ChemComm

COMMUNICATION

RSCPublishing

View Article Online View Journal | View Issue

Cite this: Chem. Commun., 2013, 49, 3899

Received 8th January 2013, Accepted 22nd March 2013

DOI: 10.1039/c3cc00159h

www.rsc.org/chemcomm

Charge transfer in cross conjugated 4,8-dithienylbenzo[1,2-b:4,5-b']dithiophene based organic sensitizers[†]

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Two novel cross-conjugated isomers based on 4,8-dithienylbenzo-[1,2-b:4,5-b']dithiophene have been designed and successfully synthesized. It was found that the charge transfer interaction was much stronger in the benzodithiophene direction as compared with the other perpendicular direction.

Charge transfer in conjugated organic systems has been widely investigated to construct organic semiconductors for optoelectronic devices, such as light-emitting diodes (LEDs),¹ photovoltaic devices,² field-effect transistors (FETs),³ nonlinear optics,⁴ and fluorescent chemosensors.⁵ Among the various applications, dye-sensitized solar cells (DSSCs) have attracted extensive attention in the last two decades since the breakthrough by O'Regan and Grätzel.⁶ The key component in a DSSC device is the sensitizer which consists of an electron donor and acceptor connected by a π -conjugated bridge. Such a push–pull configuration lowers the band gap of the semiconductor and greatly benefits the lightharvesting capability.⁷ Most importantly, a facile charge transfer in the chromophore can make the electrons transport from the donor moiety to the acceptor moiety upon photoexcitation and then inject into the semiconductor electrode.

The cross-conjugated⁸ molecule is constructed from two "perpendicular" π -conjugated arms connected through a central aromatic core. Such a two-dimensional conjugation is currently receiving intense attention due to its unique optoelectronic properties as compared with one-dimensional linear conjugated systems. Cross-conjugated materials, such as spiro compounds,⁹ tetrasubstituted benzenes,¹⁰ paracyclophanes,¹¹ and bisoxazole derived cruciforms,¹² have been recently reported. However, much less attention has been paid to the charge transfer system in cross-conjugated organic semiconductors. Although the basic concept for charge transfer in one-dimensional systems has been well developed and established, the effect of additional conjugated pathways on charge delocalization and transfer in cross-conjugated systems is still a challenge for chemists and physicists.

4,8-Dithienylbenzo[1,2-*b*:4,5-*b'*]dithiophene (**DTBDT**) consists of four thiophene rings with a benzene core. Thus, it can be functionalized within two perpendicular directions to build cross-conjugated organic semiconductors and endow them with unique properties, such as broader absorption band, lower HOMO level and higher charge mobility. Therefore, **DTBDT** has been studied as light-harvesting materials.¹³ For example, it has been recently incorporated into copolymers to construct donor-acceptor polymers, and a power conversion efficiency (η) of 7.59% has been achieved for the corresponding polymer solar cells.^{13*a*} However, the charge transfer in the two different conjugation directions has not been studied so far. Therefore, herein, we designed and synthesized two cross-conjugated push-pull isomers (**I1** and **I2**) and systematically compared the charge transfer interactions *via* two perpendicular directions.

The synthetic approaches (Schemes S1 and S2, ESI[†]) to both isomers I1 and I2 (Fig. 1) start from 4,8-dehydrobenzo-[1,2-b:4,5-b']dithiophene-4,8-dione which contains four reactive sites at the α -position on the four thiophene rings. The α -position on the two thienyl groups is much more active than the other two fused on the benzene core. Therefore, for isomer I1, after stirring with 4-hexylthienyl-2-lithium at 0 °C followed by reacting with SnCl₂ in 10% hydrochloric acid, the key intermediate core 2 was produced in 65% yield. Two hexyl groups were incorporated in order to ensure the solubility and minimize the intermolecular interactions. Then the corresponding monoaldehyde-substituted derivative 3 was synthesized by refluxing with a Vilsmeier reagent. However, for isomer I2, to functionalize the α -position on the other two thiophene rings with less reactivity, two alkyl chains have been incorporated firstly to block the more active sites of the α-position on the thienyl rings linked to the benzene core with a single bond. Lithiation of 2-hexylthiophene with n-butyllithium at 0 °C followed by addition of 4,8-dehydrobenzo-[1,2-b:4,5-b']dithiophene-4,8-dione and subsequent stirring with SnCl₂ in hydrochloric acid produced the key core 5.

