

Synthesis and Luminescence Property of 4,4'-Bis(2,2-di(4-fluorophenyl)vinyl)biphenyl for Organic Blue-Light-Emitting Diodes

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The novel fluorinated distyrylarylene, 4,4'-bis(2,2-di(4-fluorophenyl)vinyl)biphenyl (DFPVBi), was synthesized and fully characterized. The structure was confirmed with IR, ¹H NMR, ¹³C NMR, ¹⁹F NMR and MS analyses. Its electronic and photoluminescence properties were investigated by UV-Vis absorption, cyclic voltammetry and fluorescence spectroscopy. The energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are -5.77 and -2.75 eV, respectively. The electroluminescence properties of the organic light-emitting diode fabricated by DFPVBi were also studied. The device exhibits a pure blue emission peaked at 454 nm, which indicates a maximum luminance of 5872 cd/m² at 14.2 V and a maximum current efficiency of 2.82 cd/A at 10V, respectively.

Keywords fluorinated distyrylarylene, blue-light-emitting material, electroluminescence, electronic property

Introduction

Organic light-emitting diodes (OLEDs) have received considerable attention since the Kodak research team¹ introduced the first double layer device. For full-color OLED display applications, it is essential to deliver a set of primary red, green and blue emitters with high luminous efficiency for the reason that other colors of OLED may be obtained by using color-changing medium technique.²⁻⁴ In present OLEDs, blue emitters, either fluorescent or phosphorescent materials, both remain the weakest link in the development of OLEDs.^{5,6} Blue fluorescent materials have been widely studied for a long time. There are a number of stable blue-light-emitting materials, which can be roughly categorized into several major classes of compounds, namely, metal complexes,^{7,8} diarylanthracene,⁹⁻¹¹ distyrylarylene (DSA),¹²⁻¹⁴ fluorene,¹⁵⁻¹⁷ and pyrene.^{18,19} One of the blue light emitter DPVBi (4,4'-bis(2,2-diphenylvinyl)biphenyl) has received much attention since disclosed by Idemitsu in 1995.^{20,21} But it bears a lower melting point, limiting the application to doping techniques. In this paper, we designed and synthesized a fluorinated distyrylarylene compound, 4,4'-bis(2,2-di(4-fluorophenyl)vinyl)biphenyl (DFPVBi), as a blue-light-emitting material. There are several potential benefits by replacing C—H by C—F bonds,^{22,23} such as improving sublimation performance, enhancing the electron mobility and

modifying HOMO/LUMO levels.^{24,25} The electronic, photoluminescence (PL) and electroluminescence (EL) properties were fully characterized. The results indicate that DFPVBi is a competitive blue-light-emitting material in the OLED application.

Experimental

Materials and instruments

Bis(4-fluorophenyl)methanone was purchased from Changzhou Huashan Chemical Ltd Co. and 4,4'-bis(diethoxyphosphorylmethyl)biphenyl was from Hebei Xingyu Chemical Ltd Co. All chemical reagents were commercially available and used as received, except tetrahydrofuran (THF), which was dried by sodium thread.

The ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were obtained on a Bruker AV500 NMR spectrometer. The signals have been designated as follows: s (singlet), d (doublet), t (triplet) and m (multiplet). ¹H and ¹³C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference, and ¹⁹F chemical shifts from trifluoromethane (CHF₃).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out with a simultaneous thermogravimetry-differential scanning calorimetry (Netzsch STA 449C). A quadrupole mass spectrometer (Netzsch QMS 403C), which allows to

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identify gases released during heating, was coupled to the STA 449C calorimeter for gas analysis.

The UV-Vis and fluorescence spectra were obtained on a UNICO UV-2102PCS and Edinburgh-Instruments FLS920 spectrometer, respectively. MS data were determined on an HP-5989B mass spectrometer.

The infrared (IR) spectra of the compounds (in KBr pellets) were recorded on a Nicolet NEXUS 870 FT-IR spectrometer.

Cyclic voltammetry measurements were carried out in a conventional three-electrode cell using a platinum slice working electrode of 2 mm width, a platinum wire counter electrode of 1 mm diameter, and a Ag/AgCl reference electrode on a computer-controlled MCP-1 constant potentiometer at room temperature.

