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A furan-containing conjugated polymer for high mobility ambipolar organic thin film transistors†

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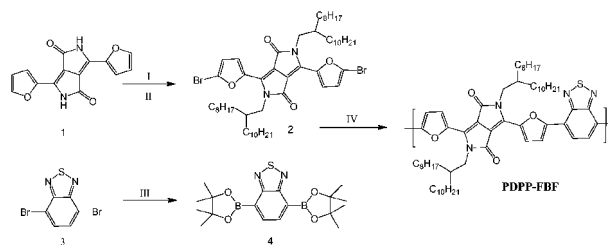
Furan substituted diketopyrrolopyrrole (DBF) combined with benzothiadiazole based polymer semiconductor PDPP-FBF has been synthesized and evaluated as an ambipolar semiconductor in organic thin-film transistors. Hole and electron mobilities as high as 0.20 cm^2 V^{-1} s^{-1} and 0.56 cm^2 V^{-1} s^{-1}, respectively, are achieved for PDPP-FBF.

Many of the polymer semiconductors used in recently reported high performance ambipolar organic thin film transistors (OTFTs) are based on thiophene and its derivatives such as thienothiophene, emeraldicene and bithiophene-imide combined with strong acceptor units.[1,2] Other five membered heterocycles such as selenophene, furan and pyrrole are also promising blocks.[3] There have been a few reports on selenophene OTFTs[4] however, furan and pyrrole have hitherto not been adequately explored for such applications. Furan is a promising block for constructing novel organic semiconductors due to its equivalent aromaticity levels compared to thiophene. The reason that furan based organic semiconductors have been paid comparatively less attention could be related to the lower stability of furan.[5] Very recently, there has been growing interest in using furan based organic semiconductors as active component inorganic electronic devices.[2b,6] Furan based materials belong to the class of green electronic materials on account of their facile synthesis from biomass precursors.[6a] Theoretical studies of effective charge transfer integral, internal reorganization energy, bandwidths and intrinsic charge carrier mobility for oligofuran indicate that ambipolar charge transport is possible in such a conjugative system.[7] These features imply that furan based organic semiconductors may be an interesting choice for ambipolar OTFTs. Recently, reasonably balanced but low mobilities of ~10^{-2} cm^2 V^{-1} s^{-1} have been reported for furan based semiconducting polymers in ambipolar OTFTs.[6e]

3,6-Di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DBF), an analogue of 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DBT) [where thiophene units on diketopyrrolopyrrole (DPP) are replaced by furan], has been successfully used lately in polymer semiconductor synthesis and has shown promising performance in unipolar p-channel[8] and ambipolar OTFTs.[6e] Some of the polymers reported by our group have exhibited hole mobilities varying in the range of 0.13–1.54 cm^2 V^{-1} s^{-1}.[8] In this study, we report the synthesis of a novel solution processable copolymer PDPP-FBF comprised of furan substituted fused aromatic DPP (electron accepting DBF block) combined with benzothiadiazole (BTZ, heteroaromatic unit) and its use in ambipolar OTFTs. DBF and BTZ moieties incorporated in the conjugated backbone could enhance the degree of coplanarity and π–π stacking through strong donor–acceptor intramolecular interactions with a large overlapping area which is favorable for charge carrier transport. These units could alter the HOMO and LUMO energies *via* hybridization of the frontier molecular orbital system, leading to HOMO/LUMO energy levels that are conducive for ambipolar OFET operation.[9]

Our preliminary results have shown that furan substituted DPP is a highly promising building block for high performance ambipolar OTFTs. Reasonably balanced high mobilities of 0.23 cm^2 V^{-1} s^{-1} and 0.56 cm^2 V^{-1} s^{-1} for holes and electrons, respectively, are achieved in OTFT devices with a PDPP-FBF polymer. The synthetic route for making the solution processable polymer semiconductor PDPP-FBF is outlined in Scheme 1.

