DOI: 10.1002/cjoc.201500385

Two Symmetrically Bis-substituted Pyrene Derivatives: Synthesis, Photoluminescence, and Electroluminescence

Xiaojie Gong,[a] Xiang Xie,[b] Naiwu Chen,[a] Chaoyue Zheng,[a] Jie Zhu,[a]
Runfeng Chen,*,[b] Wei Huang,[a,b] and Deqing Gao*,[a]

[a] *Key Laboratory of Flexible Electronics & Institute of Advanced Materials, Jiangsu National Synergistic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing, Jiangsu 211816, China*
[b] *Key Laboratory for Organic Electronics & Information Displays and Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing, Jiangsu 210003, China*

Two kinds of cyanophenyl terminated pyrene derivatives for organic light-emitting diodes were synthesized and characterized by UV/Vis, fluorescence (FL), ^{1}H NMR, MALDI-TOF, CV and TGA. Both compounds exhibited blue photoluminescence and high fluorescent quantum yield of 85% and 75% in solutions. Due to the presence of acetylene spacer, the compound distinguishes itself by high coplanarity, high thermal stability, little Stokes' shift and clear excimer formation in the solid state from the acetylene-free compound. In order to suppress the molecular aggregation, the electroluminescent properties were studied by doing the materials in PVK. The result proved that energy transfer happened from the host PVK to the materials.

Keywords pyrene, organic light-emitting diode, aggregation, energy level, doping

Introduction

Organic light-emitting diodes (OLEDs) have been widely used in display such as mobile phones and digital cameras since the first report by Tang *et al.*[1] They have attracted increasing industrial and academic interest owing to their high technological potential for next generation full-color flat panel displays and solid-state lighting.[2-4]

Among blue light-emitting materials, pyrene derivatives have rich electronic and photophysical properties and have been exploited as organic light-emitting and semiconductor materials.[5-11] The optical feature of the pyrene-based materials is that fluorescence quantum efficiency is high in dilute solution but much lower in condensed state due to heavy aggregation and excimer formation from planer molecular configuration. For example, 1,3,6,8-tetrakis(3,5-dimethylphenyl)pyrene has fluorescence quantum yield of 86% in cyclohexane but just 20% in film.[12] The well studied 1,3,6,8-tetraphenylpyrene has high fluorescence quantum yield of 90% in solution, but it showed poor OLED performance with maximum external quantum efficiency of 0.5%.[6,13-15]

One strategy to suppress the aggregation is to design twisted molecular conformation.[6,14,16] Moorthy *et al.*[6] inhibited aggregation by introducing multiple methyl and methoxyl groups on 1,3,6,8-tetraarylpyrenes molecule. Chan *et al.*[16] used 1,3-alt-calix[4]arene scaffold to arrange pyrene units orthogonal to each other and got current efficiency of 10.5 cd/A and maximum external quantum efficiency of 6.4% of a blue non-doped OLED.

A few reports are available by doping pyrene derivatives in a host material to avoid the aggregation until now.[17-19] Wee *et al.*[17] reported a series of 1- and 6-position bis-substituted pyrene derivatives as the dopants; among them, the compound with strong electron-withdrawing CN group presented the best electroluminescent property with 9,10-di(2-naphthyl)anthracene as the host. Thomas *et al.*[19] developed pyrene-fluorene chromophores with an acetylene linkage and blue or yellow electroluminescence was obtained with 4,4-bis(9*H*-carbazole-9-yl)biphenyl (CBP) as the host.

Introduction of acetylene unit as spacer between polyaromatic hydrocarbons (PAH) helps to extend the conjugation system and acquire high planarity. Both acetylene bridged tetra-substituted pyrene-fluorene and pyrene-pheyl compounds presented attractive optical properties.[19,20] Feng *et al.* reported a serial of pyrene-based Y-shaped blue emitters[21] and 1,3,5,9-tetracyanophenyl-7-*tert*-butylpyrene,[22] and found that both CN substituted derivatives had high thermal stability and excellent solid-state fluorescence quantum yield.

On the base of above analysis of literatures, we want to develop thermally stable and highly fluorescent efficient blue-emitting materials. Here we report the syn-

---

* E-mail: iamdqgao@njtech.edu.cn, iamrfchen@njupt.edu.cn; Tel.: 0086-025-83587984, Fax: 0086-025-83587984
Received May 20, 2015; accepted June 14, 2015; published online July 22, 2015.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201500385 or from the author.

thesis of two symmetrically bis-substituted pyrene derivatives **1** and **2** with CN group terminated. **1** has two directly bound cyanophenyl on pyrene core and **2** has acetylene unit inserted between pyrene core and cyanophenyl. The compounds were fully characterized and the electroluminescence property was studied by doping the material in poly(vinyl carbazole) (PVK) as the emitting layer in the OLEDs.

