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A series of short axially symmetrically 1,3,6,8-tetrasubstituted pyrenebased green and blue emitters with 4-*tert*-butylphenyl and arylamine attachments

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ABSTRACT

A series of short axially symmetrically 1,3,6,8-tetrasubstituted pyrene-based derivatives (**4a**–**4c**) with two 4-*tert*-butylphenyl segments at 1,8-positions and two hole-transporting arylamine attachments at 3,6-sites of pyrene core were designed and synthesized based on stepwise synthetic strategy. These compounds were structurally characterized and their photoelectric properties were investigated by spectroscopy, electrochemical and theoretical studies. The results show that the incorporation of different arylamine units into pyrene core can tune the electronic structures of the compounds, and polysubstituted configuration of pyrene can effectively suppress the intermolecular π – π interactions and consequently leads to relatively high absolute fluorescence quantum efficiencies. These compounds exhibit high thermal stability and can form morphologically stable amorphous thin films with glass transition temperature in the range of 156–189 °C. Solution-processed non-doped green and blue organic light-emitting diodes with maximum luminance efficiencies 4.14 cd A⁻¹ and 2.41 cd A⁻¹ were achieved for **4b** and **4c**, respectively.

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1. Introduction

Organic light-emitting diodes (OLEDs) have attracted extensive attention over the last two decades because of their potential applications in flat panel displays and general lightings [1–3]. The main research focuses in this field include the design and synthesis of new materials with excellent photoelectric properties and the efficient device fabrication techniques [4-7]. Among the many famous candidate materials for OLEDs, polyaromatic pyrene has been paid everlasting attention due to its pure blue fluorescence with high quantum yield, long fluorescence lifetime, excellent thermal stability, and high charge carrier mobility [8–10]. However, pyrene and its some derivatives tend to form excimers in solid state through $\pi - \pi$ stacking due to the flat structure of pyrene core, giving rise to the red-shifted emission, the decrease of fluorescence quantum yield and the degrade of colour purity, which brings a big obstacle for the solid state applications of such pyrene-based compounds. To obtain excellent pyrene-based OLED materials, the most effective strategies involve the control of the

Recently, we designed and synthesized three novel short axially

supramolecular structures and the optimization of functional units through the introduction of bulky peripheral attachments into the

suitable positions of pyrene core [11–14]. Indeed, a larger number of pyrene-based compounds with interesting photoelectric prop-

erties and various molecular architectures and supramolecular

structures have been designed and synthesized up to date [15–17].

Some of them have been exploited as efficient hole-transporting or

host emitting materials for high performance OLEDs [18-22].

However, the reported pyrene derivatives are almost 1-substituted

pyrenes, 1,6-disubstituted and 1,3,6,8-tetrasubstituted pyrenes

with the same group, and some non-symmetrically 1,3,6,8-

tetrasubstituted pyrenes with different peripheral segments at

1,6- and 3,8-postions of pyrene ring [23,24]. The purely 1,8-

disubstituted pyrenes are very limited due to the synthetic chal-

lenge [8]. Naturally, to the best of our knowledge, there is still no

report on short axially symmetrically 1,3,6,8-tetrasubstituted pyr-

enes with different peripheral attachments at 1,8- and 3,6-

positions of pyrene core, which can not only offer more novel

compounds but also provide one effective strategy for molecular electronic tuning, interface control and optimization of film mor-

phologies of pyrene-based photoelectric materials.







symmetrically 1,3,6,8-tetrasubstituted pyrenes with two different functional attachments at 1,8- and 3,6-positions, respectively, through the stepwise derivatization and functional transformation strategy using pyrene as the precursor (Scheme 1). The introduction of 4-*tert*-butylphenyl groups into the 1,8-positions of pyrene ring can be beneficial to the separation of pure 1,8-disubstituted pyrenes and their solution-processed property. The incorporation of different arylamines is to improve the hole-injection and transporting properties of the emitting materials. Herein, we report the design, synthesis and photoelectrical properties of the new series of short axially symmetrically 1,3,6,8-tetrasubstituted pyrenes with two different functional attachments (**4a**-**4c**). In addition, solution-processed OLEDs with two representative compounds as non-doped emitting layer were investigated.

