A non-planar pentaphenylbenzene functionalized benzo[2,1,3]thiadiazole derivative as a novel red molecular emitter for non-doped organic light-emitting diodes†

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A novel non-planar pentaphenylbenzene functionalized benzo[2,1,3]thiadiazole derivative (BPTBTD) has been designed and synthesized with only three steps, and applied into non-doped organic light-emitting diodes (OLEDs) as a red molecular emitter. The molecule exhibits good solubility in common organic solvents, excellent thermal stability and film-forming properties. The most important feature is that photoluminescence of BPTBTD shows excellent stablity in different solvents, at different concentrations and in different solid states. Red organic light-emitting diodes were fabricated in a facile non-doped configuration with different thicknesses of emission layers. Saturated red-emission was observed with an emission peak at 621 nm, a maximum external quantum efficiency of 1.0% and a maximum brightness of 1572 cd m^{-2}. Especially, the properties of devices with thick emission layers are two times better than those of the devices with thin emission layers. These results indicate that the non-planar pentaphenylphenyl functional groups substantially suppressed the tendency for molecular aggregation in thin solid films, leading to a very stable photoluminescence and higher efficiency of devices with thicker layers.

Introduction

Organic electroluminescent materials and light-emitting diodes (OLEDs) have been the universal subject of intense research and attracted significant attention because of their potential applications in colorful flat panel displays and solid state white illuminations. Since the first small molecular OLEDs and polymeric OLEDs were pioneered by Tang and Van Slyke[1] and Friend and co-workers,[2] numerous conjugated organic molecules have been designed and synthesized to fabricate OLEDs with high electroluminescent (EL) efficiencies, good thermal properties and long lifetimes as well as pure color coordinates ranges.[3–6]

For full-color displays, not only is the brightness important, but color saturation is crucial. However, it is difficult to produce highly efficient devices with pure luminescence actually. Many organic emitters exhibit high fluorescent quantum yields in solution, but they show little or no fluorescence in highly concentrated solution or solid states.[7] The phenomenon is named "concentration quenching", which will also cause emission spectrum broadening and a bathochromic phenomenon.[8] The effect is especially strong in organic red emitters,[3] because red organic conjugated emitting materials are always constructed with an intramolecular charge transfer (ICT, donor–π-acceptor) group or an extended big π-conjugation structure, which are easy to aggregate in highly concentrated solutions and solid states because of either effective π–π stacking or dipole–dipole interactions.[9] To weaken the concentration effect, the doping approach has been invented and used in fluorescence and phosphorescence systems to produce high efficiency OLEDs.[10] But the process of doping is difficult to control. Red non-doped emitters have been a hot point,[11–15] because they can be pristine thin films with vacuum deposition, which will simplify the procedure of preparing devices. However, most of them are still fabricated with donor and acceptor groups. Though a red non-doped OLED with good performance has been reached, the ICT molecular structure still affects the efficiency of devices. To improve the color purity, the thickness of the emitting layer should be increased, while it will lead a decrease in the efficiency of the device. The color purity and efficiency are usually compromised. Therefore, the idea to resolve this problem should be changed to a structural point to design red molecular emitters without a donor–acceptor structure.[16]

From this point, we sought to design a new red-emitting molecular structure. Using developing modern organic synthetic methods, we can organize different functional groups to fabric suitable molecular structures for special aims. Benzo[1,2,5]thiadiazole is an attractive heterocycle with a high electron affinity.[17] The synthesis and modification of the ring system is easy, so many small molecules and polymers have been obtained. Thiophene-benzo[1,2,5]thiadiazole (BTB), which is one of important benzo[1,2,5]thiadiazole derivatives, has a red-shift luminescence at 576 nm with a fluorescence quantum yield 95%.[18] And the BTB derivatives have shown good performances in optical electronic