Experimental

General

Pyrene, 4-bromobenzenecarbonitrile, methyltrioctylammonium chloride, tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), cuprous iodide (CuI), [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) chloride ($Pd(dppf)Cl_2$), triphenylphosphine (PPh_3), *trans*-dichlorobis(triphenylphosphine)palladium(II) ($Pd(PPh_3)_2Cl_2$) and trimethylsilyl acetylene (TMSA) were purchased from Energy Chemical. Bis(pinacontato) diboron (B_2Pin_2) was purchased from Sukailu Chemical. Bromine, potassium acetate, DMSO, anhydrous $MgSO_4$, diisopropylamine, sodium carbonate, and potassium carbonate were purchased from Sinopharm Chemical Reagent. They were used without any further purification. Poly(3,4-ethylnenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was obtained from Luminescnece Technology Corp., PVK was obtained from Sigma-Aldrich, 1,3,5-tri(1-phenyl-1*H*-benzo[d]imidazol-2-yl)phenyl (TPBI) was obtained from Nichem Fine Technology Co. Ltd. Anhydrous toluene and THF were obtained by distilling the corresponding solvent previously treated with sodium and diphenylmethanone.

The ^1H NMR (300 MHz) spectra were recorded on Bruker AMX400 spectrometer in $CDCl_3$. UV/Vis spectra were recorded on Shimadzu UV-1750. Fluorescence spectra were recorded on Hitachi F-4600. Fluorescence quantum yields (Φ_f) were calculated using coumarin 1 as primary standard ($\Phi_f = 0.99$ in ethyl acetate). Cyclic voltammetry (CV) experiments were performed with a CHI-621B electrochemical analyzer. All measurements were carried out at room temperature with a conventional three electrode configuration consisting of a platinum working electrode, an auxiliary electrode and a non-aqueous $Ag/AgNO_3$ reference electrode. The solvent was $CHCl_3$ in CV measurement and CH_2Cl_2 in other experiments. The supporting electrolyte was 0.1 mol/L tetrabutylammonium hexafluorophosphate. TGA measurements were performed on a Perkin Elmer TGA7 thermal analyzer at a heating rate of 10 ℃/min under a dry nitrogen flow.

Synthesis of compound 1

1,6-Dibromopyrene A solution of bromine (2.0 ml) in dichloromethane (50 mL) was dropwise added to a solution of pyrene (4.0 g) in dichloromethane (70 mL) at room temperature over 2 h. The solution was then stirred overnight. The white precipitate was collected by filtration. 1,6-Dibromopyrene was purified by recrystallization from toluene for several times with the yield of 50%. ^1H NMR ($CDCl_3$, 300 MHz, 298 K) δ: 8.46 (d, $J = 9$ Hz, 2H), 8.27 (d, $J = 9$ Hz, 2H), 8.12 (d, $J = 9$ Hz, 2H), 8.06 (d, $J = 9$ Hz, 2H).

4,4,5,5-Tetramethyl-2-(4-cyanophenyl)-1,3,2-dioxaborolane Following the literature,[23] the mixture of 4-bromobenzenecarbonitrile (1.82 g), potassium acetate (2.34 g, 30 mmol), bis(pinacontato) diboron (2.80 g, 11 mmol), $Pd(dppf)Cl_2$ (0.036 g, 0.030 mmol) in DMSO (25 ml) was heated under N_2 at 80 ℃ overnight. The reaction mixture was cooled to room temperature, then cool water was added. The solution was extracted by ethyl acetate and the combined organic phase was dried over anhydrous $MgSO_4$. After the solvent was evaporated and with column chromatography (silica gel, ethyl acetate/petroleum ether = 1/8, *V*/*V*) the product was collected as white solid with the yield of 75%. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): 7.88 (d, $J = 6$ Hz, 2H), 7.64 (d, $J = 9$ Hz, 2H), 1.35 (s, 12H).

Compound 1 The mixture of 1,6-dibromopyrene (0.36 g, 1 mmol), 4,4,5,5-tetramethyl-2-(4-cyanophenyl)-1,3,2-dioxaborolane (0.6 g, 3 mmol), one drop of methyl trioctyl ammonium chloride, dry toluene (25 mL) and 2 mol/L Na_2CO_3 aqueous solution (25 mL) was bubbled with N_2 for 10 min. Then $Pd(PPh_3)_4$ (46 mg, 0.04 mmol) was added. The mixture was heated at 100 ℃ for 24 h. The mixture was cooled to room temperature and the solution was extracted by dichloromethane. The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated. The crude product was purified by column chromatography (silica gel, dichloromethane/petroleum ether = 1/1, *V*/*V*) to get compound **1** as greenish yellow solid with the yield of 33%. ^1H NMR ($CDCl_3$, 300 MHz, 298 K) δ: 8.26 (d, $J = 9$ Hz, 2H), 8.11 (s, 4H), 7.98 (d, $J = 6$ Hz, 2H), 7.88 (d, $J = 6$ Hz, 4H), 7.77 (d, $J = 6$ Hz, 4H). MS (MALDI-TOF) *m/z*: calcd for $C_{30}H_{16}N_2$ 404.47, found 404.97 (M^+).