2. Experimental section

2.1. General

Dichloromethane was distilled from calcium hydride. All chemicals used were purchased from commercial sources and used without further purification. ¹H and ¹³C NMR spectra were collected on a Bruker-400 MHz or Bruker-600 MHz spectrometer in CDCl₃ solution with TMS as an internal standard. Mass spectra were obtained on a Bruker Ultraflextreme MALDI TOF/TOF mass spectrometer. Elemental analyses (C, H, N) of the dried solid samples were carried out using an Elementary Vario El analyser. UV–Vis spectra were recorded on Shimadzu UV-3600 with a UV–VIS–NIR spectrophotometer. Emission spectra were performed by a HITACHI fluorescence spectrometer (F-4600). The absolute fluorescence quantum yields (Φ_F) were determined by FM-4P-TCSPC Transient State Fluorescence Spectrometer using an integrating sphere for dilute dichloromethane solution and thin films which obtained by drop-casting on quartz plate. Cyclic voltammetry experiments were



Scheme 1. The strategy for new symmetrically pyrene-based photoelectric materials, where arylamine attachment is diphenylamino (**4a**), 4-(diphenylamino)phenyl (**4b**) and 4-(carbazol-9-yl)phenyl (**4c**).

performed with a CHI660A electrochemical work station. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum auxiliary electrode and a calomel reference electrode. The solvent in all experiments was dry dichloromethane and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophpsphate. The glass-transition temperatures (T_g) of the compounds were determined with differential scanning calorimetry (DSC) under a nitrogen atmosphere by using a DSC6000 (PerkinElmer). Samples were heated to 400 °C at a rate of 10 °C min⁻¹ and cooled at 10 °C min⁻¹ then heated again under the same heating conditions as used in the initial heating process. Decomposition temperature (T_d) were determined with thermogravimetric analysis (TGA) under a nitrogen atmosphere by using a DTG-60AH (Shimadzu). Samples were heated to 800 °C at a rate of 10 °C min⁻¹. The ground state geometries of all molecules were fully optimized using density functional theory (DFT) at the B3LYP/ 6-31G (d, p) level, as implemented in Gaussian 09W software package [25]. The electronic transitions were calculated using the time-dependent DFT (B3LYP) theory and the 6-31G (d, p) basis set.

2.2. OLED fabrication and performance evaluation

Poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) (Baytron PAI 4083) and 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) were purchased from Heraeus Precious Metals GmbH Co. KG and Luminescence Technology Corp., respectively. The OLEDs have a structure of indium tin oxide (ITO)/PEDOT:PSS (40 nm)/4b or 4c (40 nm and 50 nm)/TmPvPB (50 nm)/LiF (1 nm)/Al (150 nm) [26]. For the device fabrication, a 40 nm-thick PEDOT:PSS layer was spin-coated from an aqueous dispersion of PEDOT:PSS onto the pre-cleaned ITO substrate and then annealed at 120 °C for 30 min in air condition. Subsequently, the EML was spin-coated with two different thickness from its fresh tetrahydrofuran solution at a spin speed of 1200 rpm or 1500 rpm and then annealed at 100 °C for 30 min to remove the residual solvent at nitrogen atmosphere in a glove box. Finally, the structure of TmPyPB(50 nm)/ LiF(1 nm)/Al(150 nm) was thermally deposited in sequence in a vacuum chamber at a pressure less than 4×10^{-4} Pa through a shadow mask with an array of 14 mm² openings. The current density-voltage-luminance (I-V-L) characteristics were measured using a Keithley source measurement unit (Keithley 2400) with a calibrated silicon photodiode. The EL spectra of the devices were measured using a SpectraScan PR650 spectrophotometer. All measurements were carried out at room temperature under ambient conditions.

2.3. Synthesis

2.3.1. Synthesis of 1,8-bis(4-tert-butylphenyl)pyrene (2a)

Under the atmosphere of nitrogen, the mixture of 1,8dibromopyrene (85%) and 1,6-dibromopyrene (15%) (1.80 g, 5 mmol) [27], 4-*tert*-butylphenylboronic acid (2.14 g, 12 mmol), Pd(PPh₃)₄ (0.12 g, 0.1 mmol) and 2 M potassium carbonate solution (12 mL) were dissolved in toluene (80 mL) and refluxed for 24 h. After the reaction finished, the mixture was poured into water and extracted with dichloromethane. The organic layer was dried over MgSO₄ and the solvent was removed under vacuum. Then, the crude products were purified by silica gel column chromatography using hexane/dichloromethane mixture as eluent afforded a mixture of **2a** and **2b**. Finally, the mixture was recrystallized from dichloromethane/ethanol (1:2) solution and the pure compound **2a** was obtained as white needle-like crystals. Yield: 1.7 g, 73%. ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 8.0 Hz, 2H), 8.21 (s, 2H), 8.13 (s, 2H), 8.03 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 16 Hz, 8H), 1.48 (s, 18H). ¹³C



Scheme 2. Procedures for the syntheses of compounds 4a-4c.



