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Incorporation of Furan into Low Band-Gap Polymers for Efficient Solar Cells

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Abstract: The design, synthesis, and characterization of the first examples of furan-containing low band-gap polymers, PDPP2FT and PDPP3F, with substantial power conversion efficiencies in organic solar cells are reported. Inserting furan moieties in the backbone of the conjugated polymers enables the use of relatively small solubilizing side chains because of the significant contribution of the furan rings to overall polymer solubility in common organic solvents. Bulk heterojunction solar cells fabricated from furan-containing polymers and $PC_{71}BM$ as the acceptor showed power conversion efficiencies reaching 5.0%.

Polymer bulk heterojunction (BHJ) solar cells have attracted significant attention because of their potential for achieving large-area, flexible photovoltaic devices through low-cost solution deposition techniques.[1,2] Much of the recent research effort has focused on the development of low band-gap donor polymers that have broad absorption spectra.[3–5] The search for new building blocks for semiconducting polymers continues as we gain mechanistic understandings and establish design rules relevant to organic electronic applications.[6–8] For example, the ideal polymer should (i) have sufficient energy level offsets with fullerenes for efficient charge separation while maximizing the open-circuit voltage,[8,9] (ii) display an absorption spectrum extending across the visible spectrum and into the near-IR, and (iii) maintain high extinction coefficients over this spectral range.[6] At the same time, it has become increasingly apparent that a balance among the competing effects of solution processability, miscibility with the fullerene component, and solid-state packing needs to be established.[10–12] Both the chemical structure of the backbone repeat units and the choice of the solubilizing side chains critically impact the above-mentioned criteria.[13,14] For example, while the use of longer and bulkier alkyl substituents improves solubility, it also increases lamellar and π-stacking distances, hindering intermolecular ordering and affecting the transport of charge carriers across the polymer stacks.[13,15,16] In this regard, strategies to reduce the length, bulkiness, and density of solubilizing side chains along the conjugated polymer backbone are well worth exploring.

A survey of state-of-the-art BHJ solar cells reveals that most high-performance polymers reported so far rely on thiophene or thiophene-based heterocycles.[17–23] While thiophene-based conjugated materials have attracted much attention in the area of organic electronics, only a limited number of studies have examined furan-containing materials potentially useful for device applications.[24–26] Recently, furans have been used as an alternative to thiophenes in organic dyes for dye-sensitized solar cells and have shown very similar optical and electronic properties.[27,28] Furan-based heterocycles have also been introduced as peripheral substituents on one of the highest performing small molecules for photovoltaics.[29] The sparsity of studies examining polymer backbones containing furans in this field is surprising, given that furans exhibit similar energy levels and a comparable degree of aromaticity relative to their thiophene counterparts.[24,30] Importantly, furan derivatives can be synthesized from a variety of natural products; hence, they fall into the category of renewable and sustainable synthetic resources.

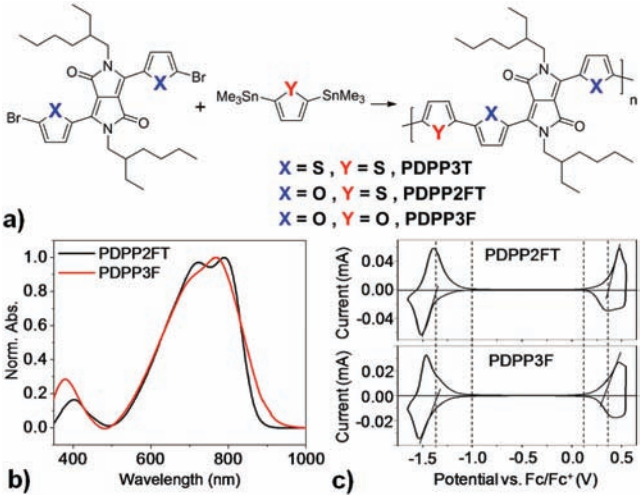

Figure 1. (a) Synthetic scheme and polymeric structures used in this study (polymerization protocol: Pd_2dba_3, P(*o*-tol)$_3$, chlorobenzene, 110 °C, 24 h). (b) Thin-film absorption spectra and (c) cyclic voltammograms of PDPP2FT and PDPP3F.

