A novel amorphous oligo(phenylenevinylene) dimer with a biphenyl linkage center and fluorene end groups for electroluminescent devices

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A new type of oligo(phenylenevinylene) dimer, 2,5,2′,5′-tetra(9,9′-dihexylfluorenyl)biphenyl (**TFB**), with a biphenyl linkage center and four fluorene end groups, has been synthesized by the Wittig reaction. The full characterization of its structure and optical properties, as well as the performance of its electroluminescent devices are presented. **TFB** shows strong blue fluorescence both in solution and as a solid film. High-quality films of **TFB** for light-emitting devices (LEDs) can be fabricated both by vacuum evaporation and the spin-coating technique, which is very special and interesting. Single-layer and multi-layer light-emitting devices using **TFB** as the active layer all show efficient blue emission.

Introduction

Conjugated organic materials such as poly(phenylenevinylene)s (PPVs) have attracted considerable attention in recent years due to their applications in organic light-emitting devices (OLEDs).[1–5] As model compounds for the corresponding polymers and active materials themselves, oligomers have induced great interest because their conjugation length can be defined and adjusted, and consequently the color of the emission can be easily controlled. Trimeric phenylenevinylene (TPV) and its derivatives have been widely investigated,[6–8] which has resulted in the deep understanding of the important conjugated polymer poly(phenylenevinylene) (PPV), while TPV itself is also a bright pure blue emitter. Unfortunately, however, the excellent luminescent properties of TPV, *e.g.* a photoluminescence (PL) efficiency of over 90%, are only obtained in dilute solution; in the solid state it emits very weakly. This solid state fluorescent quenching behavior has been associated with the formation of intermolecular aggregates, especially those arranged in a side-by-side fashion (H-aggregates).[9] This means that the stacking of TPV molecules plays a determining role in the physical properties of these materials. Much work has been done to prevent the aggregation of TPV, which aims to achieve high-efficiency emission in the solid state and in films.[10,11] This involves either the introduction of a chemical substitutent to TPV,[12] forming a tetrahedral linkage of four TPVs, *i.e.* tetrakis(4-*tert*-butylstyrylstilbenyl)methane (C(^tBuSSB)_4)[13] or forming covalent assemblies of four TPVs around a calix[4]arene core.[14] Some of them *e.g.* C(^tBuSSB)_4, have been used in the fabrication of devices,[15] however, the device performance in this case is not as good as expected from its high PL efficiency in the solid state (42%), likely to be due to low carrier mobility induced by a central sp^3-hybridized carbon atom.

Recently, we developed a versatile synthesis of a new class of dimeric TPVs in which two TPVs are linked through the phenyl–phenyl bond of the central phenylene ring to form a crossing dimeric structure with a twist angle of ∼70° between the planes of the two TPVs.[16] High photoluminescence efficiencies for these new solid TPV oligomers and high-performance blue electroluminescent (EL) devices using the new oligomers as the active layer have been demonstrated. In this paper, we report the synthesis of a new oligo(phenylenevinylene) with a biphenyl linkage center and fluorene end groups, **TFB**, and its optical and EL properties. The four fluorene end groups in **TFB** strongly improve its solubility in common solvents and high quality films can be fabricated by solution spin-coating and also by vacuum evaporation. Generally, LEDs can be fabricated from small organic molecules by a vacuum-deposition technique[15,16] and by a spin-coating technique for conjugated polymers, which has the advantage of relative simplicity and suitability for large-area flat displays.[17,18] Therefore, **TFB** combines the advantages of small organic molecules, *e.g.* well-defined molecular structure and easy purification, with the advantages of conjugated polymers, *e.g.* easy device fabrication.

Experimental

Materials

Fluorene, *N*-bromosuccinimide (NBS), 1-bromohexane, *n*-butyllithium (1.6 M hexane solution), and sodium *tert*-butoxide were purchased from Aldrich and used without further purification unless otherwise noted. Tetra(phosphonate) **5** was prepared according to our previous report.[16] Tetrahydrofuran (THF) was dried and purified by fractional distillation over sodium/benzophenone and *N*,*N*-dimethylformamide (DMF) was vacuum-distilled over P_2O_5. Column chromatography was performed using silica gel (200–300 mesh).