Fig. 1. Absorption spectra (left) and normalized emission spectra (right) of the compounds 4a-4c recorded in dichloromethane at 1×10^{-5} M concentration.

NMR (101 MHz, CDCl₃) δ 138.22 (s), 137.54 (s), 136.93 (s), 130.80 (s), 130.47 (s), 129.07 (s), 128.38 (s), 127.72 (s), 127.35 (s), 125.36 (s), 125.29 (s), 124.74 (s), 21.29 (s). MALDI TOF-MS: *m/z* 466.271 [M]⁺. Elemental analysis: anal. calcd for C₃₆H₃₄: C, 92.66; H, 7.34; Found: C, 92.62; H, 7.38. The by-product **2b** was obtained as white crystals. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, J = 9.2 Hz, 2H), 8.22 (d, J = 7.6 Hz, 2H), 8.04 (dd, J = 15.7, 8.6 Hz, 4H), 7.62 (s, 8H), 1.48 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 150.13 (s), 138.31 (s), 137.75 (s), 130.30 (s), 128.90 (s), 127.83 (s), 127.33 (s), 125.33 (t, J = 6.3 Hz),

124.42 (s), 34.70 (s), 31.51 (s). MALDI TOF-MS: *m*/*z* 466.270 [M]⁺. Elemental analysis: anal. calcd for C₃₆H₃₄: C, 92.66; H, 7.34; Found: C, 92.59; H, 7.37.

2.3.2. Synthesis of 3,6-dibromo-1,8-bis(4-tert-butylphenyl)pyrene (3)

 Br_2 (6.3 mmol, 1.13 g) in 15 mL DMF was added dropwise into a solution of compound **2a** (3 mmol, 1.40 g) in 15 mL DMF. After stirring for 15 h at room temperature, water was added. The

Table I		
Physical	parameters of the compounds 4a – 4c .	

Com.	$\lambda_{abs}^{a}(nm)$	$\lambda_{em}^{a}(nm)/(\Phi_{F}^{c}(\%))$	$\lambda_{em}^{b}(nm)/(\Phi_{F}^{c}(\%))$	Stokes shift (cm ⁻¹)	$E_{\rm g}{}^{\rm d}/E_{\rm g}$ cal. ^e (eV)	HOMO/LUMO(eV) ^f	$T_{\rm g}/T_{\rm d}{}^{\rm g}(^{\circ}{\rm C})$
4a	258, 300, 437	488 (67.43)	491 (29.31)	2349	2.50/2.99	-5.16/-2.66	183/409
4b	251, 301, 405	483 (87.45)	485 (56.47)	3944	2.78/3.10	-5.65/-2.87	189/500
4c	241, 294, 391	437 (95.43)	464 (73.87)	2692	2.96/3.23	-5.74/-2.81	156/514

^a Measured in dichloromethane.

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^b Measured as drop-coated film.

^c Absolute quantum yield measured using integrating sphere.

^d Calculated from the absorption edge, $E_{\rm g} = 1240/\lambda_{\rm onset}$.

^e Obtained from the quantum chemical calculation using TDDFT/B3LYP/6-31G (d,p).

^f HOMO values were deduced from the relation: HOMO = E_{ox} + 4.8. LUMO values were calculated from the relation band LUMO = HOMO - E_{g} .

 $^{\rm g}\,$ Obtained from DSC/TGA measured at 10 $^\circ C\,min^{-1}$ under $N_2.$

precipitated solid was collected and used without further purification. ¹H NMR (600 MHz, CDCl₃) δ 8.59 (s, 2H), 8.32 (s, 2H), 8.13 (s, 2H), 7.58–7.53 (m, 8H), 1.44 (s, 18H). ¹³C NMR (151 MHz, CDCl₃) δ 150.81 (s), 138.95 (s), 136.61 (s), 132.24 (s), 130.19 (s), 129.01 (s), 128.26 (s), 127.39 (s), 126.04 (s), 125.54 (s), 125.43 (s), 34.72 (s), 31.44 (s). MALDI TOF-MS: *m*/*z* 624.339 [M]⁺. Elemental analysis: anal. calcd for C₃₆H₃₂Br₂: C, 69.24; H, 5.17; Found: C, 69.19; H, 5.19.

