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Syntheses and properties of π-conjugated oligomers containing furan-fused and thiophene-fused aromatic units

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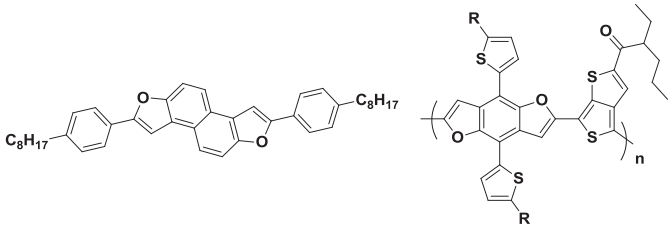
ABSTRACT

π-conjugated oligomers **1a**–**b** and **2a**–**b**, containing furan-fused and thiophene-fused aromatic units, were systematically designed and successfully synthesized. Their physicochemical properties were thoroughly investigated. Experimental results showed that different furan/thiophene ratios and fused-aromatic skeletons strongly affected the HOMO energy levels, fluorescent quantum yields and aggregation behaviors of the oligomers. Single crystal structures revealed compound **1b** adopted typical herringbone structure with strong C–H···π, S···π and S···S interactions in the crystals. **2a** formed slipped π-π stacking in the crystals, and strong π···π and O···O interactions were observed.

1. Introduction

π-Conjugated organic semiconductors have found wide applications in organic light-emitting diodes (OLEDs), organic solar cells (OSCs) and organic thin film transistors (OTFTs).[1–8] Till now, though great progress has been made, the lack of high performance organic semiconductors is still one of the bottleneck for their practical applications.[9–11] The optimum approaches to obtain high performance of organic semiconductors need the joint research in molecular design engineering (chemical modification) and morphology control process technology (physical modulation).[12,13] From the molecular design perspective, it is essential and desirable to figure out the relationship between molecular structures and properties of organic semiconductors, so that we can rationally design molecules to achieve high performance. Actually, many efforts have been made to investigate the structure-property relationship of organic semiconductors, and some generally acknowledgement in specific systems (such as fused-ring aromatic compounds and oligo-/polythiophenes) has been widely accepted.[14–20] With the aim to explore new type of high performance organic semiconductors, it is great interested and significant important to extend the structure-property relationship to other systems.[21,22]

Recently, several research groups have reported the introduction of selenium heteroatom into organic semiconductors could lead to higher carrier mobility comparing with the corresponding sulfur containing semiconductors in thin film transistors.[23–30] It is widely believed that the higher performance of selenium containing semiconductors is due to the higher polarizability and larger atomic radius of selenium atom than that of sulfur atom, which is called 'chalcogene atom effects'.[31] Consequently, furan containing materials are regarded as less advantageous for charge transport because of the lower polarizability and shorter atomic radius of oxygen atom. However, some recently results demonstrated that furan contained small molecules and polymers could exhibit high hole-mobility in OTFTs and excellent PCE in OPVs as well.[32–39] For example, DPNDF (chemical structure see Scheme 1) displayed high hole-mobility up to 3.6 cm^2/ Vs in solution-processed single crystal field-effect transistors[39] and benzodifuran-based polymers PBDFTT–CF–T (chemical structure see Scheme 1) exhibited PCE of 6.26% in hetero-junction solar cells.[36] Therefore, furan-based materials deserve much more attention to organic optoelectronics.



DPNDF PBDFTT-CF-T

Scheme 1. Some representative furan-containing organic semiconductors.

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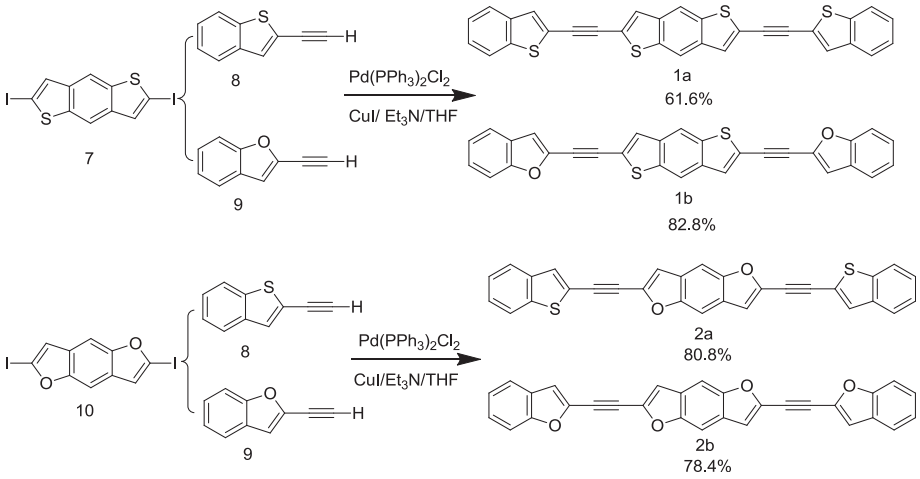
So far, the study on furan-based semiconductors has been mainly focused on oligofurans and furan contained fused-ring compounds.[40–44] With the aim to obtain high performance furan-containing organic semiconductors and further investigate their applications in organic electronics, herein, four small molecules composing of benzo[1,2-b:4,5-b′]dithiophene, benzo[1,2-b:4,5-b′]difuran, benzothiophene and benzofuran units (chemical structures see Scheme 2) were strategically designed and synthesized. These compounds possessed different furan/thiophene ratios and fused-aromatic skeletons, which is in favor of investigating the effects of furan-fused aromatic units on the properties of organic semiconductors. Experimental results showed that furan-fused aromatic units exerted significant impacts on the optical and electrochemical property of materials as well as the molecular packing model in the single crystals.

