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Enhanced Photovoltaic Response in Hydrogen-Bonded All-Organic Devices

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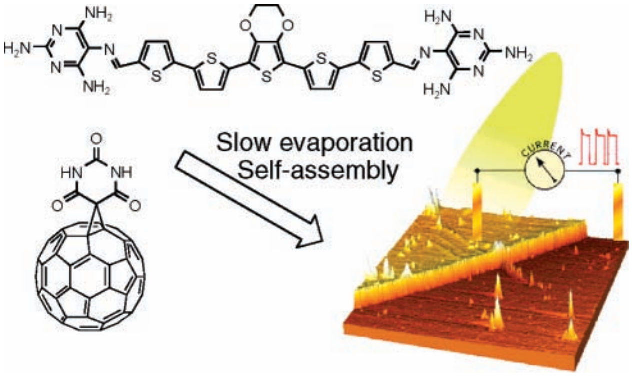
ABSTRACT



Straightforward synthetic methodologies are reported for the functionalization of oligothiophenes with hydrogen-bonding motifs. Codeposition from a solution of symmetric melamine-terminated electron-donor oligomers with a complementary barbiturate-labeled electron-acceptor fullerene resulted in homogeneous films. Incorporation into photovoltaic devices gave a 2.5-fold enhancement in light energy to electrical energy conversion when compared to analogous systems with the non-hydrogen-bonding parent C_{60}.

Complementary binding sites can, in principle, be used to program the self-assembly of electroactive donor and acceptor components into molecular heterojunctions, leading to the deliberate formation of functional architectures of low dimensionality that could build themselves from the nanometer-level upward.[1] Furthermore, it has been suggested that current amorphous organic photovoltaic systems could be improved if, following photoinduced charge separation, electron and hole movement was facilitated due to the regimented orientation of electroactive components.[2] In this approach, the use of non-self-complementary hydrogen-bonding motifs present in melamine−barbituric acid assemblies offers the possibility to further control the exact geometries of electron donor and acceptor even beyond the photoactive dyad.[3] The formation of hydrogen-bonded ribbons, in which the barbiturate and melamine moieties occupy opposing sides of a one-dimensional structure, is particularly interesting as this separation can be used to greater benefit than conventional covalent synthesis to induce ordering beyond the molecular level.[4]

To be of interest, molecular recognition units should be introduced in good yield in a minimum number of steps. Herein, we describe a straightforward synthetic methodology for the introduction of complementary, yet non-self-complementary, molecular recognition motifs based on the

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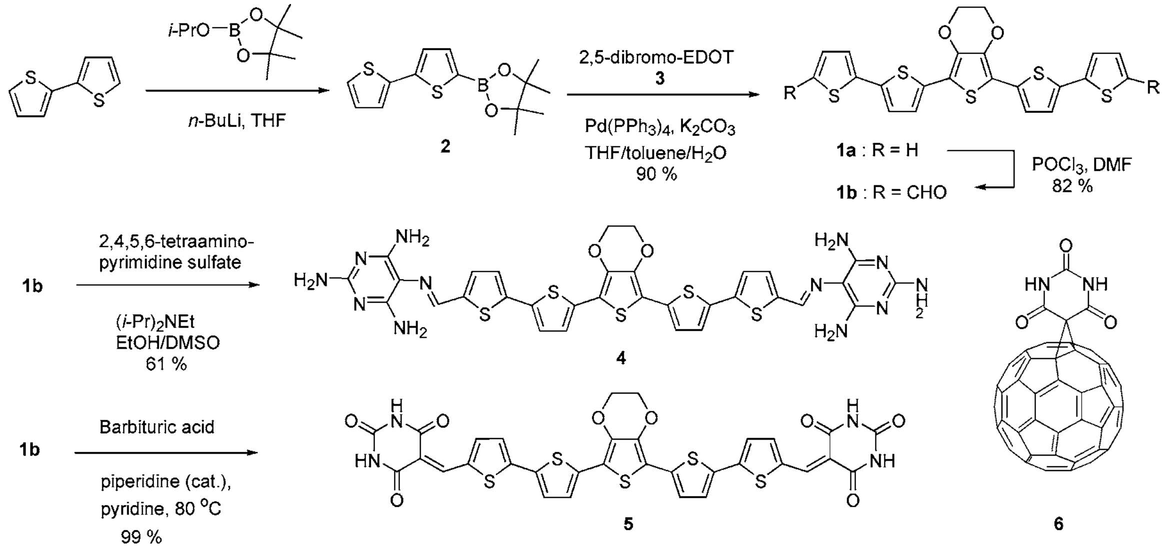
(1) See for example: (a) Beckers, E. H. A.; van Hal, P. A.; Schenning, A. P. H. J.; El-ghayoury, A.; Peeters, E.; Rispens, M. T.; Hummelen, J. C.; Meijer, E. W.; Janssen, R. A. J. *J. Mater. Chem.* **2002**, *12*, 2054. (b) Segura, M.; Sanchez, L.; de Mendoza, J.; Martin, N.; Guldi, D. M. *J. Am. Chem. Soc.* **2003**, *125*, 15093. (c) Haider, J. M.; Chavarot, M.; Weidner, S.; Sadler, I.; Williams, R. M.; De Cola, L.; Pikramenou, Z. *Inorg. Chem.* **2001**, *40*, 3912.

