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PII: S0143-7208(16)31169-X

DOI: 10.1016/j.dyepig.2017.05.017

Reference: DYPI 5979

To appear in: Dyes and Pigments

Received Date: 11 November 2016

Revised Date: 20 April 2017

Accepted Date: 5 May 2017

Please cite this article as: Li YF, Xie X, Gong XJ, Liu ML, Chen RF, Gao DQ, Huang W, Two bipolar blue-emitting fluorescent materials based on 1,3,5-triazine and peripheral pyrene for organic light-emitting diodes, *Dyes and Pigments* (2017), doi: 10.1016/j.dyepig.2017.05.017.

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Two bipolar blue-emitting fluorescent materials based on 1,3,5-triazine and peripheral pyrene for organic light-emitting diodes

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Abstract: Two blue-emitting materials, bipolar composed of the electron-withdrawing triphenyl-triazine core and the peripheral electron-donating 1-position substituted and 2-positon substituted pyrene moieties respectively, were designed, synthesized, and fully characterized by spectroscopies, cyclic voltammetry (CV) and Gaussian 03 molecular orbital calculations. The relationship between the structure and property was clearly demonstrated from the observed spectroscopic features (UV/Vis, photoluminescence and the solvatochromism) and molecular configuration. 1-Position substituted analogue exhibited a large twist angle of 52.0° and a strong electronic coupling between the core and the peripheral moieties, resulting in the strong dipolar property and the high fluorescent quantum efficiency of over 80% in the solution and the solid state. With the 1-position substituted analogue as the guest, the doped electroluminescence device showed a stable and efficient blue

emission with the maximum luminance of 4306 cd/m^2 , the current efficiency of 1.15 cd/A, the external quantum efficiency of 0.97% and the CIE coordinate of (0.13, 0.06).

Keywords: Blue light-emitting materials; Triazine; Pyrene; Substitution position; Solvatochromism.

1. Introduction

Since CW. Tang first reported on organic light-emitting diodes (OLEDs) in 1987 [1], OLEDs have gained considerable attention because they possess great promise to realize full-color flat-panel display and solid-state lighting [1-3]. As we all know, red, green and blue (RGB) are the primary colors, which of them are important for full-color displays. Blue OLEDs are necessary for the white emission and full-color display [3-7]. However, owing to the intrinsic wide band-gap nature, the performances (for example, the color purity and luminous efficiency) of the conventional blue OLEDs are relatively poor in contrast to green and red ones. Thus, blue light emitters with good color purity, high electroluminescence efficiency and stable thermal property are very essential for making a high efficient device.

Recently, more attention has been focused on the bipolar materials with bipolar charge-transporting properties in OLEDs [8-9]. The performances and operational stability of the devices could be enhanced by using bipolar materials as the emitting layers [10]. The most widely used means to achieve bipolar materials is incorporating

donor (D) and acceptor (A) moieties into the same molecule, which facilitates the injection and transport of both holes and electrons [10-12]. Besides, using bipolar materials as the light-emitters may promote the emission efficiency because the incorporation of a donor and an acceptor extends the π -conjugation of the molecule structure. But one problem exists that a D-A material might lead to a huge bathochromic effect [13]. Therefore, the major challenge is to prohibit the red-shift in developing the bipolar blue-emitting materials with D-A structures, while one can achieve and even promote their photoluminescence quantum efficiency.

Pyrene is a member of the polycyclic aromatic hydrocarbon family. Owing to the large π -conjugation, pyrene has the strong π electron delocalization energy and the efficient fluorescence property [14]. Its derivatives have been mostly utilized as the hosts [15] and the dopants [16] in blue doped OLEDs with high brightness and good efficiency. In the pyrene chemical structure exists a nodal plane which is perpendicular to the molecule through the 2- and 7-positions in the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). The substituents at 2-, and 7-positions should exert less perturbation on the electronic properties of the pyrene moiety than substituents at the 1-, 3-, 6- and 8-positions [17-19]. For example, 2-substituted pyrene-modified deoxyuridine nucleoside retained the optical properties of pyrene, whereas 1-substituted pyrenyl analogue exhibited the strong electronic interaction between pyrene and uridine moieties [20]. A lot of pyrene derivatives substituted at the 1-, 3-, 6- and 8-positions were used as

light-emitting materials [21-26], but just a few of analogues substituted at 2-, and 7-positions were reported [27-28]. To our knowledge, the direct comparison of optoelectronic properties of 1-, and 2-position's substituted pyrene analogues has not been reported.

It was well confirmed that triazine has larger electron affinity than those of other typical electron-deficient heteroaromatic units (e.g., pyridine and pyrimidine) [29-31]. Owing to this reason, triazine unit has been used as the acceptor moiety of D-A structures to promote their electron-injection and electron-transportation abilities. In addition, compounds containing triazine unit exhibit good thermal stability [32-35].

