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## COMMUNICATION

## Synthesis and photo- and electroluminescence properties of 3,6-disubstituted phenanthrenes: alternative host material for blue fluorophores<sup>†</sup>

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Three deep-blue fluorescent 9,10-bis(4-*tert*-butylphenyl)phenanthrenes with diphenyl, -naphthyl, and -pyrenyl moieties at C3 and C6 positions were synthesized and used as the host for doped blue fluorescent devices; one of these devices reveals excellent external quantum efficiency of 7.7% and current efficiency of 9.8 cd  $A^{-1}$  with low efficiency roll-off, deep-blue color coordinates (0.14, 0.14) and long operational lifetime.

Organic light-emitting diodes (OLEDs) have attracted great attention due to their application in high-resolution, full-color, flat-panel displays and lighting.<sup>1–3</sup> The search for stable and efficient three primary color (red, green, and blue) emitters and devices is particularly important for OLED products to be commercialized.<sup>4</sup> Recently, red and green electroluminescent devices with high efficiencies, long lifetimes, and proper CIE (Commission International de l'Eclairage) coordinates have been developed. For the known blue phosphorescent devices, high external quantum efficiencies (EQEs) can be achieved, but there are still some drawbacks such as high CIE coordinates (*y*-coordinate value >0.30) and short device lifetimes that require further improvement. Therefore, to achieve the market-able OLEDs, the hunt for blue fluorescent materials and devices is still a subject of current interest.

It is well known that the device efficiency, color coordinates, and operational stability of a blue fluorescent device can be significantly improved by using a doped emitter.<sup>5</sup> Nevertheless, in the dopant/host system, the phase separation upon heating has become an issue leading to the degradation of efficiency.<sup>6,7</sup> The host material has shown great influence on the efficiency and life time of the blue-doped fluorescent devices. Thus, it is crucial to find blue fluorescent host materials with outstanding properties.

Several sky blue-blue doped fluorescent devices using anthracene derivatives as the host materials with high performance have been reported.<sup>8–10</sup> A deeper blue fluorescent device with high external quantum efficiency (EQE) and current efficiency ( $\eta_c$ ) of 5.1% and 5.4 cd A<sup>-1</sup> at CIE (0.14, 0.13) was demonstrated by Chen *et al.*<sup>1c</sup> In addition, Yoon *et al.* and Liu *et al.* reported pure blue devices (CIE (y) = 0.14) with EQEs ( $\eta_c$ ) of 3.47% (3.7 cd A<sup>-1</sup>) and 4.24% (5.0 cd A<sup>-1</sup>), respectively.<sup>11,12a</sup> The search for efficient and stable blue fluorescent materials with excellent CIE coordinates (y-coordinate value < 0.15) is important but examples are still relatively rare.<sup>11,12</sup>

We have been interested in the application of polyaromatic compounds for blue fluorescent materials in organic light-emitting devices.<sup>13</sup> Previously, we and Liu's group employed pyrene- or triphenylene-containing materials as blue host emitters and as the host for doped blue devices.<sup>4,12,14</sup> As previous reports demonstrated, the anthracene moiety is the most common core structure for blue fluorescent materials.<sup>8–10,12,15</sup> However, only few blue fluorescent materials employing phenanthrene, a structural isomer of anthracene, as the core structure have been known to date.<sup>16–19</sup> It is important to note that phenanthrene is one of the most stable fused aromatics.<sup>16,20</sup> Thus, we wish to report in this communication the synthesis of phenanthrene derivatives and their application as stable and very efficient host for organic blue fluorescent devices.

Three phenanthrene derivatives, 3,6-diphenyl-9,10-bis-(4-*tert*-butylphenyl)phenanthrene (TPhP), 3,6-di(naphthalen-2-yl)-9,10-bis(4-*tert*-butylphenyl)phenanthrene (TNaP) and 3,6-di(pyrene-1-yl)-9,10-bis(4-*tert*-butylphenyl)phenanthrene (TPyP), were synthesized from Suzuki coupling of 3,6-dibromo-9,10-bis(4-*tert*-butylphenyl)phenanthrene (see ESI†)<sup>16</sup> with phenyl-, 2-naphthyl- and 1-pyrenylboronic acid, respectively, as shown in Scheme 1. The core phenanthrene structure incorporates two *tert*-butylphenyl groups at C-9 and C-10 positions to prevent extensive intermolecular  $\pi,\pi$ -interaction of the compounds in the solid state. In addition, the introduction of end-capping substituents provides effective tuning of the emission wavelength, quantum yield and thermal property of the materials.