Synthesis of 2-bromofluorene (2)

A mixture of fluorene (5 g, 60 mmol) and $FeCl_3$ (0.26 g, 4.4 mmol) was dissolved in anhydrous DMF (50 mL) in a 100 mL round-bottomed flask, which was equipped with a magnetic stirring bar and capped with a rubber septum. A solution of *N*-bromosuccinimide (0.090 g, 0.8 mmol) in DMF (50 mL) was added dropwise to the reaction flask at room

temperature in the dark. The reaction mixture was stirred at room temperature for 24 h, the resulting solution treated with HCl (0.1 M, 10 mL), neutralized with $NaHCO_3$, and then extracted with chloroform several times. After filtration and solvent evaporation, the residual solid was recrystallized from hexane, to give a white crystalline solid (yield 56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.766–7.751 (d, 1H, ArH), 7.682 (s, 1H, ArH), 7.650–7.634 (d, 1H, ArH), 7.546–7.531 (d, 1H, ArH), 7.510–7.491 (d, 2H, ArH), 7.398–7.368 (t, 1H, ArH), 7.342–7.310 (t, 1H, ArH), 3.890 (s, 2H, $ArCH_2Ar$). Anal.: calcd for $C_{13}H_9Br$: C, 63.70; H, 3.70; found: C, 63.59; H, 3.76.

Synthesis of 2-bromo-9,9′-dihexylfluorene (3)

Compound **2** (1 g, 4.08 mmol), 1-bromohexane (1.7 mL, 12 mmol), *tert*-butylammonium bromide (0.129 g, 0.4 mmol) and NaOH (0.48 mL, 50% w/w) were mixed in a 100 mL round-bottomed flask under a nitrogen atmosphere. The mixture was heated at 90 °C for 24 h. After the mixture was cooled to room temperature, water was added to the resulting solution and it was extracted with chloroform several times. The organic phase was dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the yellow liquid was purified by column chromatography (silica gel, cyclohexane) to afford a colorless oil (yield 41%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.670–7.651 (m, 1H, ArH), 7.560–7.542 (d, 1H, ArH), 7.469 (s, 1H, ArH), 7.336–7.275 (m, 4H, ArH), 1.95–1.92 (m, 4H, CH_2), 1.12–1.09 (m, 4H, CH_2), 1.04–1.03 (m, 8H, CH_2), 0.78–0.75 (m, 6H, CH_3), 0.59–0.57 (m, 4H, CH_2) ppm.

Synthesis of 9,9′-dihexylfluorene-2-carbaldehyde (4)

Compound **3** (0.413 g, 1 mmol) was dissolved in THF (15 mL) and the flask purged with nitrogen. A 15% solution of *n*-BuLi in hexane (0.7 mL, 1.4 mmol) was added dropwise at −78 °C. After 3 h at this temperature, dry degassed DMF (0.4 mL) was added, and the reaction was allowed to continue for an additional 12 h at 0 °C. The resulting solution was evaporated under reduced pressure, and solid residue was stirred with 10 mL CH_2Cl_2 and 10 mL HCl (3 mol L^{-1}) at room temperature for 20 min. The organic layer was separated, washed with saturated $NaHCO_3$, dried with Na_2SO_4, and the solvent removed under reduced pressure. The crude product was purified by column chromatography using dichloromethane as solvent to give a colorless oil (yield 66%). ^{1}H NMR (500 MHz, DMSO): δ = 10.05 (s, 1H, CHO), 8.05–8.04 (d, 1H, ArH), 7.97 (s, 1H, ArH), 7.96–7.94 (d, 1H, ArH), 7.93–7.91 (d, 4H, ArH),), 7.52–7.51 (d, 1H, ArH), 7.44–7.38 (m, 2H, ArH), 2.07–2.02 (m, 4H, CH_2), 1.03–0.95 (m, 12H, CH_2), 0.72–0.69 (m, 6H, CH_3), 0.47–0.44 (m, 4H, CH_2) ppm.

Synthesis of 2,5,2′,5′-tetra(9,9′-dihexylfluorenyl)biphenyl (TFB)

Compound **4** (0.217 g, 0.6 mmol) and tetra(phosphonate) **5** (0.158 g, 0.1 mmol) were dissolved in a mixture of anhydrous ethanol (10 mL) and THF (10 mL) in a 100 mL oven-dried round-bottomed flask, equipped with a magnetic stirring bar and capped with a rubber septum. A freshly prepared 5% solution of sodium ethoxide in ethanol (0.090 g, 0.8 mmol) was added dropwise to the reaction flask *via* a syringe at room temperature. The reaction mixture was stirred at room temperature under an argon atmosphere. The resulting solution was twice precipitated from methanol to give a light yellow solid (yield 60%). ^{1}H NMR (500 MHz, DMSO): δ = 7.78–7.28 (m, 42H), 2.09–1.93 (m, 16H, CH_2), 0.98–0.85 (m, 48H, CH_2), 0.71–0.62 (m, 24H, CH_3), 0.60–0.49 (m, 16H, CH_2) ppm.