As an ideal blue light-emitting material, the D-A bipolar compound should have a small emission red-shift and a high photoluminescence quantum yield. In this report, we designed and synthesized two star-shaped D-A compounds which are composed of the donor (three peripheral pyrenyl groups) and the acceptor (2,4,6-triphenyl-1,3,5-triazine, abbreviated as the triphenyl-triazine core, considering that it has a rigid skeleton to ensure high symmetry [13]) moieties. One is 1-position substituted pyrenyl compound 1 and the other is 2-positon substituted pyrenyl compound 2 (as seen in Scheme 1). In contrast to the reported compound which has the similar backbone as 1 [36], the introduction of the *tert*-butyl groups at the structural end aimed at enhancing the electron-donating, thermal and soluble abilities. By characterizing the materials with UV/Vis, fluorescence (FL), CV, molecular calculations and thermaogravimetric analysis (TGA), the influence of the substitution

position on properties was analyzed in detail. It was proven that two compounds were the high-performance blue-emitting materials. This work will play an important role for guiding the design of pyrene-based materials in the future.

2. Experimental section

2.1. Materials and instruments

Pyrene, 4-bromobenzonitrile, methyltrioctylammonium chloride, tetrakis(triphenylphosphine) palladium(0) $[Pd(PPh_3)_4],$ [{Ir(μ -OMe)cod}₂], (1,5-cyclooctadiene)(methoxy)iridium(I) dimer and 4,4'-di-tert-butyl-2,2'-dipyridyl (dtbpy) were purchased from Energy Chemical. Bis(pinacolato) diboron (B₂Pin₂) was purchased from Sukailu Chemical. Bromine, anhydrous MgSO₄ and sodium carbonate were purchased from Sinopharm Chemical Reagent. They were used without any further purification. Poly(3,4-ethylnenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was obtained Luminescence from Technology Corp.. 1,3,5-Tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPb) and 9,9'-(1,3-phenylene)-bis-9H-carbazole (MCP) were purchased from Shanghai Han Feng Chemical Technology Corp..

Nuclear magnetic resonance (NMR) (300 MHz) spectra were recorded on Bruker AMX400 spectrometer in CDCl₃. UV/Vis spectra were recorded on Shimadzu UV-1750. Fluorescence spectra were recorded on Hitachi F-4600. Fluorescence

quantum yields ($\Phi_{\rm f}$) of the solutions and of the solid films were measured through the integrated sphere method with coumarin 1 as the primary standard ($\Phi_{\rm f}=0.99$ in ethyl acetate) by using the Edinburgh FLS-920 Instruments. Cyclic voltammetry (CV) measurements were performed with a CHI-621B electrochemical analyzer. The surface morphology of the thin films was studied by atomic force microscopy (AFM, Dimension 3100 V (Veeco, CA)) under tapping mode with a Si tip (resonance frequency: 320 kHz; spring constant: 42 N·m⁻¹) at a scanning rate of 1 Hz. 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/AgCl reference electrode. CHCl₃ was chosen as the solvent in CV measurement and CH₂Cl₂ was in others. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. Thermaogravimetric analysis (TGA) was performed on a Perkin Elmer TGA7 thermal analyzer at a heating rate of 10 °C/min under dry N_2 flow. Differential scanning calorimetry (DSC) measurement was performed on NETZSCH DSC214 Polyma instrument under a heating rate of 5 °C/min and a nitrogen flow rate of 20 cm³/min. Commission international de l'éclairage (CIE 1931) coordinates of the devices were measured by a PR650 spectroscan spectrometer.

2.2.Synthesis

2-Tert-butylpyrene. According to the literature [37], a mixture of pyrene (5 g, 24.2 mmol) and 2-chloro-2-methylpropane (2.62 g, 3.23 mL) in CH₂Cl₂ (40 mL) was

cooled down to 0 \square and stirred for 20 min. Then the anhydrous AlCl₃ (3.62 g, 27.2 mmol) was added slowly. The reaction system was stirred for 3 h at room temperature, afterwards the solution was poured into a large excess of ice/water. The reaction mixture was extracted with CH₂Cl₂ (3 x 50 mL). The combined organic layer was washed with water and saturated NaCl solution, dried with anhydrous MgSO₄. After the solvent was evaporated, the residue was purified by column chromatography (the eluent: hexane) and pure 2-*tert*-butylpyrene (5.28 g) was obtained with the yield of 82% as a white powder. ¹H NMR (300 MHz, CDCl₃): δ = 8.23 (s, 2H), 8.16 (d, *J* = 9 Hz, 2H), 8.06 (m, 4H), 7.97 (t, *J* = 15 Hz, 1H), 1.60 (s, 9H).