Synthesis of compound 2

4-Ethynylbenzonitrile According to the literature,[24] 4-bromobenzenecarbonitrile (1.82 g, 10 mmol) was dissolved in the mixture of toluene (20 mL) and diisopropylamine (10 mL). The system was bubbled with N_2 for 10 min and then $Pd(PPh_3)_4$ (577.8 mg, 0.50 mmol) and CuI (95.2 mg, 0.50 mmol) were added. TMSA (1.2 g, 12 mmol) was added by syringe. The mixture was heated under N_2 at 80 ℃ overnight. The reaction was cooled to room temperature, and then NH_4Cl aqueous solution was added. The solution was extracted by dichloromethane. The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated. The crude product was purified by column chromatography (silica gel, dichloromethane/petroleum ether = 1/3, *V*/*V*) to get yellow solid (0.92 g, 93%). The yellow solid (0.598 g, 3.0 mmol) was added to a mixture of THF (7 mL) and MeOH (7 mL), then K_2CO_3 (4.2 g, 30 mmol) was added. The mixture was stirred at room temperature overnight. NH_4Cl aqueous solution was added and the product was extracted with dichloromethane. The combined organic phase was dried over anhydrous $MgSO_4$ and then evaporated. The crude product was purified by column chromatography (silica gel, dichloromethane/petroleum ether＝1/2, *V*/*V*) to get pure 4-ethynylbenzonitrile as white solid with the yield of 85%. ^1H NMR ($CDCl_3$, 300 MHz, 298 K) *δ*: 7.56－7.64 (m, 4H), 3.30 (s, 1H).

Compound 2 The mixture of 1, 6-dibromopyrene (0.36 g, 1 mmol) and 4-ethynylbenzonitrile (0.40 g, 2.5 mmol) in dry THF (25 ml) and diisopropylamine (10 mL) was bubbled with N_2 for 10 min. Then PPh_3 (50 mg, 0.2 mmol), CuI (25 mg, 0.2 mmol) and $Pd(PPh_3)_2Cl_2$ (50 mg, 0.05 mmol) were added. The mixture was heated at 80 ℃ for 24 h. The mixture was cooled to room temperature and the solution was extracted by dichloromethane. The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated. The crude product was purified by column chromatography (silica gel, dichloromethane/petroleum ether＝2/1, *V*/*V*) to get compound **2** as yellow solid (100 mg) with the yield of 25%. ^1H NMR ($CDCl_3$, 300 MHz, 298 K) *δ*: 8.67 (d, *J*＝9 Hz, 2H), 8.18－8.31 (m, 6H), 7.78 (d, *J*＝9 Hz, 4H), 7.72 (d, *J*＝9 Hz, 4H). MS (MALDI-TOF) *m/z*: calcd for $C_{36}H_{16}N_2$ 452.52, found 453.20 (M^+).

OLED device fabrication and measurement

Patterned indium tin oxide (ITO) substrates (10 Ω/□, Thin Film Devices, Inc.) were cleaned sequentially in an ultrasonic bath of the detergent, deionized water, acetone and ethanol. After dried in an oven at 120 ℃ for 20 min, the substrates were treated with UV-Ozone for about 5 min. A certain volume of the stock solution of **1** (or **2**) with concentration of 1 mg/mL in chlorobenzene was added into the stock solution of PVK with concentration of 12 mg/mL in chlorobenzene and a mixture solutions with concentration of 8% (*w*/*w*) of **1** (or **2**) were ready for spin coating. A thin layer of PEDOT:PSS of 30 nm thick was prepared by spin coating onto the ITO at 600 r/min for 6 s and 3000 r/min for 60 s and baked at 130 ℃ for 30 min. A layer of the emitting material (PVK, **1** doped PVK, or **2** doped PVK) was spin-coated on the top of PEDOT:PSS layer. The samples were then loaded into a deposition chamber. A sequence of TPBI (30 nm), LiF (1 nm) and Al (100 nm) were thermally deposited at a vacuum of 3×10^5 mbar. Electroluminescent (EL) devices fabricated in this work had a configuration of device **A**: ITO/PEDOT:PSS (30 nm)/**1**:PVK (8%, *w*/*w*) (50 nm)/TPBI (30 nm)/Al (100 nm), device **B**: ITO/PEDOT:PSS (30 nm)/**2**:PVK (8%, *w*/*w*) (50 nm)/TPBI (30 nm)/Al (100 nm), and device **C**: ITO/PEDOT:PSS (30 nm)/PVK (50 nm)/TPBI (30 nm)/Al (100 nm); where PEDOT:PSS was the hole injection material, TPBI was the electron transporting material and PVK was the hole transporting and host material. The film thickness was controlled by a quartz oscillating thickness monitor. The emission area of the devices was 0.09 cm^2. The EL spectra and brightness–current density–voltage characteristics of devices were measured by using a SpectraScan PR 650 spectrophotometer and a computer-controlled voltage-current source, Keithley 2400, under ambient condition.

Results and Discussion

The synthesis of two pyrene derivatives **1** and **2** started with bromination of pyrene (as shown in Figure 1). The product, 1,6-dibromopyrene, was obtained by recrystallization in toluene with several times. The boron reagent, 4,4,5,5-tetramethyl-2-(4-cyanophenyl)-1,3,2-dioxaborolane, was synthesized with 4-bromobenzenecarbonitrile as the starting material. 1,6-Dibromopyrene and the boron reagent reacted by Suzuki coupling mechanism to produce compound **1** with the yield of 33%. The intermediate for the synthesis of compound **2**, 4-ethynylbenzonitrile, was prepared by subsequent Sonogashira coupling reaction and the cleavage of acetylene protecting group trimethylsilyl with the yield of 79%. 1,6-Dibromopyrene and 4-ethynylbenzonitrile reacted by Sonogashira coupling mechanism to produce compound **2** with the yield of 25%. Due to large planer structure, **1** and **2** are only slightly soluble in toluene and CH_2Cl_2.