Characterization methods

The ^{1}H NMR spectra were recorded on a AVANCE 500 spectrometer at 298 K with deuterated chloroform or dimethyl sulfoxide (DMSO) as the solvent and tetramethylsilane (TMS) as the standard. The compounds were characterized on a Flash EA 1112 CHNS–O elemental analysis instrument. IR spectra were recorded on a Perkin–Elmer spectrophotometer in the 400–4000 cm^{-1} region using a powdered sample on a KBr plate. The LC–MS and MS–TOF mass spectra were recorded using a Applied Biosystems QSTAR instrument. UV–Vis absorption spectra were recorded on a UV-3100 spectrophotometer. Fluorescence measurements were carried out with a RF-5301PC instrument. Differential scanning calorimetry (DSC) analysis was carried out using a NETZSCH (DSC-204) instrument at 10 °C min^{-1} whilst flushing with nitrogen. Electrochemical measurements were performed with a Bioanalytical Systems BAS 100 W instrument, using a glassy carbon working electrode, a platinum wire auxiliary electrode with a porous ceramic wick, and a Ag/Ag^+ reference electrode, standardized for the redox couple ferricinium/ferrocene. Cyclic voltammetric studies of **TFB** were carried out in MeCN containing 0.1 M NBu_4PF_6 (tetra-*n*-butylammonium hexafluorophosphate) as the supporting electrolyte. The electrochemical investigations on the oligomer were carried out on a thin layer of material deposited on glassy carbon from a $CHCl_3$ solution.

Devices fabricated by spin-coating

The typical device configuration fabricated by spin-coating was ITO/PEDOT/**TFB**/Ba/Al. Indium–tin oxide (ITO)-coated glass with a sheet resistance of $< 50 \Omega \square^{-1}$ was used as the substrate. Pre-treatment of ITO included a routine chemical cleaning using detergent and alcohol in sequence, followed by oxygen plasma cleaning. The PEDOT (3,4-polyethylenedioxythiophene–polystyrenesulfonate) layer was deposited onto the ITO-coated substrate as the buffer layer. The **TFB** film was formed on the PEDOT layer by spin-coating a toluene solution with a concentration of 5 mg mL^{-1} to give a film thickness of 50–70 nm. The Ba cathode was deposited by thermo-evaporation and was followed by a thick Al capping layer.

Devices fabricated by vacuum evaporation

The typical device configuration fabricated by vacuum evaporation was ITO/NPB/**TFB**/BCP/LiF/Al. The organic layer was deposited by high vacuum (10^{-6} Torr) thermal evaporation onto a cleaned ITO glass substrate. The layer thickness of the deposited material was monitored *in situ* using an oscillating quartz thickness monitor. Finally a LiF buffer layer and Al cathode were vapor-deposited onto the organic films at a background pressure of 10^{-6} Torr. The EL spectra and Commission Internationale de l'Éclairage (CIE) coordinates of these devices were measured by a PR650 Spectroscan spectrometer. The luminance–current density–voltage characteristics were recorded simultaneously with the EL spectra by combining the spectrometer with a Keithley model 2400 programmable voltage–current source. All measurements were carried out at room temperature under ambient conditions.