7-*Tert*-butylpyrene-2-boronic acid pinacol ester. According to the literature [18], dtbpy (0.027 g, 0.10 mmol) and B₂pin₂ (0.05 g, 0.2 mmol) were dissolved in hexane (2 mL) under N₂ in a Schlenk flask. Into the solution was added the hexane solution (10 mL) of 2-*tert*-butylpyrene (1.01 g, 3.91 mmol) and B₂pin₂ (1.27 g, 5.0 mmol). After {Ir(μ -OMe)cod}₂ (0.034 g, 0.051 mmol) was added, the reaction was stirred at 80 \Box for 16 h. The system was cooled down to room temperature and was extracted with CH₂Cl₂. The combined organic layer was washed with water and saturated NaCl aqueous solution, and dried with anhydrous MgSO₄. After the evaporation, the residue was purified by column chromatography (silica gel, hexane/CH₂Cl₂ = 5:1) and recrystallized from hexane, 7-*tert*-butylpyrene-2-boronic acid pinacol ester (1.31 g) was obtained with the yield of 88% as a white powder. ¹H NMR (300 MHz, CDCl₃): δ = 8.60 (s, 2H), 8.20 (s, 2H), 8.08 (d, *J* = 9 Hz, 2H), 8.03

(d, *J* = 6 Hz, 2H), 1.58 (s, 9H), 1.46 (s, 12H).

1-Bromo-7-tert-butylpyrene. According to the literature [38], 2-tert-butylpyrene (4 g, 15.48 mmol) was dissolved in the degassed anhydrous CH₂Cl₂ (30 mL), then a solution of Br₂ (0.79 mL, 15.48 mmol) in anhydrous CH₂Cl₂ (80 mL) was slowly added at -78 \square under N₂ atmosphere. The reaction mixture was allowed to slowly warm up to room temperature and stirred overnight. Afterwards, an aqueous 0.3 M $Na_2S_2O_3$ was added to the reaction solution to neutralize remaining Br₂. The reaction was extracted with CH_2Cl_2 . The organic layer was washed with water and brine, and dried with anhydrous MgSO₄. After the evaporation, the residue was purified by column chromatography with the eluent of hexane and recrystallization. The product 1-bromo-7-tert-butylpyrene (4.6 g) was obtained with the yield of 88% as a white powder. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.41$ (d, J = 9 Hz, 1H), 8.27 (d, J = 3 Hz, 2H), 8.14-8.20 (m, 2H), 8.08 (d, J = 9 Hz, 1H), 7.96-8.01 (m, 2H), 1.60 (s, 9H).

7-*Tert*-butylpyrene-1-boronic acid pinacol ester. According to the literature [39], 1-bromo-7-*tert*-butylpyrene (4 g, 11.87 mmol) was dissolved in THF (50 mL) at -78 \Box . Into the solution was slowly added n-BuLi (1.6 M, 18.9 mmol, 11.87 mL). Afterwards, the reaction system was stirred for further 2 hours, and then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.8 mL, 28.1 mmol) was slowly added. The mixture was allowed to warm up to ambient temperature and stirred for overnight. The reaction was poured into H₂O (20 mL), extracted with

CH₂Cl₂, washed with brine and water, then dried with anhydrous MgSO₄. The organic phase was evaporated, and the residue was purified by column chromatography (silica gel, dichloromethane/petroleum ether = 1/9, v/v). The pure 7-*tert*-butylpyrene-1-boronic acid pinacol ester was obtained with the yield of 80% as a white powder. ¹H NMR (300 MHz, CDCl₃): δ = 9.03 (d, *J* = 9 Hz, 1H), 8.50 (d, *J* = 9 Hz, 1H), 8.24 (d, *J* = 3 Hz, 2H), 8.02-8.14 (m, 4H), 1.59 (s, 9H), 1.50 (s, 12H).

2,4,6-Tris(4-bromophenyl)-1,3,5-triazine. According to the literature [40], into the flask were quickly added dry CHCl₃ (20 mL) and trifluoromethanesulfonic acid (6.0 g, 40 mmol). The solution was cooled down to 0 \square . Then, a solution of 4-bromobenzonitrile (3.64 g, 20 mmol) in dry CHCl₃ (120 mL) was dropwise added to the pre-cooled solution. After the solution was stirred for 0.5 h at 0 \square , the reaction system was warmed up to room temperature and stirred for 24 h continuously. Afterwards, into the reaction mixture was added the aqueous ammonia solution (30%) to neutralize the unreacted trifluoromethanesulfonic acid. After the addition, the precipitate was formed. The precipitate was filtrated and washed with ethanol, hexane and chloroform to give 2,4,6-tris(4-bromophenyl)-1,3,5-triazine with the yield of 85% as a white powder. ¹H NMR (300 MHz, CDCl₃): δ = 8.61 (d, *J* = 9 Hz 6H), 7.72 (d, *J* = 9 Hz, 6H).

