

ChemComm

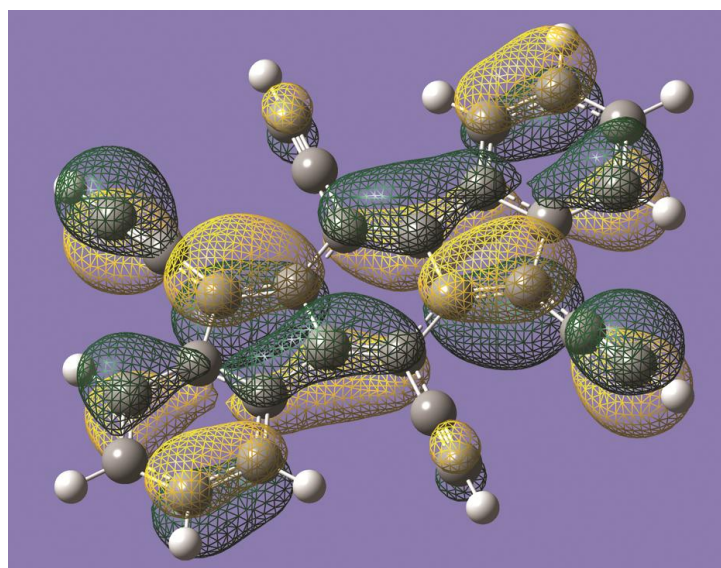
This article is part of the

Aromaticity web themed issue

Guest editors: Nazario Martín, Michael Haley and
Rik Tykwinski

All articles in this issue will be gathered together
online at

www.rsc.org/cc/aroma



Cite this: *Chem. Commun.*, 2012, **48**, 8919–8921

www.rsc.org/chemcomm

Synthesis of 3,7-diiodo-2,6-di(thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]difurans: functional building blocks for the design of new conjugated polymers†

Brandon M. Kobilka,^a Anton V. Dubrovskiy,^a Monique D. Ewan,^a Aimée L. Tomlinson,^b Richard C. Larock,^a Sumit Chaudhary^c and Malika Jeffries-EL^{*a}

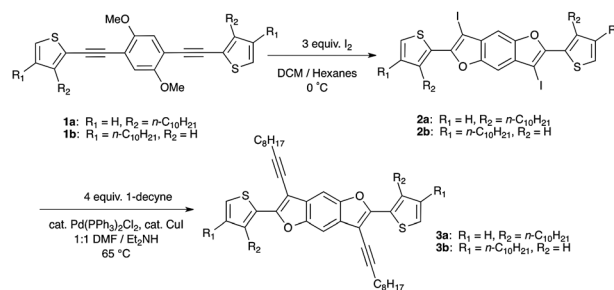
Received 7th June 2012, Accepted 20th July 2012

DOI: 10.1039/c2cc34070d

3,7-Diiodo-2,6-di(thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]difurans are efficiently prepared by an iodine-promoted double cyclization. This new heterocyclic core is readily modified by the attachment of alkyl chains for improved solubility. The use of these compounds for the synthesis of new conjugated polymers is also reported.

Organic semiconductors are finding widespread use as replacements for their inorganic counterparts in a range of applications, including field effect transistors (OFETs), light-emitting diodes (OLEDs), and photovoltaic cells (OPVCs).¹ These materials offer advantages in the form of facile device fabrication *via* solution-based techniques and energy levels that can be tuned by chemical synthesis. Tuning can be accomplished through the synthesis of materials with alternating electron-donating and electron-accepting moieties.² Among electron-donating building blocks, benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) is particularly promising, due to its planar conjugated structure that facilitates π - π stacking, leading to higher hole mobility.³ Bulk heterojunction photovoltaic cells (BHJ-PVCs) using BDT copolymers as donors have achieved power-conversion efficiencies (PCE)s up to 7.4%.^{3c}

Recently, furan-containing molecules have been explored for the design of organic semiconductors.⁴ Furan is an attractive alternative to thiophene, since it is isoelectronic, while possessing a Dewar resonance energy of 18.0 kJ mol⁻¹, which is less aromatic than that of thiophene (27.2 kJ mol⁻¹).⁵ Thus, replacing thiophene with furan is expected to favor the formation of quinoid structures, leading to a reduction in the band gap of the resulting materials. Although benzo[1,2-*b*:4,5-*b'*]difurans (BDFs) are known in the literature, the lack of methods for the synthesis of substituted derivatives has prevented their widespread use.⁶ Encouraged by some of our earlier studies on iodocyclization, we explored this approach for synthesizing BDFs.⁷ Herein, we report the synthesis of functional BDFs and their polymerization with isoindigo, an electron-deficient moiety that has been used in several polymers with high PCE, when used as donor materials in BHJ-PVCs.⁸



Scheme 1 Synthesis of 3,7-diiodo-2,6-di(thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]difurans **2a** and **2b** and their subsequent alkylation.

