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Undoped, red organic light-emitting diodes based on a *N*,*N*,*N*', *N*'-tetraphenylbenzidine (TPD) derivative as red emitter with a triphenylamine derivative as hole-transporting layer

Xingbo Cao^{a,b}, Yugeng Wen^{a,b}, Yunlong Guo^{a,b}, Gui Yu^a, Yunqi Liu^a, Lian-Ming Yang^{a,*}

^a Beijing National Laboratory for Molecular Sciences, Laboratory of New Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China ^b Graduate School of Chinese Academy of Sciences, Beijing 100049, China

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1. Introduction

Organic light-emitting diodes (OLEDs) have been the subject of intense research since the first reports of molecular [1] and polymeric OLEDs [2] as the compounds offer potential application in flat-panel displays. Primary light-emitting materials for OLEDs not only display high electroluminescent (EL) efficiency [3-16] but also must possess good thermal properties, long lifetime and high chroma. Whilst many organic emitters exhibit high fluorescent quantum yields in dilute solution, in contrast, they display either weak or even no fluorescence in both highly concentrated solution and the solid state [17]. This particular phenomenon, which is known as concentration quenching, is especially pronounced in the case of red organic emitters which commonly comprise an intramolecular charge transfer (ICT) donor- π -acceptor group or an extensively π -conjugated structure and which, also, are prone to aggregation in the solid state through either dipole-dipole interactions or intermolecular π -stacking. As a result, doping is universally employed in the fabrication of efficient, red OLEDs [18]. However, doping is difficult to control because the optimum dopant

ABSTRACT

A novel dicyanovinyl-functionalized *N,N,N',N'*-tetraphenylbenzidine (TPD) derivative, *N,N'*-bis[4-(1,1-dicyanovinyl)phenyl]-*N,N'*-bis[4-fluorophenyl)benzidine and a novel triphenylamine-based derivative, 4,4',4"-tris{[di(*p*-tolyl)amino]phenyl}triphenylamine were synthesized and employed as red molecular emitter and hole-transporting layer, respectively, in an undoped organic light-emitting diode devices. The device based on the TPD-FCN emitter and DBTPA hole-transporting material, which was fabricated in a facile non-doped configuration, achieved maximum luminance of 3400 cd m⁻² at a driven voltage of 17.5 V and maximum luminous efficiency of 3.04 cd A⁻¹. Interestingly, the device reached a brightness of 1399 cd m⁻² and luminous efficiency of 2.85 cd A⁻¹ at the low current density of 20 mA cm⁻².

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concentration is usually low and the effective doping range is extremely narrow. The resolution of concentration quenching lies in the design of novel red fluorescent materials which do not aggregate and which can themselves be employed as the lightemitting layer in OLEDs, thus resulting in so-called 'host-emitting. undoped' red OLED devices. Whilst in recent years, undoped red emitters have attracted increasing attention [17–23], novel red emitters of high are still sought from the viewpoints of their ease of synthesis and purification as well as high efficiency, brightness, color purity, stability, etc.

This paper concerns the use of a novel dicyanovinyl-functionalized TPD derivative, *N*,*N*'-bis[4-(1,1-dicyanovinyl)phenyl]-*N*,*N*'-bis(4-fluorophenyl)benzidine (**TPD-FCN**), as red-emitting material in an undoped red OLED. The *N*,*N*,*N*',*N*'-tetraphenylbenzidine (TPD) molecule is an excellent non-planar donor, as it can be considered as an electron-rich, propeller-shaped, dimeric triphenylamine (TPA) and the 1,1-dicyanovinyl group is an excellent acceptor group. It was considered that 1,1-dicyanovinylfunctionalized TPD derivatives, of $A-\pi-D-\pi-A$ structure, should be non-planar and possess a pair of antiparallel dipoles which will effectively prevent aggregation occurring through intermolecular $\pi-\pi$ stacking or dipole–dipole interactions, their fluorescence concentration quenching in the solid state would be substantially suppressed. Meanwhile, a novel, triphenylamine-based derivative,

^{*} Corresponding author. Tel.: +86 10 62565609. *E-mail address:* yanglm@iccas.ac.cn (L.-M. Yang).

