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Synthesis, Characterization and Properties of a Novel Triphenylamine Substituted Oligo(phenylene vinylene)

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A novel hole transport material of triphenylamine-substituted oligo(phenylene vinylene) of 4,4'-*bis*-[2-[4-[N,N-*bis*-(4-bromophenyl-amino)]-phenyl-1-yl]-vinyl-1-yl]-1,1'-biphenyl was synthesized. Its molecular structure was characterized by FTIR and ^{1}H NMR spectra as well as elemental analyses. Its spectroscopic and electrochemical properties were measured. The dual-layer photoreceptors taking oxotitanium phthalocyanine as the charge generation material and the compound as the charge transport material were fabricated, whose photosensitivity was 1.11 cm^2 μJ^{-1} at 762 nm, 1.6 times higher than that from N,N'-diethyl-4-aminobenzaldehyde-1-phenyl-1'-(α-naphthyl)hydrazone as charge transport material. This indicates that the triphenylamine substituted oligo(phenylene vinylene) compound may be a promising candidate for application in optoelectronic devices.

Key Words: Triphenylamine, Oligo(phenylene vinylene), Synthesis, Hole transport.

INTRODUCTION

Recently, there is increasing interest in triphenylamine substituted oligo(phenylene vinylene)s because of their applications in optoelectronic devices such as organic light emitting diodes (OLEDs), organic photoreceptors and organic solar cells[1-4]. The important feature of these applications is the development of suitable materials having excellent properties like hole transport property in combination with processability, electrochemical stability and transparency. To develop such materials, introduction of halogen substituents into the skeleton has been reported as an effective way[5,6]. However, there have been few studies of brominated triphenylamine substituted oligo(phenylene vinylene). In order to search for new triphenylamine substituted oligo(phenylene vinylene) with good hole transport property, herein, the synthesis, characterization and properties of 4,4'-*bis*[2-[4-[N,N-*bis*(4-bromophenylamino)]-phenyl-1-yl]-vinyl-1-yl]-1,1'-biphenyl (Fig. 1) are reported.

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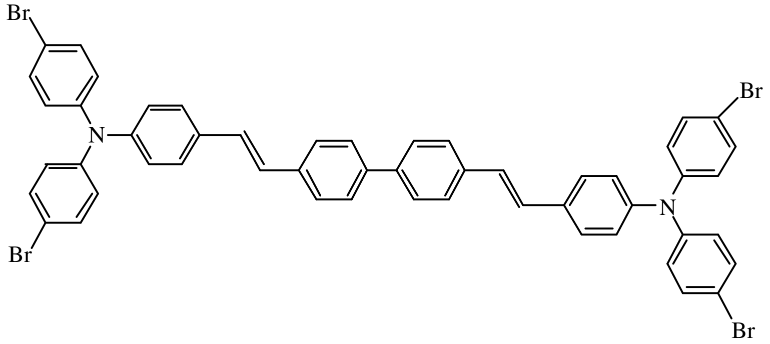

Fig. 1. Molecular structure of 4,4'-*bis*[2-[4-[N,N-*bis*(4-bromophenylamino)]phenyl-1-yl]-vinyl-1-yl]-1,1'-biphenyl

EXPERIMENTAL

Oxotitanium phthalocyanine (TiOPc) was prepared and purified in our laboratory according to earlier method[7]. N,N'-diethyl-4-aminobenzaldehyde-1-phenyl-1'-(α-naphthyl)hydrazone (BAH) was commercially available and recrystallized before use. Acetonitrile was purchased from Merck and freshly distilled over P_2O_5 before use. Other reagents were commercially available and used as received.

FTIR spectra were recorded on a VA 360 spectrophotometer in KBr pellet. ^1H NMR spectra were measured on a Bruker Avance 400/500 DMX spectrometer with TMS as an internal standard in $CDCl_3$. Elemental analyses were obtained on an EA 1110 elemental analyzer. Melting points were measured by a Yanaco micro melting point apparatus. UV-vis spectra were taken on a Lambda 20 spectrometer. Photoluminescence (PL) spectra were recorded on a Shimadzu RF-540 spectrofluorimeter. Cyclic voltammetry (CV) measurements were carried out on a CHI600A electrochemical workstation, using millimolar solutions in CH_3CN containing 0.1 mol L^{-1} supporting electrolyte of tetrabutylammonium perchlorate in a three-electrode cell, the saturated calomel electrode (SCE) was taken as reference electrode and the scanning rate was 50 mV s^{-1}. Photoconductivity measurements were carried out by using the photoinduced xerographic discharge technique on a GDT-II model photoconductivity measuring device.

