

Synthesis and Properties of A Novel Triphenylamine Derivative

Qing XU, Hong Zheng CHEN*, Jing Zhi SUN, Mang WANG*

Department of Polymer Science and Engineering, State Key Lab of Silicon Materials,
Zhejiang University, Hangzhou 310027

Abstract: A novel triphenylamine derivative of 4, 4'-bis-[2-[4-[N, N-bis-(4-methoxyphenyl-amino)] phenyl-1-yl]-vinyl-1-yl]-1, 1'-biphenyl (DMPAVBI) was synthesized. The chemical structure was confirmed by IR, ¹H NMR spectroscopy and elemental analysis. Its properties were studied by UV-Vis spectroscopy, photoluminescence spectroscopy and cyclic voltammetry methods.

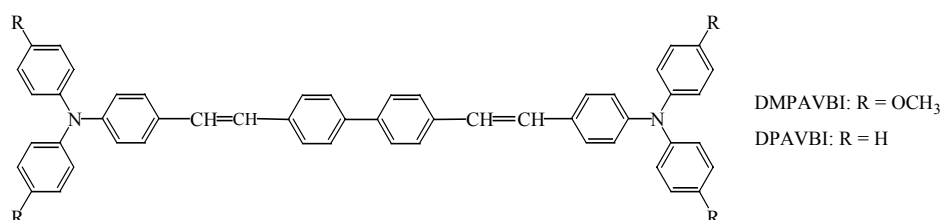
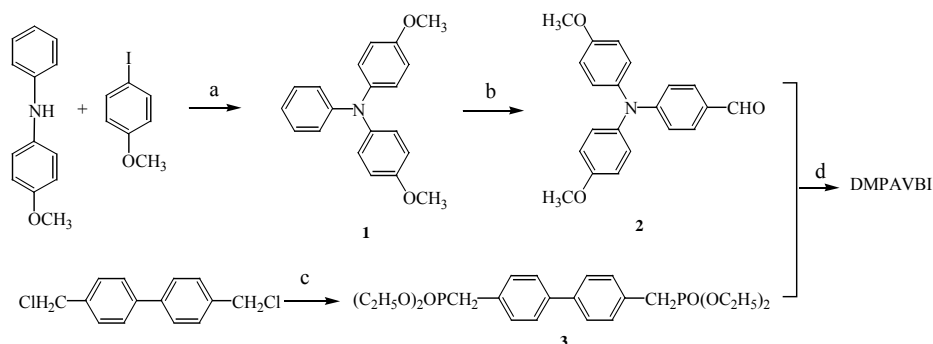
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Organic light-emitting diodes (OLEDs) based on multi-layers of low molecular weight organic materials have attracted much attention because of their great potential applications in full color flat-panel display^{1,2}. In the simplest bilayer configuration, an OLED consists of one electron transport layer and one hole transport layer³. The organic hole transport material is either in the form of a π -conjugated polymer⁴ or an electron-rich triarylamine derivative⁵. The OLED application requires the necessary material properties like high hole-transport mobility, high fluorescence efficiency, thermal stability, non-crystallinity or amorphous film-forming nature and electrochemical reversibility in addition to high electronic-grade material purity. Based on π -conjugated polymers and triarylamine derivatives, we designed 4, 4'-bis-[2-[4-[N, N-bis-(4-methoxy-phenylamino)] phenyl-1-yl]-vinyl-1-yl]-1, 1'-biphenyl (DMPAVBI) (**Figure 1**). It is expected that DMPAVBI is oligomeric triphenylamine, it could be easy to purified; DMPAVBI contains π -conjugated bonds and two triphenylamine groups, it could have high hole-transport mobility and good electroluminescent property; DMPAVBI contains four methoxy groups, it could have good solubility.

The preparation of the triphenylamine derivative is sketched in **Scheme 1**.

Compound **1** was obtained by Ullmann reaction. 4-Methoxydiphenylamine (2.19 g, 11 mmol), 1-methoxy-4-iodobenzene (2.34 g, 10 mmol), copper powder (0.64 g, 10 mmol), potassium carbonate (1.38 g, 10 mmol) and 18-crown-6 (0.26 g, 1 mmol) in o-dichlorobenzene (3 mL) were put into a 50 mL three-neck flask. The mixture was reacted under nitrogen at 210°C for 24 h. The product was purified by column chromatography with silica gel to yield **1** (2.74 g, 90%). Data for **1**: IR (KBr, cm⁻¹): 2950, 2833, 1594, 1505, 1317, 1267, 1241, 1179, 1036, 829, 750, 696. Elemental Anal.: Calcd. for C₂₀H₁₉NO₂: C 78.69; H 6.23; N 4.59; found: C 78.82; H 6.20; N 4.80.