In this contribution, we demonstrate that furan heterocycles can be advantageously incorporated into conjugated polymer backbones without hindering their photovoltaic device performance. In addition, we show that furans can be employed to dramatically reduce the amount of aliphatic side-chain material necessary to solubilize polymer backbones that otherwise require the presence of long and bulky substituents. This concept is exemplified by the synthesis and characterization of two furan-containing semiconducting polymers: PDPP2FT and PDPP3F (see Figure 1a). These polymers contain a diketopyrrolopyrrole (DPP) unit[22,31–33] and are structurally analogous to the low band-gap polymer PDPP3T previously reported by Janssen et al.[34] Importantly, these furan-containing derivatives were synthesized with 2-ethylhexyl substituents, whereas PDPP3T (as initially reported[34]) was appended with 2-hexyldecyl solubilizing groups.

While exploring the use of furans as alternatives to thiophenes in low band-gap conjugated polymers involving DPP, we found

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that soluble high-molecular-weight PDPP2FT could be readily obtained (M_n = 66 kDa, see Supporting Information). The use of 2-ethylhexyl substituents was sufficient to impart PDPP2FT with appropriate solubility in common organic solvents (e.g., tetrahydrofuran, chloroform, chlorobenzene) for device fabrication. In contrast, the all-furan derivative PDPP3F, synthesized using the same polymerization protocol (M_n = 29 kDa, see Supporting Information), was found to possess slightly reduced solubility in the same organic solvents. While the improved solubility of oligofurans over oligothiophenes has been reported,[35] it appears that the ratio of furan to thiophene in mixed oligomers also impacts solubility.[36,37] As a control experiment, we attempted to synthesize the 2-ethylhexyl-substituted derivative of the all-thiophene PDPP3T following the same polymerization procedure as that used for PDPP2FT and PDPP3T. However, the polymerization yielded only low-molecular-weight fractions that were minimally soluble in all common organic solvents (M_n = 2 kDa, see Supporting Information).

The onset of optical absorption of PDPP2FT in a thin film was measured to be 880 nm (E_g = 1.41 eV), while the λ_{max} was observed at 789 nm (see Figure 1b), which is comparable to the optical properties of PDPP3T reported earlier by Janssen et al. (E_g = 1.3 eV).[34] PDPP3F also possesses similar optical properties, with E_g = 1.35 eV and λ_{max} at 767 nm. Figure 1c shows the cyclic voltammograms of the two polymers. The onsets of oxidation and reduction of PDPP2FT were observed at +0.28 and −1.34 V vs Fc/Fc$^+$, corresponding to HOMO and LUMO levels at −5.4 and −3.8 eV vs vacuum. For PDPP3F, the onsets were observed at +0.35 and −1.34 V, corresponding to HOMO and LUMO levels at −5.5 and −3.8 eV. These values are comparable to those obtained for the low-molecular-weight all-thiophene analogue, PDPP3T (see Supporting Information).

Solar cells were fabricated using PDPP2FT as the electron donor and [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) as the electron acceptor, with the device structure ITO/PEDOT:PSS/polymer:PCBM/LiF/Al. The active layers were spin-coated from chlorobenzene, and, in some cases, a small amount of the high-boiling-point additive 1-chloronaphthalene (CN) was added to optimize blend morphology for enhanced device performance. The $J-V$ curves and external quantum efficiency (EQE) spectra of PDPP2FT:$PC_{61}BM$ devices are shown in the Supporting Information. Without any postfabrication treatment, the PDPP2FT:$PC_{61}BM$ device spin-coated from pure chlorobenzene afforded 3.4% power conversion efficiency (PCE) under AM 1.5 G, 100 mW cm^{-2} illumination. The use of chlorobenzene containing 1 vol % CN for spin-coating led to a slight improvement to 3.7% PCE, mostly through an increase in the photocurrent. The best device was obtained from a blend of PDPP2FT:$PC_{61}BM$ in a 1:3 weight ratio and gave a PCE of 3.8%, with an open circuit voltage (V_{oc}) of 0.76 V, a short-circuit current density (J_{sc}) of 9.0 mA cm^{-2}, and a fill factor (FF) of 55%. The EQE showed a sharp onset at the optical band gap of the polymer and reached a maximum value of 33%. For BHJ devices containing a 1:3 blend of PDPP3F:$PC_{61}BM$, chloroform was found to be a better solvent, and an average efficiency of 3.0% was achieved (see Supporting Information).