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devices, such as OLEDs,[19–24] organic field-effect transistors (OFETs)[25] and solar cells.[26,27] In OLEDs, BTB is often used as a monomer for polymer materials, but seldom for small molecules.[21,22] The reason is that BTB shows weak photoluminescence (PL) in films, though it has a high fluorescence quantum yield in solvent, which is associated with aggregates. From a structural point, a strong luminescence for BTB films should be reached if the intermolecular π–π stacking can be effectively prevented. Pentaphenylphenyl (Müllen-type)[28–33] dendrimer is a three-dimensional non-planar functional group, which is both shape-persistent and chemically stable. So, it can exclude π-stacking at lower dendritic generations and inhibit the formation of molecular aggregation. Thomas *et al.* firstly reported star-shaped molecules featuring hexaarylbenzene based triarylamine donors and a dithienyl benzothiadiazole acceptor.[34] The fluorescence quantum yield of these star-shaped molecules could reach 66%. Recently, as an excellent construction block, pentaphenylphenyl has been successfully incorporated into both small molecules[35–38] and polymer materials[28,30,31] for OLEDs.

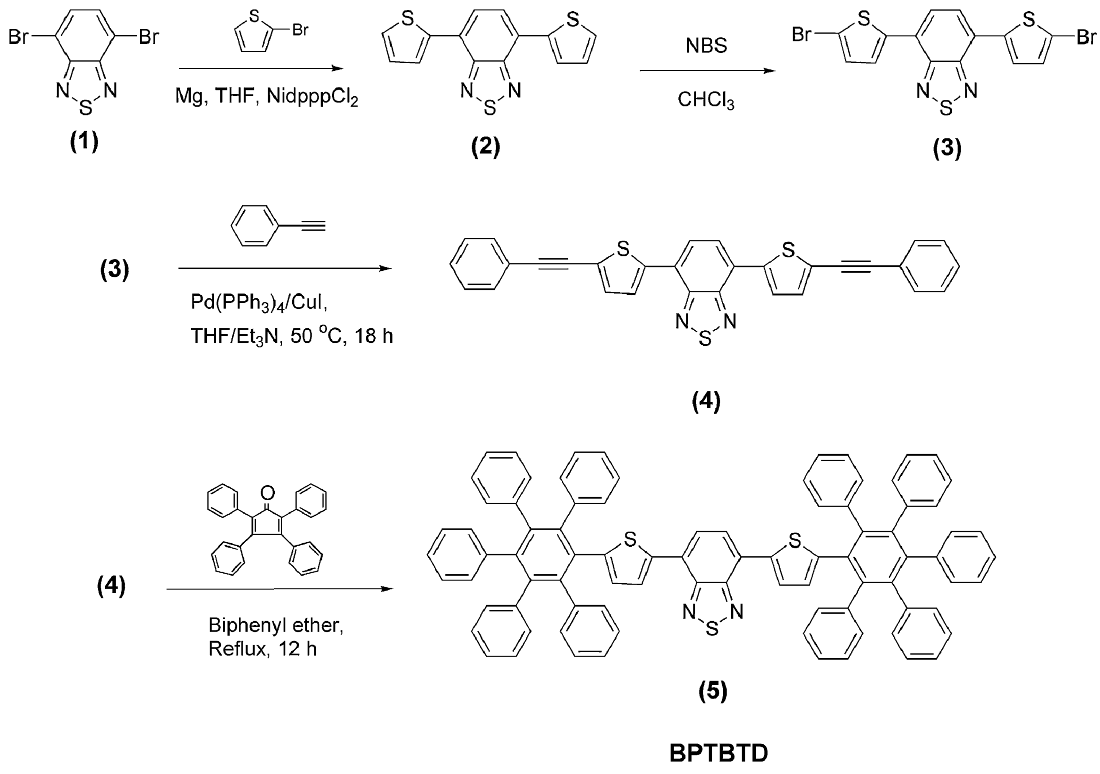
In this study, we have utilized pentaphenylphenyl groups to functionalize thiophene-benzo[1,2,5]thiadiazole to develop a new red-emitting structure, BPTBTD (shown in Scheme 1). The thermal and electronic properties of BPTBTD were investigated by TGA and cyclic voltammetry. The relationships of molecular structures and photophysical properties were discussed by ultraviolet-visible (UV-vis) absorption and photoluminescence spectra. In addition, red non-doping electroluminescent devices based on BPTBTD were obtained by a facile vacuum vapor deposition, and discussed using different thicknesses of emitting layers.