(2) (a) Brédas, J.-L.; Beljonne, D.; Coropceanu, V.; Cornil, J. *Chem. Rev.* **2004**, *104*, 4971. (b) Fox, M. A. *Acc. Chem. Res.* **1999**, *32*, 201.

(3) Simanek, E. E.; Li, X.; Choi, I. S.; Whitesides, G. M. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Ed.; Pergamon: New York, 1996; Vol. 9, Chapter 17.

10.1021/ol050966l CCC: $30.25

Scheme 1. Synthesis of **1**−**5** and Structural Formula of **6**



melamine−barbituric acid system from readily available starting materials using Schiff base formation or the Knoevenagel condensation.

Typically, the synthesis of substituted melamine derivatives relies on the availability of suitably substituted amine starting materials, which are notoriously difficult to prepare and purify in the case of conjugated oligomers due to rapid oxidation. We reasoned that the formation of a stable Schiff base between 2,4,5,6-tetraaminopyrimidine and formylated oligomers (the latter are easily obtained in good yields by Vilsmeier−Haack formylation) should proceed selectively with the more reactive 5-amino group. The π-conjugated oligomer used in this study is based on a pentameric oligothiophene containing a central EDOT unit (**1a**). Like the well-studied sexithiophene,[5] the pentameric unit offers attractive electronic properties, notably the capacity to participate in photoinduced electron-transfer reactions with C_{60}. The incorporation of a central EDOT unit augments the solubility and diminishes the oxidation potential with respect to the parent pentathiophene ($E_{ox} = 0.31$ V vs ferrocene, see Supporting Information).[6,7]

The synthesis of oligothiophene **1b** was carried out as shown in Scheme 1, via a Suzuki cross-coupling reaction between boron ester **2** and 2,5-dibromo-EDOT **3**, followed by formylation. Compared to the use of other organometallic cross-coupling methods such as the Kumada[8] or Stille reaction,[9] **1a** was obtained in high yield (90%) and did not require purification by column chromatography.

Subsequent introduction of the melamine unit was achieved using a Schiff base reaction to give **4**. As Schiff base formation is an equilibrium process, high yields of the most stable adduct can be obtained on reaction with 2,4,5,6-tetraaminopyrimidine. Equally, quantitative preparation of the symmetric complementary barbituric acid-terminated oligomer **5** was possible in one step by Knoevenagel condensation with barbituric acid.