Synthesis of 4,4-bis(2,2-di(4-fluorophenyl)vinyl)biphenyl (DFPVBi)

In a 100 mL three-neck round-bottomed flask equipped with a mechanical stirrer, a thermometer and a condenser, bis(4-fluorophenyl)methanone (4.6 g, 0.022 mol) was added to the mixture of 4,4'-bis(diethoxyphosphorylmethyl)biphenyl (4.5 g, 0.01 mol), sodium hydride (NaH) (1.0 g, 0.04 mol) and 50 mL of THF. The mixture was heated at reflux for 2 h under being stirred. The reaction was continued till the starting material 4,4'-bis(diethoxyphosphorylmethyl)biphenyl was completely consumed, as monitored with TLC. After being cooled to room temperature, the reaction mixture was poured into ice water, adjusted with 1 mol·L⁻¹ hydrochloric acid till pH value approached 7 and filtrated. The filter cake was washed with water until the filtrate reached neutrality, and finally washed with methanol. The crude product was dried in vacuum and purified by recrystallization in toluene to give 5.0 g of DFPVBi with the purity of 99.4% (HPLC) in 85.9% yield. m.p. 224–225 °C. ¹H NMR (CD₃COCD₃, 500 MHz) δ: 7.06 (s, 2H), 7.10 (d, ³J=8.0 Hz, 4H), 7.09–7.13 (m, 4H), 7.15–7.19 (m, 4H), 7.21–7.24 (m, 4H), 7.34–7.40 (m, 4H), 7.46 (d, ³J=8.0 Hz, 4H); ¹³C NMR (CDCl₃, 126 MHz) δ: 115.18 (²J_{C-F}=21.38 Hz), 115.83 (²J_{C-F}=21.38 Hz), 126.36, 127.85, 129.20 (³J_{C-F}=7.92 Hz), 129.90, 132.09 (³J_{C-F}=7.92 Hz), 136.04 (⁴J_{C-F}=3.52 Hz), 136.19, 138.73, 139.34 (⁴J_{C-F}=3.02 Hz), 140.64, 161.43 (¹J_{C-F}=21.0 Hz), 163.40 (¹J_{C-F}=21.5 Hz); ¹⁹F NMR (CDCl₃, 470 MHz) δ: -114.52 (m, 1F), -114.09 (m, 1F); IR (KBr) ν: 3099, 3067, 3037, 1598, 1505, 836, 824 (aromatics); 3024, 809, 791 (ethylene bond), 1222 (C–F) cm⁻¹; MS (70 eV) *m/z* (%): 583 (M⁺+1, 43), 582 (M⁺, 100), 291 (15).

Fabrication of OLEDs and measurements of the EL characteristics

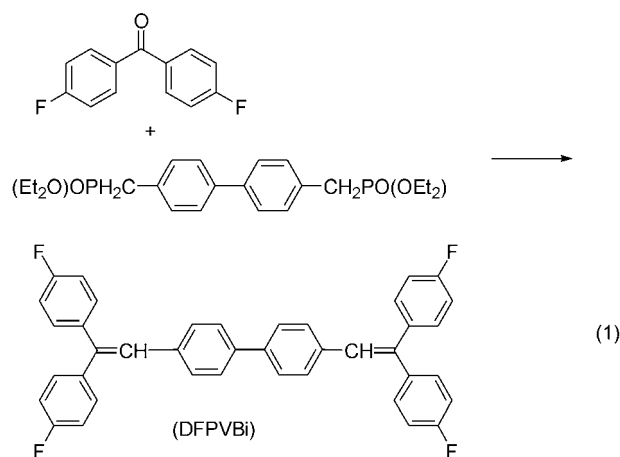
Indium tin oxide (ITO)-coated glass slides used as the substrates of the OLEDs were cleaned and exposed to oxygen plasma for 30 min. On each substrate, hole transporting material of *N,N'*-di-1-naphthyl-*N,N'*-diphenylbenzidine (NPB), blue-light-emitting material of DFPVBi, the electron transporting material of tris-

transporting material of tris-(8-quinolinolato)aluminum (AlQ₃) and the cathode of LiF-Al were successively deposited in turn by thermal evaporation in a vacuum chamber at *ca.* 210⁻⁴ Pa. The evaporating rate was kept at 0.2–0.3 nm/s for organic layers and 1 nm/s for the cathode, respectively. EL spectra were measured with a Hitachi MPF-4 fluorescence spectrophotometer. The data of the current-voltage-luminance (I-V-L) were measured with a 3645 dc power supply combined with a 1980A spot photometer. All measurements were carried out in air at room temperature.