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[†] Electronic supplementary information (ESI) available: Synthesis and characterization details for isomers **I1** and **I2**. See DOI: 10.1039/c3cc00159h







However, our further introduction of an aldehyde group by a Vilsmeier reagent is not applicable due to the low reactivity. An alternative procedure to obtain compound 6 was carried out upon addition of a stoichiometric amount of n-butyllithium to the solution of compound 5 in tetrahydrofuran (THF) at -78 °C. Then guenching with N,N-dimethylformamide and subsequent acidic hydrolysis produced the corresponding monoaldehydesubstituted derivative 6. Subsequently, for both isomers I1 and I2, the electron donor, N,N-bis(4-hexyloxyphenyl)phenylamine, was attached via C-H bond activation,14 which provided the precursors. It should be noted that a recently developed C-H bond activation¹⁴ was utilized to synthesize the precursors in high yield, which shortened the synthetic procedure by two steps. In the last step, the obtained precursors were converted to the corresponding isomers I1 and I2 by Knoevenagel condensation in the presence of cyanoacetic acid and piperidine. All the target compounds were characterized using ¹H NMR, ¹³C NMR spectroscopy, and mass-spectrometry, and were found to be consistent with the proposed structures.

Compounds I1 and I2 can easily dissolve in common organic solvents, such as dichloromethane, toluene, THF, and chloroform, and produce orange and deep red solutions, respectively. Fig. 2 shows the UV-vis absorption spectra of the resulting isomers in toluene solutions (ca. 10^{-5} M). It can be found that both compounds exhibit two distinct absorption bands. The absorption band in the high-energy region (<400 nm) corresponds to the π - π * electronic transition of the conjugated backbone, and the other one in the low-energy region (>400 nm) can be assigned to an intramolecular charge transfer from the electron donating unit to the electron-withdrawing group through the cross-conjugated bridge. As shown in Fig. 2, I1 displays the maximum absorption wavelength at 441 nm. Upon changing the electron donor and acceptor to the other perpendicular direction, I2 demonstrates the maximum absorption wavelength at 476 nm with a bathochromic shift of 35 nm. Such a significant bathochromic shift can be explained by the molecular planarization. As shown in Fig. S1 (ESI⁺), the dihedral angle between the 4,8-substituted thienyl ring and the benzene core is around 34°, while the



benzo[1,2-*b*:4,5-*b'*]dithiophene is coplanar. Thus, the conjugation is more delocalized in the benzodithiophene direction in comparison to the dithienylbenzene direction, which results in stronger charge transfer interactions in **I2** and bathochromically shifted the absorption band. Moreover, when the isomeric dyes are attached on nanocrystalline TiO₂ films, isomers **I1** and **I2** display the hypsochromically shifted maximum absorption band at 419 and 450 nm, respectively (Fig. S2, ESI[†]), due to the deprotonation of the carboxylic acid.

The photoluminescence (PL) spectra of the two crossconjugated isomers in toluene solutions were also measured. The maximum emission band is located at 564 nm for isomers both **I1** and **I2**. However, as illustrated in Fig. S3 (ESI[†]), both isomers display solvent-dependent PL spectra, and bathochromic shifts of 20 and 31 nm are observed in the PL spectra of isomers **I1** and **I2**, respectively, when the solvent polarity was increased from toluene to chloroform. Such a bathochromic shift is characteristic for an efficient charge transfer from the electron donor to the acceptor through the cross-conjugated bridge.¹⁵ The larger solvatochromic effect in **I2** as compared with **I1** suggests stronger charge transfer interactions in **I2**.