Preparation of N-(4-formylphenyl)diphenylamine (1): Triphenylamine (4 g; 16.4 mmol) and $POCl_3$ (4 mL; 44 mmol) were dissolved in 40 mL of dried DMF under nitrogen atmosphere. The reaction solution was stirred at 0 °C for 1 h, then was reacted at 90 °C for 12 h. After the solution was cooled to room temperature, 20 % NaOH solution was added until pH-7. The mixture was stirred for 1 h and was poured into H_2O (160 mL). The mixture was filtered and purified by column chromatography with silica gel (ethyl acetate/petroleum ether = 1/20 v/v) to provide **1** as yellow powder (3.12 g, 70 %). Data for **1**: FTIR (KBr, cm^{-1}): 1689 ν(C=O), 1584 and 1487 ν(C-C), 1330 ν(C-N), 825 δ(C-H), 756 and 700 δ(C-H). Elemental analysis calculated for $C_{19}H_{15}NO$ (m.w. 273): C, 83.42; H, 5.49; N, 5.12. Found: C, 83.24; H, 5.75; N, 5.15.

Preparation of 4-aldehyde-4',4''-dibromotriphenylamine[8] (2): N-(4-formyl phenyl)diphenylamine (**1**) (2.2 g; 8 mmol) was dissolved in 80 mL of methylene chloride and bromine (0.832 mL; 16 mmol) was added with vigorous stirring at room temperature. The mixture was stirred at room temperature for 12 h and then was reacted at 35 °C for 3 h. After the mixture was cooled to room temperature, the mixture was poured into large excess 1 mol L^{-1} potassium hydroxide solution. The methylene chloride layer was then separated. After methylene chloride was removed by distillation using a rotary evaporator, the product was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20 v/v) to yield **2** of a yellow solid (2.78 g, 80 %). Data for **2**: FTIR (KBr, cm^{-1}): 1685 ν(C=O), 1577 and 1486 ν(C-C), 1072 ν(C-Br), 825 δ(C-H). Elemental analysis calculated for $C_{19}H_{13}NOBr_2$ (431): C, 52.93; H, 3.04; N, 3.25. Found: C, 53.33; H, 3.33; N, 3.01.

Preparation of 4,4'-*bis*(diethoxyphosphonomethyl)biphenyl (3): 4,4'-Dichloromethyl diphenyl (5 g, 20 mmol) and triethyl phosphate (34 mL, 200 mmol) was heated and stirred at 150 °C for 4 h under nitrogen atmosphere. The excess triethyl phosphate was removed by filtration of the hot reaction mixture and the residue was recrystallized from ethyl acetate/petroleum ether (1/3 v/v) for three times to yield **3** of a white solid (7.81 g, 86 %). Data for **3**: FTIR (KBr, cm^{-1}): 1238 ν(P=O), 1023 ν(P-O-C), 823 δ(C-H). Elemental analysis calculated for $C_{22}H_{32}O_6P_2$(454): C, 58.15; H, 7.05. Found: C, 58.11; H, 7.00.

Preparation of the title compound (4): At 0 °C **2** (2.37 g; 5.5 mmol), **3** (1.25 g; 2.7 mmol) and CH_3ONa (0.45 g) were dissolved in dried DMF (10 mL) under nitrogen atmosphere. After stirring for 0.5 h, the mixture was stirred at room temperature for 10 h. Then the product was washed with hot CH_3OH and further purified by silica gel column chromatography using toluene as eluent to yield 4 of a yellow solid (2.21 g, 80 %; m.p. = 219-221 °C). Data for **4**: FTIR (KBr, cm^{-1}): 3028 ν(C-H), 1583 and 1507 ν(C-C), 1311 ν(C-N), 1072 ν(C-Br), 962 δ(*trans*-vinylene C-H), 822 δ(C-H). ^1H NMR ($CDCl_3$, 500 MHz, δ ppm): 7.61-7.63 (d, 4H, *J* = 8.3 Hz), 7.56-7.57 (d, 4H, *J* = 8.3 Hz), 7.35-7.43 (m, 12H), 6.96-7.12 (m, 16H). Elemental analysis calculated for $C_{52}H_{36}N_2Br_4$ (1008): C, 61.93; H, 3.60; N, 2.78. Found: C, 61.78; H, 3.60; N, 2.73.

Photoconductivity measurements: Photoconductivity was studied in function separated dual-layer photoreceptors. The photoreceptors were made by coating the charge generation layer (CGL) and the charge transport layer in turn on an aluminum substrate. The 1 μm thick charge generation layer was formed from the dichloroethane slurry containing 50 wt % oxotitanium phthalocyanine (TiOPc) in a polyvinyl butyral matrix. The charge transport layer consisted of 50 wt % the title compound or N,N'-diethyl-4-aminobenzaldehyde-1-phenyl-1'-(α-naphthyl)hydrazone (BAH) in polycarbonate matrix; its thickness was 25 μm. Photoconductive measurements were carried out by using the photoinduced xerographic discharge technique. The photoconductivities were evaluated by their photoinduced discharge curves under illumination of monochromatic lights with different wavelengths, where the time from the original surface potential to half under illumination ($t_{1/2}$) was obtained. In the measurement, the surface of the double-layered device was negatively charged in the dark and the intensity of exposure light (I) was tuned at 3 μW cm^{-2}. The photosensitivity (S) is defined as $(t_{1/2}\ I)^{-1}$. A good desired photoreceptor should have a large S value.