2.3.3. Synthesis of 3,6-bis(N,N-diphenylamino)-1,8-bis(4-tertbutylphenyl)pyrene (**4a**)

Under the atmosphere of nitrogen, a mixture of compound 3 (1.24 g, 2 mmol), diphenylamine (0.64 g, 3.8 mmol), bis(dibenzylideneacetone)palladium (Pd(dba)₂) (50 mg, 0.08 mmol), P(t-Bu)₃ (0.1 g/mL in toluene, 0.24 mL, 0.12 mmol), sodium tert-butoxide (0.38 g, 4 mmol) and toluene (50 mL) were heated at 80 °C for 8 h. After the reaction finished, the mixture was poured into water and extracted with dichloromethane. Then, the organic layer was dried over MgSO₄ and the solvent was removed under vacuum. The crude products were purified by silica gel column chromatography using hexane/dichloromethane mixture as eluent. The product 4a was obtained as a yellow powder solid. Yield: 1.29 g, 81%. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (s, 2H), 8.10 (s, 2H), 7.85 (s, 2H), 7.54 (s, 8H), 7.22-7.20 (m, 8H), 7.09 (d, I = 8.0 Hz, 8H), 6.94 (t, I = 7.2 Hz, 4H), 1.42 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.50 (s), 140.50 (d, J = 10.9 Hz), 138.99 (s), 130.53 (s), 129.70 (s), 129.17 (s), 128.36 (s), 128.08 (s), 127.43-127.11 (m), 124.95 (s), 123.76 (s), 122.07 (s), 121.79 (s). MALDI TOF-MS: *m*/*z* 800.574 [M]⁺. Elemental analysis: anal. calcd for C₆₀H₅₂N₂: C, 89.96; H, 6.54; N, 3.50; Found: C, 89.89; H, 6.59; N, 3.43.



Fig. 2. Normalized emission spectra of the compounds 4a-4c recorded as thin films.

2.3.4. Synthesis of 3,6-bis[4-(diphenylamino)phenyl]-1,8-bis(4-tert-butylphenyl)pyrene (**4b**)

A mixture of the compound 3 (1.24 g, 2 mmol), 4-(diphenylamino)phenylboronicacid (1.21 g, 4.2 mmol), Pd(PPh₃)₄ (46 mg, 0.04 mmol) and 2 M potassium carbonate (4.2 mL) in toluene (40 mL) was heated to reflux for 24 h under nitrogen. After the reaction finished, the mixture was poured into water and extracted with dichloromethane. Then, the organic layer was dried over MgSO₄ and the solvent was removed under vacuum. Finally, the crude products were purified by silica gel column chromatography using hexane/dichloromethane mixture as eluent afforded 4b as a green powder solid. And then the compounds was recrystallized from dichloromethane/ethanol (1:1) mixture. Yield: 1.69 g, 89%. ¹H NMR (600 MHz, CDCl₃) δ 8.33 (s, 2H), 8.23 (s, 2H), 8.06 (s, 2H), 7.65 (d, J = 8.4 Hz, 4H), 7.58 (dd, J = 8.4, 2.4 Hz, 8H), 7.34 (t, J = 7.9 Hz, 8H), 7.27–7.24 (m, 12H), 7.09 (t, J = 7.3 Hz, 4H). 1.45 (s, 18H). ¹³C NMR (151 MHz, CDCl₃) δ 150.17 (s), 147.78 (s), 147.06 (s), 138.17 (s), 137.13 (s), 136.74 (s), 135.18 (s), 131.48 (s), 130.34 (s), 129.54 (s), 129.35 (s), 129.06 (s), 128.25 (s), 128.03 (d, J = 8.3 Hz), 126.16 (s), 125.32-125.23 (m), 124.50 (s), 123.49 (s), 122.98 (s), 34.68 (s), 31.49 (s). MALDI TOF-MS: m/z 952.474 [M]⁺. Elemental analysis: anal. calcd for C72H60N2: C, 90.72; H, 6.34; N, 2.94. Found: C, 90.68; H, 6.39, N, 2.92.

