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Two novel diketopyrrolopyrrole (DPP) small molecules DPPTT-F and DPPTT-H were synthesized and characterized. Thin film transistor characteristics showed DPPTT-H exhibited p-channel behavior, and DPPTT-F displayed ambipolar characteristics with balanced hole and electron mobility in air.
Perfluorohexyl Containing Diketopyrrolopyrrole (DPP) Small Molecule for High Performance Ambipolar Transistors with Balanced Hole and Electron Mobility

Yuanyuan Wang, Qiuliu Huang, Zhiqiang Liu, Hongxiang Li

Two novel diketopyrrolopyrrole (DPP) small molecules DPPTT-F and DPPTT-H were synthesized. With the change of substituent from hexyl to perfluorohexyl, the HOMO and LUMO energy levels of DPPTT-F lowered, but the bandgap of DPPTT-H and DPPTT-F was nearly the same, which was proved by absorption spectra and electrochemistry. Thin film transistor characteristics showed DPPTT-H exhibited p-channel behavior with a hole mobility about 0.2 cm$^2$/Vs, while DPPTT-F displayed ambipolar characteristics with balanced hole and electron mobility in air. The mobility of DPPTT-F was 0.012 cm$^2$/Vs for hole and 0.011 cm$^2$/Vs for electron. The microstructure and morphology of the thin films were also investigated. All these results demonstrated the unique property of perfluoroalkyl chains and their potential application in high performance organic ambipolar semiconductors.

Introduction

Ambipolar organic semiconductors, which can fabricate light-emitting transistors and complementary metal-oxide semiconductor (CMOS)-like logic circuits in simple way at low-cost, have attracted great attentions recently. Though continuous progress has been made, the lack of ambient stable and high performance ambipolar semiconductors is still one of the bottlenecks for their practical applications, especially the one with balanced hole and electron mobility. Hence, it is vital and needed to develop novel high performance ambipolar semiconductors with balanced hole and electron mobility under ambient condition.

Diketopyrrolopyrrole (DPP) has fused planar structure and is an excellent building block for high performance polymer Semiconductors. Recently, DPP based small molecules have caught the attentions owing to their well defined structure and promising charge transport performance. For instance, vacuum deposited thin films of DPP derivative 1a (Scheme 1) showed a high hole mobility of 0.7 cm$^2$/Vs and a current on/off ratio of 10$^6$ under ambient conditions. Till now, most of the reported DPP based small molecules exhibited p-channel behavior, ambipolar materials are rarely reported and most of them are measured under vacuum or in inert atmosphere. Compound 1b (Scheme 1) displayed one of the highest ambipolar performance among DPP based small molecules with balanced electron and hole mobility about 10$^{-3}$ cm$^2$/Vs in vacuum by using Au as source and drain electrodes. It is well known that the fluorine-contained substituents can effectively lower the energy level of molecules and influence their orientation in the solid state, and thus affect the charge-transport behavior of materials. However, no much attentions has been paid to fluorine-containing DPP based small molecules. Y. Suna firstly introduced fluorine substituents into DPP based small molecules and synthesized compound 1c (Scheme 1). Though the performance of 1c was not high (electron mobility: 10$^{-4}$ cm$^2$/Vs, hole mobility: 10$^{-3}$ cm$^2$/Vs), it can be operated in ambient condition which is crucial to fabricate ambipolar transistors easily with low cost. Herein, two novel DPP derivatives DPPTT-F and DPPTT-H (Scheme 2) were successfully synthesized. Both compounds have same conjugation backbone, but their alkyl chain substituents are different. The alkyl chain substituents are hexyl for DPPTT-H and perfluorohexyl for DPPTT-F. Absorption spectra and electrochemistry results showed the replacement of hexyl with...
A mixture of 8 mL perfluorohexyl lowered the HOMO and LUMO energy levels of DPPTT-F, but the HOMO-LUMO energy bandgaps of DPPTT-H and DPPTT-F were nearly the same. Thin film transistor characteristics showed DPPTT-H exhibited p-channel behavior with hole mobility about 0.2 cm²/V·s, while DPPTT-F based transistors showed ambipolar properties with balanced hole and electronic mobilities in air. The maximum hole and electron mobility of DPPTT-F were 0.012 cm²/V·s and 0.011 cm²/V·s, respectively, one of the highest value for DPP based ambipolar transistors in air. Their thin film microstructure and morphology were also investigated.