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Scheme 1 *Reagents and conditions*: (I) K$_2$CO$_3$, 2-octyl-1-dodecyl bromide, anhydrous DMF, 120–130 °C, overnight; (II) bromine, chloroform, room temperature, overnight, 73%; (III) PdCl$_2$(dppf), 1,4-dioxane, 80 °C for 20 h, 46%; (IV) Pd(PPh$_3$)$_4$, aliquat 336, 2 M K$_2$CO$_3$, toluene, 80 °C for 72 h, phenylboronic acid, bromobenzene, 74%.

The first compound 3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1) was easily synthesized using reported procedures,[8] which was then converted to 3,6-bis-(5-bromo-furan-2-yl)-N,N'-bis(2-octyldodecyl)-1,4-dioxo-pyrrolo[3,4-c]pyrrole (2) via alkylation and bromination. 4,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxoborolan-2-yl) benzo[c][1,2,5]thiadiazole (4) was prepared from 4,7-dibromo benzo[c][1,2,5]thiadiazole (3) using bis(pinacolato)diboron, PdCl$_2$(dppf) and KOAc in 1,4-dioxane. Suzuki coupling polymerization of compounds 2 and 4 results in polymer poly{3,6-difuran-2-yl-2,5-di(2-octyl-dodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-alt-benzothidiazole} (PDPP-FBF) in 67% yield (Scheme 1). PDPP-FBF was purified by sequential Soxhlet extraction using methanol, acetone, and hexane in order to remove the catalytic impurities and oligomer fractions from the bulk polymer sample. Finally the polymer was obtained by dissolving in chloroform, followed by precipitation from methanol. The number average (M_n) and weight average molecular weight (M_w) measured by gel permeation chromatography (GPC) are 204 615 and 450 408 g mol^{-1}, respectively, at a column temperature of 40 °C with a mixture of THF and chloroform as eluent and polymethylmethacrylate (PMMA) as standard. The thermal properties of PDPP-FBF were examined by the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques respectively. TGA showed a decomposition temperature of 399 °C under nitrogen, indicating the high thermal stability of this polymer. During the heating scan of DSC measurement, an exothermic transition temperature was observed at 297 °C, whereas upon cooling, an endothermic peak was observed at 282 °C.

PDPP-FBF in chloroform showed the maximum absorption peak (λ_{max}) at 880 nm, while its thin film showed almost an identical λ_{max} at 878 nm (Fig. 1a). The optical band gap calculated for PDPP-FBF from their absorption cut-off (~980 nm) is 1.26 eV. The HOMO and LUMO energy levels for PDPP-FBF determined from a cyclic voltammogram using oxidation and reduction onset potentials are 5.37 eV and 3.74 eV respectively (Fig. 1b). The HOMO energy value calculated from CV for PDPP-FBF is also confirmed by photoelectron spectroscopy in air (PESA) measurement which shows the HOMO level to be 5.42 eV. The relatively low-lying LUMO energy level is due to the strong electron accepting nature of the DPP and BTZ moieties. Molecular organization of PDPP-FBF was studied by 2-D XRD measurements via X-ray irradiation parallel to the polymer flakes. As shown in Fig. 2, the primary diffraction peak at $2\theta = 5.27°$ corresponds to a d-spacing of 16.78 Å, whereas the broad peak located from $2\theta = 18°$ to 28° suggests that this copolymer is not highly crystalline. The distance calculated from the broad peak is 4.2–4.66 Å. The broad peak reflects simply the short range intermolecular distance. It may also indicate that not all polymer backbones are aligned normal to the substrate. Similar broad peaks were also observed for other furan DPP based copolymers studied earlier.[8]

The field effect transistor characteristics of devices with PDPP-FBF as channel semiconductors were evaluated using a bottom-gate, top-contact OTFT configuration. A heavily p-doped conductive silicon wafer with a layer of ~200 nm SiO$_2$ on the surface was used as the substrate. The SiO$_2$ functions as the gate insulator and the doped Si as the gate. The active polymer thin film (~100 nm) was deposited on top of an octyltrichlorosilane
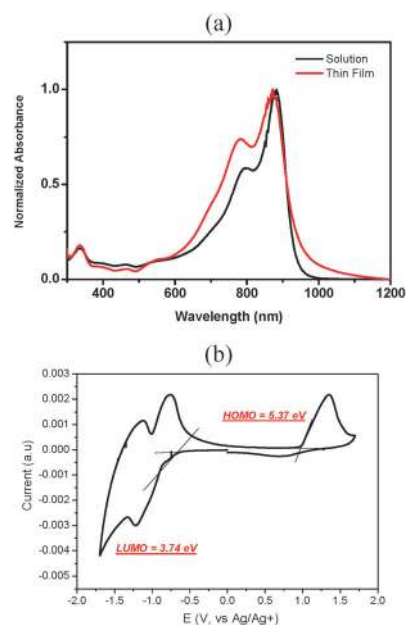

