Efficient 9-alkylphenyl-9-pyrenylfluorene substituted pyrene derivatives with improved hole injection for blue light-emitting diodes

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Two efficient blue-light-emitting materials with stable diarylfluorene and hole-transporting pyrene groups, 9-alkoxyphenyl-9-pyrenylfluorene substituted pyrenes (EHOP1 and EHOP2), have been synthesized by Suzuki coupling reaction and have been fully characterized. They have extreme thermal stability in nitrogen with onset decomposition temperature over 430 °C. They are amorphous materials with T_g of 103 and 191 °C for EHOP1 and EHOP2, respectively. They show stable bright blue emission in the solid state. Due to the non-conjugated pyrene groups at C9 of the fluorene moieties, the absorption spectra of the two compounds showed some characteristic peaks and they showed improved hole-injection ability than conjugated fluorene derivatives. A preliminary simple three-layer blue light-emitting diode, *i.e.* ITO/TCTA (8 nm)/EHOP1 (30 nm)/BCP (45 nm)/Mg:Ag, was obtained without the need for a hole-injection layer, with high luminance of 11620 cd m⁻², turn-on voltage of 4.0 V and current efficiency of 3.04 cd A⁻¹. Furthermore, the device still had a considerable efficiency of 1.74 cd A⁻¹, when the luminescence reaches its maximum.

1. Introduction

Since the fabrication of the first efficient molecule-based organic light-emitting diodes (OLEDs), reported by Tang and Van Slyke,¹ intense research and development have brought OLEDs to the brink of penetrating the market of flat panel displays,² which is currently dominated by liquid crystal materials. Whether to polymer or to small molecule materials, only the red and green ones have shown sufficient efficiencies and lifetimes to be of commercial value.³ The performance of blue electroluminescent emitters is usually inferior to that of green or red emitters, due to large bandgap energy. Because of the high photoluminescence (PL) efficiency, much research into blue-emitting materials has centred on conjugated fluorene derivatives, and aryl groups were introduced at C9 position of fluorene to improve the stability of the mateials.⁴

As a large conjugated aromatic ring, pyrene not only has the advantage of high PL efficiency,⁵ high carrier mobility, but also has the much improved hole-injection ability than oligofluorenes or polyfluorene.⁶ Very recently, some pyrene derivatives have been used in OLEDs in order to improve hole-transporting ability because of its electron-rich property.⁷ However, the pyrene itself is not suitable to act as blue emitter in the OLEDs because it is easy to crystallize. On the other hand, as mentioned above, conjugated diarylfluorene

derivatives have excellent thermal stability. In this paper, we report the synthesis and characterization of the two novel 9-(4'-(2"-ethylhexyloxyphenyl))-9-pyrenylfluorene substituted



Scheme 1 Reagents and conditions: (i), 2-ethylhexyl bromide, K_2CO_3 , DMF, 70 °C, 24 h; (ii), (1) Mg, I_2 , THF, (2) 2-bromofluorenone or 2,7-dibromofluorenone, THF, (3) saturated NH₄Cl, H₂O, reflux; (iii), pyrene (5 equiv), CHCl₃,CH₃SO₃H (1 equiv), 60 °C 20 min⁻¹; (iv), 4a/5 (1 : 1), Pd(PPh_3)_4, toluene, K_2CO_3 (2.0 M aqueous), 90 °C, 48 h; v. 4b/5 (1 : 2), Pd(PPh_3)_4, toluene, K_2CO_3 (2.0 M aqueous), 90 °C, 48 h.

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pyrenes (EHOP1 and EHOP2) (Scheme 1). Our motivation of designing the two materials is to combine the high thermal stability of diarylfluorene with the high efficiency and holeinjection ability of pyrene. We also expect that the long chain alkyloxy group can give a better solubility and a low tendency to crystallize in the devices. Due to the non-conjugated pyrene groups at C9 of the fluorene moieties, the absorption spectra of the two compounds showed some characteristic peaks and they showed improved hole-injection ability than conjugated fluorene derivatives. Preliminary results based on a simple three-layer blue OLED, i.e. ITO/TCTA (8 nm)/EHOP1 (30 nm)/BCP (45 nm)/Mg:Ag, was obtained with low turn-on voltage of 4 V, high maximum luminance of 11620 cd m^{-2} . and high current efficiency of $3.04 \text{ cd } \text{A}^{-1}$ in ambient air, and the high performance of the OLED is originated from the elaborate combination of 9-alkylphenyl-9-pyrenylfluorene and pyrene groups.