2.3.5. Synthesis of 3,6-bis[4-(carbazol-9-yl)phenyl]-1,8-bis(4-tert-butylphenyl)pyrene (**4c**)

The compound was synthesized with the same method as for compound **4b** by using (4-(9*H*-carbazol-9-yl)phenyl)boronic acid (1.21 g, 4.2 mmol). Accordingly, a yellow solid was obtained and then recrystallized from dichloromethane/ethanol (1:1) mixture. Yield: 1.61 g, 85%. ¹H NMR (600 MHz, CDCl₃) δ 8.44 (s, 2H), 8.34 (s, 2H), 8.23–8.20 (m, 6H), 7.97 (d, *J* = 8.4 Hz, 4H), 7.80 (d, *J* = 8.3 Hz, 4H), 7.71 (d, *J* = 8.2 Hz, 4H), 7.64–7.61 (m, 8H), 7.50 (t, *J* = 7.6 Hz, 4H), 7.36 (t, *J* = 7.4 Hz, 4H), 1.48 (s, 18H). ¹³C NMR (151 MHz, CDCl₃) δ 150.44 (s), 140.91 (s), 140.29 (s), 137.95 (s), 137.57 (s), 136.92 (s), 136.29 (s), 128.06 (s), 126.95 (s), 126.14 (s), 120.07 (s), 129.39 (s), 125.34 (d, *J* = 2.8 Hz), 123.51 (s), 120.41 (s), 120.07 (s), 109.91 (s), 31.50 (s). MALDI TOF-MS: *m*/*z* 948.444 [M]⁺. Elemental analysis: anal. calcd for C₇₂H₅₆N₂: C, 91.10; H, 5.95; N, 2.95. Found: C, 91.05; H, 5.89, N, 3.03.

3. Results and discussion

3.1. Synthesis

The synthetic routes of the intermediates and target compounds are shown in Scheme 2 using pyrene as the starting material. Firstly, a mixture of 1,8-dibromopyrene (**1a**, 85%) and 1,6-dibromopyrene (**1b**, 15%) was obtained from pyrene after six times recrystallization. Even though, we still start the experiments using the mixture

Table 2	
Absorption and emission properties of compounds 4a-4c in different	solvents

$\lambda_{max} (nm)/\lambda_{em} (nm)/Stokes shift (cm^{-1})$								
Com.	TOL	DCM	THF	CHL	MeCN	DMF	DMSO	
4a 4b 4c	441/480/1842 405/460/2952 391/437/2692	437/488/2391 405/483/3987 391/437/2692	438/484/2170 401/473/3796 387/438/3009	437/483/2179 402/470/3590 386/437/3023	433/494/2852 398/506/5362 389/435/2718	437/497/2763 405/508/5006 394/440/2653	438/500/2831 409/511/4880 395/443/3742	



Fig. 3. UV-vis absorption (left) and Emission spectra (right) of the compound 4a recorded in different solvents at 1×10^{-5} concentration.



Fig. 4. UV-vis absorption (left) and Emission spectra (right) of the compound 4b recorded in different solvents at 1×10^{-5} concentration.



Fig. 5. UV-vis absorption (left) and Emission spectra (right) of the compound 4c recorded in different solvents at 1×10^{-5} concentration.

because it is possible to obtain the final pure 1,8-disubstituted pyrene-based compounds in the flowing steps based on their

obvious difference in solubility. Secondly, the mixture of dibromopyrenes were transformed to a mixture of 1,8-(4-tert-



Fig. 6. Correlation between the Stokes shift and solvent parameter $E_{T}(30)$ for compounds **4a**–**4c**.

butylphenyl)pyrene (**2a**) and 1,6-(4-*tert*-butylphenyl)pyrene (**2b**) through Suzuki coupling reaction. There is a significant difference of solubility in dichloromethane and ethanol (1:2) solution for **2a** and **2b**, and therefore the pure key intermediate **2a** was relatively readily obtained. Thirdly, compound **2a** was brominated with liquid bromine, yielding the another key intermediate 3,6-dibromo-1,8-bis(4-*tert*-butylphenyl)pyrene (**3**) in a very high yield of 95%, which was used directly without further purification. Finally, the target products **4a**–**4c** were prepared by Buchwald–Hartwig and Suzuki coupling reaction between the compound **3** and the corresponding arylamine or aryl boronic acid with yields of 80–90%. These compounds show excellent solubility in organic solvents, which makes them promising candidates for solution-processed OLEDs.

