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Noncrystalline blue-emitting 9,10-diphenylanthracene end-capped with triphenylamine-substituted fluorene

Yujian Zhang[a], Yanxian Jin[b], Ru Bai[c], Zhenwei Yu[a], Bin Hu[a], Mi Ouyang[a,*], Jingwei Sun[a], Chunhui Yu[a], Junlei Liu[a], Cheng Zhang[a,*]

[a] State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Chaowang Road 18#, Hangzhou, PR China
[b] School of Pharmaceutical and Chemical Engineering, Taizhou University, Linhai, PR China
[c] School of Electronic Information, Hangzhou Dianzi University, Hangzhou, PR China

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ABSTRACT

Two blue-emitting oligomers, namely **FDPA1** and **FDPA2** containing 9,10-diphenylanthracene core end-capped with triphenylamine-substituted fluorene has been synthesized and characterized. The spiro-configuration end-capping groups imparts two compounds with pronounced morphological stability (T_g > 185 °C, T_d > 420 °C) and excellent hole injection ability (E_{HOMO} > −5.27 eV) with the advantageous optical characteristics of corresponding core. Scanning electron microscope (SEM) and X-ray diffraction (XRD) reveal that the two oligomers form excellent amorphous films and possess good morphological stability after annealing.

1. Introduction

Organic light-emitting devices (OLEDs) based on small molecules have attracted great attention in the past decades, due to their potential applications in flat-panel displays and solid state lighting resources [1–3]. Among the three primary-color emitters in OLEDs, blue-light emitting materials are of particular importance, which cannot only be used as a blue light source [4,5] but also as a host materials to generate colors else by downhill energy transfer to a suitable emissive dopant [6,7]. Unfortunately, the intrinsically wide band-gap of blue materials makes it difficult to inject carriers (holes or electrons) into emitters. As a result, the performance of blue OLEDs remains relatively poor in comparison with that of red and green OLEDs [8,9]. Additionally, the durability, which strongly depends on the thermal and morphological stability of materials, is another key factor for the device operation efficiency and lifetime [10]. Whereas, amorphous materials, thanks to their high glass transition temperature (T_g), are receiving special attention due to the effectively suppression of the crystallization for the film.

Excellent electrochemical stability and photoluminescence (PL) make anthracene derivatives attract the intensive attention and have been developed as an attractive building block and starting material in OLEDs [11–15]. Among them, 9,10-diphenylanthracene (DPA) is one of the most representative blue fluorescent materials for its excellently fluorescent properties both in solution and in the solid state [16–18]. However, an obvious deficiency of tendency to crystallize in thin film limit the further application of the DPA in blue OLEDs due to its crystal formation resulting in rough surface, grain boundaries or pin holes that eventually lead to device failure [19–21]. To date, various strategies have been developed to suppress the formation of crystal, such as the introduction of sterically hindered *t*-butyl groups [22,27], bulky substituents [21,24,25] and spiro-annulated structures [26]. Nevertheless, there are few reports on DPA derivatives end-capped with nonplanar molecular structures, which directly avoid their close packing and crystallization. Another intractable issue is the high ionization potential of anthracene-based compounds [23,27,28], which produces a relatively large hole-injection barrier from indium tin oxide (ITO) (−4.8 eV). To overcome the problem, hole-injection/transporting triarylamines were incorporated into the C2, C6 or C9, C10-positions of anthracene [28–32]. Unfortunately, such direct substitution of electron-donor groups decreases energy gap significantly due to extended conjugation lengths, which ultimately results in unwanted red-shift of

* Corresponding authors. Tel.: +86 571 88320027; fax: +86 571 88320027.
E-mail addresses: ouyang@zjut.edu.cn (M. Ouyang), czhang@zjut.edu.cn (C. Zhang).

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emission peak. Thus, the development of new approaches that can lead to stabilization of amorphous state and excellent hole-injection/transportation ability is particularly critical for obtaining highly efficient blue-emitting anthracene-based materials without the decrease of optical performance.