Results and discussion

Design and synthesis

The process used to prepare the desired compound BPTBTD is shown in Scheme 1. The symmetric product consists of a fluorophore at the center coupled with two identical pentaphenylphenyl moieties at two sides. The classical heteroaromatic fluorophore 4,7-di(2-thienyl)-benzo[2,1,3]thiadiazole (**2**) was chosen as the parent compound, which was prepared by the traditional nickel-catalyzed Kumada coupling reaction between compound **1** and freshly prepared 2-thienylmagnesium bromide. Non-planar pentaphenylphenyl group was used as the most important functional group for three reasons: the first one is to bathochromically shift luminescence to the red region by extending the molecular conjugated structure; the second is to suppress the formation of molecular aggregates and minimize intermolecular π–π stacking in the solid state by having a non-planar three-dimensional structure;[30,31,34] the third is to give the molecule good thermal stability and film-forming properties as has been proved by other research groups.[8,38] Therefore, it is expected to have a high thermal stability, good film-forming ability and excellent solid luminescence. Finally, our molecule can be seen as a simple line-shaped small molecule containing seven aryl groups as a framework modified with four benzyl groups as side groups. Red emission should come from the large conjugated structure instead of a traditional donor–acceptor ICT structure.

As shown in Scheme 1, BPTBTD could be easily synthesized with only three steps: first, the key reactive intermediate **3** was prepared in a yield of 70% by treatment of compound **2** with



Scheme 1 Synthetic route to the compound BPTBTD.

N-bromosuccinimide (NBS)–$CHCl_3$. Then, the tolane derivative **4** was synthesized by Pd(0)-catalyzed Hagihara–Sonogashira coupling of compound **3** with phenylacetylene. At low temperatures the reaction led selectively to the formation of compound **4** in high yield (89%). Finally, BPTBTD was obtained by an intermolecular Diels–Alder reaction between compound **4** and tetraphenylcyclopentadienone at high temperature.[28] Pure BPTBTD was obtained through silica-gel column purification and by train sublimation. All intermediates and final products were characterized unambiguously with ^{1}H NMR spectroscopy, elemental analysis and mass spectroscopy. For the large molecular weigh of BPTBTD, we employed a MALDI-TOF/MS measurement, which is to characterize the structure and molecular weight of the new compound directly. Functionalized by the non-planar pentaphenylphenyl group, BPTBTD has good solubility, and could be dissolved in many normal organic solvents, such as toluene, chloroform, and THF, *etc.*

Thermal and electrochemical properties

The thermal stability of BPTBTD was investigated by thermogravimetric analysis (TGA). The decomposition temperature (T_d) was estimated at about 340 °C (ESI†, Fig. S1). The excellent thermal stability indicates that BPTBTD can form thermally stable films by vacuum sublimation. The electronic properties of BPTBTD were investigated by cyclic voltammetry. When potential cycling was applied, the compound is electrochemically stable in THF solution. The onset potentials for reduction ($E^{\text{red}}_{\text{onset}}$) of BPTBTD is about −1.21 eV. The LUMO of BPTBTD was estimated at about −3.60 eV, according to the equation $E_{\text{LUMO}} = -(4.8\ \text{eV} - E_{\text{FOC}} + E^{\text{red}}_{\text{onset}})$. The corresponding HOMO was calculated by the LUMO value and the energy gap (E_g = 2.16 eV) from the edge of the absorption spectrum, and was found to be about −5.76 eV. The relatively low LUMO energy level suggests that BPTBTD would benefit electron injection and electron-transport, when is used as an active layer in devices.