To gain a deep insight into the structure-property relationship at the molecular level, density functional theory (DFT) calculations were performed to evaluate the positions and energies of frontier orbits for **1** and **2**, using the Gaussian 03 program at the B3LYP/6-31G(d) level. For **1** and **2**, the largest coefficients of HOMO orbitals are mainly positioned on the pyrene core, and the coefficients of LUMO orbitals are spread across the entire π-conjugated skeleton, as the case of 1,3,5,9-tetracyanophenyl-7-*tert*-butylpyrene.[22] As observed from the geometries, phenyl twists in relative to pyrene in **1** with the dihedral angle of 52.3°, while phenyl and pyrene in **2** are coplanar. The extended conjugation system by inserting acetylene may explain why **2** has a smaller energy gap than **1**.

Thermogravimetric analysis (TGA) was carried out under nitrogen atmosphere to evaluate the thermal stability of **1** and **2**. The onset decomposition temperatures (T_d) of **1** and **2** were estimated to be 191.8 ℃ for **1** and 256.2 ℃ for **2**. It indicates that the acetylene linkage in **2** serves as a spacer, relieves the steric strain between the pyrene and phenyl units and enhances the stability, in agreement with acetylene linked pyrene-fluorene compound.[19]

UV-vis absorption spectra and PL spectra in dilute CH_2Cl_2 solution and in powder were carried out at room temperature. In CH_2Cl_2 solution (Figure 3), **1** has the absorption spectrum at 242, 289 and 366 nm which is associated with the π-π* transition of the pyrene backbone, and emission spectrum at 427 nm. With extended conjugation structure, **2** has fine-structured absorption spectrum with maximum at 432 nm which is associated with the π-π* transition of the conjugated backbone, and emission spectrum at 448 nm and a shoulder at 475 nm, which resembles to those of 1,3,6,8-tetrakis[(triisopropylsilyl)ethynyl]pyrene[25] and 1,6-bis(phenylethynyl)-pyrene-phenothiazine dyad.[26] Compared with **1**, **2** has both bathochromicly shifted absorption and emission peaks because acetylene extends the conjugation system, as reported pyrene-acetylene compounds.[27] It is observable that **2** has the Stokes' shift of 826.7 cm^{-1} and **1** has the Stokes' shift of 3903.2 cm^{-1}, suggesting the remaining planar configuration for the singlet ground state (S_0) and the first excited singlet ground state (S_1) states of **2**.[13] In powder, **1** has an emission peak at 478 nm while **2** has a broad emission peak at 537 nm with a shoulder at 561 nm, indicating that **2** has strong J-aggregation through intermolecular π-π stacking in the solid state.[25] **2** shows a strong bathochromic shift of 89 nm of the emission in powder from that in solution, being much larger than 51 nm in the situation of **1**. This suggests that the excimers between pyrene moieties of **2** are formed in the solid state. It could be explained that **2** has higher coplanarity and has more tendency to have strong π-π staking in the solid, in agreement with the literature.[12] This experimental result gets supported by the DFT theoretical calculations (Figure 2). **1** has a large dihedral angle of 52.3° between phenyl and pyrene ring, thus resulting in severe steric congestion. The phenyl and pyrene ring in **2** are coplanar and the planar molecular structure is prone to close packing and excimer formation in the solid state, thereby resulting in the drastically bathochromic shift in the PL spectrum of its film in comparison with its emission in solution. The fluorescence quantum yields of both compounds in CH_2Cl_2 solution are high, 85% from **1** and 75% from **2**, respectively (see Table 1). Relatively lower value from **2** than **1** can be explained by the observation that **2** has larger overlap of absorption and emission spectra and therefore stronger self absorption (Figure 3). The emission of **1** and **2** in a serial of from-nonpolar-to-polar solvents was tested (Figure S3) and only minimal solvatochromism was found in contrast to the reported result,[28] suggesting small change of polarity from the ground state to the excited state of **1** and **2** due to symmetrical substitution.[29]

The electrochemical property of **1** and **2** was examined by cyclic voltammetry (CV). The measurements of the compounds displayed one reversible oxidation process in $CHCl_3$ solution, but no obvious reduction peaks were detected, as the reported observations.[12] So, we only adopted anodic scan from 0 to 2.0 V to detect the