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4,4',4"-tris{[di(*p*-tolyl)amino]phenyl}triphenylamine (**DBTPA**), was used as hole-transporting material so as to achieve high luminous efficiency at low driven voltage.

2. Experimental

2.1. General procedures

¹H and ¹³C NMR spectra were obtained on a Bruker DMX-400 NMR Spectrometer using tetramethylsilane as internal standard. Mass spectra (EI or MALDI-TOF) were recorded on a Micromass GCT-MS spectrometer and a Bruker BIFLEX III Mass Spectrometer, respectively. UV-vis absorption and fluorescence spectra were obtained with Hitachi U-3010 and Hitachi F-4500 fluorescence spectrometer. Elemental analyses were carried out on a Carlo-Erba 1160 elemental analyzer. TGA measurements were carried out on a TA SDT 2960 instrument under a dry nitrogen flow, heating from room temperature to 500 °C with a heating rate of 10 °C min⁻¹. DSC measurements were performed on DSC 2010 instrument under a dry nitrogen flow, heating from -50 to 280 °C at a rate of 10 °C min $^{-1}$ and then cooling from 280 to -50 °C at a rate of 40 °C min⁻¹, and again heating from -50 to 280 °C at a rate of 10 °C min-¹. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using Pt button working electrode of 2 mm diameter, a platinum wire counter electrode, and a Ag/AgCl reference electrode on a computercontrolled CHI660C instruments at room temperature. Reduction CV of the target compounds was performed in CH₂Cl₂ containing Bu_4NPF_6 (0.1 M) as a supporting electrolyte. The energy levels were calculated using the ferrocene (E_{FOC}) value of -4.8 eV as standard, while *E*_{FOC} was calibrated to be 0.45 V vs. Ag/AgCl electrode in CH₂Cl₂ solution. The energy levels of the lowest unoccupied molecular orbitals (LUMOs) were calculated by the HOMO value and the energy gap (E_g) from the edge of the absorption spectrum. Reagents and solvents were available commercially and used as received. Triphenylamine [24], 4-formyl-4'-fluorotriphenylamine (1) [25] and 4-[N,N-di(p-tolyl)amino]phenyl boronic acid [26] were synthesized according to the literature.

2.2. Synthesis of materials

2.2.1. 4-(1,1-Dicyanovinyl)-4'-fluorotriphenylamine (2)

A mixture of 4-formyl-4'-fluorotriphenylamine (1) (1.46 g, 5 mmol), malononitrile (0.66 g, 10 mmol) and NH₄OAc (0.77 g, 10 mmol) in anhydrous ethanol (30 ml) was refluxed for 3 h. After being cooled to room temperature, the mixture was filtered and the precipitate washed with anhydrous ethanol, providing the product **2** as an orange solid in 90% yield (1.53 g). Mp: 151–152 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.74 (d, 2H, *J* = 8.8 Hz), 7.52 (s, 1H), 7.39 (t, 2H, *J* = 7.7 Hz), 7.24 (t, 1H, *J* = 7.6 Hz), 7.21–7.15 (m, 4H), 7.09 (t, 2H, *J* = 8.5 Hz), 6.91 (t, 2H, *J* = 8.8 Hz). MS (EI): *m/z* 339 (M⁺, 100%).