Photophysical properties

Non-planar pentaphenylphenyl group was used to functionalize the fluorophore to achieve stable luminescence. UV-vis absorption and PL spectra are very important data to testify our design. The UV-vis absorption and PL spectra of BPTBTD in CH_2Cl_2 shows that BPTBTD exhibits two absorption peaks located at 332 and 483 nm, which may be deduced to be π–π transitions of the pentaphenylphenyl group and the core 4,7-di(2-thienyl)-benzo[2,1,3]thiadiazole, respectively. Benzo[2,1,3]thiadiazole derivates are always used as electron-withdrawing functional groups, but no ICT band appeared in the absorption spectrum of BPTBTD. So, BPTBTD is not an ICT material, and the red luminescence is the result of conjugated structure enlargement. As shown in Fig. 1, there is only one emission peak in the PL spectrum of the solution, which is located at 609 nm. Its fluorescent quantum yield was measured to be 32% in a CH_2Cl_2 solution relative to fluorescein in water, with a quantum yield of 0.92 at pH > 8.[39] To testify the molecular structure directly, spectra of BPTBTD in different polar solvents were measured. Fig. 1 shows the photophysical properties in solvents of different polarities. In a solvent of low polarity (toluene), the absorption peaks are located at 328 and 475 nm, and the emission peak is at 594 nm. With moderately polar solvents (THF and CH_2Cl_2), similar absorption peaks are located at 332 and 483 nm, and the emission band is near to 609 nm. When measured in a strong polar solvent (acetonitrile), the absorption peaks are still centered at 333 and 485 nm, and the emission peak is at 618 nm. The absorption and emission wavelength of BPTBTD changed little with the polarity of the solvent increasing. It resulted in only a 10 nm shift to the absorption and 20 nm to the emission peaks. For comparison, the emission wavelength of 4,7-di(2-thienyl)-benzo[2,1,3]thiadiazole derivative Btza has been shifted about 70 nm ranging from hexane to CH_2Cl_2.[21] Obviously, excited-state solvatochromism of BPTBTD is very weak. This result clearly shows that BPTBTD possesses weak dipole–dipole interactions and/or minimal intermolecular π–π stacking. The PL spectra in solutions with different concentrations and in solid films could indicate this view further. As shown in Fig. 2, BPTBTD shows bright red fluorescence both in solutions with different concentrations and in solid films. When the concentration of the solution is changed from 1 × 10^{-6} M to 1 × 10^{-3} M, the emission peaks are changed by only 5 nm, which are located at 609–614

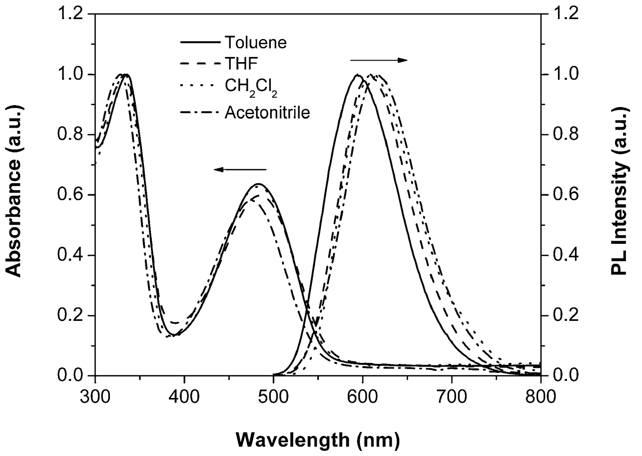


Fig. 1 UV-vis absorption and photoluminescence spectra of BPTBTD in solvents of different polarities (1 × 10^{-5} M).

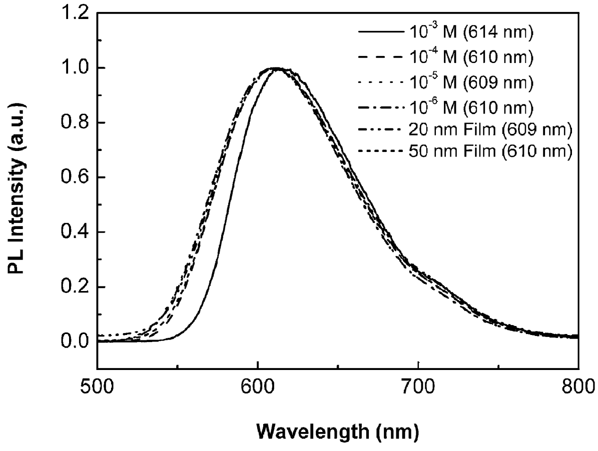


Fig. 2 Photoluminescence spectra of BPTBTD in CH_2Cl_2 solutions with different concentrations and in the solid films.

nm. In the film state, there is nearly no difference in the emission peaks with different thicknesses. The emission peaks are centered at 609–610 nm with thicknesses changed from 20 nm to 50 nm, which are similar to those in solution. Based on these phenomena, we could make a decision that BPTBTD is a very stable emitter, which shows little change of emission peaks in different solvents with different polarity and concentration, even in solid films. Therefore, BPTBTD can be a good red-emitting candidate for non-doped OLEDs.

