ORGANIC
LETTERS

2010
Vol. 12, No. 4
660−663

Synthesis of Isoindigo-Based Oligothiophenes for Molecular Bulk Heterojunction Solar Cells

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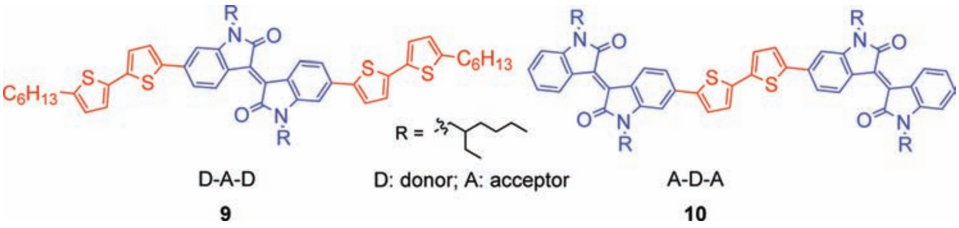
Received November 2, 2009

ABSTRACT



Isoindigo, as a new electron acceptor unit for organic electronic materials, was integrated into two low-energy gap oligothiophenes. Optical and electrochemical studies of the newly synthesized oligomers demonstrate broad absorption through the visible spectrum, along with appropriate energy levels, as desired for light harvesting donors for organic solar cells when blended with [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{60}BM$). Molecular heterojunction solar cells were fabricated using these oligomers and exhibit a power conversion efficiency up to 1.76% with a V_{oc} of 0.74 V, I_{sc} of 6.3 mA/cm^2 and fill factor of 0.38.

Conjugated polymer-based bulk-heterojunction (BHJ) solar cells have received considerable attention as potential alternative renewable energy sources,[1] due to their suitability for low-cost, fast solution processing techniques and their compatibility with flexible substrates. Significant efforts are being put forth to develop conjugated polymers that meet various criteria for high performance photovoltaic applications.[2] Currently, state-of-the-art polymer-based BHJ solar cells have reached power conversion efficiencies (PCE) of 6%.[3] However, these numbers are still significantly lower than the critical efficiencies of 10−12% many believe are required for commercial utility.[4] The strong motivation for approaching such efficiencies is driving various research efforts in the area of organic based BHJ solar cells.[1−5] Molecular crystalline semiconductors as alternatives to conjugated polymers offer several intrinsic advantages in solution-processable BHJ solar cells. Owing to their monodisperse nature with well-defined chemical structures, together with no end-group contaminants or batch-to-batch variations molecular organic semiconductors can be repro-

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(1) (a) Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474–1476. (b) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58–77. (c) Gunes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324–1338. (c) Cheng, Y.; Yang, S.; Hsu, C. *Chem. Rev.* **2009**, *109*, 5868–5923.

(2) (a) Bundgaard, E.; Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 954–985. (a) Kroon, R.; Lenes, M.; Hummelen, J. C.; Blom, P. W. M.; Boer, B. D. *Poly. Rev.* **2008**, *48*, 531–582. (c) Liang, Y.; Feng, D.; Wu, Y.; Tsai, S.-T.; Li, G.; Ray, C.; Yu, L. *J. Am. Chem. Soc.* **2009**, *131*, 7792–7799.

(3) (a) Hou, J.; Chen, H.-Y.; Zhang, S.; Chen, R. I.; Yang, Y.; Wu, Y.; Li, G. *J. Am. Chem. Soc.* **2009**, *131*, 15586–15587. (b) Park, S. H.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photonics* **2009**, *3*, 297–302.

(4) Scharber, M. C.; Wuhlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. L. *Adv. Mater.* **2006**, *18*, 789–794.

(5) (a) Scherf, U.; Gutacker, A.; Koenen, N. *Acc. Chem. Res.* **2008**, *41*, 1086–1097. (b) Taranekar, P.; Qiao, Q.; Jiang, H.; Ghiviriga, I.; Schanze, K. S.; Reynolds, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 8958–8959. (c) Lee, J. K.; Ma, W. L.; Brabec, C. J.; Yuen, J.; Moon, J. S.; Kim, J. Y.; Lee, K.; Bazan, G. C.; Heeger, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 3619–3623. (d) Kose, M. E.; Mitchell, W. J.; Kopidakis, N.; Chang, C. H.; Shaheen, S. E.; Kim, K.; Rumbles, G. *J. Am. Chem. Soc.* **2007**, *129*, 14257–14270.