* E-mail: hzchen@zju.edu.cn, mwang@zju.edu.cn

Figure 1 Molecular structures of DMPAVBI and DPAVBI.**Scheme 1** Synthetic route of DMPAVBI

Reagents and conditions: (a) Cu, K₂CO₃, 18-crown-6, *o*-dichlorobenzene, 210 °C, 24 h, N₂ (b) (i) POCl₃, DMF, 55 °C, 6 h, N₂ (ii) NaOH, H₂O, 0 °C, 1 h (c) P(OC₂H₅)₃, 150 °C, 4 h, N₂ (d) CH₃ONa, DMF, room temperature, 24 h, N₂.

Compound **2** was prepared by Vilsmeier-Haack reaction. **1** (1.53 g, 5 mmol), POCl₃ (1.37 mL, 15 mmol) and dried DMF (13.5 mL) were put into a 50 mL flask. The reaction solution was stirred for 1 hour at 0 °C under nitrogen. Next, the solution was heated to 55 °C and stirred for 6 h, cooled, 20% NaOH solution was added until pH ≈ 7, and stirred for 1 hour, poured to H₂O (200 mL). The mixture was filtered and purified by column chromatography with silica gel to provide **2** (1.18 g, 71%) as yellow solid. Data for **2**: IR (KBr, cm⁻¹): 2953, 2835, 2741, 1687, 1593, 1505, 1131, 1294, 1243, 1160, 1033, 826. Elemental Anal.: Calcd. for C₂₁H₁₉NO₃: C 75.68; H 5.71; N 4.20; found: C 75.80; H 5.75; N 4.15.

Compound **3** was obtained by Michaelis-Arbusov reaction. Triethyl phosphate (34 mL, 0.2 mol) and 4, 4'-dichloromethyl-diphenyl (5 g, 20 mmol) were put into a 100 mL flask. This was heated and stirred at 150 °C for 4 h under nitrogen. The solution was cooled. This was recrystallized three times to yield **3** (7.8 g, 86%). Data for **3**: IR (KBr, cm⁻¹): 2982, 2907, 1504, 1390, 1238, 1161, 1060, 1023, 960, 861, 823, 766. Elemental Anal.: Calcd. for C₂₂H₃₂P₂O₆: C 58.15; H 7.05; found: C 58.11; H 7.00. DMPAVBI was prepared by Wittig-Horner reaction. **2** (1 g, 3 mmol), **3** (0.55 g, 1.2 mmol) and CH₃ONa (0.38 g) and dried DMF (2 mL) were put into a 50 mL flask. The reaction solution was stirred with a magnetic stirrer for 0.5 h at 0 °C in nitrogen gas atmosphere. Next, the reaction was stirred at room temperature for 24 h. The product was purified by column

Figure 2 UV-Vis absorption spectra (dotted line) of DMPAVBI in 1, 2-dichloroethane, and photoluminescence spectra of DMPAVBI in 1, 2-dichloroethane (broken line) and in film (solid line) (excited at 380 nm).

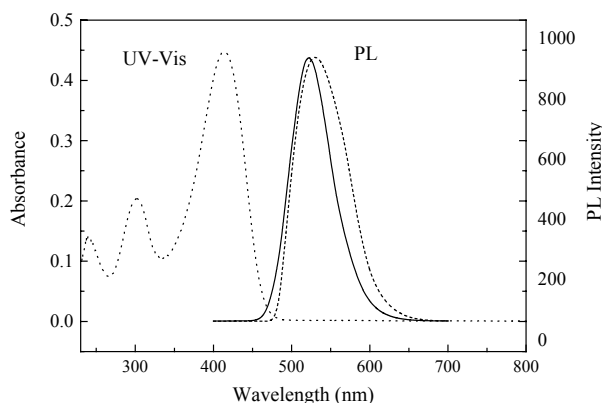
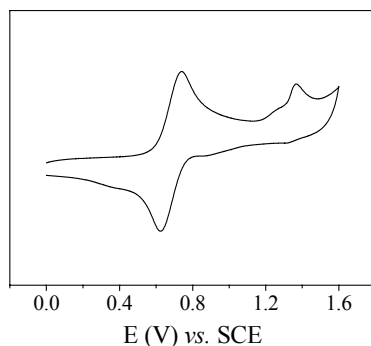