Our synthetic route to the BDFs is shown in Scheme 1. This approach offers several benefits, including: (1) the use of easily prepared starting materials and inexpensive catalysts; (2) the enhanced solubility afforded by the alkyl chains on the flanking thiophene rings; and (3) the opportunity to generate a variety of new substituted BDFs from a common intermediate *via* cross-coupling reactions. Compounds **1a** and **1b** have been prepared by the Sonogashira cross-coupling of 1,4-dibromo-2,5-dimethoxybenzene and either 2-ethynyl-3-decyl-thiophene or 2-bromo-3-decyl-5-ethynylthiophene (see the ESI†). The iodine-induced double cyclization of compounds **1a** and **1b** afforded 3,7-diiodo-2,6-di(thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]difurans **2a** and **2b** in 70 and 82% yield respectively.⁷ Both regioisomers are easily purified by recrystallization. The Sonogashira cross-coupling reactions of **2a** and **2b** with 1-decyne afforded **3a** and **3b** in 96% and 92% yield respectively. Crystals of **2a** suitable for X-ray analysis were obtained by recrystallization. Detailed crystallographic data can be found in the ESI.† In addition to confirming the identity of this new compound, the X-ray analysis indicated that the BDF ring system is planar, which is beneficial to promoting efficient π -stacking and improving the charge transport of materials derived from this intermediate. The torsion angles between the BDF and thiophene rings are approximately 175.3°.

The remaining synthetic steps to the desired polymers are shown in Scheme 2. The hydrogenation of the alkynyl BDFs **3a** and **3b** afforded the alkylated derivatives **4a** and **4b** each in ~95% yield. Subsequent stannylation afforded **5a** and **5b** each in ~94% yield. The Stille cross-coupling polymerization of **5a** or **5b** with 6,6'-dibromo-*N,N'*-(2-octyldodecanyl)-isoindigo **6**⁹

^a Department of Chemistry, Iowa State University, Ames, IA 50011, USA. E-mail: malikaj@iastate.edu; Fax: +1 515-294-0105

^b Department of Chemistry, North Georgia College & State University, Dahlonega, GA 30597, USA

^c Department of Electrical Engineering, Iowa State University, Ames, IA, USA

† Electronic supplementary information (ESI) available: Experimental details, calculations, and spectroscopy. See DOI: 10.1039/c2cc34070d

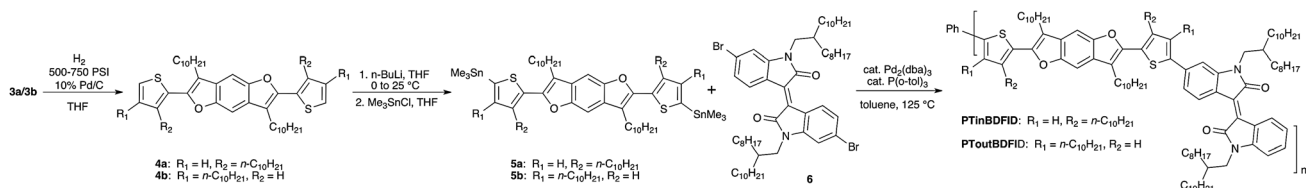


Table 1 Reaction conditions and molecular weight data for PTBDFIDs

Polymer ^a	Catalyst	Yield ^b (%)	M_w^c	M_w/M_n	DP _n
PT _{out} BDFID	Pd(PPh ₃) ₄	82	20 500	1.3	12
PT _{out} BDFID	Pd ₂ (dba) ₃	86	33 100	1.9	19
PT _{in} BDFID	Pd(PPh ₃) ₄	79	35 000	1.9	21
PT _{in} BDFID	Pd ₂ (dba) ₃	84	76 200	2.3	45

^a [Monomer] = 0.2 M in toluene, and Pd catalyst loading = 2 mol%.
^b Isolated yield. ^c Molecular weight data were obtained by GPC (see ESI).

afforded the polymers **PT_{in}BDFID** and **PT_{out}BDFID** in excellent yields after purification by Soxhlet extraction with methanol, followed by acetone, to remove residual catalyst and low molecular weight materials. Of the catalysts evaluated, Pd₂(dba)₃ gave the best results (Table 1). The polymers are soluble in standard organic solvents, such as THF and chloroform, at room temperature. Monomer **5a** consistently produced polymers with higher molecular weights. Presumably, this is due to the reduced steric hindrance at the 2- and 2'-positions of the BDF moiety.