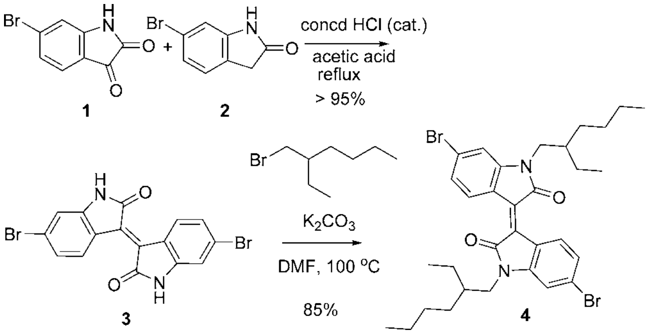
10.1021/ol902512x

ducibly prepared, functionalized and purified. Despite the fact that the highest PCEs to date for small molecule based solar cells remain lower than their polymer-based analogs, the considerations above make molecular crystalline semiconductors attractive as active materials in BHJ solar cells.[6]

Encouraged by recent reports on diketopyrrolopyrrole oligothiophenes as donor materials in molecular BHJ solar cells, where PCEs of 2.2−4.4% have been demonstrated by Nguyen and co-workers,[7] we here report the synthesis and characterization of isoindigo-based oligothiophenes and their use as donor materials in molecular BHJ solar cells.

Isoindigo is a structural isomer of the famous pigment indigo and is often found as an intermediate in drug development. In this communication, the isoindigo unit is used as an electron acceptor to form donor−acceptor−donor (DAD) and acceptor−donor−acceptor (ADA) isoindigo-based oligothiophenes in conjunction with bithiophene as an electron donor.

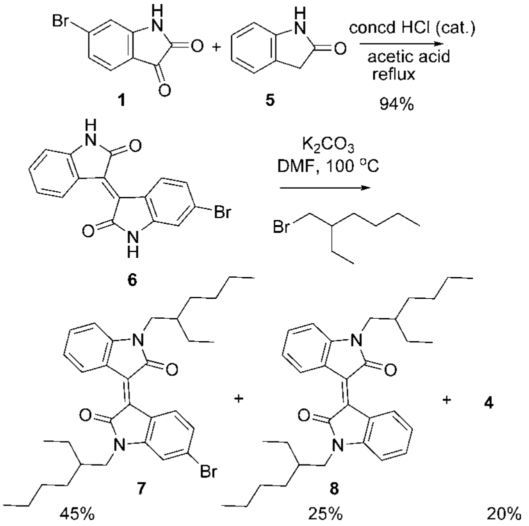
Scheme 1. Synthesis of 6,6′-Dibromoisoindigo



The work starts with the acid-catalyzed adol condensation and dehydration of commercially available 6-bromoisatin **1** and 6-bromooxindole **2** in acetic acid under argon,[8] yielding 6,6′-dibromoisoindigo **3** in almost quantitative yield (Scheme 1). Due to the existence of strong $\pi-\pi$ interactions and hydrogen bonding, compound **3** is slightly soluble in common organic solvents. Subsequently shown is the *N*-alkylation of **3** using branched alkyl bromide and efficient formation of highly soluble 6,6′-dibromoisoindigo derivative **4** in 85% yield.

The same approach has also been utilized to prepare alkylated 6-bromoisoindigo **7** (Scheme 2). Interestingly, isoindigo **8** and 6,6′-dibromoisoindigo **4** were also observed, in addition to the desired product **7**, upon reaction of 6-bromoisatin and oxindole followed by alkylation. Fortunately, the mixture can be easily separated by chromatography. The unexpected formation of **8** and **4** is likely due to acid- or base-promoted retro-adol/adol sequences that scrambled the product distribution under the existing conditions.[9] To test this hypothesis, an equimolar mixture of **8** and **4** was mixed and subjected to the two-step reaction conditions, respectively. The experiments revealed that crossover was indeed observed and **7** was produced in DMF with K_2CO_3 at 100 °C, whereas no crossover was observed in the acidic condition. It was further found that use of anhydrous DMF and fresh-dried base can minimize the scrambling.

Scheme 2. Synthesis of 6-Bromoisoindigo[a]



[a] Mole ratio of compound **7, 8** and **4** (∼2:1:1).