Synthesis of compound 1. 2,4,6-Tris(4-bromophenyl)-1,3,5-triazine (0.5 g, 0.92 mmol), 7-*tert*-butylpyrene-1-boronic acid pinacol ester (1.41 g, 3.68 mmol) and a little aliquat were added to the Schlenk flask, then the flask was degassed and

suffused with N₂. Into the mixture, toluene (30 mL) and sodium carbonate solution (5.5 mL, 2 M), tetrakis(triphenylphosphine) palladium(0) (32 mg, 0.03 mmol) were added. The reaction mixture was heated at 90 \Box for 36 h. After cooled down, the mixture was extracted with CH₂Cl₂, water and brine, and dried with anhydrous Na₂SO₄. Then the precipitate was filtrated and purified by solid-liquid extraction sequentially with refluxing hexane and chloroform to give compound **1** in 70% yield (0.69 g) as a yellowish solid. ¹H NMR (300 MHz, CDCl₃): δ = 9.09 (d, *J* = 6 Hz, 6H), 8.24-8.27 (m, 12H), 8.12 (s, 6H), 8.08 (d, *J* = 3 Hz, 3H), 8.07 (d, *J* = 3 Hz, 3H), 7.93 (d, *J* = 6 Hz, 6H), 1.61 (s, 27H). ¹³C NMR (300 MHz, 1,2-dichlorobenzene-d4): δ = 170.53, 148.07, 144.82, 135.53, 134.19, 131.98, 130.81, 130.38, 129.93, 129.87, 129.82, 128.28, 127.17, 127.08, 126.91, 123.96, 123.68, 123.60, 122.16, 121.53, 121.21, 30.64, 28.84. Elemental analysis calcd. (%) for C₈₁H₆₃N₃: C, 90.21; H, 5.89; N, 3.90; found: C, 90.15; H, 5.82; N, 3.90; MS (MALDI-TOF): *m/z* calcd. for C₈₁H₆₃N₃: 1077.50; found: 1077.54 (M⁺).

Synthesis of compound 2. 2,4,6-Tris(4-bromophenyl)-1,3,5-triazine (0.5 g, 0.92 mmol), 7-*tert*-butylpyrene-2-boronic acid pinacol ester (1.41 g, 3.68 mmol) and a little aliquat were added to the Schlenk flask, then the flask was degassed and suffused with N₂. Into the mixture, toluene (30 mL) and sodium carbonate solution (5.5 mL, 2M), tetrakis(triphenylphosphine) palladium(0) (32 mg, 0.03 mmol) were added. After the reaction mixture was heated at 90 °C for 36 h, the reaction was cooled down to room temperature. The mixture was extracted with CH₂Cl₂, water and brine,

and dried with anhydrous MgSO₄. The organic layer was evaporated and the residue purified column with was by chromatography the eluent of dichloromethane/petroleum ether (1:10) to afford a yellowish solid in 57% yield (0.56 g). ¹H NMR (300 MHz, CDCl₃): δ = 9.01 (d, J = 3 Hz, 6H), 8.47 (s, 6H), 8.24 (s, 6H), 8.13 (d, J = 3 Hz, 6H), 8.11 (d, J = 3 Hz, 6H), 8.09 (d, J = 3 Hz, 6H), 1.62 (s, 27H). ¹³C NMR (300 MHz, 1,2-dichlorobenzene-d4): $\delta = 170.35$, 148.12, 144.58, 136.41, 134.31, 131.65, 130.78, 130.49, 130.08, 127.16, 127.03, 123.18, 122.35, 121.74, 121.40, 30.66, 28.85. Elemental analysis calcd. (%) for C₈₁H₆₃N₃: C, 90.21; H, 5.89; N, 3.90; found: C, 90.16; H, 5.80; N, 3.90. MS (MALDI-TOF): m/z calcd. for C₈₁H₆₃N₃: 1077.50; found: 1078.02 (M⁺).





Scheme 1. Reaction routes of the two compounds 1 and 2.

2.3. OLED device fabrication and measurement

Indium tin oxide (ITO) substrates were cleaned in an ultrasonic bath of detergent, deionized water, acetone and ethanol sequentially. After dried in an oven at $120 \square$ for 20 min, the substrates were treated with UV-Ozone for about 5 min. The certain volume of the stock solution of **1** (or **2**) with the concentration of 5 mg/mL in 1,2-dichlorobenzene was added into the stock solution of MCP with the concentration of 15 mg/mL in 1,2-dichlorobenzene, and a mixture solution with the concentration of