In an attempt to increase the breadth of the photoactive spectrum and the overall photocurrent, we fabricated solar cells with the more light-absorbing fullerene derivative $PC_{71}BM$. Figure 2 shows the $J-V$ curves and the EQE spectra of optimized devices fabricated from blends of PDPP2FT:$PC_{71}BM$ at a 1:3 weight ratio in chlorobenzene. Interestingly, without any additive, the $PC_{71}BM$ devices performed poorly, with an average PCE of only 0.86%. However, with the addition of high-boiling CN to the blend solution, device performance improved by more than 5-fold, with much higher J_{sc} and an average PCE of 4.7%. The best device was obtained with the addition of 9% CN by volume relative to chlorobenzene, and it achieved a V_{oc} of 0.74 V, a J_{sc} of 11.2 mA cm^{-2}, a FF of 60%, and a PCE of 5.0%, results comparable to that obtained by Janssen et al. with PDPP3T.[34] The J_{sc} value calculated from the integration of the EQE spectrum of the best device is 11.4 mA cm^{-2}, which closely matches the J_{sc} value obtained from the $J-V$ measurement under white light illumination. Solar cells containing a blend of PDPP3F and $PC_{71}BM$ were also fabricated and achieved an average PCE of 3.8% (max 4.1%) after optimization. Here again, the device performance was <1% without the addition of CN. These device results strongly support the potential of furan-based polymeric systems in organic photovoltaic devices.

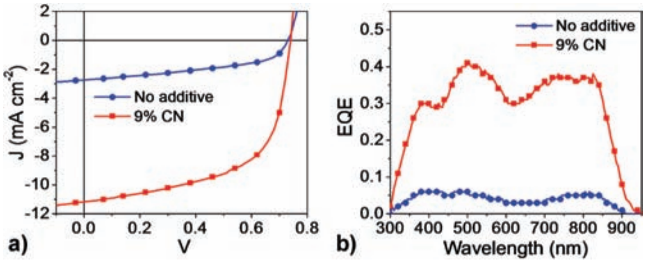

Figure 2. (a) $J-V$ curves of optimized PDPP2FT:$PC_{71}BM$ devices spin-coated out of chlorobenzene (with no additive and with 9 vol % CN). (b) External quantum efficiency spectra of optimized devices.

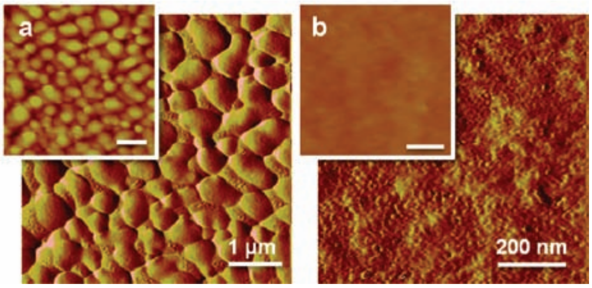

Figure 3. AFM phase images of 1:3 PDPP2FT:$PC_{71}BM$ blend films spin-coated (a) from chlorobenzene only and (b) from chlorobenzene + 9 vol % CN. Inset: Height images of the same films. The data scale is 0−60 nm.

The dramatic difference in device performance with and without the CN additive is most likely due to the optimization of blend morphology. Figure 3 compares the atomic force microscopy (AFM) images of blend films of PDPP2FT:$PC_{71}BM$ at the optimized ratio. The blend without additive exhibits coarse phase separation between the polymer and $PC_{71}BM$, with large micrometer-sized domains. In contrast, the addition of CN led to much finer phase separation between the two materials and the formation of fiber-like interpenetrating morphologies at the length scale of ∼20 nm, which is close to the ideal domain size, assuming an exciton diffusion length of 5−10 nm.[38−40] The thin-film absorption of PDPP2FT also red-shifts and displays more distinct vibronic structures when CN is added to the solution before spin-coating (see Supporting Information). The red-shift in absorption is indicative of increased intermolecular ordering and planarity in the polymer backbone and could be another reason for the improved performance of devices fabricated with CN.

