

Combination of Two Diketopyrrolopyrrole Isomers in One Polymer for Ambipolar Transport

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Supporting Information

Diketopyrrolo[3,4-*c*]pyrrole (DPP1, Figure 1) has shown promise as a versatile building block of π -conjugated

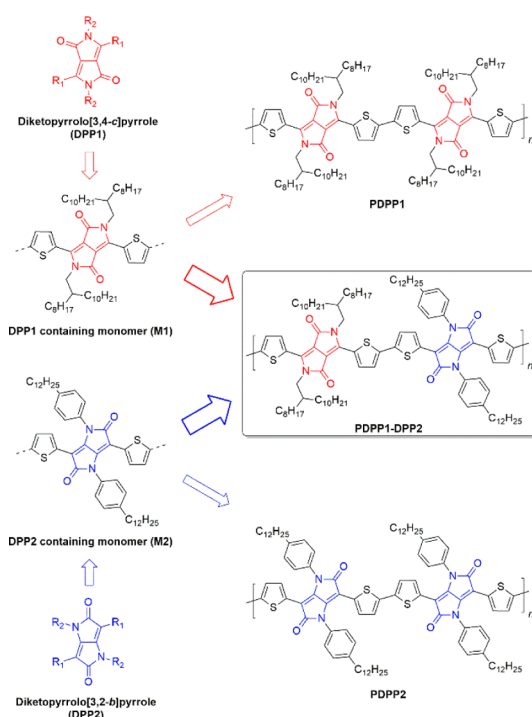


Figure 1. Evolution of molecular structures from two DPP isomers to substituted DPP monomers for polymerization and to three DPP-based polymers studied in this work.

polymers with impressive performance in both organic field-effect transistors (OFETs) and polymer solar cells (PSCs).^{1–4} DPP1 has a coplanar geometry and can form hydrogen bonds with the neighboring units in the polymer backbone, which favors intermolecular π – π stacking.⁵ In particular, many DPP1-containing polymers exhibited high and balanced hole and electron mobilities,^{6–11} being attractive for ambipolar OFETs. Thereby, both p-type and n-type channels could be realized in one device with simplified circuit design and fabrication processes.¹⁰ DPP1 was first reported in 1974,¹² and an ambipolar transporting polymer containing dithienyl-substituted DPP1 coupled with two 3-dodecylthiophenes was presented in 2008.⁶ Since then, numerous DPP1-based polymers have been synthesized and applied in OFETs as well as in PSCs with excellent device performance.^{13–18}

Inspired by the versatility and excellence of DPP1 in organic optoelectronics, researchers have recently focused on another regioisomer of DPP1, namely diketopyrrolo[3,2-*b*]pyrrole (DPP2, Figure 1) with “switched” position of the carbonyl group and the nitrogen atom.¹⁹ The DPP2 was found as a part of the structure of a natural dye in lichens^{20,21} and was synthesized around 25 years ago.²² Subsequent studies concentrated on improved synthetic strategies and the preparation of derivatives with different substituents.^{19,23–25} Until 2011, DPP2 was utilized to synthesize conjugated polymers with a variety of comonomers.²⁶ Then a series of polymers containing DPP2 in the main chain and their optoelectronic properties were reported in 2012.²⁷ Subsequently, the synthesis and application of several promising DPP2-based small molecules^{21,28} and donor–acceptor (D–A) polymers^{29–31} were presented. As a regioisomer of DPP1 whose polymers can be used as ambipolar transporters in many cases, DPP2-containing polymers should also exhibit ambipolarity upon appropriate molecular design which, however, is so far elusive.

In view of the key role of well-established DPP1 and the potential of DPP2 in the design of conjugated polymer semiconductors, it appears highly appropriate to combine these two isomers in one polymer main chain. Herein, we report a copolymer (PDPP1-DPP2, Figure 1) containing two DPP isomers separated by a bithiophene unit in one polymer backbone. The two “homo”-polymers (PDPP1 and PDPP2) incorporating only one DPP isomer coupled with bithiophene are also prepared for studying contribution of each isomer to optoelectronic behavior of PDPP1-DPP2. Optical and electrochemical studies indicate that PDPP1-DPP2 exhibits an absorption band and an energy gap located in between those of PDPP1 and PDPP2. OFETs based on PDPP1-DPP2 show ambipolar charge carrier transport, affording both hole and electron mobilities up to 0.02 cm²/(V s) resulting from its high order and close packing distance of 0.38 nm, as revealed by X-ray studies in bulk and in the thin film.