30% (w/w) of 1 (or 2) was ready for spin coating. A thin layer of PEDOT:PSS of 25 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 \Box for 30 min. A layer of the emitting material (1, 2, 1 doped MCP, or 2 doped MCP) was spin-coated on the top of PEDOT:PSS layer. The samples were then loaded into a deposition chamber. A sequence of TmPyPb (30 nm), LiF (0.5 nm) and Al (100 nm) were thermally deposited at a vacuum of 3 x 10^{5} mbar. Electroluminescent (EL) devices in this work were designed with the non-doped emitting layer: ITO/PEDOT:PSS (25 nm)/1 or 2/TmPyPb (30 nm)/LiF (0.5 nm)/Al (100 nm), and with the doped emitting layer: device A: ITO/PEDOT:PSS (25 nm)/1:MCP (30%, w/w) (40 nm)/TmPyPb (30 nm)/LiF (0.5 nm)/Al (100 nm), device B: ITO/PEDOT:PSS (25 nm)/2:MCP (30%, w/w) (40 nm)/TmPyPb (30 nm)/LiF (0.5 nm)/Al (100 nm); where PEDOT:PSS was the hole transporting layer, MCP was the host and TmPyPb was the electron transporting layer. The film thickness was the 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 spectra-photometer and a computer-controlled voltage-current source, Keithley 2400, under ambient condition.

3. Results and Discussion

The synthesis routes for two compounds **1** and **2** were shown in Scheme 1. The starting material pyrene was first alkylated by Friedel-Crafts reaction to give 2-*tert*-butylpyrene by following the literature [37]. 1-Bromo-7-*tert*-butylpyrene was

obtained by the bromination of 2-*tert*-butylpyrene with bromine (equal equiv.) in CH_2Cl_2 at -78 \Box with the yield of 88% as a white powder [38]. 1-Bromo-7-*tert*-butylpyrene was further reacted with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and

7-tert-butylpyrene-1-boronic acid pinacol ester was obtained with the yield of 80% as a white powder [39]. 7-Tert-butylpyrene-2-boronic acid pinacol ester was obtained by the direct reaction between 2-tert-butylpyrene and B₂pin₂ with the yield of 88% as a white powder [18]. 2,4,6-Tris(4-bromophenyl)-1,3,5-triazine was synthesized efficiently by modifying the method [40]. 4-Bromobenzonitrile was treated with the reagent trifluoromethane sulfonic acid in dry CHCl₃ for 24h at room temperature, and then aqueous ammonia solution (30%) was added to neutralize the unreacted trifluoromethane sulfonic acid. The yield was improved from 65% to 85%. 2,4,6-Tris(4-bromophenyl)-1,3,5-triazine respectively reacted with 7-tert-butylpyrene-1-boronic acid pinacol ester and 7-tert-butylpyrene-2-boronic acid pinacol ester by Suzuki coupling mechanism to produce compound 1 and 2 with the yield of 70% and 57%. Compound 1 was purified by solid-liquid extraction sequentially with refluxing hexane and chloroform as a yellowish solid. Compound 2 purified column chromatography with the was by eluent of dichloromethane/petroleum ether (1:10) as a yellowish solid. Due to the large conjugation structure, 1 and 2 are slightly soluble in common solvents and the solubility of 2 is a little better than 1. The chemical structures of two compounds were

identified by NMR, elemental analysis and MALDI-TOF. Due to too low concentration to collect NMR data, 1,2-dichlorobenzene-d4 was used for ¹³C NMR instead of CDCl₃ for ¹H NMR measurement. As shown in Supporting Information, two compounds exhibited the characteristic singlets at 170.35-170.53 ppm in ¹³C NMR spectra which can be attributed to the carbon atoms of the triazine ring, as observed by the literature [13].

3.1. Molecular orbital calculation

To obtain a better insight into the relationship between structure and property at the molecular level, density functional theory (DFT) calculations by using the Gaussian 03 program at the B3LYP/6-31G(d) level were carried out to evaluate the positions and energies of frontier orbits for **1** and **2** (as shown in Figure 1). As observed from the geometries, the dihedral angle between phenyl and triazine are close to 0° , indicating the triphenyl-triazine core is nearly planar for compound **1** and **2**. The dihedral angle between the pyrene ring and the triphenyl-triazine core are 52.0° and 37.1° in **1** and **2**, respectively. This is consistent with the structure feature of pyrene molecule, that is, 2-position has a large space for the substitution and the sterically induced twist between the substituent and the parent pyrene plane is small, whereas the substitution at 1-position causes much steric hindrance [27]. It is obvious that a large coefficient of HOMO orbital is mainly positioned on the pyrene moiety and the bridged carbon atom between the pyrene moiety and the triphenyl-triazine core for **1**, but a large coefficient of HOMO orbital is only positioned on the pyrene

moiety for 2. This results in that 1 possesses a large orbital overlap and a delocalized orbital between the triphenyl-triazine core and 1-position substituted pyrene moiety, and 2 has a negligible orbital overlap and a strictly localized orbital between the triphenyl-triazine core and 2-position substituted pyrene moiety. Even though the acceptor triphenyl-triazine core and the donor pyrene moiety are covalently connected in the compounds, 1 has a significant electronic coupling in between in contrast to 2, in agreement with the report [18]. Correspondingly the coefficients of LUMO orbitals are located mainly on the triphenyl-triazine core and partially on pyrene moiety for 1, but only on the triazine core for 2.