With **4** and **7** in hand, isoindigo-based DAD and ADA oligothiophenes **9** and **10** were successfully obtained by incorporating electron rich bithiophene units via Suzuki coupling (Scheme 3).[10] The structures of **9** and **10** were confirmed by ^{1}H- and ^{13}C NMR, MALDI-TOF mass spectrometry, and elemental analysis. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) revealed that **9** and **10** melt at 181 and 230 °C, respectively, and are both stable to greater than 350 °C.

UV−vis absorption spectra of the oligomers, both in THF solution and as films on indium−tin oxide coated glass were measured (Figure 1). Compound **9** and **10** broadly absorb at wavelengths up to 688 and 655 nm in solution with molar

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(6) (a) Silvestri, F.; Irwin, M. D.; Beverina, L.; Facchetti, A.; Pagani, G. A.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 17640–17641. (b) Zhang, J.; Yang, Y.; He, C.; He, Y.; Zhao, G.; Li, Y. *Macromolecules* **2009**, *42*, 7619–7622. (c) Roquet, S.; Cravino, A.; Leriche, P.; Aleveque, O.; Frere, P.; Roncali, J. *J. Am. Chem. Soc.* **2006**, *128*, 3459–3466. (d) Ma, C.-Q.; Fonrodona, M.; Schikora, M. C.; Wienk, M. M.; Janssen, R. A. J.; Bauerle, P. *Adv. Funct. Mater.* **2008**, *18*, 3323–3331. (e) Roncali, J. *Acc. Chem. Res.* **2009**, *42*, 1719–1730.

(7) (a) Tamayo, A. B.; Walker, B.; Nguyen, T.-Q. *J. Phys. Chem. C* **2008**, *112*, 11545–11551. (b) Walker, B.; Tamayo, A. B.; Dang, X.-D.; Zalar, P.; Seo, J. H.; Garcia, A.; Tantiwiwat, M.; Nguyen, T.-Q. *Adv. Funct. Mater.* **2009**, *19*, 3063–3069. (c) Tamayo, A. B.; Tantiwiwat, M.; Walker, B.; Nguyen, T.-Q. *J. Phys. Chem. C* **2008**, *112*, 15543–15552.

(8) Christos, P.; Xaver, B. *Helv. Chim. Acta* **1988**, *71*, 1079–1083.

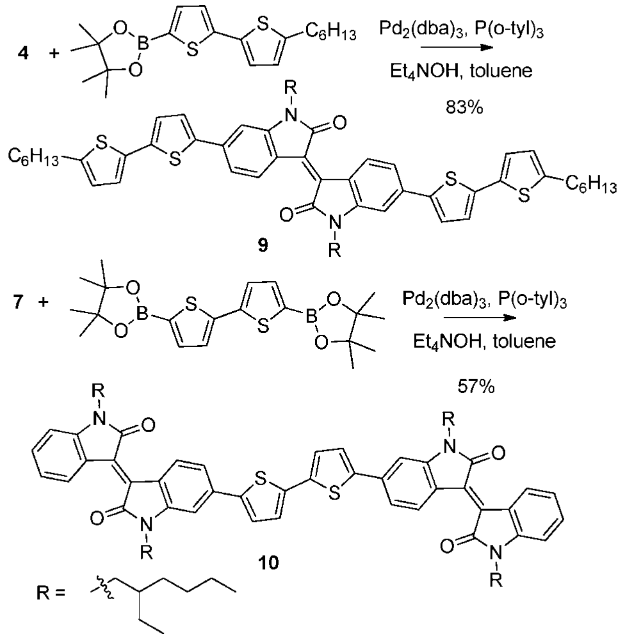
(9) (a) Komata, T.; Matsunaga, K.; Hirotsu, Y.; Akiba, S.; Ogura, K. *J. Fluorine Chem.* **2007**, *128*, 902–909. (b) Overman, L. E.; Peterson, E. A. *Tetrahedron* **2003**, *59*, 6905–6919.

(10) Perzon, E.; Zhang, F.; Andersson, M.; Mammo, W.; Inganäs, O.; Andersson, M. R. *Adv. Mater.* **2007**, *19*, 3308–3311.

(11) Jayakannan, M.; Paul, A. v. H.; René, A. J. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 251–261.

(12) Thompson, B. C.; Kim, Y.-G.; McCarley, T. D.; Reynolds, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 12714–12725.