We anticipated that the differences in the regiochemistry of the BDFs would result in differences in the optical spectra. Compounds **2b**, **3b**, and **4b**, with the alkyl substituents on the 4 and 4' positions of the thiophene rings, have less interaction with the pseudo-peri iodine, alkyne, or alkane substituents, and exhibit greater vibrational structure than analogs **2a–4a** (see ESI[†]). Arguably, this is due to the greater rigidity of the overall aromatic chromophore, *i.e.* reduction of out-of-plane rotation of the thiophene moieties. The dramatically different band shapes between the members of each pair mean that comparison of λ_{\max} between “a” and “b” analogs is not particularly meaningful. However, the leading edge of the onset of strong S1 absorption for each “a–b” pair of compounds extrapolates to a very similar wavelength, with each pair distinct from the other two. This reflects the intrinsic electronic similarities between each pair of isomers.

As expected, the additional conjugation of the alkynyl groups of **3a** and **3b** produces a red shift in the onset of absorption and λ_{\max} of the S1 absorption band. Compared to the alkyl substituents in compounds **4a** and **4b**, the iodo substituents in **2a** and **2b** induce a red-shift – albeit smaller than that of the alkyne – consistent with a reduction in conjugation length and orbital overlap (see ESI[†]). The UV–vis absorption spectra of **PT_{in}BDFID** and **PT_{out}BDFID** in solution and in thin films are shown in Fig. 1 and the optical and electronic properties are summarized in Table 2. Both polymers exhibit two main absorption bands. The high energy bands can be attributed to the π – π^* transition, whereas the low energy bands are due to intramolecular charge transfer between the donor and acceptor units. In solution, the λ_{\max} of **PT_{in}BDFID**'s low energy band is red-shifted 18 nm relative to **PT_{out}BDFID**, whereas the λ_{\max} of **PT_{in}BDFID**'s high energy band is blue-shifted 21 nm relative to **PT_{out}BDFID**. In the

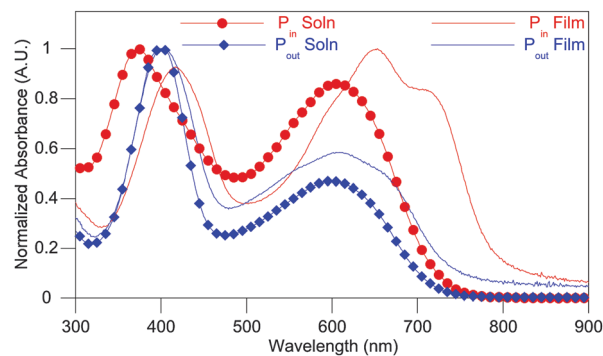


Fig. 1 UV-vis absorption of the polymers in solution and thin films.

Table 2 Electronic and optical properties of PTBDFIDs

Polymer	Media	λ_{\max} (nm)	HOMO ^a (eV)	LUMO ^b (eV)	E_g^{optc} (eV)	E_g^{ECd} (eV)
PT _{out} BDFID	THF	399, 582				
PT _{out} BDFID	Film	403, 612	–5.7	–3.8	1.7	1.9
PT _{in} BDFID	THF	378, 600				
PT _{in} BDFID	Film	415, 653	–5.7	–3.8	1.6	1.9

^a HOMO = $-(E_{\text{onset}}^{\text{ox}} + 5.1)$ (eV). ^b LUMO = $-(E_{\text{onset}}^{\text{red}} + 5.1)$ (eV).
^c Estimated from the optical absorption edge. ^d Onset of potentials (*v.s.* Fc).

solid state, the λ_{\max} for the low energy band of **PT_{out}BDFID** is blue-shifted 41 nm relative to **PT_{in}BDFID** and the difference in the high energy band is only 12 nm. These results suggest that **PT_{out}BDFID** has a more twisted backbone than **PT_{in}BDFID**. The optimized geometries obtained for isoindigo–BDF oligomers calculated using density functional theory also support the notion that **PT_{out}BDFID** has a more twisted structure (see ESI[†]). The similarity of **PT_{out}BDFID**'s solution and film spectra indicates that the steric interaction between the out facing side chain and the isoindigo group inhibits planarization.