3.2. Thermal properties

The thermal properties of the two fluorescent materials were determined by

thermaogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. As shown in Figure 2 (a), the two compounds exhibited good thermal stabilities with the decomposition temperature (T_d) at 518 \Box and 535 \Box for 1 and 2, respectively, which are close to those of two *tert*-butyl group terminated star-shaped derivatives with triazine core and peripheral carbazole moiety [13]. From DSC measurement, compound 1 exhibited the glass transition temperature at 248 \Box , the crystallization temperature (Tc) at 289 \Box , and the melting temperature (Tm) at 383 \Box in the first heating scan (Figure 2(b)); in the second heating scan compound 1 showed only a T_g at 248 \Box , but no crystallization temperature. We speculate that it may become a completely amorphous state with temperature cooling down after melted in the first heating scan, and it was difficult to crystallize again. A similar phenomenon was observed in the literature [41]. Compound 2 presented the glass transition temperature at 253 \Box in the second heating scan.





Figure 2. (a) TGA (10 /min) and (b and c) DSC (10 /min) curves of compounds 1 and 2. Inset

in Figure 2(c): the enlarged second heating scan.

3.3. Optical and electrochemical properties

UV/Vis absorption spectra of compounds 1 and 2 in dilute CHCl₃ solutions and thin films coated on quartz substrates are displayed in Figure 3. In CHCl₃ solution compound 2 exhibited an absorption maximum at 342 nm, while compound 1 showed

a red-shifted absorption with maximum at 367 nm. The reason is that 1 has a stronger electronic coupling between the triphenyl-triazine core and the pyrene moiety than 2, in agreement with the literature [20]. Both are ascribed to the π - π * transition of the pyrene backbone [42]. For compound 2 the absorption shoulder at 258 nm corresponds to the absorption of triphenyl-triazine moiety [34], while for compound 1 the absorption shoulder is located at 282 nm. In the solid-state, the UV-Vis absorption exhibited a red shift by 10 nm for 1 and 6 nm for 2 compared to the absorptions in the solution state, respectively. The phenomena of the red-shift and the broadening of the bands indicate the existence of the enhanced intermolecular interactions in the solid state. It is noteworthy that compound 1 presented a new absorption shoulder at 400 nm which can be assigned to the intramolecular charge transfer (ICT) complex transition $S_0 \rightarrow {}^1CT$ [13] which is attributed to the stronger electronic coupling in 1 instead of 2.



Figure 3. UV/Vis absorption spectra in dilute CHCl₃ solutions and thin films on quartz substrates

of compounds 1 and 2.

As shown in Figure 4, in the $CHCl_3$ solution 2 displayed the emission maximum at 453 nm and 1 displayed the emission maximum at 469 nm, the red-shift being attributed to the fact that 1 has a stronger electronic coupling between the triphenyl-triazine core and the pyrene moiety than 2, in agreement with the literature [20]. In the solid state, the emission showed the slight red-shift with the maxima at 474 and 460 nm for 1 and 2 relative to those in solutions, respectively. By using coumarin 1 as the primary standard ($\Phi_f = 0.99$ in ethyl acetate), in CHCl₃ solution the fluorescence quantum yields (Φ_f) were measured to be 89% and 18% for 1 and 2, respectively. The 1-position substituted pyrenyl derivative 1 is a very efficient light-emitter, indicating that the extended π -conjugation at 1-positon substitution prominently promoted the emission efficiency, in agreement with the properties of the bipolar derivatives of 1,3,5-triazine and carbazole [13]. 2-Positon substituted pyrenyl analogue 2 showed the 4-fold lower quantum yield than 1-position substituted pyrenyl derivative 1, because the non-radiative deactivation for the excited state in 2-postion substituted 2 caused the low emission efficiency, as the conclusion in the literature [27]. In the solid state $\Phi_{\rm f}$ was measured to be 81% for 1, being close to that in solution due to the negligible concentration quenching of the twisted molecular structure of **1**. In contrast to the reported derivatives of 1,3,5-triazine and carbazole which have much lower efficiency in the film ($\Phi_{\rm f} \sim 0.20$ -0.33) than in the solution ($\Phi_{\rm f}$ ~ 0.85) [13], compound 1 retains the high quantum yield besides a slight red-shift in

the solid state, demonstrating that **1** is an ideal blue fluorescent emitter. Interestingly, in the solid state compound **2** displayed the PL quantum yield of 56% which is higher than that in solution. This may be ascribed to the Aggregation Induced Emission Enhancement [43], considering the less twisted structure of compound **2**. The two structural components of compound **2**, triphenyl-triazine core and the pyrene moieties, have much free rotation around the single-bond axis in solution which serves as a relaxation channel for the excited state to decay; but in the aggregates, the rotation is restricted due to the physical constraint, which blocks the non-radiative path and activates the radiative decay, as the conclusion in the literature [44].