Scheme 3. Synthesis of Isoindigo-Based Oligothiophenes



absorptivities of 19 500 and 47 300 L M^{-1} cm^{-1} at 579 and 560 nm, and are, thus, strongly absorbing through most of the visible spectrum as desired for potential solar cell applications. Markedly different from other donor−acceptor systems,[7,11] there exists only a very shallow absorption valley between two absorption bands for both molecules, which makes them appear virtually black in solution. The spectra broaden and extend to 744 and 703 nm in the solid state with a peak emerging at 660 and 636 nm for **9** and **10**, indicating strong $\pi-\pi$ interactions in their crystalline forms.[7a] Upon annealing at 100 °C for 20 min, a slight decrease in absorption intensity was observed for both oligothiophenes (see Supporting Information). From the absorption onsets in the solid state, the optical energy gaps are estimated to be 1.67 eV for the DAD molecule and 1.76 eV for the ADA molecule. Both **9** and **10** are fluorescent, emitting with maxima at 780 and 749 nm in chloroform, respectively (see Supporting Information).

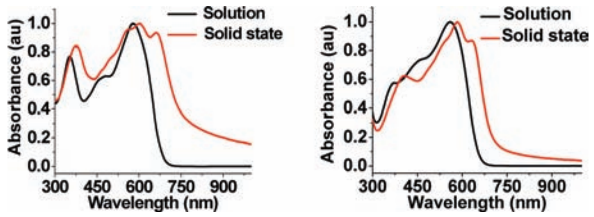


Figure 1. Normalized solution and solid state absorption spectra of **9** (left) and **10** (right).

The redox behavior of the oligomers was investigated by cyclic voltammetry (CV) in a 0.1 M solution of TBAPF$_6$/dichloromethane (DCM) solution (Figure 2). Both oligothiophenes present two consecutive quasi-reversible reduction peaks with $E_{1/2}^{\mathrm{red}}$ of −1.31 and −1.71 V for **9**, and of −1.35 and −1.74 V for **10**. In the oxidation region, two oxidation waves appear in the CV of **9** with $E_{1/2}^{\mathrm{ox}}$ of 0.47 and 0.58 V; while only one oxidation wave was observed for **10** with $E_{1/2}^{\mathrm{ox}}$ of 0.52 V. This is in accordance with the more electron donating contribution in the DAD molecule than the ADA molecule. The LUMO and HOMO energies of **9** and **10**, estimated by CV,[12] are −3.9 and −5.5 eV, and −3.8 and −5.5 eV, respectively.

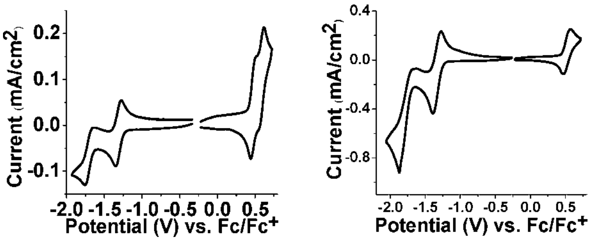


Figure 2. Cyclic voltammetry of **9** (left) and **10** (right) measured in a 0.1 M solution of TBAPF$_6$/DCM (scan rate 25 mV/s) vs Fc/Fc$^+$.

To gain more insight into the energy levels in solid state, differential pulse voltammetry (DPV) was performed on drop-cast films of **9** and **10** on Pt button electrodes (see Supporting Information). From the onset of oxidation in DPVs, HOMO levels of −5.6 eV are estimated for both **9** and **10**. Unfortunately, the first reduction wave was not observed for both molecules. Therefore, the LUMO levels were calculated using the values obtained from the solid state optical band gap, giving − 3.9 and − 3.8 eV for **9** and **10**. The solid state results are very close to the ones in solution. The appropriate energy levels and gaps, together with the

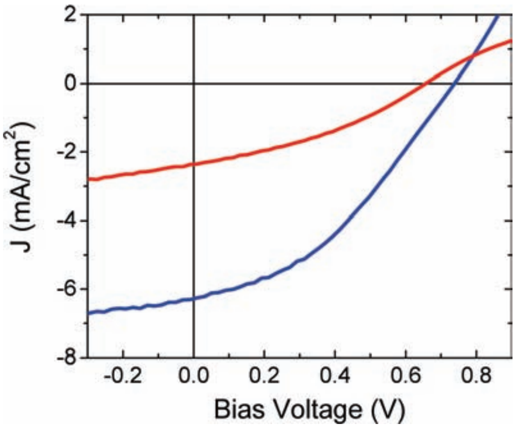


Figure 3. Performance of **9**/**10**:PC$_{60}$BM solar cells. $J-V$ characteristics under 100 mW/cm^2 white light illumination (**9** in blue and **10** in red) annealed at 100 °C for 20 min.