3.2. Photophysical properties

The UV-vis absorption and photoluminescence (PL) spectra of compounds 4a-4c in dichloromethane are shown in Fig. 1. The detailed photophysical data are presented in Table 1. The three compounds feature the longest wavelength absorptions at ca. 391-437 nm attributed to the charge transfer from amine to pyrene and the absorptions at ca. 294-301 nm ascribed to pyrene localized $\pi - \pi^*$ transitions. The absorption spectrum of compound **4a** exhibits a relative large red-shift compared with those of **4b** and **4c**, suggesting that the pyrene core directly attached by diphenylamine unit can increase the π -electron conjugation of the molecule. The energy gaps (E_g) of compounds **4a**, **4b** and **4c** estimated from the onset of the absorption spectra are 2.50, 2.78 and 2.96 eV, respectively, indicating that the different arylamines attached to the pyrene core can effectively tune the π -conjugation of the compounds. The PL spectra of compounds 4a, 4b and 4c in dichloromethane display emission peak in green, bluish-green and deep blue region, respectively. It indicates that the introduction of different arylamines into the pyrene core has obvious influence on the fluorescence properties of the compounds. Compound 4b exhibits a slightly blue-shift compared with that of 4a, which demonstrates that the incorporation of phenyl ring between the diphenylamine and the pyrene core increases the molecule twist and reduces the π -conjugation. The PL spectrum of compound **4c** shows obvious blue-shift compared with those of 4a and 4b, which suggests that the more rigid and planar conformation of carbazole

more effectively reduces the π -conjugation of the molecule. In addition, compounds **4a**–**4c** show small Stokes shifts (2349–3944 cm⁻¹ in dichloromethane), indicating less energy loss during the relaxation process and thereby ensuring efficient fluorescence. As shown in Fig. 2, the emission spectra of **4a** and **4b** in thin films exhibit a small bathochromic shift (3 nm and 4 nm) relative to those in dichloromethane solution, which indicates that the two compounds exhibit a very similar conformation in both states [11]. While compound **4c** shows an obvious red-shift (27 nm), suggesting that there exists slightly strong intermolecular π – π interactions in film state. The absence of characteristic pyrene excimer peak in these PL spectra evidences that the coplanarity and π -conjugation of the compounds have been suppressed to some extent by the twist between the functionalized moieties and pyrene core.

The absolute fluorescence quantum yields $\Phi_{\rm F}$ s of compounds **4a**–**4c** in dichloromethane and in film state were determined using an integrating sphere. These compounds show high $\Phi_{\rm F}$ s in dichloromethane with the range from 67.43 to 95.43%. The $\Phi_{\rm F}$ s of compounds **4a**–**4c** in film states (29.31–73.87%) show a decreasing tendency compared to those in dichloromethane due to the intermolecular π – π interactions in film states. Compound **4a** exhibits an obviously lower $\Phi_{\rm F}$ in film state than those of **4b** and **4c**, which indicates that the structure of diphenylamine directly attached on the pyrene backbone has a relatively weak effect on interrupt the π – π stacking of the molecule. The $\Phi_{\rm F}$ s of compounds **4b** (56.47%) and **4c** (73.87%) in film states are very high, which makes them having great potential application in solid state luminescence.

To better understand the effect of environments on the electronic spectroscopic of the compounds 4a-4c, we studied the absorption and emission spectra of the three compounds in different polar solvents such as toluene (TOL), dichloromethane (DCM), tetrahydrofuran (THF), chloroform (CHL), acetonitrile (MeCN), N,Ndimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The pertinent data are summarized in Table 2. The changes in absorption and emission profiles for compounds 4a-4c with different solvent polarities are illustrated in Figs. 3–5. In the absorption spectra, compounds **4a–4c** are insensitive to the solvent polarity with the shift below 11 nm. In the emission spectra, the emission maximum of compound 4c has no significant change with the different solvent polarities, suggesting a small transition dipole moment [21,28]. However, for compounds 4a and 4b, the solvent dependence in the emission spectra is remarkable, with large bathochromic shifts of 20 nm for 4a, 51 nm for 4b, which indicates that their excited state are more stable in polar solvent probably due to the separation of charges in the higher energy state [29]. The Stokes shifts of compounds 4a-4c in different solvents were calculated to know the structural reorganization occurring during electronic excitation. Stokes shift values in different solvents for the compounds follow the order 4c < 4a < 4b. Larger Stokes shift observed for 4b indicates appreciable structural reorganization due to photo-excitation from ground state to excited state [30]. Furthermore, the relationships of Stokes shift against the solvent parameter $E_{\rm T}(30)$ of the compounds **4a**–**4c** were investigated as shown in Fig. 6. The slopes of the correlation plots are in the order of **4c** (27.90) < **4a** (90.77) < **4b** (196.64), which indicates that more pronounced intramolecular charge transfer is occurred in compound 4b.