2.2.2. N,N'-bis[4-(1,1-dicyanovinyl)phenyl]-N,N'-bis (4-fluorophenyl)benzidine (**TPD-FCN**)

To a solution of **2** (0.85 g, 2.5 mmol) in dichloromethane (30 ml) was added solid ferric chloride (1.62 g, 10 mmol) at 0–5 °C with stirring. The ensuing mixture was stirred in an ice bath at 0–5 °C for 1 h and then poured into methanol; the precipitate was filtered and washed with methanol and water. The residue was dissolved in dichloromethane and dried over anhydrous Na₂SO₄ and the solvent was evaporated; the crude product was purified by column chromatography using silica gel employing a gradient of petroleum ether/dichloromethane (1:1, v/v), providing an orange-red solid in 80% yield (0.68 g). Mp: 228 °C. ¹H NMR (DMSO-*d*₆, 400 MHz): δ 8.23 (s, 2H), 7.84 (d, 4H, *J* = 8.9 Hz), 7.74 (d, 4H, *J* = 8.4 Hz), 7.39–7.27 (m, 12H), 6.90 (d, 4H, *J* = 8.9 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ 161.0,

158.6, 156.9, 143.5, 140.0, 136.6, 132.0, 128.0, 127.8, 127.4, 125.5, 122.2, 117.7, 116.2, 116.0, 114.0, 113.0, 75.3. MS (EI): m/z 676 (M⁺, 100%). Anal. Calcd for C₄₄H₂₆ F₂N₆: C, 78.09; H, 3.87; N, 12.42; F, 5.61. Found: C, 77.69; H, 3.88; N, 12.35; F, 5.56.

2.2.3. Tri(4-bromophenyl)amine(3)

A solution of triphenylamine (2.45 g, 10 mmol) in DMF (25 ml) was stirred at room temperature to which was added *N*-bromosuccinimide (5.2 g, 32 mmol) in 10 ml DMF in small portions (upon the addition of *N*-bromosuccinimide, the color of the reaction mixture turned to green). After stirring overnight at room temperature, the reaction mixture was poured into water and was extracted with ether. The organic layer was dried over anhydrous Na₂SO₄. After the solvent was evaporated, the crude product was purified by recrystallization from methanol to afford a write solid in 90% yield (4.35 g). Mp: 140–141 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.35 (d, 6H, *J* = 8.32 Hz), 6.92 (d, 6H, *J* = 8.28 Hz). MALDI-TOF, MS (*m*/*z*): 482.9 (M⁺).

2.2.4. 4,4',4"-tris{[di(p-tolyl)amino]

phenyl}triphenylamine (**DBTPA**)

4-[N,N-di(p-tolyl)amino]phenyl boronic acid (1.59 g, 5 mmol), **3** (0.72 g, 1.5 mmol), K₂CO₃ (1.03 g) and tetrakis(triphenylphosphine)palladium (caution: light sensitive, air sensitive; avoid strong oxidizing agents; 100 mg) were slurred in a mixture of THF (30 ml) and water (5 ml). The mixture was refluxed under a N₂ atmosphere for 12 h and, after cooling, the ensuing mixture was extracted with CH₂Cl₂, and the organic phase was washed with water, dried over Na₂SO₄ and filtered. Solvent removal by rotary evaporation, followed by column chromatography over silica gel with a mixture of petroleum ether and CH_2Cl_2 (4:1, v:v) as eluent, resulted in the product **DBTPA** as a white solid in 45% yield (0.71 g). Mp: 153–155 °C. ¹H NMR (DMSO, 400 MHz): δ 7.75 (d, 6H, *J* = 8.16 Hz), 7.52 (d, 6H *J* = 8.52 Hz), 7.15–7.05 (m, 18H), 6.97–6.90 (m, 18H), 2.26 (s, 18H). MALDI-TOF MS (m/z): 1058.6 (M⁺). ¹³C NMR (CDCl₃, 100 MHz): δ 146.24, 144.33, 132.78, 131.51, 128.90, 126.32, 126.18, 123.63, 121.89, 19.83. Anal. Calcd for C78H66N4: C, 88.43; H, 6.28; N, 5.29. Found: C, 88.49; H, 6.24; N, 5.26.