Figure 4. PL spectra in dilute CHCl₃ solutions and thin films on quartz substrates of 1 and 2.

The solvatochromism properties of **1** and **2** were studied by measuring the fluorescence emission in a serial of from-nonpolar-to-polar solvents. As shown in Figure 5, both materials displayed the strong solvatochromaticity. The spectra became broader and presented a clear bathochromic shift by 64 nm for **1** and 77 nm for **2** from

nonpolar hexane to high polar acetone, indicating that the excited states of the compounds have the large polarity which originates from the formation of an excited-state intramolecular charge transfer (ICT) where the electronic structure of the compounds are rearranged in response to environmental polarity, as well-commonly observed in the electron donor- π -acceptor (D- π -A) systems [45-46]. Interestingly, the spectrum for 1 was hypochromatic and the spectrum for 2 was further bathochromic in more polar acetonitrile solutions. As displayed in Figure 5(b) for compound 2, spectroscopic vibronic structures appeared in hexane and toluene, but disappeared in more polar solvents. The disappearance of the vibronic structures in polar solvents indicates that ICT from the pyrene moiety to the triphenyl-triazine corein 2 was enhanced when the polar solvents were used. In contrast, the emission spectrum of 1 did not exhibit any vibronic structures even in the nonpolar solvents. It can be explained by considering that the strong electronic interaction between triphenyl-triazine core and pyrene moiety in 1 results in these unstructured fluorescence bands.



Figure 5. PL spectra of 10⁻⁵ M solutions of compound 1(a) and 2(b) in hexane, toluene, chloroform, tetrahydrofuran, acetone and acetonitrile solutions ($\lambda_{ex1} = 368 \text{ nm}$, $\lambda_{ex2} = 345 \text{ nm}$).

The electrochemical behavior of the two materials was investigated by cyclic voltammetry (CV) using a standard three electrodes electrochemical cell in a 0.1 M tetrabutylammonium hexafluorophosphate in CHCl₃ solutions at room temperature under N_2 with a scanning rate of 50 mV/s. A platinum working electrode, a platinum

counter electrode and an Ag/AgCl (0.1 M) reference electrode were utilized. The measurements of the compounds displayed one oxidation process in CHCl₃ solution, but no obvious reduction peaks were detected (as seen in Figure S1 and S2 in Supporting Information). The oxidation onset potentials were measured to be 1.22 and 1.19 eV, respectively. Therefore the corresponding HOMO energy levels [HOMO= $-(4.4 + E_{onset})$] were estimated to be -5.62 and -5.59 eV for 1 and 2, respectively. The optical band gaps (E_g^{opt}) obtained from the absorption edges are 2.8 and 3.06 eV for 1 and 2, respectively. Evaluated by using the formula: HOMO = LUMO – E_g^{opt} , the LUMO energy levels were -2.82 and -2.53 eV, respectively. The relevant data were summarized in Table 1.

Compounds	$\varPhi_F(\%)$		Abs. (nm)		PL (nm)		HOMO ^c (eV)		LUMO ^c (eV)		T _d ^d (°C)	
	Sol. ^a	Film ^b	Sol. ^a	Film ^b	Sol. ^a	Film ^b						
1	89	81	367	377	469	474	-5.62	2	-2.8	32	518	
2	18	56	342	348	453	460	-5.59)	-2.5	53	535	

^{*a*}In dilute CHCl₃ solutions (*ca.* 10^{-5} mol/L).

^bFilms at a quartz substrate.

^cDetermined by cyclic voltammetry and optical energy band gaps which were obtained from the onset of absorption spectra.

^dDecomposition temperature corresponding to 5% weight loss measured by TGA.

Considering the high fluorescent quantum yield of 81% and 56% in the solid states of the two emitters, we first prepared the non-doped OLEDs with the structure of ITO/PEDOT:PSS (25 nm)/1 or 2/TmPyPb (30 nm)/LiF (0.5 nm)/Al (100 nm).

However, two compounds are slightly dissolved in common solvents, even in the high-boiling-point solvent 1,2-dichlorobenzene, and the thickness of each spin-coated film was less than 10 nm. As a result, both devices did not present expected performance with the luminance maximum of about 100 cd/m². As shown by AFM images in Figure 6, the surface morphology of the film of compound **1** was covered with many particles (Figure 6 (a)), whereas the film with 30% **1** in MCP was homogenous (Figure 6 (b)).