Fig. 1 (a) UV-vis absorption spectra of PDPP-FBF in chloroform solution and in thin film. (b) Cyclic voltammogram of PDPP-FBF thin films on a platinum electrode showing the first cathodic and anodic cycles at a scan rate of 100 mV s^{-1}. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile.
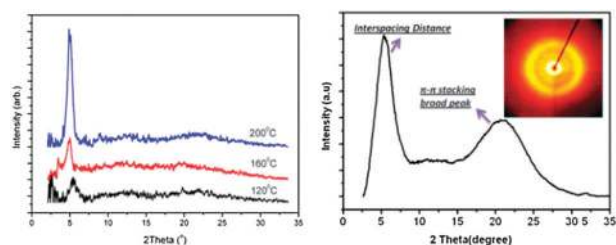

Fig. 2 XRD data obtained from spin-coated PDPP-FBF thin films (~35 nm) on OTS modified SiO$_2$/Si substrates annealed at different temperatures (left) and 2-D XRD pattern intensity graphs and 2-D XRD image (inset) obtained with the incident X-ray parallel to the thin film stack of the PDPP-FBF copolymer (right).

(OTS) modified SiO$_2$ surface by spin-coating a polymer solution in chloroform (8 mg mL^{-1}) at 1500 rpm for 1 min.

The polymer films were annealed at 120 °C, 160 °C and 200 °C, respectively, for 20 min on a hot plate under N$_2$ before Au source and drain electrodes were vacuum evaporated. The output and transfer characteristics of PDPP-FBF based ambipolar OTFTs annealed at 200 °C are shown in Fig. 3 in both hole and electron enhancement modes. The transfer curves clearly exhibit the typical V-shape in both operation modes. Hole and electron mobilities were calculated from the respective saturation regime of the transfer curves using standard procedures. It was found that the polymer thin film annealed at 120 °C exhibits balanced hole and electron mobilities of 0.18 cm^2 V^{-1} s^{-1} ($V_D = -70$ V) and 0.16 cm^2 V^{-1} s^{-1} ($V_D = +70$ V), respectively. When the film was annealed at 160 °C, the hole mobility improved slightly to 0.18 cm^2 V^{-1} s^{-1} and the electron mobility remained the same. Interestingly, when the annealing temperature was further increased to 200 °C, the hole mobility did not change whereas the electron mobility increased to 0.56 cm^2 V^{-1} s^{-1}, which is comparable to our
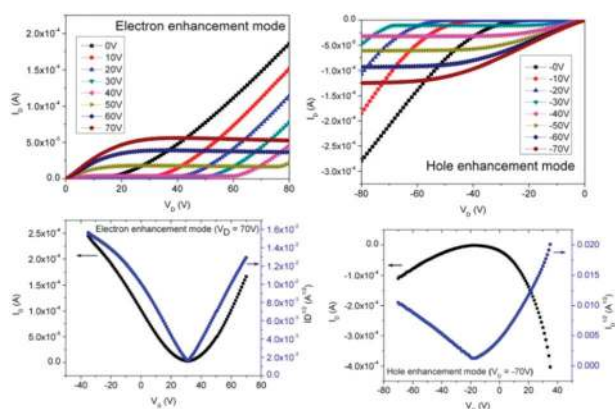
Fig. 3 Output and transfer characteristic in the hole and electron enhancement modes of a PDPP-FBF based ambipolar OTFT annealed at 200 °C on the OTS treated p ± Si/SiO$_2$ substrate. The hole and electron transfer curves were derived at drain voltages (V_D) of -70 V and $+70$ V respectively. Device dimensions: channel length = 180 μm; channel width = 3 mm.
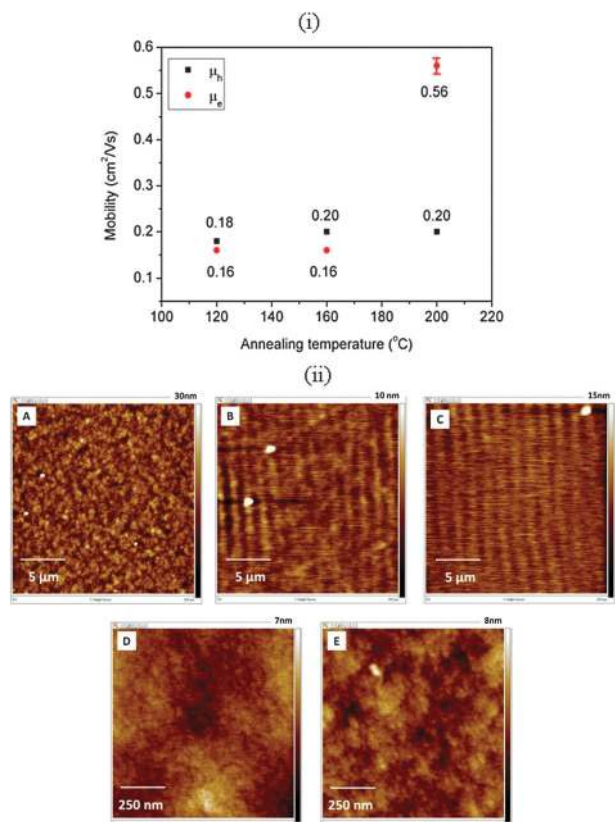
Fig. 4 (i) Effect of preannealing at various temperatures on hole and electron mobility of PDPP-FBF based ambipolar OTFT, (ii) AFM phase images of PDPP-FBF thin films annealed at (A) 120 °C, (B and D) 160 °C and (C and E) 200 °C on OTS treated p ± Si/SiO$_2$ substrates.