2. Experimental

2.1 General experimental information

All reactions were monitored by TLC using pre-coated glass sheets purchased by Yantai Huiyou Silica Gel Developing Co., Ltd (0.20 mm with fluorescent indicator UV_{254}). Compounds were visualized with UV light at 254 nm. Column chromatography was carried out using flash silica gel from Qingdao Haiyang Chemical Co., Ltd (200-300 mesh). ¹HNMR was recorded using a Varian spectrometer at 400 MHz. Molecular masses were determined by a SHIMADZU matrix-assisted laser desorption-ionization time-of-flight mass spectrometer (MALDI-TOF-MASS). Elemental analyses were performed on a Vario EL III elemental analyzer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a purged nitrogen atmosphere at a heating rate of 10 °C min⁻¹. Absorption and photoluminescence (PL) emission spectra of the materials were measured in dichloromethane using a SHIMADZU UV-3150 spectrophotometer and a SHIMADZU RF-5301PC spectrophotometer, respectively. Quantum yield was determined using solutions in dichloromethane and was calculated by comparing emission with that of a standard solution of 9,10-diphenylanthracene in cyclohexane ($\varphi = 0.9$) at room temperature. Cyclic voltammetry (CV) was performed on an Eco Chemie's Autolab. The quantum chemical calculations were performed using AM1 in the Gaussian 03, B.04 program.

Organic EL device were fabricated by using successive vacuum-deposition of the materials on top of the ITO glass substrate under a pressure of about 1×10^{-4} Pa with the deposition rate of about 0.1 nm s^{-1} . ITO glass was etched for the anode electrode pattern and cleaned in ultrasonic baths of chloroform, acetone and alcohol. The overlap area of Mg:Ag alloy cathode and ITO electrodes is 6 mm². A UV zone cleaner was used for further cleaning before vacuum deposition of the organic materials. The evaporation rate and the thickness of the film were measured with a quartz oscillator. Current–voltage–luminescence (*I-V-L*) characteristics and CIE color coordinates were measured with a Keithley SMU238 and a ST-86LA luminance-meter. EL spectra were measured with a Photo Research's PR 705.

2.2. Materials and synthesis

Commercial grade reagents were used without further purification. All the solvents for characterization were used after redistillation. THF was refluxed with sodium filament in the presence of benzophenone until a persistent blue color appears and then distilled.

1-Bromo-4-(2'-ethylhexyloxy)benzene (2). To a solution of K₂CO₃ (40.0 g, 289 mmol) and 4-bromophenol (15.0 g, 86.7 mmol) in DMF (300 mL) was added dropwise 2-ethylhexyl bromide (20.1 g, 104 mmol). The mixture was heated to 70 °C for 24 h in the dark under the nitrogen. After the solids were filtered off, the mother liquor was treated with 1 M HCl and petroleum ether. The water phase was extracted three more times with petroleum ether, and the combined extract was washed three times with 1 M HCl, then with water for three times. The mixture solution was dried with anhydrous MgSO₄. The solvents was removed by rotary evaporation, and the crude product was purified by column chromatography using petroleum ether as eluent to provide a colorless oil (18.5 g, 75%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.33–7.38 (m, 2H); 6.74-6.80 (m, 2H); 3.80 (dd, J = 5.6 Hz, 0.8 Hz, 2H); 1.68–1.75 (m, 1H); 1.24–1.55 (m, 8H); 0.92 (s, 6H).

