling of 2,7-diiodo-9,9-bis-*n*-hexylfluorene **5**[8] with 9-bromoanthracene-10-boronic acid (2.11 equiv.) followed by coupling of the resultant **6** with 4-(diphenylamino)phenyl boronic acid, and was obtained as deep yellow solids in 75% yield.



Scheme 1 Synthetic route of **1** and **2**: (i) Pd(PPh$_3$)$_4$, 2 M Na$_2$CO$_3$, THF.

Quantum chemical calculations performed using the TDDFT/B3LYP/6-31G(d,p) method revealed that all molecules adopt non-coplanar conformations. Particularly, the planar anthracene unit twists nearly perpendicular to the adjacent fluorene and triphenylamine moieties because of a steric repulsion of anthracene peri-hydrogen atoms (1,8 and 4,5 positions) with hydrogen atoms of those aromatic rings. Such structural characteristics can influence some of their electronic and physical properties such as suppression of the conjugation.

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In the HOMO orbitals of **1** and **2**, π-electrons delocalize over the anthracene and electron donor triphenylamine groups, while in their LUMO, electrons locate only on the anthracene rings.

The UV-vis spectra of **1** and **2** in solutions showed two absorption bands: strong absorption band (250–310 nm) agreeing with the π–π* local electron transition of the individual aromatic units and the less intense three absorption bands (350–400 nm) attributed to the π–π* electron transition of the anthracene–triphenylamine conjugated backbone. The HOMO–LUMO energy gaps (E_g) estimated from the onset of the absorption spectra are nearly identical (2.9 eV), despite somewhat different molecular size, indicating an equal π-conjugation length. This can be explained by an out-of-plane twisting of the fluorene unit from adjacent anthracene rings limiting the delocalization of π-electrons on the anthracene and triphenylamine units only. Both **1** and **2** showed deep blue fluorescence with high quantum yields (Φ_F) of 0.73 and 0.77, respectively. Their PL spectra are identical with a featureless pattern which is similar to what was observed for most 9,10-diphenylanthracenes. These materials showed a slight Stokes shift (85 nm) suggesting less energy loss during the relaxation process and efficient fluorescence. The thin film PL emission spectra (Fig. 1) of **1** and **2**, having bulky structures, exhibited a hypsochromic shift of about 19–26 nm compared to their solution spectra. This result may also be attributed to the aforementioned solid state packing force which prohibits the electron-vibration coupling between the triphenylamine substituent and the anthracene photoactive unit.

Electrochemical behaviours of **1** and **2** were investigated by cyclic voltammetry (CV). They were found to exhibit two quasi-reversible oxidation processes (0.95–0.96 and 1.21–1.25 V) with an identical onset potential of 0.88 V, which is very close to the data reported for most triphenylamine derivatives (0.90 V). The first oxidation wave was assigned to the removal of electrons from the peripheral triphenylamines resulting in radical cations. Their multiple CV scans revealed identical CV curves with no additional peak at lower potential on the cathodic scan (E_{pc}) being observed. This indicates no oxidative coupling or a weak oxidative coupling if any at *p*-phenyl rings of the peripheral triphenylamine led to electro-polymerization. This type of electrochemical coupling reaction can be detected in some triphenylamine derivatives with an unsubstituted *p*-position of the phenyl ring.[10] Steric hindrance of an adjacent anthracene ring might play a key role to prevent such electrochemical reactions in both molecules. The result suggests that these materials are electrochemically stable molecules. Moreover, under these CV conditions, no reduction process was observed in both cases.

The thermal properties were investigated by the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Those results suggest that **1** and **2** were thermally stable materials with temperature at 5% weight loss (T_{5d}) well over 400 °C. A DSC thermogram of **1** revealed only an endothermic baseline shift owing to glass transition (T_g) that was detected at 79 °C with no crystallization and melting peaks observed at higher temperature. The thermogram of **2** displayed T_g at 155 °C and exothermic peaks due to the crystallization (T_c) around 225 °C that gave the same crystal as obtained by crystallization from solution, which then melted at 338 °C. Their ability to form a molecular glass with the possibility to prepare good thin films by both evaporation and solution casting processes is highly desirable for application in electroluminescent devices.

