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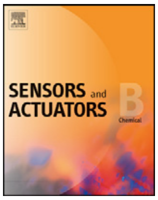

A new wide bandgap organic semiconductor and its application in organic UV sensors with tunable response wavelength

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ABSTRACT

A triphenylbenzene-containing carbazole derivative (PCP) with wide bandgap, good hole mobility, and excellent thermal stability was synthesized and used as electron donor to construct planar heterojunction organic ultraviolet sensors (UVSs), while bis(4-(4,6-diphenyl-1,3,5-triazine-2-yl)phenyl)diphenylsilane (NSN) was used as electron acceptor. The UVS ITO/PEDOT:PSS/PCP/NSN/LiF/Al/Ag showed good responses to illumination from both ITO and cathode sides. When a semitransparent cathode was applied, the response region could be further extended to deep-ultraviolet (DUV) region. When the semitransparent Al (9 nm)/Ag (30 nm) cathode was replaced by Al (13 nm), the blue-shift of the response spectra of the UVS could be found. It was especially interesting that the cutoff of response could be changed by using different kind of cathodes. This study may provide a useful guideline to achieve low-cost organic deep-ultraviolet sensors (DUVSs) with tunable spectral response.

1. Introduction

Ultraviolet sensors (UVSs) have attracted much attention due to their wide applications in fields like military, environmental pollution monitoring, fire detection and astronomical study. Commonly, UVSs are made from inorganic semiconductors including diamond, SiC, GaN, ZnO, etc. [1,2]. However, the manufacturing of the wide-gap inorganic semiconductor is rather complicated and the cost is also quite high, especially for the large-scale applications. Over the past decades, UV sensitive organic semiconductors attracted increasing attention because of the advantages like easy processing as well as low fabrication cost compared to their inorganic counterparts. Both organic small molecules [3–9] and polymers [10–13] have been proved to be alternative candidates for UVSs. Small molecules are more attractive because they are easier to synthesize and purify, compared to polymers. However, for these small molecules with the best UV sensitivity, like Alq_3 [5] and m-MTDATA [6,14], the bad solubility has increased their fabrication complexity. Therefore, development of solution processable small molecular is highly desirable. Another attraction of small molecules is that the molecule structure of the molecule can be designed. The desirable response spectra can easily obtained by tuning the conjugation scale of the molecule and the resulting change of the bandgap. For the reason that the application area of UV irradiation varies with the variation of the wavelength, the UVSs with different response spectra will get potential application in wider fields. However, up to now, most of the organic UVSs reported are lack of wave band selectivity. The most common response spectra cover the wide region from 300 nm to 400 nm, or even extend to the visible region [5–10]. For example, Lin et al. fabricated UVS based on spirobifluorene-cored material, the spectral response of which is 300–410 nm [7]. The organic UVS reported by Dai and Zhang owns spectral responses from 300 to 420 nm [9]. The poly(9,9-dihexylfluorene) based UVS responds to irradiation from the region of 300–425 nm [10]. The cutoff wavelength of the above mentioned systems all locate in the visible region and the effect of the visible light can hardly be avoided. Thus, the detecting of UV signal might be interfered with by the visible light. Only a small amount of research is about the wavelength selectivity of the organic UVSs. Though Li and co-workers shifted the response peak to 280 nm by filtering part of near-ultraviolet (NUV) radiation in the incident light, the cutoff wavelength is still in the visible region [15]. Thus, new materials are worthy to be developed to tune the response wavelength of the organic UVSs.

Rathore and co-workers [16] revealed the relationship between the cutoff of the UV absorption spectra and the effective conjugation length by studying the he UV absorption of poly-p-phenylenes with different number of phenylene moieties. With the decrease of the number of phenylene moieties from 7 to 2, the cutoff of the absorption spectra shifted from 400 nm to 300 nm. In this study,

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in order to obtain visible anti-interference UVSs with high deep-ultraviolet (DUV) sensitivity, we designed and synthesized a new wide-bandgap organic semiconductor, 3,6-di(1,1′:3′,1″-terphenyl-5′-yl)-9-(2-ethyl)hexylcarbazole (PCP), constructed by carbazole and 1,3,5-triphenylbenzene (1,3,5-TPhB) moieties. The extension of π-conjugation can be controlled by the twisted structure of 3,6-subsituted carbazole to achieve wide bandgap [17,18]. Carbazole moiety can endow the molecule with promising charge transporting property [8,19,20]. The hyper branched conjugated molecule like 1,3,5-TPhB commonly owns high thermal stability [21,22]. Thus, the mobility and the thermal stability of PCP are supposed to be guaranteed. Moreover, to improve solution processability, the 2-ethylhexyl is incorporated at the N position of carbazole.

PCP was employed as electron donor to combine with a silane-containing triazine derivative, NSN, with wide bandgap of 3.8 eV to construct a UVS with planar heterojunction structure: indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)(PEDOT:PSS)/PCP/NSN/LiF/Al/Ag. Due to the wide bandgap of the active layer, the NUV response with cutoff wavelength of 400 nm was obtained for the ITO side irradiation. Substituting Al (9 nm)/Ag (30 nm) with Al (13 nm), the cutoff can move to 370 nm. By employing the semitransparent counter electrode for the light incidence, the response region was further extended to deep ultraviolet (DUV) region. This strategy can be applied to modify the cutoff wavelength of the response spectra for the organic UVSs by using donor and acceptor with desirable bandgaps to substitute the PCP/NSN active layer. If NSN can be further replaced by solution processable organic molecule, real solution processable organic UVSs could be realized.