Electroluminescent properties

The new emitter can be easily deposited as pristine thin film by thermal deposition in a vacuum system. To achieve high performance in organic EL devices, it is necessary to attain a hole–electron transporting balance and effective recombination of holes and electrons in the emitting layer. The devices were fabricated with the following configuration ITO/NPB (30 nm)/BPTBTD (*x* nm)/TPBI (30 nm)/LiF (1 nm)/Al by a sequential thermal deposition. To improve the color purity, the thicknesses of BPTBTD were increased from 20 nm to 50 nm. Here, BPTBTD, NPB, TPBI and LiF were used as emitting layer, hole-transporting, electron-transporting materials and electron injection layer, respectively. The proposed energy level diagram provides further insight into the roles of four functional materials playing in the device (Fig. 3). In this configuration, holes and electrons are all restricted in the emission layer.

Fig. 4 shows the electroluminescence spectra of non-doped devices with different thicknesses of BPTBTD as the emission layer. For these two kinds of device, only red emission peaks were observed from BPTBTD, and no emission peak from other materials, such as NPB. When the thickness of BPTBTD is 20 nm, the emission peak is located at 609 nm, which is similar to the photoluminescence spectra in solid films. The electroluminescent peak was shifted to 621 nm with the thickness of the emission layer increasing to 50 nm. The color purity was improved obviously. There is a phenomenon that emission maximum show a 12 nm red-shift with the thickness of emission layer increasing. The peaks of the PL spectra are nearly identical in solutions and solid states, so the red-shifted spectra with different thicknesses are not due to the excimer of BPTBTD, but the optical interference from the device structure.[16,41,42] Under different applied voltages, the emission spectra are very stable (shown in Fig. 5).

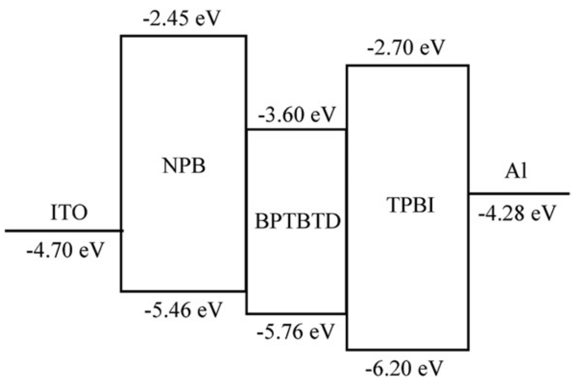


Fig. 3 Proposed energy level diagram of non-doping OLED with BPTBTD as the emitting layer (the HOMO and LUMO levels of NPB and TPBI are rooted in ref. 40)

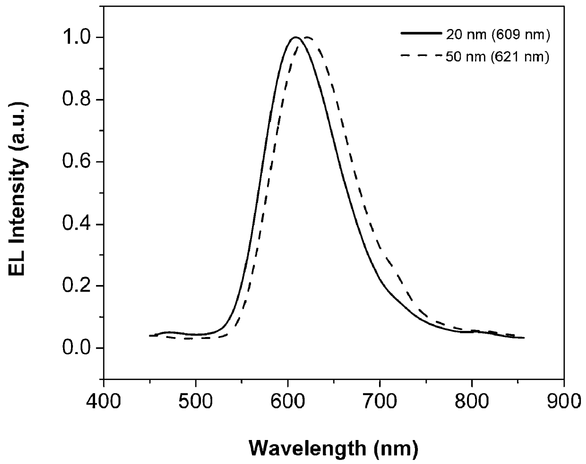


Fig. 4 EL spectra of devices ITO/NPB/BPTBTD (*x* nm)/TPBI/LiF/Al.