The electrochemical properties of the polymers have been investigated by cyclic voltammetry (CV). Both polymers exhibit measurable and reproducible oxidation and reduction processes. The electrochemical band gaps of both are approximately 0.3 eV higher than the optical band gaps (E_g^{opt}) determined *via* the tangent lines on the absorption spectra. This difference can be attributed to the electron injection barrier in the electrochemistry.¹⁰ The HOMO and LUMO values of both polymers are similar to those reported previously for **PBDT-OIO**, a related terpolymer of **6**, thiophene and BDT (LUMO –3.91 eV and HOMO –5.74 eV).¹¹ Unfortunately, we cannot arrive at a conclusion regarding the relative donor strength of BDF, as the BDT group had two electron-donating alkoxy groups on the central benzene ring. Although, the LUMO values are less than 0.3 eV lower than those of the PC₆₁BM acceptor, impeding charge transfer, the HOMO levels of both polymers are deep enough

Table 3 Photovoltaic performance of **P12** and **P13** with PCBM

Polymer	V_{OC} (V)	I_{SC} (mA)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
P _{in} BDFID	0.7366	0.208	1.66	48.6	0.590
P _{out} BDFID	0.6410	0.164	1.306	36	0.301

Polymer films were prepared from solutions in *o*-DCB, 10 mg mL⁻¹.

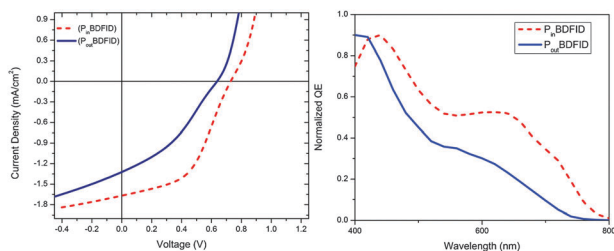


Fig. 2 Current–voltage characteristics of polymer PVCs (left). Normalized external quantum efficiency vs. wavelength curve of the PVCs (right).

to ensure air stability, while providing good open-circuit voltage (V_{oc}).¹²

The performance of both polymers in BHJ-PVCs was evaluated using PC₆₁BM as the electron acceptor with a device configuration of indium tin oxide (ITO)/poly(3,4-ethylene dioxythiophene):polystyrene sulfonate (PEDOT:PSS)/polymer:PC₆₁BM (1:4, w/w)/LiF/Al. The active layer processing conditions were chosen to yield a layer thickness less than 100 nm. In general (for P3HT systems), thicker layers (~200 nm) are better, because they absorb more light. However, since new generation donor–acceptor polymer films do not have a long-range order like P3HT, thicker layers tend to have increased recombination due to hole traps, and thus lower efficiencies.¹³ The fabrication conditions and PVC parameters (fill factor (FF), short-circuit current density (J_{sc}) and V_{oc}) are summarized in Table 3. The current–voltage (I – V) characteristics of our devices are shown in Fig. 2.

Overall, P_{T_{in}}BDFID PVCs performed better than P_{T_{out}}BDFID-based devices in all categories. This is most likely an effect of the polymer's planarity on morphology, and is currently being evaluated further. Although the performance of these devices is lower than other conjugated polymers, this is our first attempt toward fabricating PVCs from these materials. We note that the performance of most new systems can be dramatically improved by the optimization of processing parameters.

In conclusion, we report the efficient synthesis of novel electron-rich building blocks based on 2,6-di(thiophen-2-yl)-benzo[1,2-*b*:4,5-*b'*]difurans and their use for the development of donor–acceptor copolymers. The highlights of this work are the overall high yields of the reactions and the versatility of the synthetic approach. The energy levels of the new polymers are suitable for their use as donor materials in BHJ-PVCs. Preliminary device studies have shown good V_{oc} and FF, but low overall performance. We are currently working toward

optimizing the device performance in addition to developing new materials based on BDFs.

Support for this work has been provided by Iowa State University (ISU) and the 3M Foundation. We thank Dr Kamel Harrata and the ISU mass spectroscopy laboratory and Dr Arkady Ellern and the ISU X-ray crystallography facility for analyses. The PVCs were fabricated at ISU Institute for Physical Research and Technology's Microelectronics Research Center.