**Experimental section**

**Materials synthesis**

All reactions were carried out under nitrogen atmosphere unless stated otherwise. The reagents were purchased from commercial suppliers and were used directly without further purification unless otherwise noted. Compounds S1, S3 and S4 were synthesized according to the literature.

**Synthesis of compound S2**

A mixture of S1 (1.10 g, 4 mmol) and dimethyl succinate (0.29 g, 2 mmol) was added into a boiling mixture of sodium tert-pentoxide (0.75 g, 6.8 mmol) and 8 mL tert-amyl alcohol over 1.3 h. The reaction mixture was refluxed for another 2 h and then cooled to room temperature. After adding methanol and concentrated hydrochloric acid, the mixture was stirred for 30 min, and then stood overnight in refrigerator. The precipitate was filtered and washed with methanol and water, to afford crude product S2 (0.65 g), which was used directly in subsequent reactions without further purification.

**Synthesis of DPPTT-H**

A mixture of S2 (1.28 g, 2 mmol), K₂CO₃ (1.1 g, 8 mmol) and dry DMF (20 mL) was stirred at 120 °C for 4 h before 1-bromoheptane (0.77 g, 4.6 mmol) was added. Then the reaction mixture was heated at 130 °C for another 2 h and cooled to room temperature. Water was added and the reaction solution was extracted with CHCl₃. Solvent was removed under vacuum and the residue was purified by column chromatography (CHCl₃-petroleum ether, 1.5:1) to yield 0.3 g of DPPTT-H as a dark blue solid (18.7%); mp. 231 °C; ¹H NMR (CDCl₃) δ 8.90 (d, 2H); 7.22 (d, 2H); 7.13 (d, 2H); 6.72 (d, 2H); 4.06 (t, 4H); 2.8 (t, 4H); 1.78 (m, 8H); 1.28-1.37 (m, 12H); 0.83 (t, 6H); MS (MALDI-TOF): m/z 801.3; Anal Calcd for C₅₀H₅₀N₄O₈S₂: C 68.95%, H 7.55%, N 3.50%; Found: C 68.75%, H 7.40% N 3.43%.

**Synthesis of DPPTT-F**

A 50 mL Schlenk tube was charged with S3 (1 g, 1.76 mmol), S4 (0.11 g, 0.176 mmol), Pd(PPh₃)₄ (10 mg, 0.0087 mmol) and 10 mL toluene. The mixture was stirred at 130 °C for 20 h and then cooled to room temperature. The solid was filtered, washed with CHCl₃ and purified by recrystallization from o-dichlorobenzene to afford 2g (89.6%) DPPTT-F as a dark blue solid; mp. 255 °C; ¹H NMR (CDCl₃) δ 8.70 (d, 2H); 7.32 (m, 4H); 7.23 (d, 2H); 4.06 (t, 4H); 2.8 (t, 4H); 1.3-1.46 (m, 16H); 0.88 (t, 12H); MS (MALDI-TOF): m/z 801.3; Anal Calcd for C₅₀H₅₀N₄O₈S₂: C 68.95%, H 7.55%, N 3.50%; Found: C 68.75%, H 7.40% N 3.43%.

**Device Fabrication and characterization**

The transistors were fabricated in a top contact, bottom gate configuration. Heavily N-doped Si and a 300 nm thick SiO₂ layer were used as gate electrode and dielectric layer. The specific capacitance of the dielectric layer was 10 nF/cm². The substrates were cleaned and modified with OTS according to reported procedure. The DPPTT-H and DPPTT-F thin films were evaporated on the substrates under 10⁻⁷ Torr at different substrate temperatures from 25 °C to 85 °C, and the thickness of the films was 50 nm measured by a quartz crystal microbalance. The gold source/drain electrodes were deposited on the semiconductor layer by thermal evaporation using a shadow mask. The channel width and length of the transistors were 273 and 31 μm.
respectively. The electrical characterization of the devices was performed by using a Keithley 4200 semiconductor parameter analyzer in air at room temperature.

Results and discussion

The synthetic routes of DPPTT-H and DPPTT-F are outlined in Scheme 2. Compound S1 reacted with diethyl succinate in the presence of sodium tert-amyl alcohol to afford compound S2. Alkylation of compound S2 with hexyl bromide gave target compound DPPTT-H as a dark blue solid. The synthesis of DPPTT-F was accomplished by a Still coupling of S4 and stannic compound S3, and the product was purified by recrystallization from o-dichlorobenzene. DPPTT-H has good solubility in common organic solvents, while DPPTT-F was poor soluble in organic solvents, suggesting the different effect of perfluorohexyl and hexyl substituents. Both compounds were fully characterized by 1H NMR, MS and elemental analysis.