Results and discussion

Synthesis and characterization of TFB

As shown in Scheme 1, the oligo(phenylenevinylene) dimer **TFB** containing a biphenyl linkage center and fluorene end segments was prepared by a Wittig reaction. The structure of **TFB** was identified by FT-IR, ^{1}H NMR and HPLC mass spectrometry. The FT-IR spectrum of **TFB** is shown in Fig. 1.
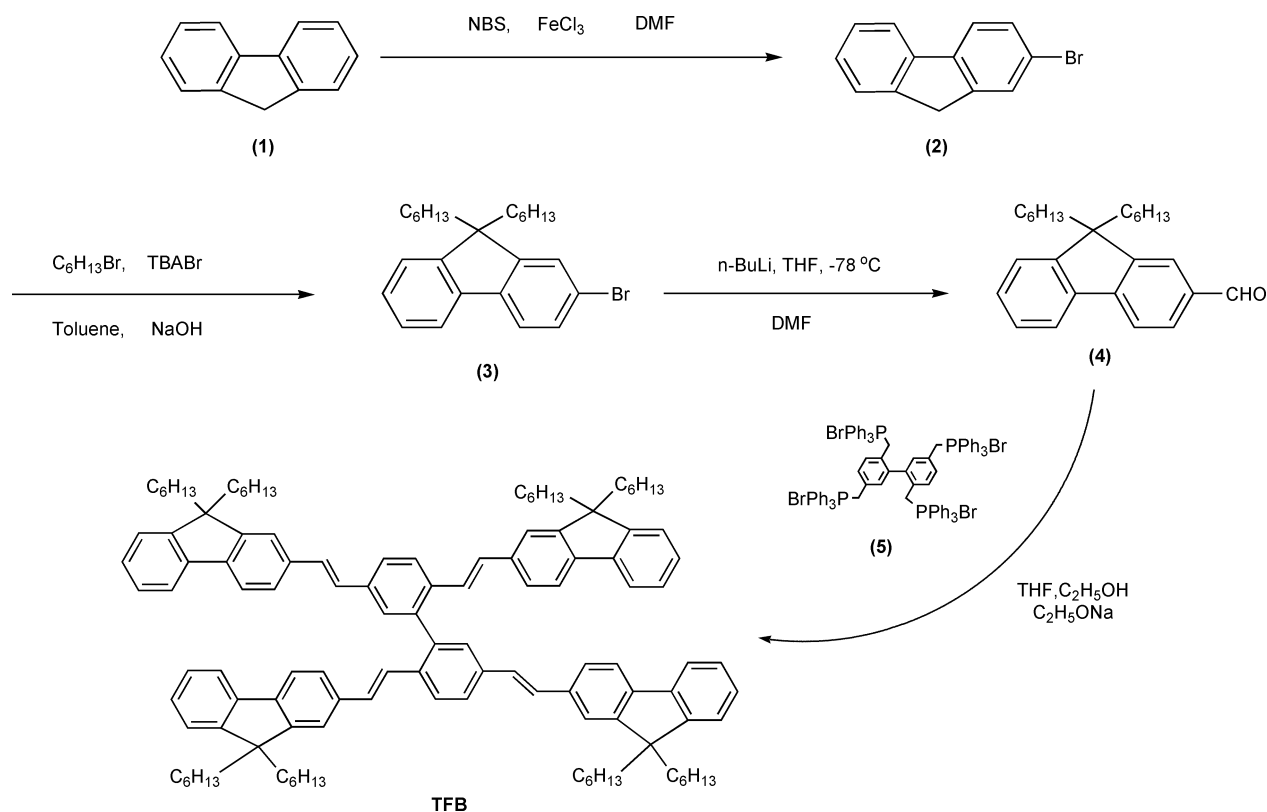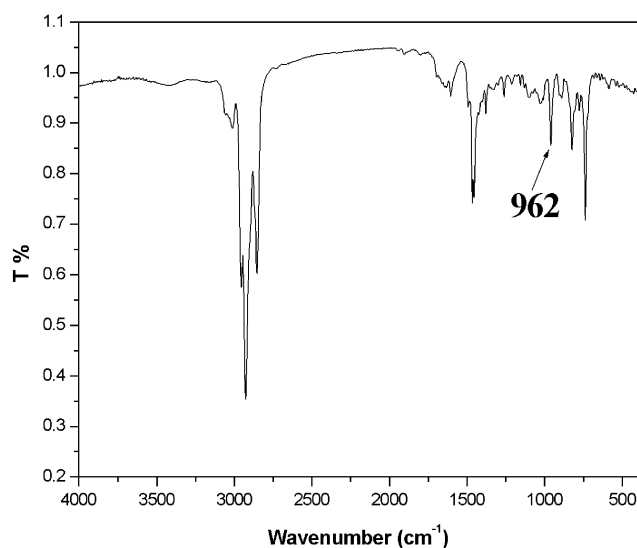
Scheme 1   Synthesis of **TFB**.

Fig. 1   The FT-IR spectrum of **TFB**.

Fig. 2   The ^{1}H NMR spectrum of **TFB**.

In particular, **TFB** showed characteristic absorption bands at 3010, 2927, 2848 (v_{C-H}); 1466, 1452, 1376 (δ_{CH_2}, δ_{CH_3}); 962 (*trans* CH=CH, γ_{C-H}); and 825, 739 (v_{ArC-H}). From Fig. 1, we could easily find the characteristic absorption bands of the *trans* double bonds at 962 cm^{-1}. This suggested that the vinylene group formed in this reaction was in the *trans* configuration.[19]