2-Bromo-9-(4'-(2"-ethylhexyloxyphenyl))-fluoren-9-ol (3a). The Grignard reagents were prepared from magnesium turnings (0.58 g, 24 mmol), a little iodine in THF (3 mL), and 1-bromo-4-(2'-ethylhexyloxy)benzene (2) (8.56 g, 30 mmol) in THF (30 mL), then the 2-bromofluorenone (4.0 g, 15.4 mmol) in THF was dropped into the Grignard solution after the Grignard solution was diluted with another THF (20 mL) and cooled. The mixture was refluxed for 5 h and hydrolyzed with saturated NH₄Cl solution for 2 h after cooling at room temperature, then was extracted with dichloromethane, washed with water, dried with anhydrous MgSO₄. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography using ethyl acetate/ petroleum ether (1 : 10) as eluent to obtain the pale-green solid (6.81 g, 95%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.62 (d, J = 7.2 Hz, 1H); 7.45-7.54 (m, 3H); 7.24-7.42 (m, 5H);6.78-6.82 (m, 2H); 3.80 (dd, J = 5.6 Hz, 0.4 Hz, 2H); 2.45 (s, 1H); 1.62–1.68 (m, 1H); 1.02–1.56 (m, 8H); 0.91 (s, 6H).

2,7-Dibromo-9-(4'-(2"-ethylhexyloxyphenyl))-fluoren-9-ol (**3b**). **3b** was synthesized according to the procedure described for **3a** using 2,7-dibromofluorenone (4.0 g, 11.7 mmol) to get a pale-green solid (6.02 g, 11 mmol) in a high yield of 94%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.48 (s, 4H); 7.44 (d, J = 0.8 Hz, 2H); 7.24 (d, J = 8.4 Hz, 2H); 6.81 (d, J = 8.8 Hz, 2H); 3.80 (d, J = 5.6 Hz, 2H); 1.64–1.74 (m, 1H); 1.24–1.56 (m, 8H); 0.91 (s, 6H).

2-Bromo-9-(4'-(2"-ethylhexyloxyphenyl))-9-pyrenylfluorene (**4a**). To a solution of pyrene (4.3 g, 21.5 mmol) and CH₃SO₃H (0.41 g, 4.3 mmol) in CHCl₃ (100 mL) was added dropwise **3a** (2.0 g, 4.3 mmol) in CHCl₃. The mixture was heated to 60 °C, and stirred for another 20 min. Then saturated sodium bicarbonate solution was added into the mixture to quench

the reaction. The organic phase was separated and washed by saturated sodium bicarbonate, and the water phase was extracted three times with dichloromethane. The combined organic solution was dried with anhydrous MgSO₄. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography using petroleum ether/dichloromethane (5 : 1) as eluent to get a white solid (2.1 g, 75%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.16 (d, J = 7.6 Hz, 1H); 8.10 (d, J = 7.6 Hz, 1H); 7.92–8.06 (m, 5H); 7.81 (d, J = 7.6 Hz, 2H); 7.70 (d, J = 8.0 Hz, 3H); 7.54–7.64 (broad, 1H); 7.38 (td, J = 7.6 Hz, 0.8 Hz, 1H); 7.23 (td, J = 7.6 Hz, 0.8 Hz, 1H); 3.80 (d, 5.6 Hz, 2H); 1.64-1.74 (m, 1H); 1.25-1.53 (m, 8H); 0.91 (s, 6H). LDI-TOF-MS (m/z): Anal. calcd. for $C_{43}H_{37}^{79}BrO$ 648.2; found 648.2. Anal. calcd. for $C_{43}H_{37}^{81}BrO$ 650.2; found 650.2. Anal. calcd. C, 79.50; H, 5.74; found C, 79.45; H, 5.80.