Fig. 6 and 7 show the electroluminescent properties of two sets of devices with different thicknesses of emitting layers. In

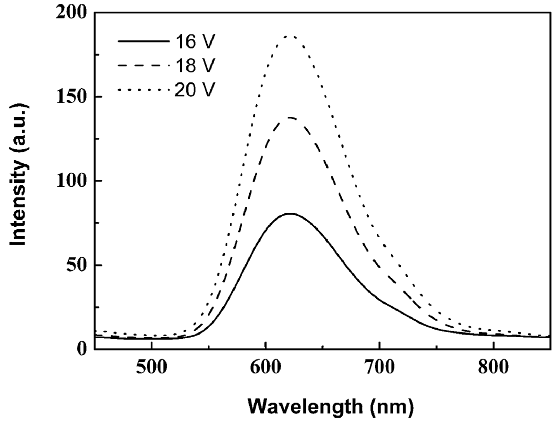


Fig. 5 EL spectra of devices ITO/NPB/BPTBTD (50 nm)/TPBI/LiF/Al under different voltages.

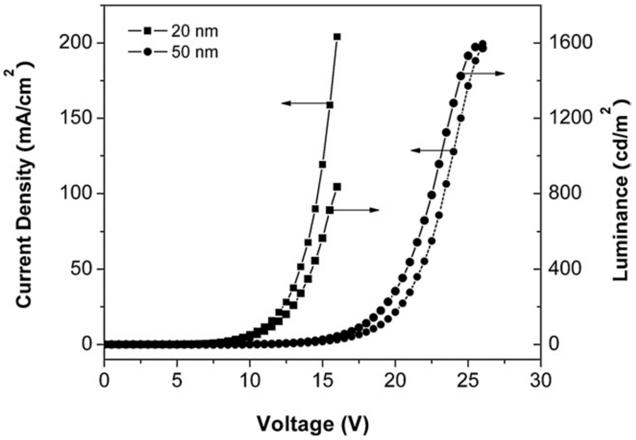


Fig. 6 Current density–voltage (a) and brightness–voltage (b) characteristics of the devices ITO/NPB/BPTBTD (*x* nm)/TPBI/LiF/Al.

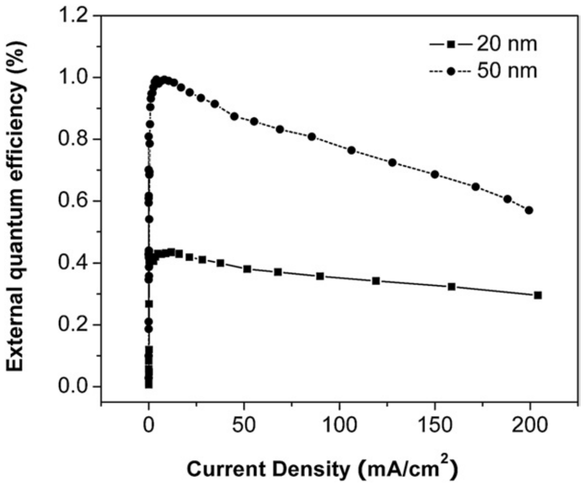


Fig. 7 External quantum efficiency–current density characteristics of the devices ITO/NPB/BPTBTD (*x* nm)/TPBI/LiF/Al.

contrast, when the thickness of the BPTBTD layer was 20 nm, a brightness of 835 cd m^{-2} at a current density of 200 mA cm^{-2} and an external quantum efficiency of 0.43% (corresponding to 0.60 cd A^{-1}) were acquired. When the thickness of BPTBTD was increased to 50 nm, a obviously improved performance of the non-doped OLEDs was obtained with a brightness of 1572 cd m^{-2} at a current density of 200 mA cm^{-2} and a maximum external quantum efficiency of 1.0% (corresponding to 1.37 cd A^{-1}). Obviously, the properties of devices with thick emission layers are two times better than those of the devices based on thin emission layers. As reported by many groups, the thickness of the organic emitting layer has much effect on the properties of devices. The electroluminescence quantum efficiency of the devices will be a function of the emitter thickness and used to determine the width of the carrier recombination zone.[43] At the same electric fields, a large emitter thickness will lead to an increase in electroluminescence quantum efficiency, because the width of the carrier recombination zone is large when the thickness is large. However, if the emitter thickness is much larger, it will normally lead a concentration quenching. This phenomenon is obviously special to red emitters. But, our results show that the electroluminescence quantum efficiency of the devices was also increased two times over the thin one, when the thickness was increased above double that of the thin one. For this point, it justly testifies our design that the molecule BPTBTD has a non-planar molecular structure, and functional pentaphenylphenyl group substantially suppressed dipole–dipole interactions and intermolecular π–π stacking. So, there is nearly no concentration quenching in our red emitting devices, when the emitter thickness is increased. The above discussions imply well that the molecule BPTBTD has excellent solid properties in the film, and BPTBTD is a good candidate for efficient and non-doped red OLEDs.