The ^{1}H NMR spectrum of **TFB** in DMSO-d_6 solution (Fig. 2) showed that the ratio of aliphatic/aromatic protons observed for **TFB** is 2.53, which is in good agreement with the calculated value (2.48). In addition, there weren't any peaks characteristic of a *cis*-double bond around 6.5 ppm in the ^{1}H NMR spectrum of **TFB**, which also confirmed that the vinylene group was in *trans* configuration.[20,21] This *trans* configuration of the vinylene group in **TFB** was propitious to
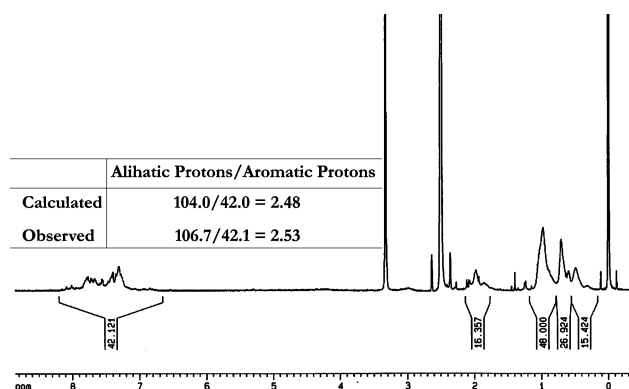
getting a high emission efficiency. Fig. 3 shows the mass spectrum corresponding to the "molecular ion" of the **TFB** molecule ($C_{120}H_{146}$). We observed the characteristic peak ($[M + H]^+$) at 1588.19. The experimentally measured isotopic distribution showed excellent agreement with that calculated (1588.14).

As depicted in Fig. 4, the wide-angle X-ray diffraction pattern for powdered specimens of **TFB** showed a broad band in the region around 20°, which revealed its entirely amorphous character. Because of this amorphous nature, molecules of **TFB** might have a weak interaction in the solid state and therefore have promise as blue-emitting materials with a weak (or no) concentration-quenching effect.

The DSC thermograms of **TFB** are shown in Fig. 5. A sample of **TFB** was heated to 150 °C with subsequent cooling to −20 °C at a rate of 10 °C min^{-1} before gathering the second heating scan at a rate of 10 °C min^{-1} from −20 °C to 100 °C. The glass phase transition T_g was found at 43 °C; similar to other fluorene based oligomers.[22]

We also investigated the electrochemical behavior of **TFB** by cyclic voltammetry (CV) to obtain information about the
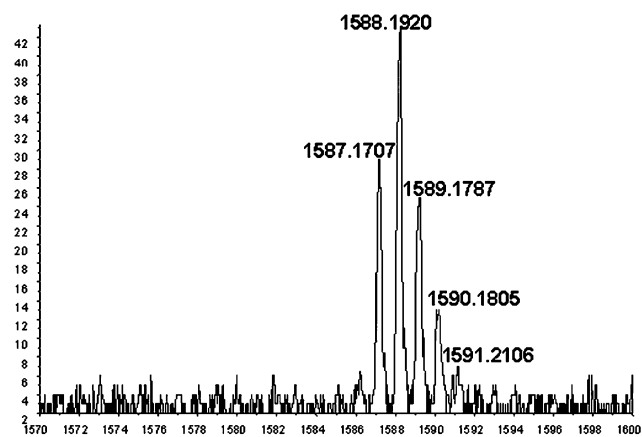
Fig. 3 The mass spectrum corresponding to the "molecular ion" of **TFB** ($C_{120}H_{146}$).
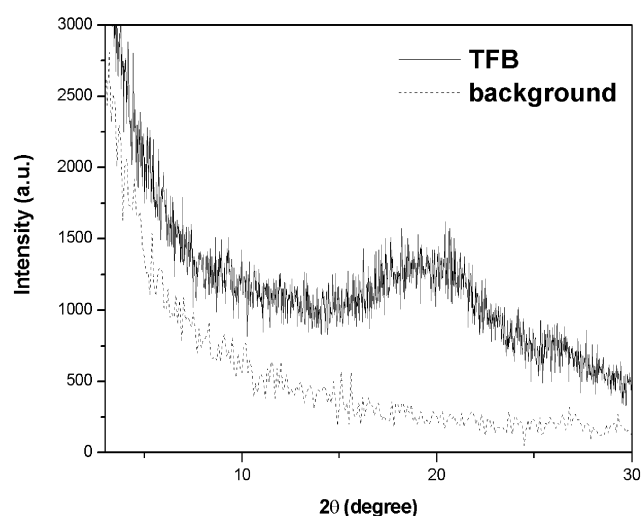

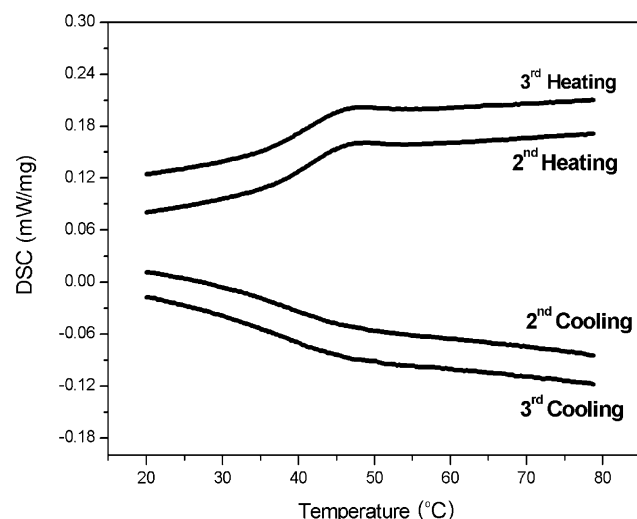**Fig. 4** Wide-angle X-ray diffraction pattern of **TFB** recorded at room temperature.