2,7-Dibromo-9-(4'-(2"-ethylhexyloxyphenyl))-9-pyrenylfluorene (4b). 4b was synthesized according to the procedure described for **4a** using 2,7-dibromo-9-(4'-(2"-ethylhexyloxyphenyl))-fluorene-9-ol (**3b**) (4.0 g, 7.3 mmol), pyrene (7.38 g, 36.5 mmol) and CH₃SO₃H (0.70 g, 7.3 mmol) to get a white solid (3.91 g, 5.4 mmol) in a yield of 73%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.17 (d, J = 7.6 Hz, 1H); 8.12 (d, J = 7.6 Hz, 1H); 7.94–8.08 (m, 5H); 7.78–7.92 (broad, 2H); 7.67 (d, J = 8.0 Hz, 4H); 7.51 (dd, J = 8.0 Hz, 2.0 Hz, 2H); 3.80 (d, J = 6.0 Hz, 2H); 1.62–1.78 (m, 1H); 1.24–1.52 (m, 8H); 0.91 (s, 6H). LDI–TOF-MS (m/z): Anal. calcd. for C₄₃H₃₆⁷⁹Br⁷⁹BrO 728.1; found 728.1. Anal. calcd. for C₄₃H₃₆⁸¹Br⁸¹BrO 730.1; found 730.1. Anal. calcd. C, 70.89; H, 4.98; found C, 70.86; H, 5.02.

9-(4'-(2"-Ethylhexyloxyphenyl))-2,9-dipyrenylfluorene **(EHOP1)**. 1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl) pyrene (5) (0.5 g, 1.5 mmol), 2-bromo-9-(4'-(2"-ethylhexyloxyphenyl))-9-pyrenylfluorene (4a) (0.97 g, 1.5 mmol), and $Pd(PPh_3)_4$ (0.05 mmol) and aqueous 2.0 M K₂CO₃ (2 mL) were mixed in a flask containing with nitrogen saturated toluene (50 mL). The reaction mixture was stirred at 90 °C for 48 h. After it was cooled to room temperature, the reaction mixture was guenched with saturated sodium bicarbonate solution and extracted twice with dichloromethane. The combined organic extracts were dried with anhydrous MgSO₄. The crude product was purified by column chromatography using petroleum ether/dichloromethane (4 : 1) as eluent to provide a pale green powder (0.92 g, 80%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.08–8.22 (m, 4H); 7.83–8.07 (m, 15H); 7.75 (d, J = 9.6 Hz, 1H); 7.68 (d, J = 7.6 Hz, 2H); 7.46 (t, J = 8.8 Hz, 1H); 7.16–7.35 (m, 4H); 6.74–6.88 (m, 2H); 3.80 (d, J = 5.6 Hz, 2H); 1.65–1.78 (m, 1H); 1.23–1.53 (m, 8H); 0.92 (s, 6H). ¹³CNMR (400 MHz, CDCl₃) δ (ppm): 158.41, 152.89, 140.76, 139.93, 139.55, 137.87, 131.65, 131.17, 131.07, 130.72, 130.62, 130.24, 129.89, 129.02, 128.58, 128.18, 127.97, 127.78, 127.68, 127.58, 127.52, 126.72, 126.13, 125.34, 125.30, 125.21, 125.12, 125.05, 124.92, 124.81, 120.82, 120.70, 115.02, 70.67, 66.54, 39.66, 30.77, 29.96, 29.35, 24.10, 23.29, 14.34, 11.38. LDI - TOF-MS (m/z): Anal. calcd. for C59H46O 770.4; found 770.6. Anal. calcd. C, 91.91; H, 6.01; found C, 91.90; H, 6.03.