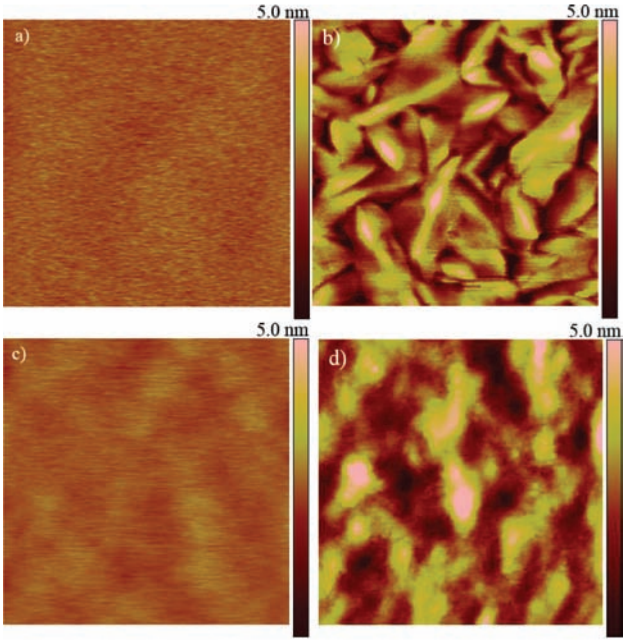


Figure 4. AFM height images of **9**:PC$_{60}$BM (50:50) spin-coated from chlorobenzene (a) as cast, and (b) annealed at 100 °C for 20 min; **10**:PC$_{60}$BM (60:40) spin-coated from chlorobenzene (c) as cast, and (d) annealed at 100 °C for 20 min. All images are 1 × 1 μm with 5 nm height scales. RMS surface roughness values of the AFM images are (a) 0.15 nm, (b) 0.98 nm, (c) 0.14 nm, and (d) 0.95 nm.

high absorption coefficients, suggest the new isoindigo-based oligothiophenes should be effective electron donors in BHJ solar cells.

Molecular BHJ solar cells were fabricated by spin-coating **9**/**10**:PC$_{60}$BM blends from chlorobenzene onto a clean ITO/PEDOT:PSS bottom electrode on a glass substrate. Optimization experiments exploring different blend ratios, annealing temperatures, and solution concentrations resulted in the highest power conversion efficiencies (PCEs) for **9**/**10**:PC$_{60}$BM blend ratios of 50:50 (**9**) and 60:40 (**10**), an annealing temperature of 100 °C, and a total solution concentration of 18 mg/mL.

The BHJ cells made from **9** performed significantly better than devices made from **10**. After annealing at 100 °C, solar cells made from **9** showed a PCE of up to 1.76%, with a V_{oc} of 0.74 V, J_{sc} of 6.3 mA/cm^2, and fill factor of 0.38. Annealed photovoltaic devices (100 °C) of **10** had PCEs of up to 0.55%, with a V_{oc} of 0.66 V, J_{sc} of 2.4 mA/cm^2, and fill factor of 0.36. Preannealed devices were less efficient with PCEs of 0.72 and 0.11% for **9** and **10** respectively. The $J-V$ characteristics for annealed devices are shown in Figure 3.

The AFM height images of the blend films before and after annealing are presented in Figure 4. These images show that upon annealing the surface of the films become rougher and more ordered domains appear to form. It is suspected that **9** performs better than **10** in solar cells in part due to a higher degree of ordering, and a lower energy gap.

In conclusion, we report the synthesis and characterization of isoindigo-based oligothiophenes, and their utilization as electron donors in molecular BHJ solar cells for the first time. These devices exhibit very promising power conversion efficiencies for solution-processed small molecule solar cells. We are currently working to fine-tune the optical and electronic properties of isoindigo-based donor−acceptor materials through molecular design, to bridge chemical structure, film morphology and photovoltaic response, as well as to optimize processing conditions suitable for small molecules.

Acknowledgment. We gratefully acknowledge AFOSR (FA9550-09-1-0320) for financial support. Thanks to Prof. Aaron Aponick at University of Florida (UF) for useful suggestions and to Dr. Quentin Bricaud at UF for his assistance in device testing. K.R.G. and R.S. acknowledge the University Alumni Awards Program for a fellowship.

Supporting Information Available: Detailed procedures, characterization details, optical spectra of blends, and device fabrication. This material is available free of charge via the Internet at http://pubs.acs.org.

OL902512X