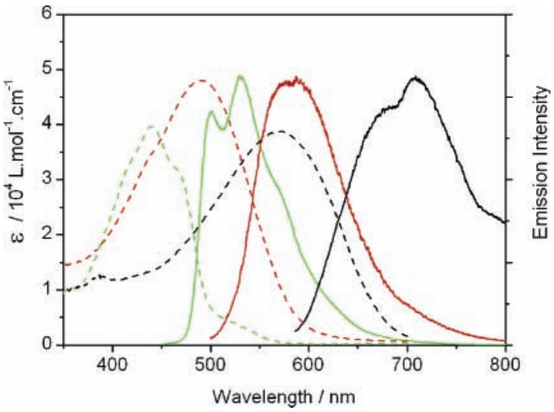


Figure 1. (a) Absorption (dashed lines) and fluorescence (solid lines) spectra of **1a** (green, $\lambda_{ex} = 440$ nm), **4** (red, $\lambda_{ex} = 490$ nm), and **5** (black, $\lambda_{ex} = 575$ nm) in DMSO.

The absorption and emission spectra of **1a**, **4**, and **5** are shown in Figure 1. An important observation is that the

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(4) (a) Bassani, D. M.; Darcos, V.; Mahony, S.; Desvergne, J.-P. *J. Am. Chem. Soc.* **2000**, *122*, 8795. (b) Vida, Y.; Suau, R.; Perez-Inestrosa, E.; Bassani, D. M. *Chem. Commun.* **2004**, 1270.

(5) (a) Kalinowski, J.; Stampor, W.; Di Marco, P.; Garnier, F. *Chem. Phys.* **1998**, *237*, 233. (b) Marks, R. N.; Muccini, M.; Lunedi, E.; Michel, R. H.; Murgia, M.; Zamboni, R.; Taliani, C.; Horowitz, G.; Garnier, F.; Hopmeier, M.; Oestreich, M.; Mahrt, R. F. *Chem. Phys.* **1998**, *227*, 49.

(6) (a) Apperloo, J. J.; Groenendaal, L. B.; Verheyen, H.; Jayakannan, M.; Janssen, R. A. J.; Dkhissi, A.; Beljonne, D.; Lazzaroni, R.; Brédas, J.-L. *Chem. Eur. J.* **2002**, *8*, 2384. (b) Turbiez, M.; Frére, P.; Blanchard, P.; Roncali, J. *Tetrahedron Lett.* **2000**, *41*, 5521. (c) Groenendaal, L. B.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481.

(7) Facchetti, A.; Yoon, M. H.; Stern, C. L.; Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 13480.

(8) Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Chem. Mater.* **1996**, *8*, 882.

(9) Turbiez, M.; Frére, P.; Roncali, J. *J. Org. Chem.* **2003**, *68*, 5357.

increased conjugation in **4** and **5**, compared to **1a**, extends the absorption envelope further into the visible portion of the spectrum. This is of significance because it implies that it is not necessary to synthesize longer oligomers to obtain materials with an absorption spectrum that is well-matched to incident solar radiation, ca. 40% of which is in the visible region. The emission spectra of **4** and **5** display a large Stokes' shift indicative of a polar excited state, presumably due to the electron-withdrawing nature of the end groups. These results indicate that the molecular recognition units are conjugated with the oligomer π-system.

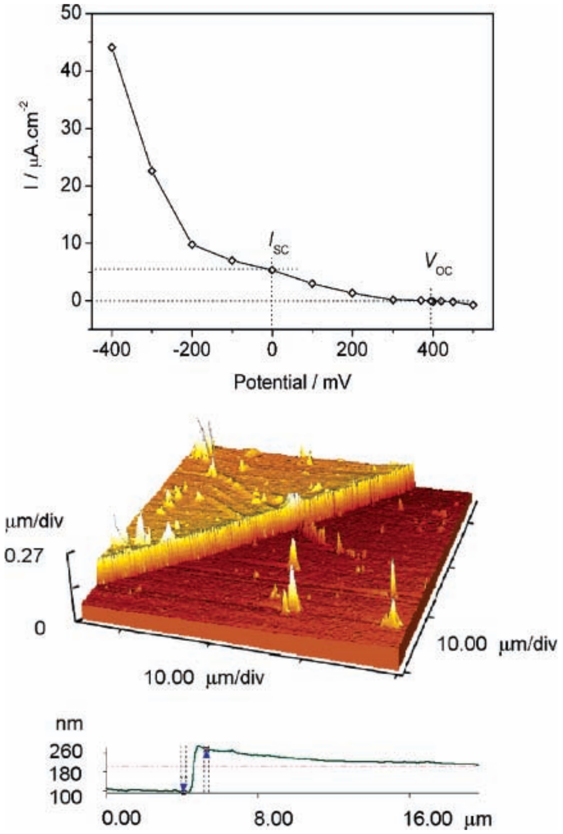

Figure 2. *I*/*V* curve obtained from a drop-cast film of **4** on Au and AFM image of the film showing its thickness.