ambipolar polymer PDPP-TBT reported earlier.[1a] In addition, hole and electron mobilities of 0.61 cm^2 V^{-1} s^{-1} and 0.67 cm^2 V^{-1} s^{-1} have been measured for 200 °C annealed samples at gate voltage -80 V. The effect of annealing temperature on charge carrier mobility is shown in Fig. 4(i). An on-to-off current ratio (I_{on}/I_{off}) of $\sim 10^3$ is calculated for all of the devices.

AFM was conducted to elucidate the effects of annealing on morphology. The AFM height images in Fig. 4(ii) show that the

120 °C annealed polymer thin film exhibits less organized morphology. As the annealing temperature was increased to 160 and 200 °C, the morphology becomes more organized and exhibits well aligned ~ 1.5 μm wide microstripes. Sharpening of the 2θ peak at 5.27° at 200 °C annealing also supports this observation. Under a higher resolution, it is evident that the microstripes are composed of firmly held crystalline nanograins, which are considered favorable for efficient intergranular charge transport. Ideal HOMO–LUMO energy levels, strong intramolecular interactions and preferred molecular organization make PDPP-FBF a very suitable candidate for high performance ambipolar OFETs with respectable charge carrier mobility.

We have demonstrated that furan is a promising building block for high performance semiconducting polymers for use in ambipolar OTFTs. With the incorporation of an electron-withdrawing furan-containing DPP moiety into benzothiadiazole the resulting polymer PDPP-FBF has shown high and balanced hole and electron mobilities of 0.20 cm^2 V^{-1} s^{-1} and 0.56 cm^2 V^{-1} s^{-1}, respectively. These results clearly reveal that the furan substituted DPP is a promising conjugated building block for designing novel high performance ambipolar semiconductors for organic electronic applications.

