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Invited paper

Functionalization of diketopyrrolopyrrole with dendritic oligothiophenes: Synthesis, photophysical properties, and application in solar cells

Wei Gao[a,d], Junkai Wang[b], Yi Lin[c], Qun Luo[a], Yuchao Ma[a], Junyan Dou[a], Hongwei Tan[b,*], Chang-Qi Ma[a,*], Zheng Cui[a,*]

[a] Printable Electronics Research Center, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Collaborative Innovation Center of Suzhou Nano Science and Technology, 398 Ruoshui Road, SEID SIP, Suzhou, Jiangsu 215123, PR China
[b] College of Chemistry, Beijing Normal University, No. 19, XinJieKouWai St., HaiDian District, Beijing, 100875, PR China
[c] Department of Chemistry, Xi'an Jiaotong Liverpool University, 111 Ren Ai Road, SEID SIP, Suzhou, 215123, PR China
[d] University of Chinese Academy of Sciences, Beijing, 100049, PR China

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ABSTRACT

Diketopyrrolopyrrole (DPP) is one of the most widely used organic dye moieties in conjugated organic semiconductors for use in organic electronics. To enrich the library of DPP based organic semiconductors and to further understand the structure-property-performance relationship of this type materials, in this paper, the diketopyrrolopyrrole moiety was functionalized with three-dimensional (3D) π-conjugated dendritic oligothiophenes (DOTs), and four diketopyrrolopyrrole compounds decorated with dendritic oligothiophenes (DOT-c-DPPs) were obtained and characterized in detailed. Results show that all these four compounds are monodisperse with defined molecular structure. Spectroscopy and cyclic voltammetry measurement results showed that the introduction of dendritic oligothiophene unit on the DPP unit improves the light absorption ability over 350–500 nm, and decreases the optical band gap slightly, which are in good accordance with theoretical calculation results that the frontier molecular orbitals are mainly located at the central DPP unit. Solution processed organic solar cells using these DOT-c-DPPs as the electron donor were fabricated and tested. Improved device performance was found for the bigger molecule for its less aggregation tendency.

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1. Introduction

Diketopyrrolopyrrole (DPP) is one of the most widely used building blocks for constructing π-conjugated materials for solution processed organic field effect transistors (OFETs) and organic solar cells (OSCs) [1–5]. High ambipolar charge carrier mobility ($\mu_h = 17.8\,cm^2\,V^{-1}\,s^{-1}$; $\mu_e = 7.0\,cm^2\,V^{-1}\,s^{-1}$) [6,7] and power conversion efficiencies (PCE) of 9.4% have been reported for the DPP based polymers [8]. Recently, π-conjugated small molecules attracted also much attention for use in organic electronic devices owing to their advantages of monodisperse and defined molecular structure, high purity, and low batch-to-bath performance variation [9,10]. For example, Würthner et al. reported a p-type organic semiconductor based channel organic field-effect transistors based on DPP small molecules DPP(CN)$_2$, which exhibited a high hole mobility of $\mu_h = 0.7\,cm^2\,V^{-1}\,s^{-1}$ [11]; Park et al. reported high-performance n-type organic field-effect transistors based on dicyanovinylene functionalized DPP small molecule DPP-T-DCV, which exhibit an electron mobility μ_e up to $0.96\,cm^2\,V^{-1}\,s^{-1}$ [12]. For use in organic solar cells, Cao et al. reported a high PCE of 7% for a π-conjugated moiety end-capped D2-A2-D1-A1-D1-A2-D2 type DPP molecule NDPPFBT [13]. Whereas Peng and coworkers achieved high PCE of 8% in a single-junction photovoltaic device based porphyrin-cored DPP dimer DPPEZnP-THE [14], which was further improved to 9.06% when using DPPEZnP-TBO as the electron donor [15]. A high-performance solution-processed, tandem solar cell based on DPPEZnP-TBO as electron donor materials in the rear subcell achieved a power conversion efficiency of 12.50% (verified 12.70%) under 1 sun condition [16], demonstrating a promising application prospect of DPP based small molecules.