Figure 6. AFM images of the spin-coated films of compound **1**(a) and of **1**:MCP with the concentration of 30% of **1**(b) in 1,2-dichlorobenzene solvent.

Compounds **1** and **2** were tested as the guests in the host-guest system. MCP was chosen as the host which possesses the good hole-transporting property. The efficient energy transfer was proven by studying the overlap of the UV-Vis absorption spectra of the guests **1** and **2** and the PL spectrum of the host MCP. As shown in Figure 7 (a), the PL emission of MCP film extended from 330 to 550 nm with a maximum at 368 nm and well overlaps with the absorption spectrum of **1** or **2**, meeting the requirement of Förster energy transfer [47]. The film of **1** or **2** doped MCP was prepared by

spin-coating the blend of **1** or **2** and MCP. **1** doped MCP had the PL emission at 470 nm, and **2** doped MCP had the PL emission at 453 nm. The emission of each blend was consistent with the corresponding guest and no emission from MCP was observed, meaning the complete energy transfer from MCP to **1** or **2**.

The electroluminescence spectra of the fabricated devices A and B were presented in Figure 7 (b). With the doping concentration of 30%, device A has the maximum emission at 460 nm and device B has the maximum emission at 451 nm. Compared with PL spectra in Figure 7 (a), we can conclude that the emission of the device A is contributed from **1** and the emission of device B is contributed from **2**, even though by slightly blue-shifted relative to the emission of the corresponding blend film.





Figure 7. (a) UV/Vis absorption spectra (left) in films on quartz substrates of **1** and **2** and PL spectra (right) of MCP, **1**:MCP and **2**:MCP in films which were prepared by spin-coating the corresponding solution with the concentration of 30% of **1** or **2** on quartz substrates; (b) EL spectra of device **A** and **B** (at 5, 6, 7 and 8 V).

Figure 8 shows the current density-voltage (*J-V*) and luminescence-voltage (*L-V*) of devices. Device A had a turn-on voltage of 3.5 V and presented the maximum luminance of 4306 cd/m² at 9.5 V. Device B gained a turn-on voltage of 3.5 V and the highest brightness of 1273 cd/m² at 10.5 V. In comparison with device B, device A showed the higher current density. This should be attributed to that fact that the electron injection from the electron transporting material TmPyPb is easier into **1**:MCP layer than into **2**:MCP layer, as deduced by analyzing the energy levels of the functional materials in the devices. As shown in Scheme 2, the LUMO of **1** is -2.82 eV which stays lower than that of LUMO at -2.7 eV of TmPyPb, while the

LUMO of **2** is -2.53 eV which is higher than the LUMO of TmPyPb. What's more, device A exhibited the highest current efficiency of 1.15 cd/A and the maximum external quantum efficiency of 0.97% (as shown in Figure S14), being superior to device B. This could be explained by the higher fluorescence quantum efficiency of 81% of **1** in contrast to 56% of **2** in the solid states. Device A showed a stable blue emission with the Commission Internationaled'Eclairage (CIE_{x,y}) color coordinates of (0.13, 0.06) at 5 V.





Figure 8. (a) Luminescence-voltage (L-V) (left) and current density-voltage (J-V) (right) characteristics of device **A** and **B**; (b) Current Efficiency and CIE color coordinates for device A.



Scheme 2. Energy levels of device A (a) and of device B (b). Inset: the molecular structures of

MCP and TmPyPb.

4. Conclusions

Two bipolar efficient blue-emitting fluorescent materials were designed and synthesized. The structures were composed of the electron-withdrawing triphenyl-triazine core and the electron-donating peripheral pyrene moieties. In the host-guest system, the diode with 1-position substituted derivative 1 presented the maximum luminance of 4306 cd/m^2 , the current efficiency of 1.15 cd/A, the external quantum efficiency of 0.97% and the CIE coordinate of (0.13, 0.06). Considering that the materials exhibited the high fluorescent quantum yield of 81% and 56% in the solid states and the high color-purity blue photoluminescence, the overall electroluminescent performance was not satisfied. The main reason could be that the compounds 1 and 2 were not well soluble in the common solvents and the spin-coated films had defects. Now we put effort to increase the solubility by incorporating branched alkyl chains instead of *tert*-butyl groups at the structural ends.

Acknowledgement

This work was supported by the National Natural Science Foundation of China under grant No. 21371096.

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Two bipolar blue-emitting fluorescent materials based on 1,3,5-triazine and peripheral pyrene for organic light-emitting diodes

- 1. Two bipolar blue-emitting materials of 1,3,5-triazine core and peripheral pyrene.
- 2. Fluorescent quantum efficiency of over 80% in the solution and the solid state.
- 3. Comparison between 1-position and 2-position substituted pyrene analogues.