Notes and references

1 (a) P. Sonar, S. P. Singh, Y. Li, M. S. Soh and A. Dodabalapur, *Adv. Mater.*, 2010, **22**, 5409; (b) J. D. Yuen, J. Fan, J. Seifter, B. Lim, R. Hufschmid, A. J. Heeger and F. Wudl, *J. Am. Chem. Soc.*, 2011, **133**, 20799; (c) Z. Chen, H. Lemke, S. Albert-Seifried, M. Caironi, M. Nielsen, M. Heeney, W. Zhang, I. McCulloch and H. Sirringhaus, *Adv. Mater.*, 2010, **22**, 2371; (d) J. Bijleveld, A. Zoombelt, S. Mathijssen, M. Wienk, M. Turbiez, D. de Leeuw and R. Janssen, *J. Am. Chem. Soc.*, 2009, **131**, 16616; (e) Z. Chen, M. J. Lee, R. Shahid Ashraf, Y. Gu, S. Albert-Seifried, M. Meedom Nielsen, B. Schroeder, T. D. Anthopoulos, M. Heeney, I. McCulloch and H. Sirringhaus, *Adv. Mater.*, 2012, **24**, 647; (f) H. Bronstein, Z. Chen, R. S. Ashraf, W. Zhang, J. Du, J. R. Durrant, P. S. Tuladhar, K. Song, S. E. Watkins, Y. Geerts, M. M. Wienk, R. A. J. Janssen, T. D. Anthopoulos, H. Sirringhaus, M. Heeney and I. McCulloch, *J. Am. Chem. Soc.*, 2011, **133**, 3272.
2 (a) A. R. Mohebbi, J. Yuen, J. Fan, C. Munoz, M. F. Wang, R. S. Shirazi, J. Seifter and F. Wudl, *Adv. Mater.*, 2011, **23**, 4644; (b) P. M. Beaujuge and J. M. J. Frechet, *J. Am. Chem. Soc.*, 2011, **133**, 20009; (c) X. G. Guo, R. P. Ortiz, Y. Zheng, Y. Hu, Y. Y. Noh, K. J. Baeg, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, 2011, **133**, 1405.
3 L. I. Bellenkii and V. N. Gramenitskaya, The Literature of Heterocyclic Chemistry, part-VIII, 1999–2001, *Adv. Heterocycl. Chem.*, 2004, **87**, 1.
4 (a) M. Shahid, T. McCarthy-Ward, J. Labram, S. Rossbauer, E. B. Domingo, S. E. Watkins, N. Stingelin, T. D. Anthopoulos and M. Heeney, *Chem. Sci.*, 2012, **3**, 181; (b) H. W. Lin, W. Y. Lee and W. C. Chen, *J. Mater. Chem.*, 2012, **22**, 2120.
5 R. M. McConnell, W. E. Godwin, S. E. Baker, K. Powell, M. Baskett and A. Morara, *Int. J. Polym. Mater.*, 2004, **53**, 697.
6 (a) O. Gidron, A. Dadvand, Y. Sheynin, M. Bendikov and D. F. Perepichka, *Chem. Commun.*, 2011, **47**, 1976; (b) J. T. Lin, P. C. Chen, Y. S. Yen, Y. C. Hsu, H. H. Chou and M. C. P. Yeh, *Org. Lett.*, 2009, **11**, 97; (c) B. Walker, A. B. Tomayo, X. D. Dang, P. Zalar, J. H. Seo, A. Garcia, M. Tantiwiwat and T. Q. Nguyen, *Adv. Funct. Mater.*, 2009, **19**, 3063; (d) C. H. Woo, P. M. Beaujuge, T. W. Holcombe, O. P. Lee and J. M. J. Frechet, *J. Am. Chem. Soc.*, 2010, **132**, 15547; (e) 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.
7 S. Mohakud, A. P. Alex and S. K. Pati, *J. Phys. Chem. C*, 2010, **114**, 20436.
8 (a) Y. Li, P. Sonar, S. P. Singh, W. Zeng and M. S. Soh, *J. Mater. Chem.*, 2011, **21**, 10829; (b) P. Sonar, S. P. Singh, E. L. Williams, Y. Li, M. S. Soh and A. Dodabalapur, *J. Mater. Chem.*, 2012, **22**, 4425.
9 S. P. Singh, A. Sellinger and A. Dodabalapur, *J. Appl. Phys.*, 2010, **107**, 044509.