The absorption spectra of compounds **1a**–**b** and **2a**–**b** were obtained in dilute hot chlorobenzene solutions. As shown in Fig. 1b, all compounds displayed three main absorption peeks in the range from 300 nm to 500 nm. Compounds **1a** and **1b** showed nearly the same absorption spectra, and their onset absorption was red-shifted comparing with compounds **2a** and **2b**. The absorption of **2b** exhibited a slightly 4 nm blue-shift comparing with that of **2a**. The HOMO–LUMO bandgaps calculating from the absorption spectra were 2.86 eV for **1a**, 2.88 eV for **1b**, 2.90 eV for **2a** and 2.93 eV for **2b**, which showed the introduction of benzo[1,2-b:4,5-b′]difuran and benzofuran can slightly broaden the bandgaps. Fig. 1c illustrated the thin film absorptions of compounds **1a**–**b** and **2a**–**b**. The maximum peaks of **1a**–**b** and **2a**–**b** on thin films were 396, 374, 370, 451 nm, respectively. Comparing with that of solutions, the maximum absorption of **1a** thin film exhibited a red-shift



Scheme 2. Synthesis of compounds **1a**–**b** and **2a**–**b**.

2. Results and discussion

The synthetic routes of compounds **1a**–**b** and **2a**–**b** were shown in Scheme 2. They were synthesized by palladium catalyzed Sonogashira cross-coupling reactions and obtained in medium to high yields. All compounds were characterized by ^{1}H NMR spectra, mass spectra and elemental analyses. Due to the large π-conjugated and rigid planar structures, these compounds had poor solubility in common organic solvents and the attempts to get their ^{13}C NMR spectra failed.

The cyclic voltammetry (CV) experiments of compounds **1a**–**b** and **2a**–**b** were conducted in dilute hot chlorobenzene solutions (Fig. 1a). All compounds displayed one irreversible oxidation peak in the potential range of 0 V–1.8 V. The onset oxidation potentials were 1.34 V for **1a**, 1.36 V for **1b**, 1.42 V for **2a** and 1.44 V for **2b**. The CV results showed that **1b** and **2b** exhibited more positive oxidation potentials than **1a** and **2a** by 0.02 V, respectively, indicating that benzofuran unit was slightly electron-poorer than benzothiophene. The oxidation potentials of **2a** and **2b** were higher than that of **1a** and **1b** by 0.08 V, respectively, further confirmed that the furan-fused aromatic units lowered the HOMO energy levels of oligomers. The HOMO energy levels calculated from CV were −5.75 eV for **1a**, −5.77 eV for **1b**, −5.83 eV for **2a** and −5.85 eV for **2b** (calibrated using Fc/Fc^+=0.39 V vs SCE). It could be seen the two terminal benzofuran units lowered the HOMO energy levels of 0.02 eV, and the central benzo[1,2-b:4,5-b′]difuran unit decreased the HOMO energy levels of 0.08 eV, and a synergistic effect on the HOMO energy levels were observed from **1a** to **2b**.

of 15 nm, and a large red-shift of 63 nm was observed for **2b** thin film, suggesting that J-aggregations were dominated in the thin films. On the contrary, the thin film maximum absorptions of **1b** and **2a** were blue shifted of 7 nm and 22 nm, respectively, and new shoulder absorptions at longer wavelength appeared, indicating that **1b** and **2a** adopted H-aggregations in thin films. These results indicated furan-fused aromatic units strongly affected the intermolecular interactions and molecular packing of organic semiconductors.

Fig. 1d illustrated the fluorescent emission spectra of compounds **1a**–**b** and **2a**–**b** performed in extra-dilute CH_2Cl_2 solutions. Similar as that of solution absorption spectra, compound **1a** and **1b** displayed the same emission spectra and the maximum emission peaks of **2a** was slightly red shifted comparing with that of **2b**. The fluorescence quantum yields estimated from CH_2Cl_2 solutions with 9,10-diphenylanthracene as internal standard were 0.18 for **1a**, 0.31 for **1b**, 0.39 for **2a** and 0.40 for **2b**.[45] It was evident that the replacement of benzothiophene with benzofuran strongly enhanced the quantum yield from 0.18 to 0.31 for **1a** and **1b**. Replacement of the central benzo[1,2-b:4,5-b′]dithiophene with benzo[1,2-b:4,5-b′]difuran improved the quantum yield from 0.18 to 0.39 for **1a** and **2a**. However, unlike that of the HOMO energy levels, no synergistic effect on fluorescence quantum yield was observed for benzo[1,2-b:4,5-b′]difuran and benzofuran. The smaller increase of quantum yield from 0.31 to 0.40 for **1b** and **2b** as well as from 0.39 to 0.40 for **2a** and **2b**, suggested that only the first introduction of furan unit strongly improved the fluorescence quantum yield. Nonetheless, benzo[1,2-b:4,5-b′]difuaran was more efficient and