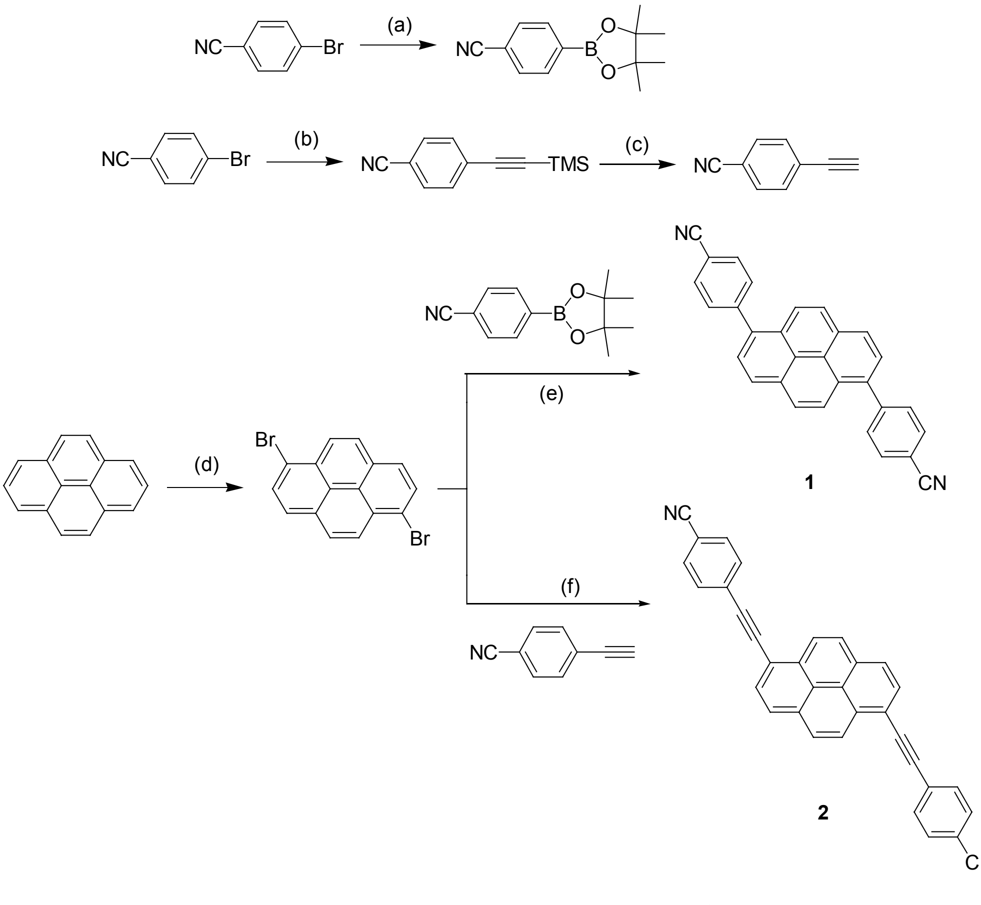


Figure 1 Synthesis of compound **1** and **2**: (a) $Pd(dppf)Cl_2$, B_2Pin_2, KOAc, DMSO, 80 ℃, 75%; (b) $Pd(PPh_3)_4$, TMSA, CuI, *i*-Pr_2NH, toluene, 93%; (c) K_2CO_3, MeOH/THF, 85%; (d) Br_2, 50%; (e) $Pd(PPh_3)_4$, K_2CO_3, H_2O/toluene, 33%; (f) $Pd(PPh_3)_2Cl_2$, *i*-Pr_2NH, CuI, PPh_3, toluene, 25%.

Table 1 Photophysical properties, frontier molecular orbital energy levels and thermal stability

λ_{abs}	Soln[a]	λ_{em} Soln[a]	Solid[b]	Φ_{F} Soln[c]	HOMO[d]	LUMO[d]	T_{d}[e]
1	366, 289, 242	427	478	85%	−5.70	−2.62	191.8
2	432, 413, 281	448, 475	538, 561	75%	−5.71	−2.94	256.2

[a] In dichloromethane solution (*ca.* 10 μmol/L). [b] In powder at a quartz substrate. [c] The fluorescent quantum yield (Φ_{F}) was determined in dichloromethane using Coumarin 1 as primary standard ($\Phi_{\mathrm{f}}=0.99$ in dichloromethane). [d] Determined by cyclic voltammetry and optical energy band gap obtained from the onset of absorption spectra. [e] Decomposition temperature corresponding to 5% weight loss measured by TGA.

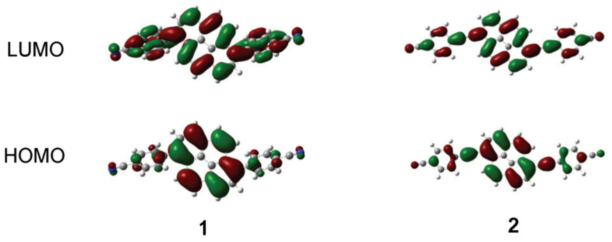


Figure 2 Spatial distributions of the compounds **1** and **2** frontier orbits.

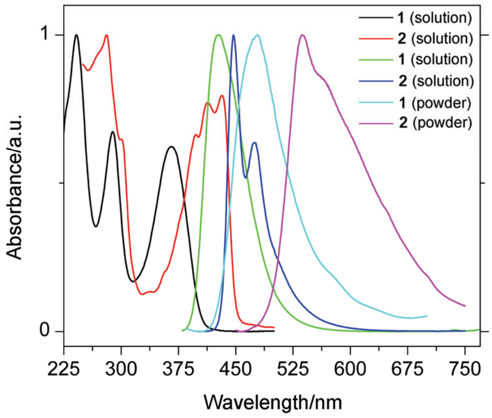


Figure 3 UV/Vis absorption spectra (left) and PL spectra (right) in dilute CH_2Cl_2 solution, and PL spectra (right) in powder on quartz substrates of **1** and **2**.

HOMO.[22] **1** and **2** have nearly identical onset oxidation potential (E_{onset}), meaning that they have identical HOMO level. From E_{onset} the HOMO energy levels [$\mathrm{HOMO}=-(4.4+E_{\mathrm{onset}})$] are calculated as −5.70 and −5.71 eV for **1** and **2**, respectively. The LUMO energies were evaluated using standard approximations by the formula: $\mathrm{HOMO}=\mathrm{LUMO}-E_{\mathrm{g}}^{\mathrm{opt}}$, as –2.62 and –2.94 eV for **1** and **2**, respectively. The optical energy band gap ($E_{\mathrm{g}}^{\mathrm{opt}}$) was obtained from the onset of the absorption spectra.