To further investigate the electronic properties of the two cross-conjugated compounds, the electrochemical behavior was studied using cyclic voltammetry (CV). As shown in Fig. 3, both cross-conjugates exhibit one reversible oxidative wave at lower potential attributed to the oxidation of the triphenylamine moiety and one quasi-reversible oxidative wave at higher potential assigned to the oxidation of the DTBDT core. The first half-wave potential $(E_{1/2})$ for I1 and I2, which is taken as the HOMO levels of the isomers, was determined to be 0.77 and 0.81 V (vs. NHE, the same below), respectively. Correspondingly, calculated from HOMO levels and the optical band gap,¹⁶ the LUMO energy level of **I1** and **I2** is -1.54 and -1.38 V, respectively. Moreover, the second $E_{1/2}$ for I1 and I2 is determined to be 1.27 and 1.33 V, respectively. It can be clearly observed that both the first and the second oxidative potential values of I2 are higher than those for I1. This is due to the more delocalized conjugated system in I2, which lowers the electron density and results in a higher oxidative potential.¹⁷ The more delocalized conjugation in I2 also suggests stronger charge transfer interactions.





Fig. 4 J-V curves for the DSSCs based 11 and 12. IPCE spectra are shown in the inset.

Dye-sensitized solar cells were constructed using the resulting isomers with push–pull configuration as the sensitizer on transparent conductive glass (F-doped SnO₂, FTO). As shown in Fig. 4, the DSSC with **I1** as the sensitizer produced a short circuit photocurrent density (J_{sc}) of 10.01 mA cm⁻², an open circuit voltage (V_{oc}) of 0.76 V, and a fill factor (FF) of 0.73, corresponding to an η of 5.5%. Under the same conditions, **I2** based DSSC offered a J_{sc} of 12.46 mA cm⁻², a V_{oc} of 0.79 V, and an FF of 0.71, corresponding to an η value of 7.0%.

To understand the enhancement of the J_{sc} value, action spectra of the incident photon-to-current conversion efficiencies (IPCE) as a function of incident wavelength for the two DSSCs are recorded and shown in the inset of Fig. 4. The DSSCs based on **I1** and **I2** display almost identical highest IPCE value of over 85%. However, the IPCE spectrum for the DSSC based on **I2** is much broader than that for **I1**, which is in good agreement with their absorption spectra. The integral current densities from IPCE spectra are calculated to be 8.28 and 10.25 mA cm⁻², for **I1** and **I2** based DSSCs, respectively, which are lower than the corresponding J_{sc} values from J-V curves. The experimental error between J_{sc} from the J-V curve and that from IPCE is around 17%, which is probably attributed to the spectral mismatch between the simulated and standard AM1.5G solar light.

Since V_{oc} is related to the conduction band position of TiO₂ and the charge recombination rate in DSSCs, to explain the difference of another important performance parameter (V_{oc}), the electron lifetime against charge density for the DSSCs (Fig. S4, ESI[†]) was investigated since the relative conduction band positions are generally identical for the DSSCs based on sensitizers with similar chemical structures. At the same charge density, the electron lifetime of **I2** based DSSC is longer than that of **I1**. Consequently, the reduced charge recombination rate constant will reduce electron loss at an open circuit. When more charge is accumulated in TiO₂, the Fermi level moves upward and V_{oc} becomes larger.

In summary, two cross-conjugated isomers based on the **DTBDT** unit were designed and synthesized. It was found that the charge transfer interaction was much stronger in the benzodithiophene direction as compared with the other dithienylbenzene direction. As a result, the DSSC based on isomer **I2** exhibited a power conversion efficiency of 7.0% which was much higher than that for the DSSC based on isomer **I1**. Our findings provide insight into the push-pull effects in the cross-conjugated system and will guide the design of the organic semiconductors based on cross-conjugated materials.

This work was financially supported by the National Basic Research Program (2011CB933302) of China, the National Natural Science Foundation of China (90922004 and 51273045), Shanghai Pujiang Project (11PJ1401700), STCSM (12JC1401500), Shanghai Leading Academic Discipline Project (B108), and Jiangsu Major Program (BY2010147).

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