In summary, we have shown that furans can be advantageously used as an alternative to thiophenes and thiophene-based building units in the design and synthesis of low band-gap conjugated polymers with efficient solar cell performance. The polymers examined, PDPP2FT and PDPP3F, exhibit nearly identical optical and electronic properties and demonstrate power conversion efficiencies approaching 5% in BHJ devices with PC$_{71}$BM. The incorporation of furan into the conjugated backbone allowed for shorter solubilizing groups to be used, compared to those required to solubilize the all-thiophene polymer PDPP3T. In particular, polymer solubility was found to improve substantially when a combination of thiophene and furan heterocycles is incorporated. The ca. 4% efficiency achieved with the all-furan low band-gap polymer PDPP3F clearly demonstrates the potential of furans as thiophene alternatives in the design of high-performance organic solar cell materials, paving the path for the design and production of organic electronic materials from sustainable synthetic resources.

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Supporting Information Available: Experimental details, synthesis of monomers and polymers, device fabrication and characterization, additional device data, and AFM images. This material is available free of charge via Internet at http://pubs.acs.org.

References

(1) Dennler, G.; Scharber, M. C.; Brabec, C. J. *Adv. Mater.* **2009**, *21*, 1323–1338.
(2) Arias, A. C.; MacKenzie, J. D.; McCulloch, I.; Rivnay, J.; Salleo, A. *Chem. Rev.* **2010**, *110*, 3–24.
(3) Chen, J. W.; Cao, Y. *Acc. Chem. Res.* **2009**, *42*, 1709–1718.
(4) Cheng, Y. J.; Yang, S. H.; Hsu, C. S. *Chem. Rev.* **2009**, *109*, 5868–5923.
(5) Roncali, J. *Macromol. Rapid Commun.* **2007**, *28*, 1761–1775.
(6) Heremans, P.; Cheyns, D.; Rand, B. P. *Acc. Chem. Res.* **2009**, *42*, 1740–1747.
(7) Vandewal, K.; Tvingstedt, K.; Gadisa, A.; Inganäs, O.; Manca, J. V. *Nat. Mater.* **2009**, *8*, 904–909.
(8) Scharber, M. C.; Wuhlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. L. *Adv. Mater.* **2006**, *18*, 789–794.
(9) Veldman, D.; Meskers, S. C. J.; Janssen, R. A. J. *Adv. Funct. Mater.* **2009**, *19*, 1939–1948.
(10) Nguyen, L. H.; Hoppe, H.; Erb, T.; Gunes, S.; Gobsch, G.; Sariciftci, N. S. *Adv. Funct. Mater.* **2007**, *17*, 1071–1078.
(11) Gadisa, A.; Oosterbaan, W. D.; Vandewal, K.; Bolsee, J. C.; Bertho, S.; D'Haen, J.; Lutsen, L.; Vanderzande, D.; Manca, J. V. *Adv. Funct. Mater.* **2009**, *19*, 3300–3306.
(12) Wu, P. T.; Ren, G.; Jenekhe, S. A. *Macromolecules* **2010**, *43*, 3306–3313.
(13) Zoombelt, A. P.; Leenen, M. A. M.; Fonrodona, M.; Nicolas, Y.; Wienk, M. M.; Janssen, R. A. J. *Polymer* **2009**, *50*, 4564–4570.
(14) Huo, L. J.; Hou, J. H.; Chen, H. Y.; Zhang, S. Q.; Jiang, Y.; Chen, T. L.; Yang, Y. *Macromolecules* **2009**, *42*, 6564–6571.
(15) Piliego, C.; Holcombe, T. W.; Douglas, J. D.; Woo, C. H.; Beaujuge, P. M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2010**, *132*, 7595–7596.
(16) Chen, M. H.; Hou, J.; Hong, Z.; Yang, G.; Sista, S.; Chen, L. M.; Yang, Y. *Adv. Mater.* **2009**, *21*, 4238–4242.
(17) Hou, J.; Chen, H. Y.; Zhang, S.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16144–16145.