Figure 1. a) UV-vis absorption spectra of DPPTT-H and DPPTT-F in o-dichlorobenzene solution (10⁻⁴ mol/L) and on thin films (50 nm thickness, deposited on a quartz substrate at 55 ºC); b) Cyclic voltammetry of DPPTT-H and DPPTT-F in o-dichlorobenzene solution. 0.1 M Bu₄NPF₆ as electrolyte, SCE as reference electrode, Pt as working electrode.

The UV-vis absorption spectra of DPPTT-H and DPPTT-F in o-dichlorobenzene solution and on thin films are shown in Figure 1. Both compounds have strong absorption in the range of 460-780 nm in solution. Though perfluorohexyl chain has stronger electron withdrawing ability than that of hexyl group, surprisingly DPPTT-H and DPPTT-F displayed nearly the same absorption spectra in the solution, suggesting the replacement of perfluorohexyl group does not affect the HOMO-LUMO energy gap of the molecules. The optical energy gap estimated from solution spectra is about 1.89 eV. Comparing with that of solution, the absorptions of DPPTT-H and DPPTT-F based thin films were largely blue shifted. The maximum absorptions of DPPTT-H and DPPTT-F were blue shifted ~113 nm and 76 nm respectively, indicating strong intermolecular interactions exist in the solid state. Additionally, a shoulder absorption at 630 nm for DPPTT-H and at 650 nm for DPPTT-F was observed, suggesting both compounds form H-type aggregation in the solid state.

The cyclic voltammograms (CV) of DPPTT-H and DPPTT-F were measured in o-dichlorobenzene solution with 0.1 M Bu₄NPF₆ as electrolyte, Pt electrode as working electrode, and ferrocene as internal standard (Figure 1b). DPPTT-H showed three reversible redox peaks, and the first reduction and oxidation potentials estimated from the midpoint of forward and backward scan are -1.18 V and 0.76 V respectively. The CV of DPPTT-F displayed non-reversible redox behavior, which might be ascribed to the effect of perfluorohexyl groups and the low solubility of DPPTT-F. The first oxidation and reduction peaks of DPPTT-F are at 0.98 V and -1.05 V. The HOMO/LUMO energy levels calculated from CV are -5.03 /-3.09 eV for DPPTT-H and -5.25 eV/-3.22 eV for DPPTT-F. The HOMO-LUMO energy bandgap estimated from electrochemistry is 1.92 eV for DPPTT-H and 1.97 eV for DPPTT-F, close to the optical bandgap calculated from UV. Apparently, the perfluorohexyl groups lower the HOMO and LUMO energy levels of DPPTT-F, but nearly has no influence on its HOMO-LUMO energy bandgap.

Table 1 Field-effect characteristics of DPPTT-H and DPPTT-F deposited at various substrate temperatures

<table>
<thead>
<tr>
<th>Substrate Temperature [°C]</th>
<th>DPPTT-H</th>
<th>DPPTT-F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_{sub}</td>
<td>μ_{max} (μV cm⁻¹ V⁻¹)</td>
</tr>
<tr>
<td>25</td>
<td>0.20 (0.15)</td>
<td>5.3×10⁴</td>
</tr>
<tr>
<td></td>
<td>4.9×10⁻⁷ (1.4×10⁻⁷) (c)</td>
<td>3.6×10⁻⁵ (c)</td>
</tr>
<tr>
<td></td>
<td>1.1×10⁻⁶ (4.6×10⁻⁶) (c)</td>
<td>8.4×10⁻⁶ (c)</td>
</tr>
<tr>
<td></td>
<td>2.6×10⁻⁶ (1.3×10⁻⁶) (c)</td>
<td>1.0×10⁻⁶ (c)</td>
</tr>
</tbody>
</table>

In order to investigate the charge transport property of DPPTT-H and DPPTT-F, top-contact, bottom gate transistors were fabricated. The mobility of devices was calculated in saturation regime according to the expression

\[ \mu = \frac{L}{W C_{i} (V_{G}-V_{T})^{2}} \]

where \( L \) and \( W \) are the channel length and width, respectively; \( C_{i} \) is the capacitance. Figure 2 shows the typical transfer and output curves of DPPTT-H and DPPTT-F based transistors, and their device performance is summarized in Table 1. DPPTT-H exhibited p-channel behavior, and the highest hole mobility could reach ~0.2 cm²V⁻¹s⁻¹ with \( I_{on}/I_{off} \) ratio > 10⁴ at substrate temperature (\( T_{sub} \)) = 25 ºC. When the \( T_{sub} \) was increased