Considering a strong π-π staking of both two compounds which results in intermolecular aggregation and deterioration of the electroluminescence property, a doping method with PVK as the host in the emissive layer was adopted. PVK is an excellent hole transporting material. In agreement with the report,[30] the PL emission of PVK film extends from 350 to 600 nm with a maximum at 404 nm (As shown in Figure 4 (a)) and well overlaps with the absorption spectra of **1** or **2**, meeting the requirement of Förster energy transfer.[31] The film of **1** or **2** doped PVK was prepared by spin-coating the blend of **1** or **2** and PVK. **1** doped PVK has PL emission at 439 nm and no emission of PVK, meaning the complete energy transfer from PVK to **1**. **2** doped PVK has PL emission at 455 nm and 478 nm which are attributed to **2**, and a shoulder at 375 nm which is the contribution of PVK, indicating that the energy transfer from PVK to **2** is not complete at the doping concentration of 8%.

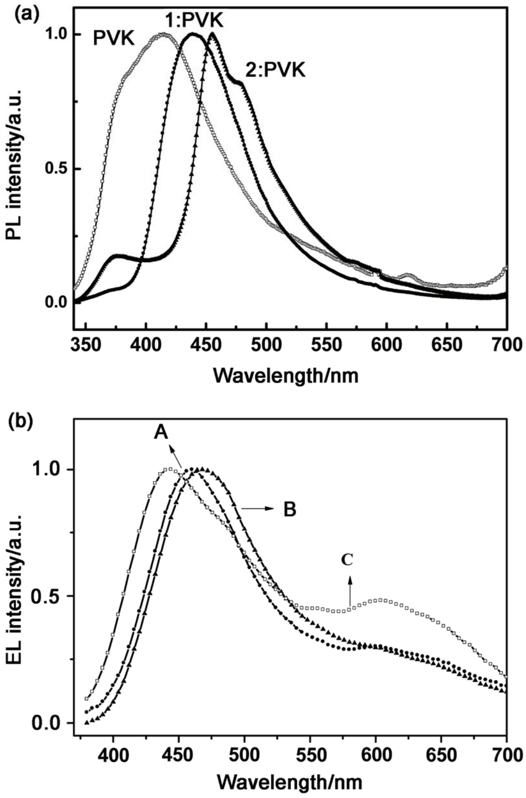


Figure 4 (a) PL spectra of PVK, **1**:PVK and **2**:PVK in films prepared by spin-coating the corresponding solution at the concentration of 8% on quartz substrates; (b) EL spectra of device **A** and **B** measured at 22 V, compared with EL spectrum of device **C** at 13 V.

As shown in Figure 4 (b), device **A** has a strong emission at 460 nm and device **B** has a strong peak at 468 nm. It is obvious that the emission of the device **A** is attributed to that of **1** and the emission of device **B** is attributed to that of **2** compared with device **C** which emits electroluminescence emission at 420 nm from PVK. Three devices have a common shoulder emission at 610 nm which is ascribed to the excimer emission from PVK. Compared with PL emission of **2** doped PVK, it is interesting that PL emission at 375 nm which is attributed to emission of PVK does not appear in EL spectrum, meaning the energy transfer from PVK to **2** is complete upon an applied bias. Either **A** or **B** has a stable emission spectrum at increasing applied voltage. It is noted that the emission from PVK did not appear, meaning that energy transfer from PVK to the compounds was efficient at a low concentration of 8%, in contrast to the literature reporting complete energy transfer at high concentration of 32% due to small overlap between PVK and the dopant.[32]

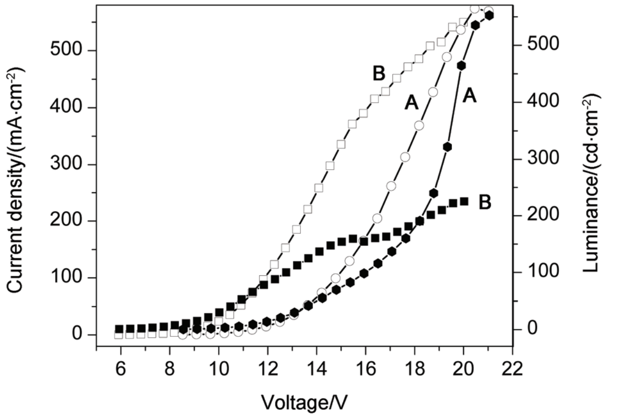
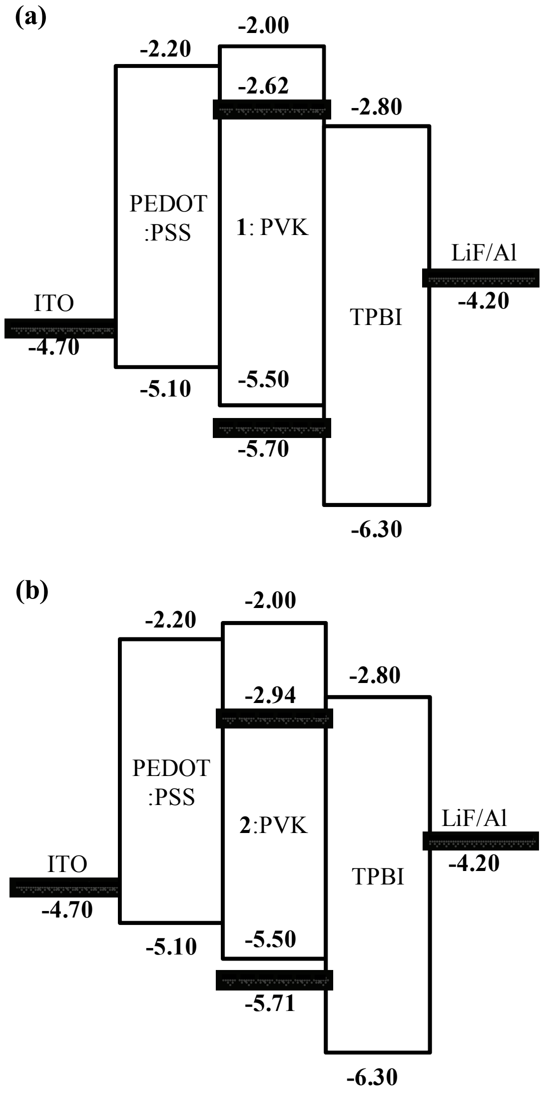