9-(4'-(2"-Ethylhexyloxyphenyl))-2,7,9-tripyrenylfluorene (EHOP2). EHOP2 was synthesized according to the procedure described for EHOP1 using 5 (0.5 g, 1.5 mmol), 2,7-dibromo-9-(4'-(2"-ethylhexyloxyphenyl))-9-pyrenylfluorene (4b) (0.51 g, 0.7 mmol), Pd(PPh₃)₄ (0.02 mmol), 2.0 M K₂CO₃ (1 mL) and toluene (30 mL). The crude product was purified by column chromatography using petroleum ether/dichloromethane (3:1)as eluent to provide a pale green powder (0.47 g, 69%). 1 H NMR (400 MHz, CDCl₃) δ (ppm): 8.09–8.31 (m, 12H); 7.90– 8.08 (m, 15H); 7.74-7.89 (m, 4H); 7.58-7.73 (broad, 2H); 7.55 (d, J = 7.2 Hz, 2H); 6.96 (d, J = 8.0 Hz, 2H); 3.88 (d, J =5.6 Hz, 2H); 1.75-1.86 (m, 1H); 1.32-1.60 (m, 8H); 1.04 (s, 6H). ¹³C NMR (400 MHz, CDCl₃) δ (ppm): 158.69, 153.53, 141.10, 139.69, 139.09, 138.85, 137.93, 131.76, 131.44, 121.20, 130.88, 130.80, 130.66, 130.18, 129.34, 128.75, 128.49, 127.92, 127.81, 127.71, 127.68, 126.91, 126.78, 126.22, 125.43, 125.37, 125.19, 125.05, 124.98, 121.04, 115.23, 70.81, 66.95, 39.79, 30.92, 29.50, 24.25, 23.43, 23.11, 14.50, 11.54. LDI-TOF-MS (m/z): Anal. calcd. for C₇₅H₅₄O 970.4, found 970.7. Anal. calcd. C, 92.75; H, 5.60; found C, 92.70; H, 5.63.

3. Results and discussion

The two 9-(4'-(2"-ethylhexyloxyphenyl))fluorene substituted pyrenes, EHOP1 and EHOP2, were synthesized according to the procedure sketched in Scheme 1. Compound 2 was synthesized by Williamson reaction (75% yield).⁸ Grignard reagent was prepared from Mg and compound 2 in THF. Then it was reacted respectively with 2-bromofluorenone and 2,7-dibromofluorenone to get the fluorene-9-ol 3a and 3b (>94% yield), which were followed by Friedel-Crafts reaction with an excess amount of pyrene in chloroform promoted by methanesulfonic acid to get the compounds 4a and 4b, respectively (>70% yield). The Suzuki coupling reaction was employed between the pyrene boric acid and monobromide 4a or dibromide 4b to achieve the target compounds EHOP1 and EHOP2 with 80 and 69% yield, respectively.⁹ Both the two compounds in this report were purified by flash column chromatography. They were fully characterized by ¹H and ¹³C NMR, MALDI-TOF-MASS and elemental analysis. The results were consistent with the proposed structures.

The thermal stability of the two materials in nitrogen was evaluated by thermogravimetric analysis (TGA). The two materials have the similar thermal decomposition temperature over 430 °C. The TGA results indicate that the materials are thermally stable enough to be used as EL materials. But the phase-transition properties the two materials were more outstanding, which is determined by DSC in nitrogen atmosphere at a heating rate of 10 °C min⁻¹ (Fig. 1). The DSC examination revealed that EHOP1 and EHOP2 are stable amorphous materials, with glass transition temperature (T_g) of 103 and 191 °C for EHOP1 and EHOP2, respectively. One more rigid pyrene at the C7 of the fluorene moiety in EHOP2 results in higher T_g than that of EHOP1. In contrast, although pyrene has the high efficiency and high carrier mobility, it is ease to crystallize, which is the reason why the direct using of pyrene as emitters in doped or non-doped OLEDs is neglected. So this result indicates that the incorporation of the more rigid



Fig. 1 The DSC traces of EHOP1 and EHOP2.

9-alkyloxyphenyl-9-pyrenylfluorene moiety onto the pyrene can significantly enhance the amorphous stability of the materials. Amorphous stability is a basic requirement for materials used in OLEDs, and the microcrystallization of the materials has detrimental effects on the device stability. So the high thermal stability may in turn improve the operating lifetime of the EL device.¹⁰