2. Experimental

2.1. Materials

3,6-Dibromocarbazole (1) [23], 3,6-dibromo-9-(2-ethylhexyl)carbazole (2) [24] were synthesized according to the literature methods. All other chemicals were purchased from commercial suppliers. The synthesis route to 3,6-di(1,1′:3′,1″-terphenyl-5′-yl)-9-(2-ethyl)hexylcarbazole (PCP) and bis(4-(4,6-diphenyl-1,3,5-triazine-2-yl)phenyl)diphenylsilane (NSN) are shown in Scheme 1.

2.2. Synthesis

2.2.1. Synthesis of 1-bromo-3,6-diphenylbenzene (3)

A mixture of 1,3,5-tribromobenzene (1.4136 g, 4.49 mmol), phenylboronic acid (1.1640 g, 9.55 mmol), $Pd(PPh_3)_4$ (0.1576 g, 0.14 mmol), 67.5 mL toluene and 22.5 mL 2 M Na_2CO_3 aqueous solution was stirred at 100 °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 $MgSO_4$. The crude product was purified by chromatography using petroleum ether and dichloromethane as eluent. Yield: 0.7357 g (60%). ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 7.71 (s, 3H), 7.63–7.60 (m, 4H), 7.49–7.39 (m, 6H). Anal. Calcd. for $C_{18}H_{13}Br$: C, 69.92; H, 4.24. Found: C, 69.65; H, 4.45.

2.2.2. Synthesis of 3,6-diphenylbenzene-1-boronic acid (4)

1.9 mL 2.2 M n-BuLi (2.5 M dissolved in hexane) was added dropwise into a solution of 3(1.0061 g, 3.26 mmol) in 25 mL THF at −78 °C. After being stirred for 2 h at this temperature, 2.6 mL triisopropylboronate was added and the mixture was stirred at −78 °C for additional 2 h. Then the mixture was allowed to warm to room temperature and stirred overnight. After being cooled to 0 °C, 24 mL 2 M HCl was added. The mixture was further stirred for 30 min and extracted with dichloromethane, washed with brine three times. The organic layer was dried over $MgSO_4$ and evaporated to dryness. The crude product was dissolved in little dichloromethane and then ultrasonic dissolved. The solid was filtered to obtain the product. Yield: 0.5004 g (56%). ^1H NMR (300 MHz, DMSO-d6, δ ppm): 8.24 (br, 2H), 8.06 (d, 2H), 7.91 (s, 1H), 7.76 (m, 4H), 7.47 (m, 4H), 7.37 (m, 2H). Anal. Calcd. for $C_{18}H_{15}O_2B$: C, 78.87; H, 5.52. Found: C, 78.95; H, 5.12.

2.2.3. Synthesis of PCP

A mixture of 2 (0.3948 g, 0.9037 mmol), 4 (0.5266 g, 1.92 mmol), $Pd(PPh_3)_4$ (41.60 mg, 0.036 mmol), 13.6 mL toluene and 4.5 mL 2 M Na_2CO_3 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 $MgSO_4$. The crude product was purified by chromatography using petroleum ether and dichloromethane as eluent. Yield: 0.5323 g (80%). ^1H NMR (500 MHz, $CDCl_3$, δ ppm): 8.48 (s, 2H), 7.94 (d, 4H), 7.85 (d, 2H), 7.76 (m, 10H), 7.50 (m, 10H), 7.40 (m, 4H), 4.22 (m, 2H), 2.18 (m, 1H), 1.40 (m, 8H), 0.91 (m, 6H). Anal. Calcd. for $C_{56}H_{49}N$: C, 91.39; H, 6.71; N, 1.90. Found: C, 90.94; H, 6.76; N, 2.00.

2.2.4. Synthesis of NSN [25]

A mixture of 2-chloro-4,6-diphenyl-1.3.5-triazine (0.59 g, 2.2 mmol), diphenyl-[4,4′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)diphenyl]silane (0.59 g, 1 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), 25 mL tetrahydrofuran (THF) and 5 mL 2 M Na_2CO_3 aqueous solution was stirred at 65 °C for 24 h under nitrogen atmosphere. The resulting mixture was cooled to room temperature and then poured into water. The organic layer was extracted with ethyl acetate and dried over $MgSO_4$. The crude product was purified by chromatography using petroleum ether and dichloromethane as eluent. Yield: 0.54 g (68%). ^1H NMR (500 MHz, $CDCl_3$, δ ppm): 8.79 (m, 12H), 7.86 (d, 4H), 7.68 (d, 4H), 7.55–7.64 (m, 12H), 7.41–7.52 (m, 6H). Anal. Calcd. for $C_{54}H_{38}N_6Si$: C, 81.17; H, 4.79; N, 10.52. Found: C, 81.43; H, 4.91; N, 10.02.

2.3. Characterization

^1H NMR spectra were recorded on a 300 MHz Varian spectrometer in $CDCl_3$. Element analysis results were taken on ThermoFinnigan Flash EA1112. UV–vis absorption spectra were obtained on a Cary Bio 100 spectrophotometer. The thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere on a PE Pyris 1 TGA at heating rates of 20 °C/min. Cyclic voltammetry (CV) measurements were recorded in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) 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 used as the reference electrode, counter electrode and working electrode, respectively. Carrier-transport properties were studied in vapor-deposited glass of PCP by space-charge limited current (SCLC) technique [26]. The samples for SCLC measurement were prepared by vacuum deposition using the structure: ITO/PCP (100 nm)/Au (40 nm).

2.4. Device fabrication and performance characterization

For the device fabrication, patterned ITO glass was used 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 15 min. Due to the properties of NSN, all the small molecules were used thermal vapor deposition method in vacuum chamber at 7×10^{-4} Pa. The thickness of every organic layer is 25 nm. Finally, LiF (0.5 nm), aluminum (9 nm)