Figure 5 Current density-voltage (*J-V*) (left) and luminescence-voltage (*L-V*) (right) characteristics of device **A** and **B**.

J-V and *L-V* of devices are shown in Figure 5. Device **A** has a turn-on voltage of 9 V and the highest brightness of 553 cd/cm^2 at 21 V. Device **B** has a turn-on voltage of 6 V and the highest brightness of 227 cd/cm^2 at 20 V. In comparison, device **B** has higher current density than device **A** till the applied bias of 18 V. This is attributed to two factors: easy electron injection from TPBI to **2** and high carrier transporting ability from **2** compared with **1**. As shown in Scheme 1, LUMO of **2** is −2.94 eV and stays lower than that of LUMO at −2.80 eV of TPBI, while the LUMO of **1** is −2.62 eV and stays higher than LUMO at −2.80 eV of TPBI. This means that electrons can be injected more easily into the **2**:PVK layer than into the **1**:PVK layer. In addition, **2** should have higher carrier transporting ability than **1** due to high coplanarity. Therefore, device **B** exhibited higher current density and lower turn-on voltage than device **A**. However, Device **B** is not good as device **A** in terms of the luminance and efficiency. The highest current efficiency of 0.22 cd•A^{-1} from device **B** is lower than that of 0.36 cd•A^{-1} from device **A**. This could be explained by the relatively lower fluorescence efficiency of 75% of **2** than that of 85% of **1**. It is noted that HOMO levels of **1** and **2** are lower than −5.50 eV of PVK in Scheme 1, indicating mismatch of energy level which can not meet the requirement to efficiently trap the excitons generated from a host in a dopant.[19] We consider to test other hosts to boost the performance of these two blue-light emitting.

Chang *et al.*[12] reported that the 1,3,6,8-tetrakis(3,5-dimethylphenyl)pyrene had a strong aggregation and the excimer which was formed upon applied voltage exhibited efficient electroluminescence properties. It is worth trying the undoped **1** or **2** as the emitting material and studying the electroluminescence from excimer.

Scheme 1 Schematic drawing of device **A** (a) and **B** (b)



Device A: ITO/PEDOT:PSS (30 nm)/**1**:PVK (8%, *w*/*w*) (50 nm)/TPBI (30 nm)/Al (100 nm), device B: ITO/PEDOT:PSS (30 nm)/**2**:PVK (8%, *w*/*w*) (50 nm)/TPBI (30 nm)/Al (100 nm). Energy levels of the functional materials are cited from the literature.[33]

Conclusions

Two pyrene-based materials were designed and synthesized. Compound **1** with directly linked phenyl and pyrene has large dihedral angle, and compound **2** with acetylene inserted between phenyl and pyrene moieties is coplanar. Optical analysis and DFT calculation confirmed that compound **2** is prone to excimer formation in the solid state due to high coplanarity. The materials exhibited blue photoluminescence and high fluorescent quantum yield of 85% and 75% in solution. The electroluminescence properties were studied with **1** or **2** doped PVK as the emitting layer. The electroluminescent emission was attributed to the material itself and it was deduced that the energy transfer from PVK to the pyrene derivatives happened.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (No. 21371096).