Results and discussion

Synthesis and thermal property

The synthetic approach of the DFPVBi is outlined in Eq. (1). Using Wittig-Horner reaction catalyzed by NaH, bis(4-fluorophenyl)methanone reacted with 4,4'-bis(diethoxyphosphorylmethyl)biphenyl under reflux for 2–3 h in THF. The obtained yellowish-green solid was purified by recrystallization in good yield of 85.9%. The product was sublimated once before structural analysis. The sublimation of DFPVBi is obviously easier than that of DPVBi. The structure was confirmed by IR, ¹H NMR, ¹⁹F NMR, ¹³C NMR and MS techniques. Molecular ion of 582 and half molecular ion of 291 were obtained in the mass spectrum. There are two chemical shifts of -114.15 and -114.09 in ¹⁹F NMR spectrum which proves that two configurations of the fluorine atom in the DFPVBi molecule. Correspondingly there are two chemical shifts of 161.43 (¹J_{C-F}=21.0 Hz), 163.40 (¹J_{C-F}=21.5 Hz) in ¹³C NMR spectrum, which belongs to carbon atom bonded to the fluorine.



Thermogravimetric analysis shows (Figure 1) that DFPVBi and DPVBi lost 5% weight at 334 and 347 °C, respectively. No decomposition gases were detected in the QMS 403C mass spectrometer. This refers that the weight loss is due to volatilization, and DFPVBi is easier to volatilize than DPVBi. The DSC results indicate that the melting temperature of DFPVBi (224.6 °C) is higher than that of DPVBi (206.9 °C).

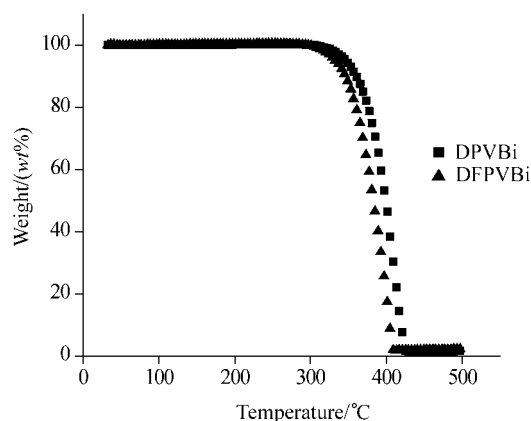


Figure 1 TGA data measured on STA 449 C calorimeter under dry argon at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

Electronic properties

The UV-Vis absorption and photoluminescence spectra were recorded in dilute CH_2Cl_2 solution at room temperature, as shown in Figure 2. The compound exhibits single absorption band peaked at 348 nm, and a fluorescence emission band peaked at 449 nm with a full width at half-maximum of 80 nm. From the onset of the absorption peak (410 nm), the optical band gap E_g ($E_g = 1240/\lambda_{\text{onset}}$) was determined to be 3.02 eV.

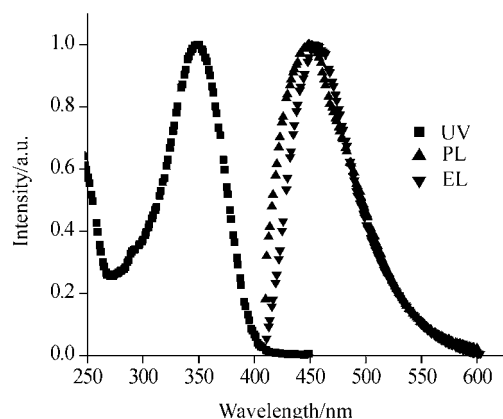


Figure 2 UV-Vis absorption and PL spectra of DFPVBi in dilute CH_2Cl_2 solution; the EL spectrum was measured on a device in configuration of ITO/NPB (40 nm)/DFPVBi (40 nm)/AIQ₃ (10 nm)/LiF (2 nm)/Al (200 nm).

