



Ultra-wide bandgap organic acceptor material and its application in organic UV photodetector



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ABSTRACT

Two fluorene derivatives, 2-(1,1':3',1''-triphenyl-5'-yl)-9,9-diphenyl-9H-fluorene (TPF) and (9,9-diphenyl-9H-fluorene-2-yl)diphenylphosphine oxide (DFPPO) with wide bandgap and good thermal stability were synthesized. The electron mobility of DFPPO is 5 times higher than that of TPF because of the introduction of the electron-withdrawing diphenylphosphine oxide group. The planar heterojunction organic ultraviolet photodetectors (UVDs) were fabricated by applying TPF or DFPPO as electron acceptor, 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT) as donor. The UVDs with structure of ITO/PEDOT:PSS/C8-BTBT/DFPPO/LiF/Al presented higher ultraviolet response compared to the TPF based counterpart. Corresponding dark to light current ratio and higher sensitivity is about 179 and 0.69 mA/W under illumination of 1 mW/cm² 365 nm UV light and bias of −0.5 V.

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1. Introduction

During the past decades, organic ultraviolet photodetectors (UVDs) have attracted much attention due to their advantages of light weight, easy processing and low cost of fabrication compared to their inorganic counterparts, as well as their potential application area including solar astronomy, missile plume detection, space-to-space transmission, sterilization monitors and so on [1–11]. Organic small molecules [12–18] and polymers [19–22] have been proved to be alternative candidates for the active layer of the UVDs. Small molecules are more attractive because their structure can be designed to control the conjugation length of the molecule and the bandgap [23,24], which favor the spectral selective detection of UV signals in various regions.

Several kinds of organic small molecules including TPBi [15], BCP [25], Bphen [26] and PBD [27] were selected to act as acceptor to construct the active layer of the UVDs. The bandgaps of these materials are in the region from 3.0 eV to 3.5 eV, so the cutoff wavelength of the response spectra of the UVDs can be tuned from 400 nm to 350 nm. Li and co-workers reported that the silane-containing triazine derivative, NSN, with wide bandgap of 3.8 eV, can be used as acceptor to fabricate UVDs sensitive to UV signals with wavelength shorter than 350 nm [28]. Up to now, the organic

acceptor material with bandgap wider than 3.5 eV is still limited, which blocks the development of the organic UVDs with selective sensitivity to deep UV signals.

In this study, in order to obtain organic acceptor material with bandgap wider than 3.5 eV, we designed and synthesized two new molecules, 2-(1,1':3',1''-triphenyl-5'-yl)-9,9-diphenyl-9H-fluorene (TPF) and (9,9-diphenyl-9H-fluorene-2-yl)diphenylphosphine oxide (DFPPO), because of the promising charge transporting property for fluorene-based molecules [17]. The influence of different lateral group, diphenylphosphine oxide and diphenylbenzene, on LUMO/HOMO level and electron transport property was studied. 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT) was selected to act as donor because of the excellent hole transport ability [29–31]. Ultraviolet photodetector with structure of ITO/PEDOT:PSS/C8-BTBT/TPF(DFPPO)/LiF/Al was fabricated. The sensitive UV response to 365 nm UV light proves the feasibility of applying organic semiconductor with ultra-wide bandgap as the acceptor part in the active layer of the UVDs.

2. Experimental

2.1. Materials

2-bromo-9,9-diphenyl-9H-fluorene and 3,6-diphenylbenzoic acid, chlorodiphenylphosphine were purchased from Aldrich, Acros, J&K Scientific Ltd., respectively. All chemicals used

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as received if not specified. The synthesis route to 2-(1,1':3',1''-triphenyl-5'-yl)-9,9-diphenyl-9H-fluorene (TPF) and (9,9-diphenyl-9H-fluorene-2-yl)diphenylphosphine oxide (DFPPO) are shown in Scheme 1.

2.2. Synthesis

2.2.1. Synthesis of 2-(1,1':3',1''-triphenyl-5'-yl)-9,9-diphenyl-9H-fluorene (TPF)

A mixture of 2-bromo-9,9-diphenyl-9H-fluorene (0.35 g, 0.9 mmol), 3,6-diphenylbenzoic acid (0.29 g, 1.05 mmol), 40 mg Pd(PPh₃)₄, 25.8 mL toluene and 15.6 mL 2 M Na₂CO₃ aqueous solution was stirred at 95 °C for 48 h under nitrogen atmosphere. The resulting mixture was cooled to room temperature and then poured into water. The organic layer was extracted with dichloromethane and dried over MgSO₄. The crude product was purified by chromatography using petroleum ether and dichloromethane as eluent. Overall yield: 57%. ¹H NMR (400 MHz, CDCl₃, δppm): 7.22–7.03(m, 12H), 7.43–7.26 (m, 7H), 7.527.66(m, 9H), ;7.70 (s, 1H), 7.78 (s, 1H), 7.70 (s, 1H). MS (MALDI-TOF): Calcd for C₄₃H₃₀(M⁺): 546.70, Found: 546.68.