Notes and references

- (a) A. Facchetti, *Chem. Mater.*, 2010, **23**, 733; (b) A. C. Grimsdale, K. Leok Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chem. Rev.*, 2009, **109**, 897; (c) Y.-J. Cheng, S.-H. Yang and C.-S. Hsu, *Chem. Rev.*, 2009, **109**, 5868.
- (a) E. E. Havinga, W. Hoeve and H. Wynberg, *Polym. Bull.*, 1992, **29**, 119; (b) E. E. Havinga, W. ten Hoeve and H. Wynberg, *Synth. Met.*, 1993, **55**, 299.
- (a) J. Hou, M.-H. Park, S. Zhang, Y. Yao, L.-M. Chen, J.-H. Li and Y. Yang, *Macromolecules*, 2008, **41**, 6012; (b) P. Sista, M. C. Biewer and M. C. Stefan, *Macromol. Rapid Commun.*, 2012, **33**, 9; (c) Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, *Adv. Mater.*, 2010, **22**, E135; (d) A. Najari, S. Beaupré, P. Berrouard, Y. Zou, J.-R. Pouliot, C. Lepage-Pérusse and M. Leclerc, *Adv. Funct. Mater.*, 2011, **21**, 718.
- (a) C. H. Woo, P. M. Beaujuge, T. W. Holcombe, O. P. Lee and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2010, **132**, 15547; (b) P. A. Peart and J. D. Tovar, *Macromolecules*, 2009, **42**, 4449; (c) H. Li, P. Tang, Y. Zhao, S.-X. Liu, Y. Aeschi, L. Deng, J. Braun, B. Zhao, Y. Liu, S. Tan, W. Meier and S. Decurtins, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 2935; (d) J. C. Bijleveld, B. P. Karsten, S. G. J. Mathijssen, M. M. Wienk, D. M. de Leeuw and R. A. J. Janssen, *J. Mater. Chem.*, 2011, **21**, 1600.
- R. S. Hosmane and J. F. Liebman, *Tetrahedron Lett.*, 1992, **33**, 2303.
- (a) Z. Liang, S. Ma, J. Yu and R. Xu, *J. Org. Chem.*, 2007, **72**, 9219; (b) L. Huo, Y. Huang, B. Fan, X. Guo, Y. Jing, M. Zhang, Y. Li and J. Hou, *Chem. Commun.*, 2012, **48**, 3318; (c) C. Yi, C. Blum, M. Lehmann, S. Keller, S.-X. Liu, G. Frei, A. Neels, J. Hauser, S. Schürch and S. Decurtins, *J. Org. Chem.*, 2010, **75**, 3350; (d) H. Tsuji, C. Mitsui, L. Ilies, Y. Sato and E. Nakamura, *J. Am. Chem. Soc.*, 2007, **129**, 11902; (e) S. Keller, C. Yi, C. Li, S.-X. Liu, C. Blum, G. Frei, O. Sereda, A. Neels, T. Wandlowski and S. Decurtins, *Org. Biomol. Chem.*, 2011, **9**, 6410.
- D. Yue, T. Yao and R. C. Larock, *J. Org. Chem.*, 2005, **70**, 10292.
- (a) R. Stalder, J. Mei and J. R. Reynolds, *Macromolecules*, 2010, **43**, 8348; (b) E. Wang, Z. Ma, Z. Zhang, K. Vandewal, P. Henriksson, O. Inganäs, F. Zhang and M. R. Andersson, *J. Am. Chem. Soc.*, 2011, **133**, 14244.
- T. Lei, Y. Cao, Y. Fan, C.-J. Liu, S.-C. Yuan and J. Pei, *J. Am. Chem. Soc.*, 2011, **133**, 6099.
- (a) C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale and G. C. Bazan, *Adv. Mater.*, 2011, **23**, 2367; (b) Y. Zhu, R. D. Champion and S. A. Jenekhe, *Macromolecules*, 2006, **39**, 8712.
- Z. Ma, E. Wang, M. E. Jarvid, P. Henriksson, O. Inganäs, F. Zhang and M. R. Andersson, *J. Mater. Chem.*, 2012, **22**, 2306.
- (a) B. C. Thompson, Y.-G. Kim and J. R. Reynolds, *Macromolecules*, 2005, **38**, 5359; (b) M. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. Heeger and C. Brabec, *Adv. Mater.*, 2006, **18**, 789.
- Z. M. Beiley, E. T. Hoke, R. Noriega, J. Dacuna, G. F. Burkhard, J. A. Bartelt, A. Salleo, M. F. Toney and M. D. McGehee, *Adv. Energy Mater.*, 2011, **1**, 954.