Fig. 5 DSC thermograms of **TFB** with sequential heating and cooling.
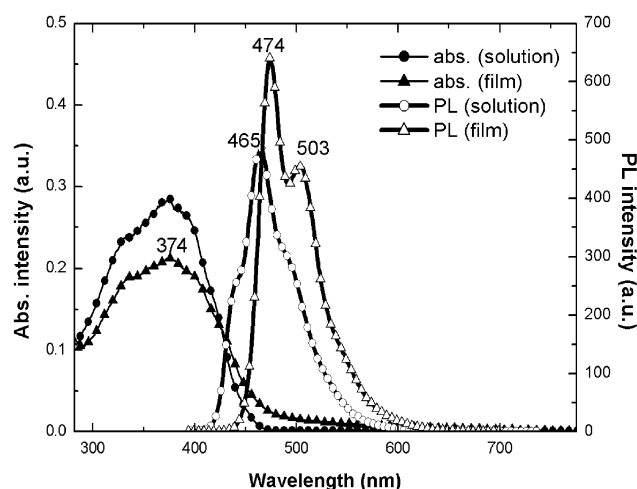

Fig. 6 UV–Vis and PL spectra of **TFB** in THF solution ($\sim 2.0 \times 10^{-4}$ M) and as a film at room temperature; the samples were excited at 375 nm.

band gap. The result showed a reversible redox peak in the reductive potential range with the reductive onset at -2.20 V and an obvious single oxidation peak in the oxidative potential range with the oxidative onset at 0.86 V. The LUMO level of **TFB** was estimated to be -2.48 eV and the HOMO level was about -5.54 eV. Therefore, the band gap of **TFB** is 3.06 eV, which is close to the value obtained from the absorption spectra (2.82 eV).

Optical properties of TFB

The absorption and emission spectra of the oligomer both in dilute THF solution and as a solid film are shown in Fig. 6; detailed data are tabulated in Table 1. The optical absorption spectrum of **TFB** in THF solution showed λ_{max} at 374 nm, which is almost the same as that of its analog 2,5,2′,5′-tetra(4′-biphenylenevinyl)biphenyl (TBVB),[16] indicating that the bulky and non-coplanar aliphatic side groups have little effect on the conjugation degree of the oligomer. The PL spectra of **TFB** in THF exhibited a maximum (λ_{em}) around 465 nm (the blue light region). The PL efficiency of **TFB** solution was about 50%, which was close to that for the homogeneous PPV oligomers that we had reported previously,[16] such as 2,5,2′,5′-tetra(styryl)biphenyl (TSB) and TBVB. As shown in Fig. 6, there are only slight differences in the absorption spectra between the solution and the film of **TFB**. The PL spectrum of the solid film of **TFB** displayed a maximum of about 474 nm and a shoulder at about 503 nm, which was only a ~ 10 nm red shift compared to that of the solution, which could be the result of self-absorption. Both in solution and in the film state, **TFB** showed a very bright blue emission. This was different from TPV, which emitted very weakly in the solid state.[9] Consequently, with its central phenylene–phenylene bond and the bulky side chain, **TFB** can efficiently avoid intermolecular aggregation.

Electroluminescence properties of TFB

TFB-based LEDs can be fabricated both by vacuum evaporation and the spin-coating technique, and two types of devices show high performance.

Table 1 Optical properties of **TFB**; the samples were excited at 375 nm

Oligomer	$\lambda_{a,\ max}$/nm (THF solution)	ε / mol L^{-1} cm^{-1}	$\lambda_{f,\ max}$/nm (THF solution)	$\lambda_{f,\ max}$/nm (film)	φ_{PL} (solution)^a
TFB	374	54.47×10^3	465	474	0.50

^{a} In dilute THF, using quinine sulfate in 0.1 M sulfuric acid as standard.