The absorption and photoluminescence spectra (PL) of TPhP, TNaP, and TPyP thin films are shown in Fig. 1, while the peak maxima of these spectra are summarized in Table 1. As revealed in Fig. 1, the absorption spectra are mainly in the

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<sup>†</sup> Electronic supplementary information (ESI) available: Experimental section, cyclic voltammograms, calculated HOMO/LUMO density maps, TGA and DSC thermograms, AFM topographic images, <sup>1</sup>H and <sup>13</sup>C NMR spectra, electroluminescence properties. See DOI: 10.1039/ c1cc12875b



Scheme 1 Synthesis of phenanthrene derivatives.



**Fig. 1** Absorption and photoluminescence emission spectra of TPhP, TNaP and TPyP in the thin film and electroluminescence spectra of devices A–D.

UV range and are due to  $\pi$ - $\pi$ \* transition, but the PL spectra span the UV and deep blue regions. Comparison of the PL spectra of these three phenanthrene derivatives indicates that as the conjugation increases, the emission maximum is red-shifted significantly.

In addition, the thin film PL spectra of TPhP and TNaP reveal mild stacking in the thin film resulting in *ca*. 14 nm redshifted compared with those in dichloromethane solution. On the other hand, the TPyP thin film shows a broadened PL spectrum red-shifted by 33 nm relative to that in the solution, suggesting an increase of  $\pi$ - $\pi$  stacking of the two end-capping pyrene moieties (see Fig. 1). Such a red-shift phenomenon of pyrene-based material has been previously reported.<sup>4</sup> The fluorescence quantum yields of these thin films (30 nm) are measured using an integrating sphere and are listed in Table 1. The results show that all these three phenanthrenes give high quantum yields and TPyP is significantly higher than TNaP and TPhP.

The electrochemical properties of TPhP, TNaP and TPyP were investigated by cyclic voltammetry (CV) (see ESI†). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels and thus the energy gaps were estimated from their oxidation and reduction potentials. The results as indicated in Table 1 are in agreement with the observed absorption and emission data showing that the HOMO/LUMO energy gap of TPyP is substantially lower than those of TPhP and TNaP owing to the longer  $\pi$  conjugation of the pyrenyl group. To gain insight into the electronic states of these phenanthrene compounds, density functionalized theory (DFT) calculation was performed. Interestingly, the results revealed that the HOMO/LUMO electron distributions of TPhP and TNaP are similar mainly on the 9,10-bis(4-*tert*butylphenyl)phenanthrene structure and to a less degree on the 3,6-disubstituted groups. In contrast, the HOMO/LUMO electron distributions of TPyP are mostly over the two pyrene groups and to a less extent over the phenanthrene structure (see ESI†). This difference in the electron distributions provides the basis for the difference in the HOMO/LUMO level, the photophysical properties and the electrochemical properties of these phenanthrene derivatives.

The thermal-property data of these compounds were measured by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) as shown in Table 1. In the DSC measurement of TPhP, the  $T_{\rm m}$  and  $T_{\rm g}$  were not detected. On the other hand, the  $T_{\rm g}$  and  $T_{\rm m}$  of both TNaP and TPyP were observed clearly and TPyP showed a very high  $T_{\rm g}$  of 211 °C and  $T_{\rm m}$  of 378 °C (see ESI<sup>†</sup>). To look into the impact of thermal stability toward the surface morphology, we used atomic force microscopy (AFM) to measure the topography of a TPyP thin film doped with 5% 4,4'-bis(9-ethyl-3-carbazovinylene)-1,1'-biphenyl (BCzVBi) at room temperature and heated at 110 °C for 18 h; we found that the root-mean-square roughness (R<sub>rms</sub>) were 0.237 and 0.220, respectively. These observations demonstrated that the doped TPyP film has no phase separation problem upon heating and formed a highquality amorphous film. We think that the phenanthrene structure attached by the tert-butylphenyl and the large rigid pyrene groups is the major reason for the high thermal and morphological stability.

To find the suitability of these phenanthrene derivatives as EL materials, we fabricated devices A–C by utilizing these derivatives as the host and BCzVBi as the dopant. The devices consist of the layers: NPB (20 nm)/TCTA (30 nm)/phenanthrene derivatives: BCzVBi (5%) (40 nm)/BCP (30 nm)/LiF (1 nm)/Al (100 nm), where NPB = N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine, TCTA = 4,4',4''-tri(9-carbazoyl) triphenylamine and BCP = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline. Devices A, B and C employing TPhP, TNaP, and TPyP as the host materials have achieved excellent EQEs of 5.2, 5.6 and 6.4%, and current efficiencies of 5.0, 6.5 and 7.7 cd A<sup>-1</sup>, respectively (see Table 2). The EQEs and current efficiencies *vs.* luminance of these devices are displayed in Fig. 2. At luminance between 10 to 10000 cd m<sup>-2</sup>, the EQE