In this contribution, the synthesis and physical and chemical properties of two thermally stable materials **FDPA1**and **FDPA2** (Scheme 1), containing DPA as main core unit, are reported. End-capping triphenylamine (TPA)-substituted fluorene (TPAF) is incorporated into DPA unit to retain the large band gap of the original DPA core. In addition, end-capping fluorene and TPA moieties are connected through the sp^3-hybridized carbon atom, which may not only hinder close packing and crystallization but also result in pronounced morphological stability of amorphous materials. Meanwhile, the hole-injection/transportation ability of molecules is efficiently improved.

2. Experimental

2.1. Chemicals and instruments

9-(4-Bromophenyl)-fluoren-9-ol [33] and 2,6-dibromoanthracene-9,10-dione [28] were synthesized as reported previously. All chemical reagents were used as received from commercial sources without further purification. And the solvents used in the reaction were purified following routine procedures. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III 500-MHz spectrometer using the chloroform-d as the solvent. High-resolution mass spectrometric measurements were carried out on a Brüker autoflex MALDI-TOF-MS spectrometer. Elemental analyses were performed using the Thermo-Finnigan Flash EA-1112 (CE, Italy) instrument. UV–vis spectra were measured using a Shimadzu UV-1800 spectrophotometer. PL spectra were obtained using a Perkin-Elmer LS-55 luminescence spectrophotometer. Thermal analysis was performed on a Diamond TG/DTA 6300 (PerkinElmer, USA) in the temperature range of 100–800 °C. The differential scanning calorimetry (DSC) analysis was performed on a TA Instruments DSC2920. A CHI 660C electrochemical analyzer was applied to conduct the electrochemical measurements. X-ray diffraction (XRD) measurements of thin films were performed on X'Pert Pro diffractometer.

2.2. Synthesis

2.2.1. 2,6-Dibromo-9,10-bis(4-butylphenyl)anthracene (*BrDPA*) [31]

The 1-bromo-4-butylbenzene (2.12 g, 10 mmol) dissolved in diethyl ether (100 mL) was mixed with 6.25 mL of n-butyllithium (1.6 M in hexane) in diethyl ether (100 mL) at −78 °C. To the suspension, 2,6-dibromoanthraquinone (1.8 g, 5.0 mmol) in diethyl ether (20 mL) was added dropwise at −78 °C. After stirring for 1 h at the room temperature, the mixture was poured into an aqueous HCl solution (2 M) and the organic phase separated. The water phase was extracted with ether (3 × 50 mL). The combined organic fractions were dried over magnesium sulfate and the diethyl ether was removed to get residue. And then, to this residue were added potassium iodide (3.0 g, 18 mmol), $Na_2H_2PO_2$ (3.0 g, 34 mmol), and acetic acid (30 mL), and the mixture was heated under reflux for 3 h. The precipitated product in the reaction vessel was filtered with a glass filter and washed with water to give compound BrDPA (0.92 g, 30.7%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 2.0 Hz, 2H), 7.58 (d, J = 9.5 Hz, 2H), 7.43 (d, J = 8.0 Hz, 4H), 7.38 (dd, J = 10.5 Hz, 2H), 7.33 (d, J = 8.0 Hz, 4H), 2.85–2.78 (m, 4H), 1.80 (dt, J = 15.5, 4H), 1.52 (dd, J = 14.5 Hz, 4H), 1.05 (t, J = 7.5 Hz, 6H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 142.7, 136.9, 134.8, 131.1, 131.0, 129.1, 129.0, 128.8, 128.7, 120.7, 35.6, 33.6, 22.6, 14.1. **MS(EI)**: m/e 600.1(M^+).

2.2.2. 4-(9-(4-Bromophenyl)-fluoren-9-yl)-N,N-di-p-tolylaniline (*4*)

A solution of CF_3SO_3H (1.84 mL, 20 mmol) in appropriate 1,4-dioxane (20 mL) was added drop wise to a mixture solution of **3** (3.4 g, 10 mL) [33] and N,N-Bis(4-methylphenyl)aniline (2.7 g, 10 mmol) in 1,4-dioxane (80 mL). The reaction mixture was stirred at 80 °C under nitrogen until starting material was no longer detectable by TLC (8 h). The mixture was poured into saturated $NaHCO_3$ solution and extracted with $CHCl_3$. After the crude product was further purified by column chromatography (EtOAc/hexane = 1/20) to give the desired product **4** (4.6 g, 77.8%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.5 Hz, 2H), 7.42–7.33 (m, 6H), 7.32–7.26 (m, 2H), 7.11 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 8.5 Hz, 4H), 6.99 (dd, J = 10.5 Hz, 6H), 6.87 (d, J = 8.5 Hz, 2H), 2.31 (s, 6H); ^{13}C NMR ($CDCl_3$ 500 MHz) δ 151.0, 146.9, 145.4, 145.1, 140.0, 137.6, 132.5, 131.2, 129.9, 129.8, 128.6, 127.7, 127.6, 126.0, 124.7, 121.8, 120.6, 120.2, 64.5, 20.8; **MS(EI)**: m/e 591.2(M^+).