3.3. Theoretical calculation

To deeply investigate the electronic structures, orbital energies, electron densities of the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) states of the compounds **4a**–**4c**, as well as to understand the absorption



Fig. 7. Electronic distributions observed for the frontier orbitals for the compounds 4a-4c.

characteristics, density functional theory (DFT) calculations (B3LYP/ 6-31G (d, p) basis set) were performed on the three compounds with the Gaussian 09W software package [25]. Three-dimensional optimized geometries and electronic distributions in the frontier molecular orbitals of compounds 4a-4c are shown in Fig. 7 and the HOMO–LUMO energy gaps (E_g cal.) were calculated and are presented in Table 1. The calculated structures of compounds 4a-4c reveal that all molecules adopt non-coplanar conformations. The planar pyrene twists by the substituents on the 1-, 3-, 6-, 8- position of the pyrene ring. Such structural characteristic is beneficial to OLED application by suppressing the undesirable intermolecular $\pi-\pi$ interactions and the crystallization hindrance to build a uniform amorphous morphology in the film state. The π -electrons in the HOMOs of compounds 4a and 4b are mainly distributed on the 3,6-bis(*N*,*N*-diphenylamino)pyrene and 3,6-bis[4-di(phenylamino) phenyl]pyrene moieties, respectively. For compound 4c, the HOMO orbital is mainly contributed by the pyrene ring and a little by the 3,6-bis[4-(carbazol-9-yl)phenyl] unit. In the LUMOs of the compounds **4a**–**4c**, the excited electrons are localized primarily on the electron-rich pyrene core. It suggests that the substituent of 3,6-bis [4-(carbazol-9-yl)phenyl] on pyrene ring has a little effect on the HOMO of the molecule. Moreover, the TDDFT calculations of compounds **4a**–**4c** have been carried out and the predicted vertical transitions and their assignments are summarized in Table S1. The results reveal that the S₁ states (S₀ \rightarrow S₁ transition) of compounds **4a**–**4c** are dominated by the HOMO \rightarrow LUMO transition.

3.4. Electrochemical and thermal studies

The electrochemical properties of compounds **4a–4c** were studied by cyclic voltammetry (CV) measurements and the onset oxidation potentials of the compounds were calculated using ferrocene as standard. The data of HOMO, LUMO energy levels and band gap energy (E_g) are summarized in Table 1. The HOMO values of compounds **4a**, **4b** and **4c** estimated from the onset potentials of oxidation peak are –5.16 eV, –5.65 eV and –5.74 eV, respectively. The LUMO values of these compounds calculated by HOMO and E_g are in the range from –2.66 to –2.87 eV.



Fig. 8. Structure of the non-doped devices and energy levels of materials 4b and 4c.

the materials used in these devices are shown in Fig. 8 and the essential performance electric parameters are demonstrated in Table 3. These data indicate that the hole-injection into the emitting layer of 4c-based devices (devices I and II) were less effective than 4b-based devices (devices III and IV) because of the larger barrier between the PEDOT:PSS (-5.2 eV) and 4c (-5.74 eV) than **4b** (-5.65 eV). The effective of electron-injection into the emitting laver of 4c- and 4b-based devices are almost equal due to the similar electron-injection barrier between TmPyPB (-2.7 eV) and 4c (-2.81 eV), 4b (-2.87 eV), respectively.

The current density-voltage-luminance (I-V-L) characteristics and the current density-efficiency curves of the devices I-IV are shown in Fig. 9. The turn-on voltages of the devices I, II, III and **IV** are very low with the values of 2.9, 2.9, 4.5 and 4.1 eV, respectively, which indicates that the performance of the devices is decent. Devices I and II show relatively lower turn-on voltages than those of devices III and IV, which may be ascribed to the better charge carrier transporting ability of compound 4b. The device II using **4b** as emitting material shows the best device performance with a maximum brightness (L_{max}) of 8741 cd/m², a maximum luminance efficiency (η_{max}) of 4.03 cd/A, a maximum power efficiency (PE) of 2.89 lm/W. The 4c-based device with the emitting

Table 3	
EL performance: ITO/PEDOT: PSS (40 nm)/EML (40 nm and 50 nm)/TmPyPB (50 nm)/LiF (1 nm)/Al (150 nm	n)

Devices	Emitters	$V_{\rm on}^{\rm a}({\rm V})$	EL _{max} ^b (nm)	FWHM ^c	$L_{\rm max}^{\rm d}$ at voltage (cd m ⁻² /V)	η_{max}^{e} (cd/A)	PE ^f (lm/W)	CIE(x,y)
I	4b (50 nm)	2.9	480	63	7878/8.6	4.14	2.86	(0.153, 0.328)
П	4b (40 nm)	2.9	480	54	8741/8.0	4.03	2.89	(0.147, 0.294)
Ш	4c (50 nm)	4.5	465	90	2438/11.0	1.89	0.95	(0.174, 0.258)
IV	4c (40 nm)	4.1	464	88	3550/9.6	2.41	1.34	(0.163, 0.246)

Turn-on voltage (V) at a luminance of 1 cd m^{-2} .

b Emission maximum.