In order to investigate the electroluminescence properties of **1** and **2**, OLEDs (devices I, II) were fabricated with the following device structure: indium tin oxide (ITO)/PEDOT:PSS/EL(50 nm)/BCP(40 nm)/LiF(0.5 nm):Al(150 nm), where these materials were used as the emitting layer (EL) and poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) act as the hole injection layer and the hole blocking layer, respectively. Both diodes exhibited deep blue emission with peaks centered at 458 and 466 nm and CIE coordinates of (0.14, 0.13) and (0.15, 0.16), respectively. The EL spectra are similar to their corresponding PL spectra in film (Fig. 1) indicating that the EL emission originates from the singlet-excited states of **1** and **2**. Significantly, a stable emission was obtained from all diodes and the EL spectra and CIE coordinates did not change over the entire applied voltage. Device II having **2** as the emitting layer showed the best performance with a high maximum brightness of 4586 cd m^{-2} at 8.8 V, a low turn-on voltage of 4.6 V, a maximum luminous efficiency of 1.65 cd A^{-1} and a maximum external quantum efficiency of 0.34%. A slightly lower device performance was observed from device I (Fig. 2, Table 1). Although many blue fluorescent emitters have been reported, high efficiency materials emitting in the deep blue region are still rare. The performance of these materials in terms of colour purity and efficiency is

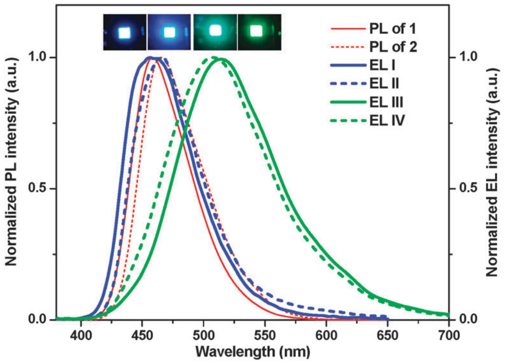

Fig. 1 PL spectra of **1** and **2** measured as a thin film obtained by vapor deposition, and EL spectra of OLEDs with **1** and **2** as EL and HTL.

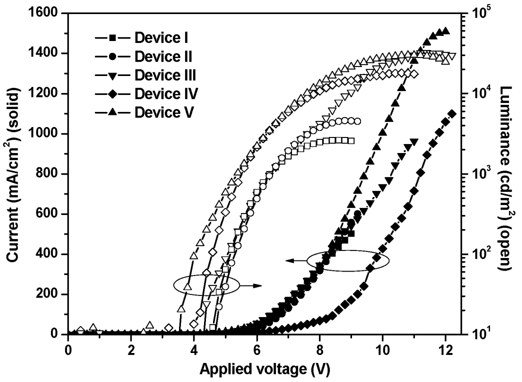

Fig. 2 *J–V–L* characteristics of OLED devices.

Table 1 Device characteristics of OLEDs with **1** and **2** as EL and HTL

Device	EL/HTL	$V_{\text{on}}{}^{a}$	$\lambda_{\text{em}}{}^{b}$	L^{c}	J^{d}	η^{e}	EQE^{f}	CIE^{g}
I	**1**	4.5	457	2621	436	1.28	0.26	0.14,0.13
II	**2**	4.6	465	4586	512	1.65	0.34	0.15,0.16
III	**1**	4.4	515	18 035	891	4.13	0.20	0.27,0.52
IV	**2**	4.0	509	32 270	894	6.25	0.30	0.26,0.49
V	NPB	3.6	515	30 044	1362	4.42	0.22	0.25,0.48

[a] Turn-on voltage (V) at a luminance of 10 cd m^{-2}. [b] Emission maximum. [c] Maximum luminance (cd m^{-2}) at the applied voltage (V). [d] Current density (mA cm^{-2}). [e] Luminance efficiency (cd A^{-1}). [f] External quantum efficiency (%). [g] CIE coordinates (x, y).