Conclusions

In conclusion, we have synthesized and characterized a novel non-planar pentaphenylphenyl group to functionalize a benzo[2,1,3]thiadiazole derivative (BPTBTD). This material exhibits good solubility in common organic solvents, excellent thermal stability and film-forming properties. In different solvents, BPTBTD exhibits very weak excited-state solvatochromism. Moreover, BPTBTD also shows stable photoluminescence with different concentrations in solution and in solid state, which indicates that the non-planar functional pentaphenylphenyl group substantially suppressed dipole–dipole interactions and intermolecular π–π stacking. With increasing thickness of emission layer for the red OLEDs, an obvious improvement was achieved in both brightness and efficiency. The experimental results indicate that BPTBTD has great potential for use in red OLEDs of high performance with facile preparation methods. Intensive studies on electroluminescent properties by optimizing the configurations of the devices (modifying the cathode to enhance the electron injection or adopting suitable thicknesses) and modifications to the structures of these derivative materials are in progress.

Experimental

Materials and instrumentation

2-Bromothiophene, phenylacetylene, 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one, tetrakis(triphenylphosphine)palladium [Pd(PPh$_3$)$_4$] and dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) [Ni(dppp)Cl$_2$] were purchased from Aldrich. Other normal chemical reagents and solvents were obtained from the Beijing Chemical Plant. Solvents for reactions and photophysical measurements (DMF, CH$_2$Cl$_2$, THF, *etc.*) were all distilled after dehydration according to conventional methods. 4,4′-Bis[*N*-(1-naphthyl)-*N*-phenyl-amino]-biphenyl (NPB) and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) were purchased and purified by sublimation prior to use.

^{1}H NMR spectra were recorded on a Bruker DMX 300 NMR spectrometer. UV-vis absorption and fluorescence spectra were obtained with Hitachi U-3010 and Hitachi F-4500 spectrometers, respectively. Mass spectra were recorded on an AEI-MA50-MS spectrometer for EI-MS and a Bruker BIFLEX III Mass Spectrometer for MALDI-TOF-MS. Elemental analyses were carried out on a Carlo-Erba 1160 elemental analyzer. Thermogravimetric analyses (TGA) were carried out using a Perkin-Elmer thermogravimeter (Model TGA7) under a dry nitrogen gas flow, heating from room temperature to 500 °C, with a heating rate 10 °C min^{-1}. Cyclic voltammetric measurements were carried out in a conventional three electrode cell using a Pt button working electrode of 2 mm in diameter, a platinum wire counter electrode, and a Ag/AgCl reference electrode on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature. Reduction CV of BPTBTD was performed in CH$_2$Cl$_2$ containing Bu$_4$NPF$_6$ (0.1 M) as a supporting electrolyte. The energy levels were calculated using the ferrocene (E_{FOC}) value of −4.8 eV as the standard, while E_{FOC} was calibrated to be 0.45 V *vs.* Ag/AgCl electrode in CH$_2$Cl$_2$ solution.

Synthesis of compounds. 4,7-Dibromo-benzo[2,1,3]thiadiazole (**1**) was synthesized according to the literature procedure.[44]