2.2.2. Synthesis of (9,9-diphenyl-9H-fluorene-2-yl)diphenylphosphine oxide (DFPPO)

1.04 mL n-BuLi (1.6 M in hexane) was added dropwise into a solution of 2-bromo-9,9-diphenyl-9H-fluorene(0.69 g, 1.8 mmol) in 20 mL THF at –78 °C. The mixture was stirred at this temperature for 2 h, followed by the addition of a solution of chlorodiphenylphosphine (0.50 mL, 2.25 mmol) under a nitrogen atmosphere. Then the mixture was warmed gradually to ambient temperature and quenched with methanol (10 mL). The mixture was washed by water. The organic layer was extracted with dichloromethane and dried over magnesium sulfate. The crude powdery product was obtained after vacuum distillation and filtration. Then the powder was dissolved in dichloromethane (50 mL) and hydrogen peroxide (10 mL), and stirred overnight at room temperature. The organic layer was separated and washed with dichloromethane and water. The extract was evaporated to dryness to produce a reseda solid. The product was purified by column chromatography (Ethyl acetate-methyl alcohol) to produce white powdery solid. Yield: 32%. ¹H NMR (400 MHz, CDCl₃, δppm): 7.06–6.99(m, 4H), 7.15–7.07 (m, 6H), 7.38–7.23(m, 7H), 7.48–7.41(s, 2H), 7.78–7.71(s, 2H), 7.60–7.49(s, 5H), 7.69–7.64(s, 1H). MS (MALDI-TOF): Calcd for C₃₇H₂₇OP (M⁺): 518.58, Found: 519.15.

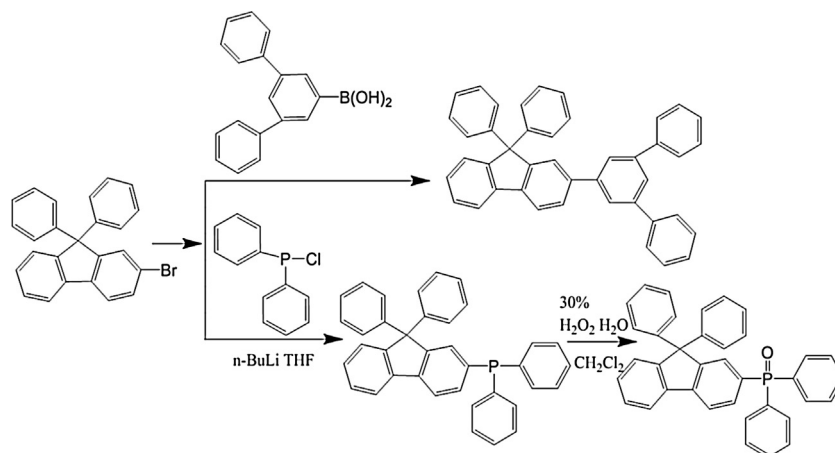
2.3. Characterization

¹H NMR spectra were recorded on a 500 MHz Varian spectrometer in CDCl₃. MALDI-TOF MS spectra were measured on a Walters Maldi Q-TOF Premier mass spectrometry. UV–vis absorption spectra was obtained on a Cary Bio 100 spectrophotometer. The thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere on a PE Pyris 1 TGA at a heating rate of 10 °C/min. Cyclic voltammetry (CV) measurements were recorded in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution at room temperature using a CHI 660C electrochemical workstation at a scan rate of 50 mV/s. A saturated calomel electrode (SCE), a platinum wire and a platinum disk were applied as the reference electrode, counter electrode and working electrode, respectively. Carrier transport properties were studied by space-charge limited current (SCLC) technique [32]. The structure of the electron only device is ITO/ZnO/TPF(DFPPO) (50 nm)/Al (100 nm). The samples for time-resolved photoluminescence measurements were fabricated in identical steps with that for organic ultraviolet photodetectors till organic molecules film deposition. Samples were photo excited by 280 nm laser beam (FLSP920, Edinburgh Instruments). The life time was fitted with a bi-exponential decay function.

2.4. Device fabrication and performance characterization

For the device fabrication, patterned ITO glass was applied as substrate, which was cleaned by detergent and a series of organic solvents (isopropanol, ethanol and acetone) with ultrasonic washer for 10 min. Then a buffer layer (40 nm) of PEDOT:PSS was spin-coated, after dealing with UV-ozone 20 min. Both donor and acceptor were deposited by thermal vapor deposition method under 4 × 10^{−4} Pa in vacuum chamber. The thickness of donor, acceptor layer was 100 nm and 50 nm, respectively. Finally, LiF (1.5 nm), aluminum (100 nm) was evaporated respectively onto the active layers under 10^{−4} Pa as the cathode.

All electrical measurements were performed in air at room temperature. The active area of the device irradiated by the light was 0.04 cm². The photo response was measured on a Keithley 236 Source-Measure Unit under the irradiation of a high pressure mercury lamp (CHG200) filtered by 365 nm bandpass filters. A 500 W Xenon lamp, a grating monochromator and a Stanford Research Systems (USA) SR830 DSP lock-in amplifier were applied to record the spectral response. The radiant power was measured



Scheme 1. Synthetic scheme of TPF and DFPPO.

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