The photovoltaic response of these materials when used in conjunction with a barbiturate-substituted fullerene derivative was investigated to assess their usefulness in the construction of devices. Regarding the nanostructuring of the binary hydrogen-bonding donor−acceptor films, in which rosettes, crinkled tapes, and linear tapes are possible, only the linear array satisfies all the hydrogen-bonding sites of **4**.[2,3] Simple photovoltaic devices were constructed using **4** and a complementary fullerene-substituted barbituric acid derivative (**6**) to test the suitability of such materials for molecule-based electronics.[10] Solutions of **4** and **6** (1:2 ratio) were prepared in polar DMSO (not conducive to formation of hydrogen-bonded structures in homogeneous solutions). Drop-casting and slow evaporation of the solvent on a gold slide resulted in the formation of a thin film whose response could be measured in a two-compartment aqueous photoelectrochemical cell, irradiating with light in the 400−500 nm region in the presence of an electrolyte and with methyl viologen acting as the electron carrier.[11]

At first, oligothiophene **4** was tested alone (device A) to verify that the there is a photovoltaic response with films of this molecule. A typical *I*/*V* graph of photocurrent generated vs applied potential is shown in Figure 2 for **4**. The thickness of the film was estimated at ca. 200 nm using AFM, which also showed that the films are even and reproducible. From the *I*/*V* curve, and using eqs 1 and 2, the open-circuit voltage conversion efficiency, $\Phi(V_{oc})$, and short-circuit quantum conversion efficiency, $\Phi(I_{sc})$, of the photovoltaic device can be estimated. Respectively, these values express the fraction of light energy that is converted into voltage and the fraction of electrons generated for every photon of light that is absorbed.[12]

$$\Phi(V_{oc}) = V_{oc}/E_{00} \tag{1}$$

$$\Phi(I_{sc}) = (\mathrm{d}n_e/\mathrm{d}t)/(\mathrm{d}n_{h\nu}/\mathrm{d}t) \tag{2}$$

where n_e and $n_{h\nu}$ are the number of charges generated and the number of photons absorbed, respectively, and E_{00} is the energy of the $S_1 \leftarrow S_0$ transition in eV. The incident light intensity was determined to be 150 mW cm^{-2}, which corresponds to an average photon flux of 5.6×10^{-8} Einstein s^{-1} (at 450 nm).

From the measured thickness of the film, it is estimated that ca. 2.7% of incident light is absorbed. From eqs 1 and 2 above and values of $V_{oc} = 0.39$ V and $I_{sc} = 6.8$ μA, one can obtain $\Phi(V_{oc}) = 0.14$ and $\Phi(I_{sc}) = 0.05$. This value is comparable to other photovoltaic devices based on similar technology (although experimental error, associated mainly with the determination of film thickness, must be taken into consideration). Identical devices were then prepared using **4** (1 equiv) in the presence of either 2 equiv of pristine C_{60} (device B) or 2 equiv of **6** (device C). It should be noted that both C_{60} and **6** are only sparingly soluble in DMSO. However, compound **6** was completely solubilized in the presence of **4**. This behavior is typical of compounds possessing complementary molecular recognition sites and is taken as an indication of interaction at the molecular level.

The response of the photovoltaic devices A, B, and C in the presence and absence of light at an applied potential of −100 mV is shown in Figure 3. As noted by others, a gain in performance (ca. 2-fold) is obtained by the incorporation

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(10) (a) McClenaghan, N. D.; Absalon, C.; Bassani, D. M. *J. Am. Chem. Soc.* **2003**, *125*, 13004. (b) McClenaghan, N. D.; Grote, Z.; Darriet, K.; Zimine, M.; Williams, R. M.; De Cola, L.; Bassani, D. M. *Org. Lett.* **2005**, *7*, 807.