Characteristics of LEDs fabricated by vacuum evaporation

The multi-layer organic light-emitting devices (OLEDs) with the structure ITO/NPB (30 nm)/**TFB** (30–40 nm)/BCP (30 nm)/LiF/Al were fabricated by thermal deposition in a vacuum chamber, in which NPB (N,N'-di-1-naphthyl-N,N'-diphenylbenzidine) acted as the hole transporting layer and BCP (bathocuprine) as the hole and exciton block layer. Fig. 7 shows the electroluminescence spectra of **TFB**. Fig. 8 shows the current density (I)–voltage (V)–luminance (L) characteristics; the insert shows the LE–V (luminance efficiency $vs.$ voltage) characteristics of the device. As for other homogeneous PPV oligomers, **TFB** exhibits blue light emission with CIE coordinates of (0.26, 0.27). The EL spectrum of **TFB** devices with a peak at 472 nm was the same as its PL spectrum. The devices based on **TFB** exhibited a turn-on voltage of 5 V with a maximum luminance efficiency of 0.66 cd A^{-1} (0.21 lm W^{-1}) and a luminance of 954 cd m^{-2}. Although the devices fabricated by vacuum evaporation showed acceptable character, some key operations should be noticed in the process; in particular, the evaporative temperature must be kept under 350 °C during device fabrication, because **TFB** might begin to decompose if the operating temperature is too high. In addition, **TFB** evaporated very slowly, which made the whole process too long. Therefore, we investigated devices formed by spin-coating in our subsequent studies.
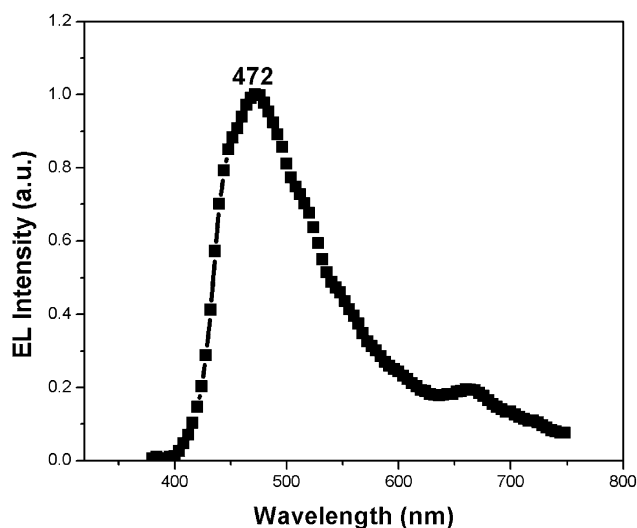
Characteristics of LEDs fabricated by spin-coating

The single-layer organic light-emitting devices (OLEDs) with the configuration of ITO/PEDOT/**TFB**/Ba/Al were fabricated to investigate the electroluminescent properties of the spin-coating oligomer devices. As shown in Fig. 9, the EL spectra of **TFB** (insert) showed a peak wavelength around 468 nm with CIE coordinates of (0.23, 0.29), which was similar to both the PL spectra and that of devices fabricated by vacuum evaporation. The spectra showed a small change in difference voltage, probably produced by Joule heat when the devices operated. The device had a turn-on voltage of 5 V with a maximum luminance of 314 cd m^{-2}, but the luminance efficiency of the single-layer organic light-emitting devices is only about 0.023 cd A^{-1}. In **TFB** LEDs, since the p-type conjugated molecules are much better hole-transporters than electron-transporters, the resulting charge imbalance may limit EL efficiency. An improvement in device efficiency could be obtained by inserting the electron injecting layer between the spin-coated **TFB** layer and the electrode metals. Fig. 10 shows the power efficiency (PE)–voltage (V)–luminance efficiency (LE) characteristics of the multi-layered ITO/PEDOT/**TFB**/PBD/Alq$_3$/LiF/Al devices, where **TFB** was fabricated by spin-coating, PBD (2-$tert$-butylphenyl-5-biphenyl-1,3,4-oxadiazole) acted as the hole and exciton block layer, and Alq$_3$ (aluminium(III) tris(8-hydroxyquinolate)) as the electron

Fig. 7 Electroluminescence spectrum of the ITO/NPB/**TFB**/BCP/LiF/Al device.