The UV-Vis absorption and photoluminescence spectra of the two materials were measured both in CH₂Cl₂ and in film and the corresponding data were summarized in Table 1. From EHOP1 to EHOP2, the onset absorption shows a red shift due to the increasing of conjugation length, resulting from a more conjugated pyrene group at the C7 of fluorene moiety in EHOP2 (Fig. 2a). The two absorption peaks at \sim 334 nm and \sim 322 nm, all resulted from the non-conjugated pyrene group at the C9 of fluorene moiety, which is consistent with the absorption of pyrene in CH2Cl2 (336 nm, 322 nm). Although the conjugation chains for EHOP1 and EHOP2 are different, they all show the absorption λ_{max} at ~351 nm. 2,7-Dipyrenyl-9,9-diphenylfluorene (DPhDPF)¹¹ has the similar conjugated chain to EHOP2, but the absorption λ_{max} is at 362 nm, thus the π - π ^{*} conjugation absorption of the EHOP1 should be covered up by the peaks at \sim 351 nm, and the EHOP2's should be the shoulder peak at the \sim 365 nm, which was also partly covered up. Except for the absorption λ_{max} at 360 nm, there is no other absorption peaks for DPhDPF. From the above comparison, we think the sharp peaks at ~ 351 nm is the characteristic absorption peak of 9-pyrenylfluorene substituted pyrenes, which might originated from the interaction of the non-conjugated pyrene groups at the C9 of the fluorene and the conjugated pyrene groups at the C2 of the fluroene moiety, and the further research is on the way.



Fig. 2 (a) UV–Vis absorption. (b) Emission spectra of pyrene, EHOP1, and EHOP2. (c) Film PL of pyrene, EHOP1, and EHOP2, also included are the PL spectra of EHOP1 and EHOP2 film after annealed at 150 $^{\circ}$ C for 24 h.

Table 1	Physical	properties	of	EHOP1	and	EHOP2.
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	Φ (%)	$\lambda_{abs,max}/nm$	$\lambda_{\rm em,max}/\rm nm$				
Substituted pyrene			Solution	Film	$\Delta E/eV$ (abs. edge/nm)	HOMO/eV	LUMO ^a /eV
EHOP1	75	351	405	467	2.98 (416)	-5.39	-2.41
EHOP2	74	352	425	459	2.83 (439)	-5.32	-2.49

The emission spectra display maxima at 405 and 425 nm, for EHOP1 and EHOP2, respectively. From the unsubstituted pyrene to substituted EHOP1 to EHOP2, the PL spectra also show a gradual red shift, concomitant with the increasing conjugation length (Fig. 2b). The PL quantum yields of the materials in dichloromethane solution were estimated to be 0.75 and 0.74 for EHOP1 and EHOP2, respectively, by using 9,10-diphenylanthrancene as the reference standard ((cyclohexane solution, $\Phi = 0.9$).¹² Although the solution emission spectra of pyrene, EHOP1 and EHOP2 were obviously different to each other, both the film PL maxima of EHOP1 and EHOP2, prepared by vacuum vapor deposition (100 nm), seem to be similar to that of pyrene (Fig. 2c), which could be attributed to the aggregation of the pyrene groups. It is also the reason that why the names of the two compounds are abbreviated to be pyrene derivatives. In addition, no obvious change in the emission film was observed even after annealing at 150 °C for 24 h under nitrogen, which indicates that we have successfully improve the luminescent stability of pyrene by incorporating the bulky 9-alkyloxyphenyl-9-pyrenylfluorene group onto the pyrene ring.

The electrochemical behavior of the materials were investigated by cyclic voltammetry (CV) with a standard three electrodes electrochemical cell in a 0.1 M tetra-n-butylammonium hexafluorophosphate (Bu₄NPF₆) in CH₂Cl₂ at room temperature under nitrogen with a scanning rate of 200 mV s⁻¹. A platinum working electrode, a platinum counter electrode and an Ag/AgNO₃ (0.1 M) reference electrode were used. The oxidation onset potentials were measured to be 0.69 and 0.66 V for EHOP1 and EHOP2, respectively. The corresponding HOMO energy levels were thus estimated to be -5.39 and -5.36 eV for EHOP1 and EHOP2,13 respectively, which indicates that the electron-rich pyrene derivatives do have obviously improved hole-injection ability than conjugated fluorene derivatives (-5.6 to -5.8 eV).⁴ The LUMOs can be estimated from the ΔE , calculated from the absorption edges. The corresponding data were also summarized in Table 1.