(11) Compare with SAM systems: (a) Hirayama, D.; Takimiya, K.; Aso, Y.; Otsubo, T.; Hasobe, T.; Yamada, H.; Imahori, H.; Fukuzumi, S.; Sakata, Y. *J. Am. Chem. Soc.* **2002**, *124*, 532. (b) Imahori, H.; Liu, J.-C.; Hosomizu, K.; Sato, T.; Mori, Y.; Hotta, H.; Matano, Y.; Araki, Y.; Ito, O.; Maruyama, N.; Fujita, S. *Chem. Commun.* **2004**, 2066.

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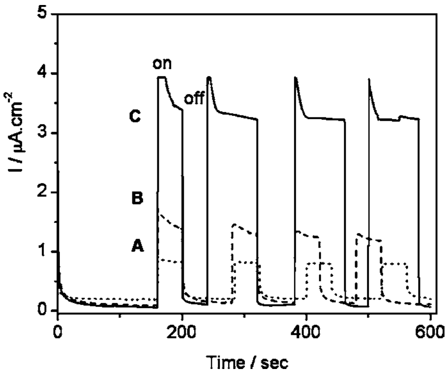


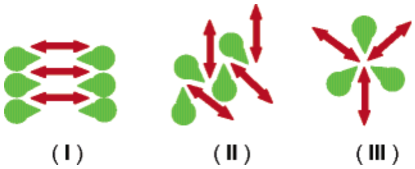
Figure 3. Illumination dependence of the photovoltaic response of devices A (solid line), B (dashed line), and C (dotted line) at an applied potential of −100 mV.

of C_{60} in conjugated polymer blends. More importantly, a 5-fold enhancement in photocurrent under identical experimental conditions is obtained from the use of the modified C_{60} (device C). This improvement is attributed to better miscibility, compared to pristine C_{60}, of **6** with the conjugated oligomer. This in turn allows a more even incorporation of C_{60} derivative in the device, leading to a greater degree of charge separation.

On the basis of the calculated efficiency of device A, one can estimate the efficiency of devices incorporating the modified C_{60} derivative **6** to be as high as 25%. This compares favorably with recent photovoltaic devices based on the layer-by-layer construction of conjugated polymers and C_{60}. However, attempts to increase the absorbance of the film by increasing its thickness resulted in a decrease in photocurrent. This is consistent with a low-charge carrier mobility in the material, in agreement with previous measurements of charge transport based on field-effect transistor devices.[13]

An important factor that became immediately apparent during this initial testing phase of the devices is their inherent stability toward air and moisture. Indeed, the photovoltaic cell setup uses an aerated aqueous solution of methyl viologen as the electron transport agent. The response of **4** (device A) is stable over time, whereas device B (**4** + pristine C_{60}) exhibits a slow (ca. 10% loss) of efficiency over a period of 1 h (see Supporting Information). During this same period, no measurable decrease in efficiency was detected for device C (**4** + **6**).

The observed improvement in photovoltaic response is attributed to the presence of complementary hydrogen-bonding between the active components. At the very least, this is expected to provide increased compatibility between otherwise poorly miscible materials. Additionally, the hydrogen-bonding pattern employed is conducive to the formation of extended organized domains, which are expected to be beneficial to charge separation and transport. Of the three architectures observed in melamine−barbituric acid systems, the tapelike structure I is the most common, and, in the case of **4** and **6**, it is also the only one that satisfies all the hydrogen-bonding requirements of both molecular constituents. Further work is in progress to provide evidence for the existence of these structures in the solid.



In conclusion, the introduction of hydrogen-bonding molecular recognition motifs in direct conjugation to an oligothiophene unit via a Schiff base reaction or Knoevenagel condensation provides a straightforward route from the corresponding dialdehyde intermediate. This strategy should be widely applicable and of interest for the preparation of ordered supramolecular devices.

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Supporting Information Available: Experimental procedures and synthesis and characterization data of **1**−**5** (^{1}H NMR, ^{13}C NMR, HRMS, IR), as well as preparation of devices (A−C). This material is available free of charge via the Internet at http://pubs.acs.org.

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