4,7-Di(2-thienyl)-benzo[2,1,3]thiadiazole (2). Magnesium (1.46 g, 60 mmol) was transferred to a three-necked round-bottomed flask and heated to 100 °C in a N_2 atmosphere for 2 h. After the flask was cooled to room temperature, dry THF (40 mL) and a catalytic amount of I_2 were added; then the mixture was left to react for 10 min. 2-Bromothiophene (6.0 mL, 60 mmol) was carefully added in parts to the solution to avoid an excessive increase in temperature, and the mixture was refluxed for 2 h to obtain the corresponding Grignard reagent. 4,7-Dibromo-benzo[2,1,3]thiadiazole **1** (5.90 g, 20 mmol) and [Ni(dppp)Cl_2] (1.02 g, 1.88 mmol) were transferred to a separate three-necked round-bottomed flask connected to a sintered glass filter. After purging with N_2, dry THF (60 mL) was added and the Grignard reagent was carefully transferred through the filter. The reaction mixture was refluxed for 20 h, left to stand at room temperature for 2 h, and then quenched with 1 N HCl. It was then filtered and the THF solvent was removed in a flash evaporator. The residue was extracted with water–CH_2Cl_2 and the organic layer was dried over anhydrous $MgSO_4$. After the solvent was evaporated under reduced pressure, the residue was purified by flash silica-gel column chromatography to afford the product. Yield: 67%. ^1H NMR (300 MHz, $CDCl_3$): $d = 8.12$ (dd, 2 H), 7.89 (s, 2 H), 7.46 (dd, 2 H), 7.22 (dd, 2 H) ppm; MS [electron impact (EI)]: m/z: 300 (M^+); elemental analysis calcd (%) for $C_{14}H_8N_2S_3$: C, 55.97; H, 2.68; N, 9.32. Found: C, 55.90; H, 2.62; N, 9.26.

4,7-Bis(5-bromo-2-thienyl)-benzo[2,1,3]thiadiazole (3). Prepared according to a method described previously.[45]

4,7-Bis-(5-phenylethynyl-2-thienyl)-benzo[2,1,3]thiadiazole (4). A mixture of compound **3** (300 mg, 1.0 mmol), phenylacetylene (0.24 mL, 2.2 mmol), $Pd(PPh_3)_4$ (117 mg, 0.1 mmol) and copper iodide (38 mg, 0.2 mmol) in THF (20.0 mL) and triethylamine (20.0 mL) was stirred at 50 °C for 18 h under N_2. Cooled to room temperature, the mixture was put into 100 mL THF and stirred for 30 min. The mixture was filtered to remove salts and concentrated by evaporating THF. The remaining solution was poured into 200 mL of methanol with stirring. A deep red solid residue was precipitated out immediately, which was filtered and dried to give the product. Yield: 66%. MS [electron impact (EI)]: m/z: 500 (M^+); elemental analysis calcd (%) for $C_{30}H_{16}N_2S_3$: C, 71.97; H, 3.22; N, 5.60. Found: C, 71.67; H, 3.32; N, 5.68.

4,7-Bis-[5-(2,3,4,5-tetraphenyl)phenyl-2-thienyl]-benzo[2,1,3]-thiadiazole (5) BPTBTD[27]. A mixture of compound **4** (500 mg, 1.0 mmol) and 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (844 mg, 2.2 mmol) was heated to 250 °C in 10 mL of diphenyl ether for 16 h. The raw product was washed with 40 mL of cold *n*-hexane and purified by flash silica-gel column chromatography to afford the red solid product. Yield: 78%. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.63$ (d, 2 H), 7.34 (s, 2 H), 6.99 (d, 10 H), 6.91 (t, 10 H), 6.82–6.88 (brs, 32 H). MS (MALDI-TOF): m/z: 1212 (M^+), 1235 (Na^+); elemental analysis calcd. (%) for $C_{86}H_{56}N_2S_3$: C, 85.11; H, 4.65; N, 2.31. Found: C, 84.73; H, 4.87; N, 2.65.

OLED fabrication and measurements

Indium tin oxide (ITO) coated glass was used as the substrate and the anode, and was washed with deionized water, acetone, and ethanol in turn. Multilayered devices were fabricated: ITO/NPB (30 nm)/BPTBTD(x nm)/TPBI (30 nm)/LiF (1 nm)/Al (100 nm). As functional layers, NPB works as the hole-transporting layer, TPBI as the hole-blocking and electron-transporting layer. Al was used as the cathode. The materials used as the emission layers and other organic functional layers were successively deposited onto the ITO/glass substrates. The emitting area of the EL devices was about 5 mm^2. Electroluminescence spectra were recorded on the Hitachi F-4500 spectrophotometer. Current–voltage characteristics for the OLEDs were measured with a HP4140B semiconductor parameter analyzer. Brightness was measured with a spectra scan PR 650 photometer. All device tests were carried out under an ambient atmosphere at room temperature.

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