 Table 1
 Photophysical and thermal properties of phenanthrene derivatives

Compound	$\lambda_{ m sol}{}^a/ m nm/(\epsilon)^b$	PL <sub>sol</sub> <sup>a</sup> /nm	${\rm PL_{film}}^c/{\rm nm}$	HOMO <sup>d</sup> /eV	LUMO <sup>d</sup> /eV	$E_{\rm g}{}^{e}/{ m eV}$	$T_{g}^{f}/T_{m}^{f}/T_{d}^{g}/^{\circ}C$	$\Phi^i$
TPhP	272 (1238), 328 (381)	380, 395	397	-5.8	-2.1	3.7	N.D <sup>h</sup> /N.D <sup>h</sup> /367	0.57
TNaP	268 (1361), 338 (433)	395, 406	418	-5.7	-2.2	3.5	134/291/438	0.64
TPyP	242 (1404), 282 (1103), 346 (872)	427	460	-5.6	-2.3	3.3	211/378/504	0.83

<sup>*a*</sup> Absorption spectra measured in CH<sub>2</sub>Cl<sub>2</sub> with concentration =  $1 \times 10^{-5}$  M. <sup>*b*</sup> Extinction coefficient ( $10^{2}$  M<sup>-1</sup> cm<sup>-1</sup>). <sup>*e*</sup> Fluorescence measured in the thin film. <sup>*d*</sup> HOMO and LUMO levels were estimated based on the CV data of each compound. <sup>*e*</sup> E<sub>g</sub> = HOMO – LUMO. <sup>*f*</sup> Glass transition temperature ( $T_{g}$ ) and melting point ( $T_{m}$ ). <sup>*g*</sup> Decomposition temperature ( $T_{d}$ ). <sup>*h*</sup> Not detected. <sup>*i*</sup> The quantum yields of the films (30 nm) were determined with an integrating sphere.

Table 2EL performance of the host materials TPhP, TNaP andTPyP

Device	EQE <sup>a</sup>	$\eta_{c}{}^{b}$	$\eta_{ m p}{}^c$	$L_{max}^{d}$	$V_{\rm on}(\mathbf{V})^e$	$\operatorname{CIE}(x,y)^f$
А	5.2	5.0	3.2	8641	3.8	0.14, 0.10
В	5.6	6.5	4.6	14912	3.6	0.14, 0.13
С	6.4	7.7	5.1	27762	3.6	0.14, 0.14
D	7.7	9.8	5.4	44750	3.5	0.14, 0.14

<sup>*a*</sup> The external quantum efficiency (%), <sup>*b*</sup> current efficiency (cd A<sup>-1</sup>) ( $\eta_c$ ), <sup>*c*</sup> power efficiency (lm W<sup>-1</sup>) ( $\eta_p$ ) and <sup>*d*</sup> brightness (cd m<sup>-2</sup>) ( $L_{max}$ ) are the maximum values of the devices. <sup>*e*</sup> Recorded at 1 cd m<sup>-2</sup>. <sup>*f*</sup> Recorded at 8 V.



Fig. 2 EQE and current efficiency versus luminance of devices A-D.

of TPhP- and TNaP- based devices A and B showed relatively high efficiency roll-off. But surprisingly, the efficiency of the TPyP-based device C increases gradually as the luminance increases from 10 to 10000 cd  $m^{-2}$ . The performance of the device C-based structure can be further improved by inserting a thin layer of MoO<sub>3</sub> (2 nm) between ITO and NPB.<sup>21</sup> Device D thus fabricated shows an EQE and current efficiency as high as 7.7% and 9.8 cd  $A^{-1}$ , respectively. The operational lifetime of device C was tested under a luminance of 500 cd m<sup>-2</sup>. The  $T_{58}$  (58% of initial luminance) of device C was about 20 h. The lifetime  $T_{67}$  (67% of initial luminance) of device D was improved drastically to 291 h under a higher luminance of 1000 cd  $m^{-2}$  as shown in the ESI.<sup>†</sup> It is known that the use of BCP as an electron-transporting layer displays typically a low device stability.<sup>1c</sup> As a result, it is necessary to search for new electron transporting materials for the present devices in order to further improve the device durability.

In summary, we have successfully synthesized three phenanthrene derivatives TPhP, TNaP and TPyP that show excellent photoluminescent and thermal properties for electroluminescent (EL) applications. In particular, the pyrene-substituted TPyP-based devices have achieved one of the highest external quantum efficiencies ever reported and excellent stability with CIE coordinates (0.14, 0.14).

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