2.3. OLED fabrication and measurements

CuPc, NPB, Alq₃, and BCP (purchased from Aldrich Chemical Co.) were purified using a train sublimation method. OLED devices were fabricated on $30 \Omega/^{TM}$ indium-tin oxide (ITO) coated glass substrates using conventional vacuum vapour deposition employing a vacuum of 2×10^{-4} Pa. The organic layers and electrodes were grown by means of conventional vacuum deposition. A quartz crystal oscillator placed near the substrate was used to measure the thickness of the thin films, which were calibrated *ex situ* using an Ambios Technology XP-2 surface profilometer. EL spectra were recorded on the Hitachi F-4500 spectrophotometer. Current-voltage characteristics for OLEDs were measured with a Keithley 4200-SCS semiconductor characterization system. Brightness was measured with a spectra scan PR 650 photometer. All device tests were carried out under an ambient atmosphere at room temperature.

3. Results and discussion

3.1. Synthesis

Two target compounds, **TPD-CN** and **DBTPA**, were prepared as shown in Figs. 1 and 2. The formylated triarylamine **1** underwent a condensation reaction with malononitrile to afford the intermediates **2** with excellent yields, which were easily purified by a simple filtration and wash with ethanol. The target compound **TPD-FCN** was obtained in 80% of isolated yield by an easy oxidative



Fig. 1. Synthetic route to the compound TPD-FCN.

coupling reaction, and the target compound **DBTPA** was obtained in 45% of isolated yield by the Pd (0)-catalyzed Suzuki reaction. The two target compounds were soluble in most organic solvents, and characterized fully by ¹H and ¹³C NMR, MS, and elemental analysis.

3.2. Thermal and electrochemical properties

Decomposition temperatures at 5 wt% loss of the materials **TPD-CN** and **DBTPA** were found to be over 400 °C from thermogravimetic analysis (TGA). Glass transitions appeared at 126 °C for **TPD-FCN** and



Fig. 2. Synthetic route to the compound DBTPA.

146 °C for **DBTPA** in differential scanning calorimetry (DSC) measurements. The excellent thermal stability indicates that all the target compounds form stable films by vacuum sublimation. The high glass transition shows that DBTPA would be a good hole-transporting material. In cyclic voltammograms (CV), the target compounds are electrochemically stable in CH₂Cl₂ solution when potential cycling was applied (shown in Fig. 3). Their energy levels of the highest occupied molecular orbitals (HOMOs) were -5.39 eV for **TPD-FCN** and -4.93 eV for **DBTPA**. The data suggested that **DBTPA** would be more favorable for hole-injection into emitting layer as compared to the usually used NPB material, and **TPD-FCN** with the relatively low LUMO energy level (-3.00 eV) would facilitate electron injection when used as an active layer in OLED devices.

3.3. Photophysical properties

UV-vis absorption and photoluminescence (PL) spectra are important parameters to testify the designed materials. The absorption peaks of **TPD-FCN** in dichloromethane are located 448 nm (shown in Fig. 4). The PL emission peak of **TPD-FCN** in dichloromethane appeared at 555 nm, and the one in thin films are located at 622 nm (shown in Fig. 5). Apparently, the salvation effects resulted in a blue-shift of 67 nm for the PL emission peak of **TPD-FCN** in dichloromethane. Importantly, there is only one PL emission peak for **TPD-FCN** whether in solution or in the thin film.

The compound **TPD-FCN** exhibits a considerably strong photoluminescence in the solid state because its molecular structure could effectively avoid the fluorescence-quenching resulting from the molecular aggregation. In contrast, **TPD-FCN** displayed a rather low fluorescent quantum yield in solutions. For example, its fluorescent quantum yield in CH₂Cl₂ (measured by using coumarin 307 as standard according to a known procedure [27,28]) was 0.10%. Such an unusual fluorescence behavior of the non-planar twin dipolar molecule was observed and explained in the previous publications [15,21].