(18) (a) Park, S. H.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photon.* **2009**, *3*, 297–302. (b) Peet, J.; Kim, J. Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, A. J.; Bazan, G. C. *Nat. Mater.* **2007**, *6*, 497–500.
(19) (a) Holcombe, T. W.; Woo, C. H.; Kavulak, D. F. J.; Thompson, B. C.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2009**, *131*, 14160–14161. (b) Woo, C. H.; Holcombe, T. W.; Unruh, D. A.; Sellinger, A.; Fréchet, J. M. J. *Chem. Mater.* **2010**, *22*, 1673–1679. (c) Kim, B. J.; Miyamoto, Y.; Ma, B.; Fréchet, J. M. J. *Adv. Funct. Mater.* **2009**, *19*, 2273–2281. (d) Woo, C. H.; Thompson, B. C.; Kim, B. J.; Toney, M. F.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2008**, *130*, 16324–16329.
(20) Liang, Y.; Feng, D.; Wu, Y.; Tsai, S. T.; Li, G.; Ray, C.; Yu, L. *J. Am. Chem. Soc.* **2009**, *131*, 7792–7799.
(21) Qin, R. P.; Li, W. W.; Li, C. H.; Du, C.; Veit, C.; Schleiermacher, H. F.; Andersson, M.; Bo, Z. S.; Liu, Z. P.; Inganäs, O.; Wuerfel, U.; Zhang, F. L. *J. Am. Chem. Soc.* **2009**, *131*, 14612–14613.
(22) Zou, Y. P.; Najari, A.; Berrouard, P.; Beaupre, S.; Aich, B. R.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2010**, *132*, 5330–5331.
(23) Huo, L. J.; Hou, J. H.; Zhang, S. Q.; Chen, H. Y.; Yang, Y. *Angew. Chem., Int. Ed.* **2010**, *49*, 1500–1503.
(24) Bunz, U. H. F. *Angew. Chem., Int. Ed.* **2010**, *49*, 5037–5040.
(25) Umeyama, T.; Takamatsu, T.; Tezuka, N.; Matano, Y.; Araki, Y.; Wada, T.; Yoshikawa, O.; Sagawa, T.; Yoshikawa, S.; Imahori, H. *J. Phys. Chem. C* **2009**, *113*, 10798–10806.
(26) Yamamoto, T.; Zhou, Z. H.; Kanbara, T.; Shimura, M.; Kizu, K.; Maruyama, T.; Nakamura, Y.; Fukuda, T.; Lee, B. L.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K.; Sasaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 10389–10399.
(27) Li, R. Z.; Lv, X. J.; Shi, D.; Zhou, D. F.; Cheng, Y. M.; Zhang, G. L.; Wang, P. *J. Phys. Chem. C* **2009**, *113*, 7469–7479.
(28) Lin, J. T.; Chen, P. C.; Yen, Y. S.; Hsu, Y. C.; Chou, H. H.; Yeh, M. C. P. *Org. Lett.* **2009**, *11*, 97–100.
(29) Walker, B.; Tomayo, A. B.; Dang, X. D.; Zalar, P.; Seo, J. H.; Garcia, A.; Tantiwiwat, M.; Nguyen, T. Q. *Adv. Funct. Mater.* **2009**, *19*, 3063–3069.
(30) Chen, Z. F.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. V. *Chem. Rev.* **2005**, *105*, 3842–3888.
(31) Zou, Y. P.; Gendron, D.; Neagu-Plesu, R.; Leclerc, M. *Macromolecules* **2009**, *42*, 6361–6365.
(32) Zou, Y. P.; Gendron, D.; Badrou-Aich, R.; Najari, A.; Tao, Y.; Leclerc, M. *Macromolecules* **2009**, *42*, 2891–2894.
(33) Zou, Y.; Najari, A.; Berrouard, P.; Beaupré, S.; Réda Aích, B.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2010**, *132*, 5330–5331.
(34) Bijleveld, J. C.; Zoombelt, A. P.; Mathijssen, S. G. J.; Wienk, M. M.; Turbiez, M.; de Leeuw, D. M.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16616–16617.
(35) Gidron, O.; Diskin-Posner, Y.; Bendikov, M. *J. Am. Chem. Soc.* **2010**, *132*, 2148–2149.
(36) Miyata, Y.; Nishinaga, T.; Komatsu, K. *J. Org. Chem.* **2005**, *70*, 1147–1153.
(37) Hucke, A.; Cava, M. P. *J. Org. Chem.* **1998**, *63*, 7413–7417.
(38) Scully, S. R.; McGehee, M. D. *J. Appl. Phys.* **2006**, *100*, 034907.
(39) Shaw, P. E.; Ruseckas, A.; Samuel, I. D. W. *Adv. Mater.* **2008**, *20*, 3516–3520.
(40) Markov, D. E.; Amsterdam, E.; Blom, P. W. M.; Sieval, A. B.; Hummelen, J. C. *J. Phys. Chem. A* **2005**, *109*, 5266–5274.

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