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[*] Corresponding authors.
E-mail addresses: hongwei.tan@bnu.edu.cn (H. Tan), cqma2011@sinano.ac.cn (C.-Q. Ma), zcui2009@sinano.ac.cn (Z. Cui).

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Conjugated dendrimers are a novel class of monodisperse macromolecules with highly branched chemical structures [17,18]. Conjugated dendrimers combine the advantages of high molecular weight of polymers and the chemically defined structure of oligomers [19]. Therefore, they display many unique properties, such as well-defined and monodisperse 3D highly branched spatial structures, tunable electronic properties, good solubility and film forming ability, superior batch-to-batch reproducibility, and isotropic charge-transport ability [20,21]. Among various conjugated dendrimers, dendritic oligothiophenes (DOTs) are highly interesting for their ease of chemical synthesis, extended π-conjugation chain over the molecule, and tunable optical and electronic properties [22]. Considering that conjugated dendrimers have the advantages of defined and monodispersed molecular structure, it is highly interesting to develop structure defined DPP-based molecules decorated with three-dimensional (3D) π-conjugated dendritic structures. In this paper, we report the synthesis and characterization of four diketopyrrolopyrrole compounds decorated with dendritic oligothiophenes (DOT-c-DPPs). The chemical structure as well as the optical and electrochemical properties of these molecules are fully characterized and described. Application of these compounds in solution processed bulk heterojunction solar cells will be also discussed. The current work enriches the DPP-based conjugated molecule library, and provides a better understanding on the structure-property-performance relationship, which would help for further design and synthesis of DPP based materials for organic electronics.

2. Experimental section

2.1. Materials

Chemicals were purchased and used without further purification: 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)dione (**Br-DPP-Br**) (Suna Tech Inc), $Pd_2(dba)_3\cdot CHCl_3$ (Sigma-Aldrich), $HP(t\text{-Bu})_3\cdot BF_4$ (Sigma-Aldrich), K_2CO_3 (Enox®). Solvents were purified and dried by usual methods prior to use and typically used under inert gas atmosphere [23].

2.2. Instruments and measurements

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 400 spectrometer (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz). Chemical shifts are denoted in δ (ppm), and were referenced to tetramethylsilane (TMS) via the residual non-deuterated solvent peaks ($CDCl_3$: ^{1}H NMR: 7.26 ppm, ^{13}C NMR: 77.0 ppm; $C_2D_2Cl_4$: ^{1}H NMR: 6.00 ppm, ^{13}C NMR: 74.0 ppm) as internal standard. The splitting patterns are designated as follows: singlet (s), doublet (d), triplet (t), and multiplet (m). Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) were performed on a Bruker Autoflex Speed using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as the matrix. High resolution mass spectrometry (HRMS) was performed on a Bruker ultraflextreme MALDI-TOF/TOF (operation mode: MALDI; matrix: DCTB). Gel Permeation Chromatography (GPC) measurement was performed on a Waters Breeze separations module apparatus with THF as the eluent (flow rate 1 mL min^{-1}, 35 °C). Number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of compounds were determined by GPC analysis relative to polystyrene standards. UV–vis spectra of these new materials in chloroform ($CHCl_3$) solution and thin film were recorded on a Perkin Elmer Lambda 750 UV–vis Spectrophotometer. For UV–vis absorption spectrum measurement in solution, three concentrated solutions (around 10^{-4} mol L^{-1}) were prepared independently, each of which were further diluted to get three diluted solutions (with concentration around 10^{-7}–10^{-6} mol L^{-1}) for UV–vis absorption measurement. The absorption spectra of the dilute solutions were recorded, and the data points of the absorbance at a certain wavelength vs. concentration were then plotted. A good linear relationship was found for all these compounds, suggesting no obvious intermolecular interaction was found in such a concentration range. The molecular molar extinction coefficient (ε) was obtained from the slope of the best-fit line over the above mentioned data points according to the Beer–Lambert's Law equation, $A = \varepsilon\cdot L\cdot c$. Thin film samples for UV–vis spectra measurement were prepared by spin-casting a chloroform solution on quartz glasses. The photoluminescence (PL) spectra of the DOT-c-DPPs in chloroform solution were obtained with an Hitachi F-4600 fluorescence spectrophotometer.