Studies on the electrochemical behaviors are essential for understanding the redox properties of the molecule which are considered as an indicator of HOMO and LUMO levels.^{26,27} The solutions of DFPVBi ($0.5\text{ mmol}\cdot\text{L}^{-1}$) and Bu_4NClO_4 ($0.1\text{ mol}\cdot\text{L}^{-1}$) in $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$ were scanned on a cyclic voltammeter from -1500 to 1600 mV at a rate of 30 mV/s . In the anodic scan region, DFPVBi gave an irreversible wave with an oxidation peak at 1.45 V and an onset potential (E_{onset}) of 1.32 V . The ionization potential or HOMO level was determined by taking the ferrocene (HOMO level -4.8 eV) as a standard material and calculating with the onset

potential. During the process of anodic scan, ferrocene showed an onset at $+0.35\text{ V}$ against the reference electrode Ag^+/Ag . In our work, the energy level of the silver electrode derived from ferrocene was -4.45 eV relative to vacuum. The estimated HOMO level ($-E_{\text{onset}} - 4.45\text{ eV}$) and LUMO level ($E_{\text{HOMO}} + E_g$) of DFPVBi was -5.77 and -2.75 eV respectively. We have also measured the redox data of DPVBi and calculated its HOMO and LUMO energy levels. The HOMO and LUMO of DPVBi were measured to be -5.75 and -2.73 eV , respectively.

Electroluminescence properties

The blue-light-emitting diodes with the structure of ITO/NPB (40 nm)/DFPVBi (40 nm)/AIQ₃ (10 nm)/LiF (2 nm)/Al (200 nm) were constructed. Figure 3 shows the current-voltage and luminance-voltage characteristics.

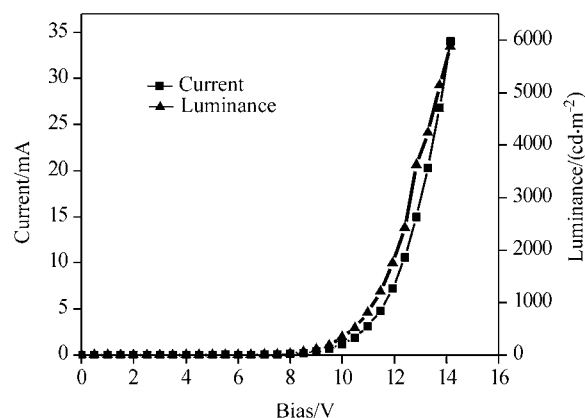


Figure 3 The current-voltage and luminance-voltage characteristics of the device ITO/NPB (40 nm)/DFPVBi (40 nm)/AIQ₃ (10 nm)/LiF (2 nm)/Al (200 nm).

The electroluminescence emission peak is at 454 nm , which has a slight bathochromic shift compared to the PL one (Figure 1). The EL emission has a narrow peak with a full width at half-maximum of 67 nm . The device gave an optimum efficiency of 2.82 cd/A at the bias of 10 V , which reached the maximum brightness up to 5872 cd/m^2 at the bias of 14.2 V . A comparing device fabricated by DPVBi with the same process and structure, gave an optimum current efficiency of 2.28 cd/A at 10.5 V , which reached the maximum brightness of 4397 cd/m^2 at 13.1 V .

The EL spectra of the device are nearly the same under various biases, indicating that the recombination zone of holes and electrons is independent of the forward biases because the blue emitter used the thicker neat film, which differed from other guest-host blue systems and there would be balance carrier injection and transport in the device structure based on DFPVBi.

In conclusion, we have shown a facile approach for the synthesis of a fluorinated distyrylarylene DFPVBi by Wittig-Horner reaction in a good yield. Its electronic,

photoluminescence and electroluminescence properties were also presented along with those of DPVBi. The absorption spectrum shows a sharp peak at 348 nm in CH₂Cl₂, and the PL spectrum peaks at 449 nm. Cyclic voltammetry results of DFPVBi indicate that its oxidation potential is at 1.45 V. The device based on DFPVBi emits blue light peaked at 454 nm with the maximum luminance up to 5872 cd/m² at 14.2 V and maximum luminescence efficiency up to 2.82 cd/A under the bias of 10 V. The EL characteristics have been obviously improved compared to DPVBi. The novel blue light emitter presents high melting point which would extend the operation lifetime of the related OLEDs.