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Moreover, in air though the LUMO energy level of the different electrical behaviors of Absolutely, the perfluorohexyl chains should be responsible for the different electrical behaviors of DPPTT-H and DPPTT-F. Moreover, DPPTT-F based ambipolar transistors can be operated in air though the LUMO energy level of DPPTT-F is -3.22 eV, further demonstrating the unique property of perfluoroalkyl chains and their potential applications in high performance organic ambipolar semiconductors. In addition, the low optimized substrate temperature (55 °C) guarantees the potential applications of these compounds in flexible transistors.

Figure 3. X-Ray diffraction of DPPTT-H and DPPTT-F films deposited on OTS modified Si/SiO2 substrates at different substrate temperatures. The wavelength for the X-Ray source is 0.154 nm.

Figure 4. AFM images of DPPTT-H (4 × 4 μm2) and DPPTT-F (3 × 3 μm2) thin films deposited on OTS modified Si/SiO2 substrates at different substrate temperature.

The thin film quality, microstructure and morphology of DPPTT-H and DPPTT-F were investigated by X-ray diffraction (XRD) and atomic force microscopy (AFM). Figure 3 illustrates the XRD patterns of the thin films deposited at different substrate temperatures. DPPTT-H thin films showed one diffraction peak when the Tsub was 25 °C and 55 °C respectively. The d-spacing estimated from XRD is 2.36 nm at Tsub = 25 °C and 2.59 nm at Tsub = 55 °C, suggesting DPPTT-H adopts different packing models on the substrate. Surprisingly, this changes has nearly no influence on the mobility and just slightly affected the threshold voltage of the devices, indicating both molecular packing models of DPPTT-H favorite charge transport. It is known the threshold voltage is strongly affected by the traps in the interfaces such as organic semiconductor - electrodes interface and organic semiconductor - dielectric layer interface, and in organic semiconductor thin film. We believe, more traps were formed in the devices at Tsub =55 °C, which led to the increase of the threshold voltage. No peaks were observed for the films deposited at 85 °C, indicating its less crystalline and being consistent with the device performance. For DPPTT-F thin films, a series of single family diffraction peaks were observed. With the increase of substrate temperature, the intensity of the peaks increased, indicating the improved crystalline of the films. The d-spacing estimated from the first diffraction peak is 2.33 nm, close to that of DPPTT-H thin film deposited at Tsub = 25 °C. Figure 4 shows the AFM images of DPPTT-H and DPPTT-F thin films. With increasing the substrate temperature from 25°C to 55 °C, the grain size of DPPTT-H increased, and the grain boundaries became larger. While the substrate temperature increased to 85 °C, the grain size as well as grain boundary further increased, and the continuity of the film became worse. The thin films with large grain sizes and short grain boundaries facilitate charge transport. The large grain boundary might be responsible for the deteriorated device performance of DPPTT-F at Tsub = 85 °C. The morphology of DPPTT-H thin films exhibited the same tendency as that of DPPTT-F with the increase of substrate temperature. The different crystalline and morphology of the thin films led to the performance variation of DPPTT-H and DPPTT-F films at different substrate temperatures.

Conclusions

In summary, two novel DPP based small molecules, DPPTT-F and DPPTT-H were prepared. Their physicochemical properties were investigated by absorption spectra and electrochemistry. Comparing with DPPTT-H, the HOMO and LUMO energy levels of DPPTT-F lowered, but the HOMO-LUMO bandgap was nearly the same, demonstrating the unique effect of perfluoroalkyl substituents to the energy levels of the frontier orbital of compounds. Thin film transistor characteristics showed DPPTT-H displayed p-channel behavior with hole mobility of 0.2 cm2V-1s-1. And DPPTT-F exhibited ambipolar characteristics with balanced hole and electron mobility in air. The maximum hole and electron mobility of DPPTT-F was 0.012 and 0.011 cm2V-1s-1 respectively, which was observed at Tsub = 55 °C, one of the highest and balanced value for DPP based small molecules.
in air. AFM image and XRD results showed the morphology and crystalline changes are responsible for the mobility variation of DPPTT-H and DPPTT-F at different substrate temperatures.

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Notes and references