Cyclic voltammetry (CV) experiments were performed with a RST-3000 Electrochemistry Workstation (Suzhou Risetech Instrument co., ltd). All CV measurements were carried out at room temperature with a conventional three-electrode configuration under nitrogen atmosphere. The electrochemical cyclic voltammetry was performed in a 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$)/dichloromethane (DCM) solution with a scan speed of 100 mV s^{-1}. A Pt disk (ϕ = 1 mm) embedded in Teflon was used as the working electrode. The surface was polished before use. A Pt sheet (~1 cm^2) and Ag/AgCl were used as the counter and reference electrodes, respectively. After the measurement, a small amount of ferrocene was added in the solution and the ferrocene/ferrocenium (Fc/Fc^+) redox couple was measured as an internal standard. Transmission electron microscopy (TEM) tests were performed on a Tecnai G2 F20 S-Twin 200 kV field-emission electron microscope (FEI). Specimens for the TEM experiments were obtained by transferring the floated blend films from the water onto the 200 mesh copper grid.

2.3. Synthesis

6T-c-DPP-Si: Compound **Br-DPP-Br** (100 mg, 98.4 μmol), **B-3T-Si** (125 mg, 241 μmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (12 mg, 11.6 μmol), and $HP(tBu)_3BF_4$ (7 mg, 24.1 μmol) were dissolved into well-degassed THF (40.0 mL). The reaction mixture was bubbled with nitrogen and a well-degassed aqueous solution of K_2CO_3 (1 M, 1.5 mL, 1.5 mmol) was added dropwise. The reaction mixture was stirred overnight at room temperature and then poured into ice water (100 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4. The solvent was removed by rotary evaporation. The residue was filtered through a short column of silical gel to remove any inorganic salts and small molecule side product (homocoupling product of **B-3T-Si**). The filtrate was concentrated and purified by SEC column chromatography eluting with THF to give the blue product (129 mg, 80%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.93 (d, *J* = 4.16 Hz; 2H), 7.34 (s; 2H), 7.32(d, *J* = 4.16 Hz; 2H), 7.18 (d, *J* = 3.44 Hz; 2H), 7.15 (s; 4H), 7.12 (d, *J* = 3.48 Hz; 2H), 4.05 (d, *J* = 7.60 Hz; 4H), 1.98 (m; 2H), 1.20–1.34 (m; 64H), 0.82–0.88 (m; 12H),0.33 (s; 18H), 0.31 ppm (s; 18H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 161.60, 142.62, 141.80, 141.73, 141.25, 139.56, 139.34, 136.66, 134.24, 134.20, 134.11, 132.66, 132.56, 128.71, 128.44, 128.17, 127.86, 124.87, 108.54, 46.36, 37.93, 31.92, 31.85, 31.34, 30.05, 29.67, 29.62, 29.55, 29.37, 29.30, 26.38, 22.69, 22.66, 14.11, −0.06, −0.15 ppm; MALDI-TOF MS: *m*/*z* calcd for $C_{90}H_{132}N_2O_2S_8Si_4$: 1640.7; found: 1640.9; HR MS: *m*/*z* calcd for $C_{90}H_{132}N_2O_2S_8Si_4$: 1640.7132; found: 1640.7197.

6T-c-DPP-H: A solution of TBAF (270 mg, 1.033 mmol) in THF (5 mL) was added dropwise to a solution of **6T-c-DPP-Si** (120 mg, 73.2 μmol) in THF at room temperature. The reaction mixture was stirred at this temperature for 10 min, and then was dropped into

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