RESULTS AND DISCUSSION

The synthetic route of the title compound is shown in Fig. 2. N-(4-formylphenyl) diphenylamine (**1**) was synthesized by a Vilsmeier-Haack formylation of triphenylamine using the DMF/$POCl_3$ complex, which was then changed to 4-aldehyde-4',4''-dibromotriphenylamine (**2**) by a bromination using Br_2 in methylene chloride. 4,4'-*Bis*(diethoxyphosphonomethyl)biphenyl (**3**) was synthesized by Michaelis-Arbuzov reaction. The title compound was obtained by a Wittig-Horner reaction of **2** and **3**.

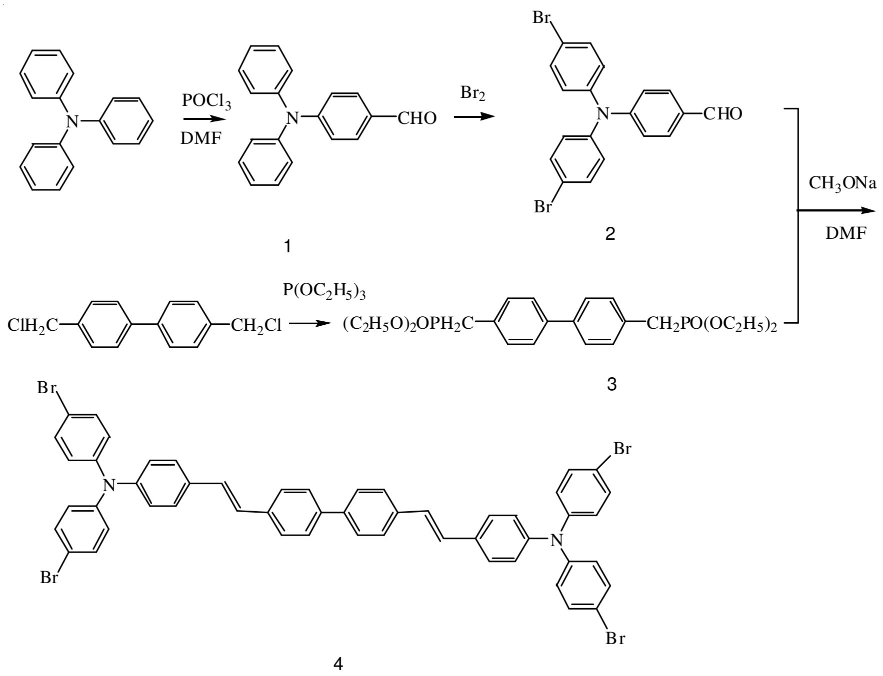

Fig. 2. Synthetic route of the title compound

The molecular structure of the title compound was verified by FTIR, ^1H NMR spectra and elemental analyses. It has good solubility in common organic solvents, such as chloroform, tetrahydrofuran, 1,2-dichloroethane, dichloromethane, toluene, DMF, *etc*. For example, the maximum solubility of the title compound in tetrahydrofuran at room temperature was several per cent (wt %). Therefore, its films can be easily formed from its solution, which is necessary for optoelectronic devices fabrication from wet processing.

Spectroscopic properties: UV-vis absorption spectra of the title compound in chloroform are shown in Fig. 3 (curve 1). It has three absorption peaks around 241, 318 and 395 nm, where the peak at 395 nm is caused by the π-π* transition of the conjugated system. The band gap (Eg) of the title compound is estimated to be 2.73 eV from the absorption edge of 455 nm[9,10]. It can emit intense blue fluorescence under the irritation of UV light of wavelength 343 nm. Fig. 3 also shows the PL spectra (curve 2) of the title compound in chloroform solution. It shows emission with a maximum at 460 nm.