3.4. Electroluminescent properties

The target compound **TPD-FCN** can easily be deposited as pristine thin films by thermal deposition in a vacuum system. In order to achieve high performances in organic EL devices, two series of devices were fabricated with the following configuration: ITO/CuPc (8 nm)/NPB (20 nm)/**TPD-FCN** (35 nm)/BCP (15 nm)/Alq3 (5 nm)/LiF (1 nm)/Al (100 nm) (the device 1), and ITO/CuPc (8 nm)/**DBTPA** (20 nm)/**TPD-FCN** (35 nm)/BCP (15 nm)/Alq3 (5 nm)/LiF (1 nm)/Al (100 nm) (the device 2). CuPc, Alq3, NPB and BCP are, respectively, copper (II) phthalocyanine, tris(8-hydroxyquinolinolato)aluminum,



Fig. 3. Cyclic voltammogram of TPD-FCN and DBTPA in CH₂Cl₂.



Fig. 4. Absorption and PL spectra of the target compounds.

N,*N*'-diphenyl-*N*,*N*'-bis(1-naphenyl)-1,1'-biphenyl-4,4'-diamine, and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline. Herein, **TPD-FCN**, CuPc, NPB or **DBTPA**, BCP, and Alq3 were used as emitting, hole-injection, hole-transporting, hole-blocking, and electron-transporting layers, respectively.

Fig. 5 shows the PL spectra of the compound **TPD-FCN** in the solid films and EL spectra of the **TPD-FCN**-based emission layer in the structurally different non-doped devices 1 and 2. Like the PL of **TPD-FCN**'s thin film, the two different devices produced only one red emission peak located nearly at 632 nm and CIE (0.61, 0.39). This phenomenon demonstrated that the EL emission spectra of **TPD-FCN**-based OLEDs are stable and not interfered by different device structures.

Fig. 6 shows the EL properties of **TPD-FCN**-based two different devices. The device 1 with NPB as hole-transporting layer only had a medium performance: the maximum luminance reached 2703 cd/m² at a driving voltage 19.5 V; the maximum luminous efficiency reached 1.79 cd/A; and a brightness of 393 cd/m² and a luminous efficiency of 1.66 cd/A at a low current density of 20 mA/cm². The device 2 with **DBTPA** as hole-transporting layer achieved higher performances. The device 2 had the maximum luminance of 3400 cd/m² at a driving voltage 17.5 V, and the maximum luminous efficiency of 3.04 cd/A, respectively. It is noteworthy that the device 2 can reach a high brightness of 1399 cd/m² and a luminous efficiency of 2.85 cd/A at a low current density of 20 mA/cm². Compared to the device 1, the device 2 with



Fig. 5. PL spectra of TPD-FCN in the solid films and EL spectra of two TPD-FCN-based OLED devices.



Fig. 6. Current density–voltage and luminance–voltage (a) and luminous efficiency– current density (b) characteristics of two **TPD-FCN**-based OLED devices.

DBTPA achieved higher brightness and higher luminous efficiency at a low driving voltage, particularly the brightness at a low current density of 20 mA/cm². The superior performance should largely be attributed to new red fluorescent material **TPD-FCN** with the low fluorescence-quenching nature and the relatively low LUMO energy level, as well as new hole-transporting material **DBTPA** with the relatively high HOMO energy level.

4. Conclusions

We have designed and synthesized dicyanovinyl-functionalized TPD derivative **TPD-FCN** as red fluorescent material and TPA-based derivative **DBTPA** as the hole-transporting layer by a simple and easy procedure. The red OLED devices based on **TPD-FCN** as red emitters were fabricated in a facile non-doped configuration with different hole-transporting layers. The device 2 with **DBTPA** as hole-transporting layer achieved a relatively high maximum luminous efficiency and high brightness at a low current density of 20 mA/cm². The red fluorescent material will be anticipated to give even better performances through further optimization of the device processing. This work would lead to the development of more new red fluorescent materials usable in OLEDs for high performances.

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