Fig. 9 The current density (I)–voltage (V)–luminance (L) characteristics of the single-layer device ITO/PEDOT/**TFB**/Ba/Al fabricated by spin-coating; the insert shows its electroluminescence spectra.
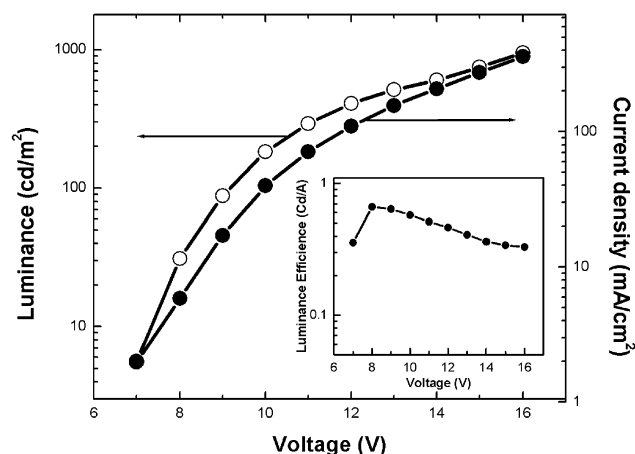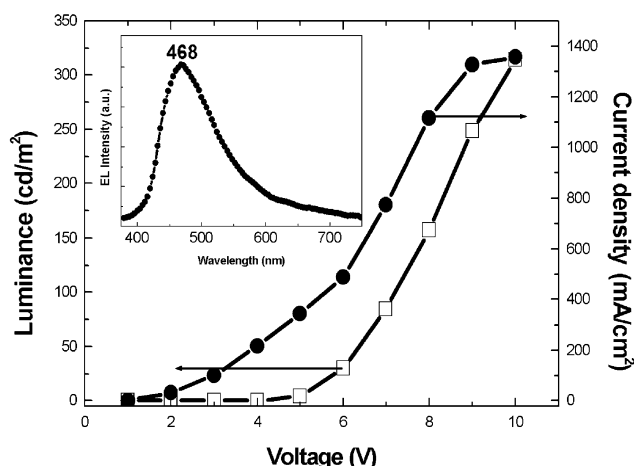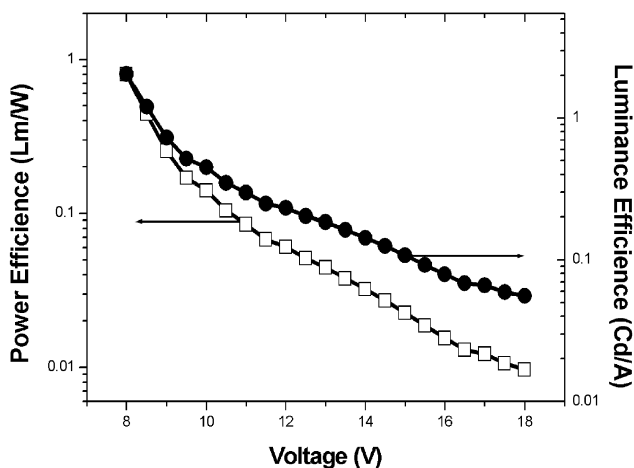

Fig. 8 The current density (I)–voltage (V)–luminance (L) characteristics of the ITO/NPB/**TFB**/BCP/LiF/Al device; the insert shows its LE–V (luminance efficiency $vs.$ voltage) characteristics.

Fig. 10 The power efficiency (P)–voltage (V)–luminance efficiency (LE) characteristics of the multi-layer device ITO/PEDOT/**TFB**/PBD/Alq$_3$/LiF/Al fabricated by spin-coating.

transporting layer. The luminance efficiency of the devices was enhanced greatly compared with that of the single-layer devices, which had a maximum luminance efficiency of 2.1 cd A^{-1} (0.80 lm W^{-1}). This efficiency was much higher than that of the vacuum evaporation devices, but the efficiency of the spin-coating devices rapidly dropped when the voltage increased. It was considered that Joule heat induced the morphological change of the **TFB** film because of the low T_g of **TFB**. Thus, the development of new directions that can lead to stabilization of the amorphous state of the oligomers is required. Further modifications of the oligomer structure are presently underway to improve the thermostability (*i.e.* increasing T_g). Above all, we have fabricated OLEDs from the oligomer both by vacuum evaporation and by the spin-coating technique, and as expected, the devices fabricated by the two different methods showed good character. The perfect behaviour in the optical and device properties can be attributed to extraordinarily low levels of intermolecular interaction, which is an outstanding property of this kind of TPV dimer. The good spectral properties and the flexible fabrication of devices indicate that **TFB** is a good candidate for blue light emitting device materials, especially after increase of its T_g through structural modification.

Conclusions

In summary, a novel PPV oligomer, **TFB**, with a biphenyl linkage center and fluorene end groups, has been synthesized. **TFB** exhibits strong blue fluorescence both in solution and the solid state, and a high-quality amorphous film of **TFB** for LED fabrication can be formed both by vacuum evaporation and solution spin-coating. The performances of the devices are fine and some of them are excellent; for example, the luminance efficiency can be up to 2.1 cd A^{-1}. We have therefore developed a new kind of blue light emitting material, which exhibits potential for luminescence-based applications, especially those requiring emission of pure blue light.

Acknowledgements

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