References

- 1 Tang, C. W.; Vanslyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.
- 2 Li, Y.; Fung, M. K.; Xie, Z.; Lee, S. T.; Hung, L. S.; Shi, J. *Adv. Mater.* **2002**, *14*, 1317.
- 3 Hosokawa, C.; Eida, M.; Matsuura, M.; Fukuoka, K.; Nakamura, H.; Kusumoto, T. *Synth. Met.* **1997**, *91*, 3.
- 4 Hosokawa, C.; Toshion, S.; Fukuoka, K.; Tokailin, H. *SID 2001 Digest*, San Jose, CA, **2001**, 522.
- 5 Wen, S. W.; Lee, M. T.; Chen, C. H. *IEEE/OSA J. Display Technol.* **2005**, *1*, 90.
- 6 Kan, Y.; Wang, L.; Duan, L.; Hu, Y.; Wu, G.; Qiu, Y. *Appl. Phys. Lett.* **2004**, *84*, 1513.
- 7 Tao, X. T.; Suzuki, H.; Wada, T. *J. Am. Chem. Soc.* **1999**, *121*, 9447.
- 8 (a) Chai, S. Y.; Zhou, R.; An, Z. W.; Kimura, F. A. K.; Matsuura, M. *Thin Solid Films* **2005**, *479*, 282.
(b) Li, Y.; Liu, Y.; Bu, W.; Lu, D.; Wu, Y.; Wang, Y. *Chem. Mater.* **2000**, *12*, 2672.
- 9 Shi, J.; Tang, C. W. *Appl. Phys. Lett.* **2002**, *80*, 3201.
- 10 Tao, S.; Xu, S.; Zhang, X. *Chem. Phys. Lett.* **2006**, *429*, 622.
- 11 Tao, S.; Hong, Z.; Peng, Z.; Ju, W.; Zhang, X.; Wang, P.; Wu, S.; Lee, S. *Chem. Phys. Lett.* **2004**, *397*, 1.
- 12 Hosokawa, C.; Higashi, H.; Nakamura, H.; Kusumoto, T. *Appl. Phys. Lett.* **1995**, *67*, 3853.
- 13 Tokailin, H.; Higashi, H.; Hosokawa, C. *US 5130603*, **1992** [*Chem. Abstr.* **1992**, 12956].
- 14 Hosokawa, C.; Tokailin, H.; Higashi, H. *J. Appl. Phys.* **1995**, *78*, 5831.
- 15 Saitoh, A.; Yamada, N.; Yashima, M.; Okinaka, K.; Senoo, A.; Ueno, K.; Tanaka, D.; Yashiro, R. *Proc. Soc. Inf. Display*, Seattle, WA, **2004**, p. 150.
- 16 Zhang, Y.; Cheng, G.; Zhao, Y.; Hou, J.; Liu, S. *Appl. Phys. Lett.* **2005**, *87*, 241112.
- 17 Wu, C. C.; Lin, Y. T.; Chiang, H. H.; Cho, T. Y.; Chen, C. W. *Appl. Phys. Lett.* **2003**, *81*, 577.
- 18 Yeh, C. C.; Lee, M. T.; Chen, H. H.; Chen, C. H. *Proc. Soc. Inf. Display*, Seattle, WA, **2004**, p. 788.
- 19 Xing, Y.; Xu, X.; Zhang, P.; Tian, W.; Yu, G.; Lu, P.; Liu, Y.; Zhu, D. *Chem. Phys. Lett.* **2005**, *408*, 169.
- 20 Hosokawa, C.; Sakamoto, S.; Kusumoto, T. *U. S. Patent 5,389,444*, **1995** [*Chem. Abstr.* **1995**, *120*, 177613].
- 21 Hung, L. S.; Chen, C. H. *Mater. Sci. Eng., R.* **2002**, *39*, 143.
- 22 (a) Grushin, V. V.; Herron, N.; LeCloux, D. D.; Marshall, W. J.; Petrov, V. A.; Wang, Y. *Chem. Commun.* **2001**, 1494.
(b) Shi, Y. W.; Shi, M. M.; Huang, J. C.; Chen, H. Z.; Wang, M.; Liu, X. D.; Ma, Y. G.; Xu, H.; Yang, B. *Chem. Commun.* **2006**, 1941.
- 23 McCoy, R. K.; Karasz, F. E.; Sarker, A.; Lahti, P. M. *Chem. Mater.* **1991**, *3*, 941.
- 24 Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.
- 25 Gurge, R. M.; Sarker, A. M.; Lahti, P. M.; Hu, B.; Karasz, F. E. *Macromolecules* **1997**, *30*, 8286.
- 26 Eckhardt, H.; Shacklette, L. W.; Jenk, Y. *J. Chem. Phys.* **1989**, *91*, 1303.
- 27 Xiang, N. J.; Lee, T. H.; Leung, L. M.; So, S. K.; Shi, J. X.; Gong, M. L. *Acta Chim. Sinica* **2006**, *64*, 1157 (in Chinese).

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