Full-width at half maximum.

d Maximum luminance (cd m^{-2}) at the applied voltage (V).

Luminance efficiency (cd A^{-1}).

Maximum power efficiency.

The thermal properties of the compounds **4a–4c** were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere, the relevant data are shown in Table 1 and Fig. S1. These compounds show high thermal stability and the decomposition temperatures (T_d) corresponding to 5% weight loss are 409, 500 and 515 °C for compounds 4a, 4b and 4c, respectively. DSC thermograms of the three compounds display remarkably high glass transition temperature (T_g) values at 183, 189 and 156 °C, respectively, and no crystallization and melting peaks being observed at higher temperatures, indicating an excellent amorphous glass state stability [31]. The high thermal and morphological stabilities of these compounds are advantageous for the construction of stable and long-life OLED devices.

3.5. Electroluminescence

Two representative compounds 4b and 4c were employed as the non-doped emitting layers (EMLs) in OLEDs with the following configuration: ITO/PEDOT: PSS (40 nm)/EML (40 nm and 50 nm)/ TmPyPB (50 nm)/LiF (1 nm)/Al (150 nm). Poly(3,4ethylenedioxythiophene):ploy(4-styrenesulfonate) (PEDOT: PSS) act as the hole injection layer, 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) is used as an electron-transporting layer, the materials 4b and 4c are conducted as emitters, respectively. The emitting materials were spin-coated with two different thickness from its fresh THF solution. The structures and the energy levels of layer thickness of 40 nm (device IV) exhibits a relatively lower device performance with a L_{max} of 3550 cd/m², a η_{max} of 2.41 cd/A, a PE of 1.34 lm/W. Generally, the EL efficiencies of 4c-based devices are lower than those of **4b**-based devices, which may derive from the higher hole-injection barrier of 4c (-0.54 eV) than that of 4b (-0.45 eV). From the EL spectra shown in Fig. 9(b), the devices I and II emit a strong bluish-green emission with λ_{EL} all peaked at 480 nm and the corresponding CIE coordinates are (0.153, 0.328) and (0.147, 0.294), respectively. While the devices III and IV exhibit a sky-blue emission with maximum emission peaks at 465 nm, 464 nm and the CIE coordinates of the devices are (0.174, 0.258) and (0.163, 0.246), respectively. The electroluminescence (EL) spectra of all devices match with their corresponding PL spectra, indicating that the EL purely originate from the emitting layers. Furthermore, it is worth to note that there is almost no emission shoulder at the longer wavelength and no significant change in the EL spectra upon varying driving voltages for all devices, which indicates that the hole-electron pairs for recombination are well confined in the emitter layer.

4. Conclusions

In conclusion, a series of short axially symmetrically 1,3,6,8tetrasubstituted pyrene-based compounds (4a-4c) with 4-tertbutylphenyl and hole-transporting arylamine attachments have been elaborately designed and successfully synthesized. The planar pyrene twists by the substituents on the pyrene ring, which can



Fig. 9. The current density–voltage–luminance curves with varying thickness of the compounds 4b and 4c (a); The electroluminescent spectrum of the compounds 4b and 4c (b); Luminance efficiency of the compounds 4b and 4c (c); Power efficiency of the compounds 4b and 4c (d).

effectively suppress the intermolecular $\pi - \pi$ interactions of the molecules. Incorporation of different arylamine units into the pyrene core can tune the electronic structures of these compounds and then influences their photoelectric properties. All the three compounds exhibit high PL absolute quantum efficiencies both in dichloromethane (67.43-95.43%) and film states (29.31-73.87%). The three compounds are also thermally and morphologically stable, showing high T_d (409–514 °C) and T_g values (156–189 °C). These compounds with a symmetrical structure show good solubility and film-forming abilities, which is beneficial to form homogeneous and smooth films for OLED device by conventional solution processing techniques. Solution processed double-layer OLEDs using two representative compounds 4b and 4c as nondoped emitting layer were fabricated and they exhibit good device performance. More short axially symmetrically as well as the long axially symmetrically pyrene-based compounds with the excellent properties are carrying out in our lab.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.03.020.

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