A typical semiempirical quantum chemical calculation methodology, Austin Model1 (AM1),¹⁴ was employed to simulate the HOMOs and LUMOs of the EHOP1, EHOP2 and DPhDPF (Fig. 3). For EHOP1 and EHOP2, the

calculated results showed that the non-conjugated pyrene groups at the C9 of the fluroene moieties make significant contribution to the HOMO energy levels. In comparison with this, the non-conjugated benzene groups and long-chain alkyloxy groups have no contribution to the HOMO, including the diphenyl groups at the C9 of fluorene moiety in DPhDPF. The special influences of the non-conjugated pyrene group at C9 of fluorene moiety are consistent with the difference between our experimental HOMO of EHOP2 (-5.32 eV) and the reported HOMO of DPhDPF (-5.7 eV).¹¹

The two materials have good hole-injection and holetransporting ability, because the HOMOs of the EHOP1 and EHOP2 are close to the common hole-injection materials such as CuPc and PEDOT:PSS (~ -5.2 eV).¹⁵ Thus in order to simplify the device architecture, a light-emitting device was obtained without the hole-injection layer, ITO/TCTA (8 nm)/ EHOP1 (30 nm)/BCP (45 nm)/Mg:Ag, where the 4,4',4"tri(N-carbazolyl)triphenylamine (TCTA) was used as a buffer and hole-transporting layer, the 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as a buffer and electron-transporting layer, considering that there is always fluorescence quenching at the interface between the metal electrode and the emitter layer. A blue emission from the EHOP1 was observed (Fig. 4), with 1931 CIE (Commission Internationale DE 1'Eclairage) coordinates of (~ 0.18 , ~ 0.23). The device has a low turn-on voltage of 4.0 V, and the maximum luminance of 11620 cd m^{-2} was obtained at the voltage of 14.6 V, with the current density of 668 mA cm⁻² (Figs 5 and 6). The maximum efficiency is 3.04 cd/A (8.8 V, 2891 cd m^{-2} and 95 mA cm⁻²). At the more practical current densities of ~ 50 and 25 mA cm⁻², the device has efficiency of 2.8 cd A^{-1} , 1.12 lm W^{-1} and 2.4 cd A^{-1} , 1.12 lm W^{-1} , respectively. It is noteworthy that the device still keeps a considerable efficiency of 1.74 cd A^{-1} , when the luminescence reaches its maximum. This implies that the device is stable enough to endure extreme operating conditions. Considering the simple three-layer device fabrication, low turn-on voltage, high luminance, high efficiency and efficiency stability when current increases, the performance of this non-doped blue OLED can competitive with the best of the doped and nondoped blue OLEDs,^{11,16} which is originated from the elaborate combination of the



Fig. 3 The calculated frontier orbitals for EHOP1, EHOP2, and DPhDPF.



Fig. 4 The EL spectra of the light-emitting device.



Fig. 5 The current-voltgate-luminane characteristic of the EL device.

9-alkylphenyl-9-pyrenylfluorene and pyrene groups. Though some further optimization of devices is required to obtain the higher luminance and efficiency, it is clear from these results



Fig. 6 The current efficiency-current density and the power efficiency-current efficiency (inset) characteristics of the EL device.

that the materials are promising materials for application to optoelectronics.

3. Conclusion

In summary, two new 9-(4'-(2"-ethylhexyloxyphenyl))-9-pyrenvlfluorene substituted pyrenes, i.e. EHOP1 and EHOP2, have been synthesized and characterized. The two materials are stable amorphous materials, with $T_{\rm g}$ of 103 and 191 °C for EHOP1 and EHOP2, respectively. Due to the non-conjugated pyrene groups at C9 of the fluorene moieties, the absorption spectra of the two compounds showed some characteristic peaks and they showed improved hole-injection ability than conjugated fluorene derivatives. The preliminary simple three-layer blue EL device, ITO/TCTA (8 nm)/EHOP1 (30 nm)/BCP (45 nm)/Mg:Ag, was obtained with high brightness (11620 cd/m^2), low turn-on voltage (4.0 V) and high efficiency (3.04 cd/A), without the need for hole-injection layers. Results of this work have also proof that we can simplify the device technology though the elaborate design of material structures.

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