2.2.3. 4-Methyl-N-(4-(9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-fluoren-9-yl)phenyl)-N-(p-tolyl)aniline (*5*)

4 (3 g, 5 mmol), 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bis(1,3,2-dioxaborolane) (1.3 g, 5.2 mmol), KOAc (1.4 g, 14.2 mmol), and $Pd(dppf)Cl_2$ (30 mg) were mixed in anhydrous DMSO (25 mL). Then, the mixture was degased by purging with N_2. The solution was heated at 80 °C for 24 h under N_2. After the reaction mixture cooled, the solvent was evaporated and the product was extracted with chloroform. The organic extracts were washed with brine, and then dried over $MgSO_4$. After, the solvent was evaporated. Finally, the crude product was purified through columnchromatography (hexane/EtOAc, 12:1) to give **5** (1.4 g, 45%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 7.5 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 7.5 Hz, 2H), 7.39–7.23 (m, 6H), 7.04 (d, J = 8.5 Hz, 4H), 6.99 (dd, J = 15 Hz, 6H), 6.85 (d, J = 8.5 Hz, 2H), 2.30 (s, 6H), 1.32 (s, 12H); ^{13}C NMR ($CDCl_3$ 500 MHz) δ 151.2, 149.5, 146.7, 145.2, 140.1, 138.3, 134.7, 132.4, 129.8, 128.7, 127.5, 127.4, 126.2, 124.6, 121.9,120.1, 83.7, 65.2, 24.8, 20.8; **MS(EI)**: m/e 639.2(M^+).

2.2.4. General procedure for the synthesis of compounds *FDPA1, FDPA2*

A mixture of anthracene-based core (1 mmol), **5** (1.4 g, 2.2 mmol), $Pd(PPh_3)_4$ (0.3 g, 0.27 mmol), Na_2CO_3 (2.0 M, 3.0 mL), and toluene (50 mL)/THF (30 mL) was stirred at 90 °C for 48 h under the atmosphere of nitrogen. After the mixture cooled, 200 mL of $CHCl_3$ was added to the reaction mixture. The organic portion was separated and washed with brine before dried over anhydrous $MgSO_4$. The solvent was evaporated off, and the solid residues were purified by column chromatography to afford the desired product.

FDPA1 (0.73, 60.8%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 7.5 Hz, 4H), 7.66 (dd, J = 6.5 Hz, 4H), 7.61 (d, J = 7.5 Hz, 4H), 7.44 (m, 8H), 7.38 (t, J = 7.5 Hz, 4H), 7.30 (dd, J = 14.5 Hz, 8H), 7.14 (d, J = 8.5 Hz, 4H), 7.05 (d, J = 8.5 Hz, 8H), 7.00 (d, J = 8.5 Hz, 8H), 6.93 (d, J = 8.5 Hz, 4H), 2.30 (s, 12H); **MALDI-TOF-MS** (m/z) 1200.5(M^+); **Anal. Calcd** for $C_{92}H_{68}N_2$: C, 91.96; H, 5.70; N, 2.33 Found: C, 91.89; H, 5.88; N, 2.23.

FDPA2 (0.46, 31.7%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.76 (t, J = 8.5 Hz, 6H), 7.57 (dd, J = 9.0, 2H), 7.43 (t, J = 7.5 Hz, 8H), 7.41–7.34 (m, 12H), 7.29 (d, J = 7.5 Hz, 2H), 7.23–7.8 (m, 6H), 7.04 (d, J = 8.0 Hz, 12H), 6.97 (d, J = 7.5 Hz, 8H), 6.86 (d, J = 8.0 Hz, 4H),