among good non-doped deep blue emitters reported. The trend in device luminous efficiencies matches very well with the observed decrease in PL quantum efficiencies (Φ_F) on going from **2** to **1**. The efficiency of an OLED depends both on the balance of electrons and holes and the Φ_F of the emitter.[11] Analysis of band energy diagrams of all devices also revealed that there is a barrier around 0.32 eV for holes to migrate from the PEDOT:PSS/EL interface suggesting that a migration of hole at that interface is more effective in both devices and the charge efficiently recombines in the EL resulting in good device performance.

As HOMO levels of these materials (5.32 eV) match well with the work function of the ITO (4.8 eV) electrode, they may potentially serve as hole-transporting material (HTM). To test this hypothesis, double-layer green OLEDs (devices III, IV) with the structure of ITO/PEDOT:PSS/HTL(40 nm)/Alq3(50 nm)/LiF(0.5 nm):Al(150 nm) were fabricated, where these materials were used as the hole-transporting layer (HTL) and tris-(8-hydroxyquinoline) aluminium (Alq3) as the green light-emitting and electron-transporting layers (ETL). The reference device (device V) with the same structure based on commonly used commercial HTM, *N*,*N*′-diphenyl-*N*,*N*′-bis(1-naphthyl)-(1,1′-biphenyl)-4,4′-diamine (NPB), as HTL was made for comparison. On comparison of HOMO and LUMO levels of layers for the devices, it was found that there is a barrier around 0.32 eV for holes to migrate from the HTL layer to the Alq3 layer, while that for electrons to transport from the Alq3 to the HTL layer is about 0.57 eV. According to this band diagram and device configuration, both compounds can transport a hole injected from ITO/PEDOT:PSS to the Alq3 emitting layer. Under applied voltage, all devices exhibited a bright green emission with peaks centered at 509–515 nm and CIE coordinates of (0.25–0.27, 0.48–0.52). The EL spectra match with the PL spectrum of Alq3 and also other reported EL spectra of Alq3 devices (Fig. 1).[12] No emission at the longer wavelength, owing to exciplex species formed at the interface of HTL and ETL materials, which has often occurred in the devices fabricated from HTL with a planar molecular structure, was detected.[13] In our case, the formation of exciplex species could be prevented by the bulky nature of both the anthracene core and triphenylamine at the periphery of the molecules. From these results and in view of the fact that barrier for electron-migration at the Alq3/HTL interface (0.57 eV) is nearly twice higher than those for hole-migration at the HTL/Alq3 interface (0.32 eV), **1** and **2** act only as HTM and Alq3 would act preferably as an electron blocker more than as a hole blocker and charge recombination is thus confined to the Alq3 layer. The device characteristics clearly demonstrate that the hole-transporting ability of **1** and **2** with superior device performance (maximum brightness and efficiency) is comparable to that of an NPB-based device (Fig. 2, Table 1). Device IV having compound **2** as HTL exhibited the best performance with a high maximum brightness of 32270 cd m^{-2} for green OLED at 11.4 V, a low turn-on voltage of 4.0 V, a maximum luminous efficiency of 6.25 cd A^{-1} and a maximum external quantum efficiency of 0.30%.

New anthracene derivatives with the combined characteristics of deep blue light-emitting and hole-transporting materials have been developed. These materials showed deep blue emission with high emission quantum efficiency over 73% in the solution and strong luminance in the solid state and were electrochemically and thermally stable with degradation temperature well above 400 °C. Non-doped blue OLEDs with a maximum efficiency of 1.65 cd A^{-1} and CIE coordinate of (0.15, 0.16), and green OLEDs with a maximum efficiency of 6.25 cd A^{-1} and CIE coordinate of (0.26, 0.49), were achieved. Their ability as HTL for green OLEDs in terms of device performance and thermal properties was greater than the common hole-transporter NPB.

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