References

[1] Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.
[2] Sun, Y. R.; Giebink, N. C.; Kanno, H.; Ma, B. W.; Thompson, M. E.; Forrest, S. R. *Nature* **2006**, *440*, 908.
[3] So, F.; Kido, J.; Burrows, P. *MRS Bull.* **2008**, *33*, 663.
[4] Reineke, S.; Linder, F.; Schwartz, G.; Seidler, N.; Walzer, K.; Lussem, B.; Leo, K. *Nature* **2009**, *459*, 234.
[5] Figueira-Duarte, T. M.; Müllen, K. *Chem. Rev.* **2011**, *111*, 7260.
[6] Moorthy, J. N.; Natarajan, P.; Venkatakrishnan, P.; Huang, D. F.; Chow, T. J. *Org. Lett.* **2007**, *9*, 5215.
[7] Zhao, Z.; Chem, S.; Lam, J. W. Y.; Lu, P.; Zhong, Y.; Wong, K. S.; Kwok, H. S.; Tang, B. Z. *Chem. Commun.* **2010**, *5*, 2221.
[8] Zhao, Z.; Chen, S.; Lam, J. W. Y.; Wang, Z.; Lu, P.; Mahtab, F.; Sung, H. H. Y.; Williams, I. D.; Ma, Y.; Kwok, H. S.; Tang, B. Z. *J. Mater. Chem.* **2011**, *21*, 7210.
[9] Tang, C.; Liu, F.; Xia, Y. J.; Xie, L. H.; Wei, A.; Li, S. B.; Fan, Q. L.; Huang, W. *J. Mater. Chem.* **2006**, *16*, 4074.
[10] Xiao, J. C.; Divayana, Y.; Zhang, Q. C.; Doung, H. M.; Zhang, H.; Boey, F.; Sun, X. W.; Wudl, F. *J. Mater. Chem.* **2010**, *20*, 8167.
[11] Xiao, J. C.; Liu, S. W.; Liu, Y.; Liu, X. W.; Zhang, H.; Sun, X. W.; Zhang, Q. C. *Chem. Asian J.* **2012**, *7*, 561.
[12] Chang, Z. F.; Ye, S. H.; He, B. R.; Bei, Z. R.; Lin, L. Y.; Lu, P.; Chen, B.; Zhao, Z. J.; Qiu, H. Y. *Chem. Asian J.* **2013**, *8*, 444.
[13] Berlman, I. B. *J. Phys. Chem.* **1970**, *74*, 3085.
[14] Wu, K. C.; Ku, P. J.; Lin, C. S.; Shih, H. T.; Wu, F. I.; Huang, M. J.; Lin, J. J.; Chen, I. C.; Cheng, C. H. *Adv. Funct. Mater.* **2008**, *18*, 67.
[15] Oyamada, T.; Uchiuzou, H.; Akiyama, S.; Oku, Y.; Shimoji, N.; Matsushige, K.; Sasabe, H.; Adachi, C. *J. Appl. Phys.* **2005**, *98*, 074506.
[16] Chan, K. L.; Lim, J. P. F.; Yang, X. H.; Dodabalapur, A.; Jabbour, G. E.; Sellinger, A. *Chem. Commun.* **2012**, *48*, 5106.
[17] Wee, K. R.; Ahn, H. C.; Son, H. J.; Han, W. S.; Kim, J. E.; Cho, D. W.; Knag, S. O. *J. Org. Chem.* **2009**, *74*, 8472.
[18] Chercka, D.; Yoo, S. J.; Baumgarten, M.; Kim, J. J. *J. Mater. Chem. C* **2014**, *2*, 9083.
[19] Thomas, K. R. J.; Kapoor, N.; Bolisetty, M. N. K. P.; Jou, J. H.; Chen, Y. L.; Jou, Y. C. *J. Org. Chem.* **2012**, *77*, 3921.
[20] Hu, J. Y.; Era, M.; Elsegood, M. R. J.; Yamato, T. *Eur. J. Org. Chem.* **2010**, *72*.
[21] Feng, X.; Hu, J. Y.; Yi, L.; Seto, N.; Tao, Z.; Redshaw, C.; Elsegood, M. R. J.; Yamato, T. *Chem. Asian J.* **2012**, *7*, 2854.
[22] Feng, X.; Hu, J. Y.; Tomiyasu, H.; Seto, N.; Redshaw, C.; Elsegood, M. R. J; Yamato, T. *Org. Biomol. Chem.* **2013**, *11*, 8366.
[23] Wu, C. J.; Xue, C.; Kuo, Y. M.; Luo, F. T. *Tetrahedron* **2005**, *61*, 4735.
[24] Brooks, A. J.; Antonio, F.; Michael, R. W.; Tobin, J. M. *J. Am. Chem. Soc.* **2007**, *129*, 15259.
[25] Zhao, Z. J.; Ye, S. H.; Guo, Y. J.; Chang, Z. F.; Lin, L. Y.; Jiang, T.; Lam, J. W. Y.; Lu, P.; Qiu, H. Y.; Liu, Y. Q.; Tang, B. Z. *Org. Electron.* **2011**, *12*, 2236.
[26] Suneesh, C. V.; Gopidas, K. R. *J. Phys. Chem. C* **2010**, *114*, 18725.
[27] Liu, F.; Tang, C.; Chen, C. C.; Li, S. Z.; Wu, H. B.; Xie, L. H.; Peng, B.; Wei, W.; Cao, Y.; Huang, W. *Org. Electron.* **2009**, *10*, 256.
[28] Niko, Y.; Cho, Y.; Kawauchi, S.; Konishi, G. *RSC Adv.* **2014**, *4*, 36480.
[29] Reichardt, C.; Welton, T. In *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2010**, pp. 359－424.
[30] Qiu, Y.; Duan, L.; Hu, X. M.; Zhang, D. Q.; Zheng, M.; Bai, F. L. *Synth. Met.* **2001**, *123*, 39.
[31] Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7.
[32] Zhou, Y.; Kim, J. W.; Kim, M. J.; Son, W. J.; Han, S. J.; Kim, H. N.; Han, S. W.; Kim, Y.; Lee, C.; Kim, S. J.; Kim, D. H.; Kim, J. J.; Yoon, J. Y. *Org. Lett.* **2010**, *12*, 1272.
[33] Behzad, S. K.; Najafi, E.; Amini, M. M.; Janghouri, M.; Mohajerani, E.; Ng, S. W. *J. Luminescence* **2014**, *156*, 219.

(Cheng, F.)