Figure 3 Cyclic voltammogram of DMPAVBI in 1, 2-dichloroethane (1 mmol/L) with 0.1 mol/L $(C_4H_9)_4NClO_4$ at room temperature.



chromatography with silica gel and washed with hot CH_3OH to yield DMPAVBI (0.63 g, 65%) of a yellow solid. Data for DMPAVBI: IR (KBr, cm^{-1}): 3025, 2951, 2833, 1596, 1504, 1319, 1280, 1241, 1177, 1035, 965, 826. 1H NMR ($CDCl_3$, 500 MHz, δ ppm): 3.80(s, 12H), 6.82-6.98(m, 14H), 7.06 (s, 10H), 7.34(d, 4H, $J=8.6$ Hz), 7.55 (d, 4H, $J=8.3$ Hz), 7.59 (d, 4H, $J=8.3$ Hz). Elemental Anal.: Calcd. For $C_{56}H_{48}N_2O_4$: C 82.76; H 5.91; N 3.45; found: C 82.46; H 6.09; N 3.20.

The introduction of methoxy groups in the benzene rings results in good solubility. DPAVBI (**Figure 1**) has poor solubility in common solvents. On the contrary, DMPAVBI has good solubility in common organic solvents such as chloroform, THF, ethyl acetate, 1, 2-dichloroethane, dichloromethane, and DMF, *etc.*

Figure 2 shows the UV-Vis absorption spectra of DMPAVBI in 1, 2-dichloroethane and photoluminescence (PL) spectra of DMPAVBI in 1, 2-dichloroethane and in film at room temperature. Three absorption bands at 414, 302, and 240 nm can be observed; the

absorption bands at 414 nm can be attributed to electronic π - π^* transition of conjugated backbone. The absorption edge can be seen around 484 nm. The band gap, e.g., is estimated from the absorption edge as -2.56 eV. The PL spectra of DMPAVBI both in solution and film are almost identical, and their maximum peaks appear at 522 nm, corresponding to green light emissions. These results indicated that DMPAVBI is an efficient emissive material.

Cyclic voltammetry (CV) was carried out in order to obtain information about the electrochemical stability and the reversibility of the redox process of DMPAVBI. **Figure 3** shows the cyclic voltammograms for the anodic oxidation of DMPAVBI (Working electrode: platinum plate; counter electrode: platinum wire; reference electrode: standard calomel electrode, SCE. Scan rate: $50 \text{ mV}\cdot\text{S}^{-1}$). DMPAVBI showed two chemical reversible oxidation and reduction peaks of $E_{\text{OX}}(1)=0.74$ and $E_{\text{OX}}(2)=1.37$ V, and the corresponding reduction peaks appeared at 0.63 and 1.30 V. The oxidative process started at 0.46 V. The energy level of the highest occupied molecular orbital (HOMO), E_{HOMO} , can be estimated from the oxidative onset potential to be -5.2 eV^5 . The E_{HOMO} of DPAVBI is -5.4 eV , which referred to the previous paper⁶. The introduction of methoxy groups in the benzene rings results in higher E_{HOMO} , which is favorable for hole injection and transport. The energy level of the lowest unoccupied molecular orbital (LUMO), E_{LUMO} , can be estimated by subtracting E_{g} from E_{HOMO} as determined by the electrochemistry. This leads to an estimate of E_{LUMO} of -2.64 eV .

In summary, the novel compound 4, 4'-bis-[2-[4-[N, N-bis-(4-methoxyphenyl-amino)] phenyl-1-yl]-vinyl-1-yl]-1, 1'-biphenyl (DMPAVBI) with good solubility, which is necessary for opto-electronic devices, was designed and synthesized. The electronic structure and photoluminescent properties of DMPAVBI suggested that this type of compounds could become promising new material for OLED application.

Acknowledgments

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