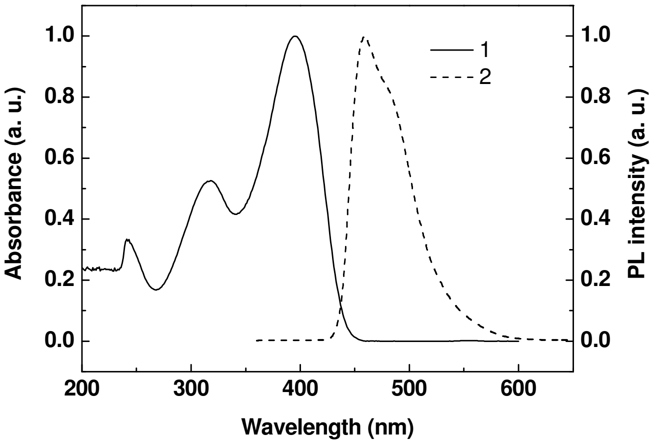

Fig. 3. UV-vis absorption spectra (1) and PL spectra (2) (excited at 343 nm) of the title compound in chloroform

Cyclic voltammetry: The electrochemical stability and the reversibility of the redox process of the title compound were studied by cyclic voltammetry (CV). Fig. 4 shows its cyclic voltammogram in CH_3CN. It exhibits a chemically reversible oxidation and reduction peak of $E_{OX} = 1.17$ V (*vs.* SCE). The oxidative process starts at 0.81 V. The energy level of the highest occupied molecular orbital (HOMO), E_{HOMO}, can be calculated from the oxidative onset potential to be -5.55 eV[11,12]. The energy level of the lowest unoccupied molecular orbital (LUMO), E_{LUMO}, can be estimated by subtracting Eg from E_{HOMO} as determined by the electrochemistry[13]. This leads to an estimation of E_{LUMO} to be -2.82 eV for the title compound. It is electrochemically stable, for the same redox potentials are observed for repeated cycles of redox processes. Such a behaviour is very important for organic photoreceptor and OLED which require stable hole transport ability.

Photoconductive property: In order to investigate the hole transport property of the title compound, the photoconductivity was studied in dual-layer photoreceptors, where TiOPc acted as the charge generation material and the title compound or BAH acted as the charge transport materials. Fig. 5 presents the effect of illumination wavelength on photosensitivity of the photoreceptors from the title compound and

BAH, respectively. It is find that, at the same illumination wavelength, the photoreceptors from the title compound show higher photosensitivity (S) than that from BAH does. Taking 762 nm for example, the photosensitivity value of the title compound is 1.11 cm^2 μJ^{-1}, whereas, that of BAH is 0.68 cm^2 μJ^{-1}, indicating the title compound has better hole transport property than BAH does. BAH has been proved to be a good hole transport material and is generally used as charge transfer material in photoreceptors for copiers and laser printers[14]. This indicates that the title compound may be a promising candidate for application in organic photoreceptors.

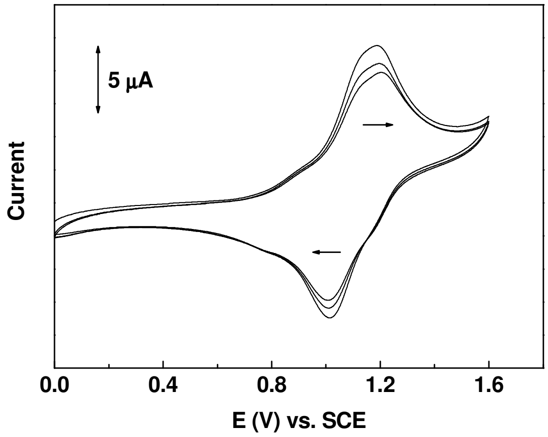

Fig. 4. Cyclic voltammograms of the title compound in CH_3CN with 0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ at room temperature. Working electrode: platinum plate; counter electrode: platinum wire; reference electrode: standard calomel electrode, SCE. Scan rate: 50 mV s^{-1}

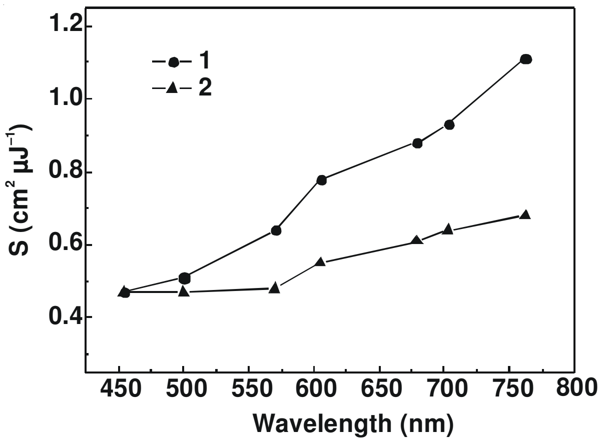

Fig. 5. Effect of illumination wavelength on photosensitivity of the photoreceptors from the title compound (**1**) and BAH (**2**), respectively. Light intensity of the exposure (I): 3 μW cm^{-2}

Conclusion

Novel triphenylamine substituted oligo(phenylene vinylene) with good processability and electrochemical stability, which are necessary for optoelectronic devices, was successfully synthesized. The title compound has better hole transport property than BAH, a common good hole transport material, suggesting a promising application in optoelectronic devices.

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