Although polymers containing DPP1 units with varying aryl substituents such as phenyl, thienyl, furyl, thienothienyl, and thiazolyl have been reported,³² most of the DPP1-based polymers with pronounced device performance are composed of DPP1 flanked with two thiophene moieties. Such a repeating unit (M1, Figure 1) with long branched alkyl chains is thus

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employed for our molecular design. On the other side, a similar DPP2-containing unit **M2** with different side chains is used as a comonomer. The backbone of polymer PDPP1-DPP2 thus deviates only slightly from those of PDPP1 and PDPP2. The PDPP1-DPP2 polymer is synthesized employing Suzuki coupling reaction between boronic pinacol ester of **M1**⁵ and dibrominated **M2**,²⁷ whereas the PDPP1 and PDPP2 are prepared according to a literature procedure.³³ The synthetic details are described in the Supporting Information. The PDPP1-DPP2 is quite soluble in common organic solvents such as chloroform, THF, toluene, and chlorobenzene. A M_n of 73 kg/mol with a PDI of 5.06 for PDPP1-DPP2 is measured by GPC in THF using a polystyrene standard. The large PDI might originate from an overestimation of M_w owing to aggregation which is commonly observed in solution for DPP1-containing copolymers.⁵ The PDPP1-DPP2 exhibits good thermal stability with 5% weight loss upon heating at 373 °C, as investigated by TGA. The measurements of molecular weights and thermal properties of the PDPP1 and PDPP2 are presented in the Supporting Information.

UV-vis-NIR absorption spectra of the three polymers in solution and as thin films are shown in Figure 2 and relevant

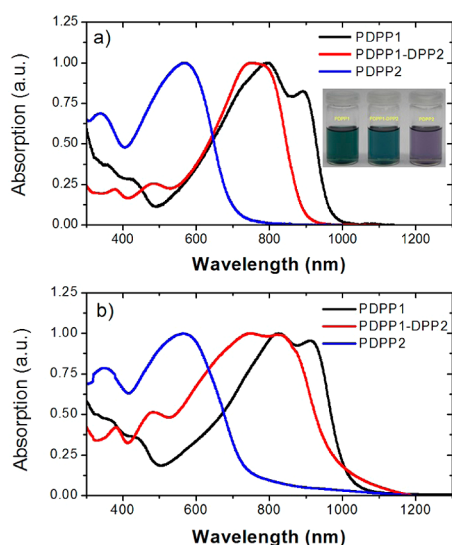


Figure 2. UV-vis-NIR absorption spectra of three DPP-based polymers: (a) in chlorobenzene solution ($\times 10^{-5}$ M of repeating unit); inset: colors of the three polymers in solution; (b) as thin films drop-cast from dichlorobenzene.

data are summarized in Table S1 in the Supporting Information. The PDPP1-DPP2 polymer exhibits an absorption band in between those of the PDPP1 and PDPP2 with λ_{\max} at 785 nm. This is reasonable in view of the alternating linkage of the DPP1 and DPP2 containing repeating units (**M1** and **M2**) in the main chains. Polymer PDPP1 displays an absorption maximum (λ_{\max}) at 892 nm with a shoulder at 796 nm in the solution, whereas the λ_{\max} of PDPP2 locates at 567 nm. The striking blue shift of the absorption bands when going from PDPP1 to PDPP2 can be partially ascribed to the difference in electronic structure of the two DPP isomer cores, as suggested by theoretical computation.³⁰ It is believed, however, that conformational changes cannot be neglected in view of the aryl side chains in PDPP2, which could twist the polymer backbone because of steric hindrance and thus hypsochromically shift the absorption band. A gradual color

change from dark green for PDPP1, to dark blue for PDPP1-DPP2, and to purple for PDPP2, is observed as shown in Figure 2a inset.

In a thin film, PDPP1 affords a slightly red-shifted (20 nm) absorption band relative to that in solution, whereas for PDPP2 an almost unchanged thin-film absorption spectrum is observed. This finding suggests that the backbone conformation of PDPP2 does not change upon going from solution to the solid state because of the aforementioned steric effect. Interestingly, PDPP1-DPP2 shows a broadened absorption band with a red shift of 40 nm in the film compared to that in solution, which is even more striking than that for PDPP1. This implies that PDPP1-DPP2 tends to aggregate in the thin film significantly stronger than the reference polymers because of the solid-state packing effect.³⁴ The absorption onset of PDPP1-DPP2 is also shifted remarkably to the red and is close to that of PDPP1 so that one arrives at similar optical band gaps for both polymers (1.23 eV for PDPP1 and 1.27 eV for PDPP1-DPP2). These results indicate that unlike the situation in PDPP2, the solid-state packing is not suppressed by the introduction of DPP2-containing building block (**M2**) into the PDPP1-DPP2 backbone, which is crucial for the charge carrier transport.

Cyclic voltammetry of the three polymers in thin films is carried out to study their electrochemical property. The CV diagrams are shown in Figure S2 in the Supporting Information. All three polymers exhibit reversible reductive and quasi-reversible oxidative waves, thus suggesting their potential as ambipolar semiconductors. The HOMO and LUMO energy levels that are estimated from the onset potentials of oxidation and reduction waves are listed in Table S1 in the Supporting Information. It appears that the energy gap (E_g) of PDPP1-DPP2 is situated between those of PDPP1 and PDPP2, while its HOMO and LUMO levels are very close to the ones of PDPP1. Density functional theory (DFT) calculations are also carried out on dimers of the three polymers to model their electron density distributions of HOMO and LUMO energy levels. A similar trend in evolution of the energy levels and E_g as observed from the CV measurements could be obtained from these calculations (see Figure S3 in the Supporting Information). These results together with the observations from the absorption behavior demonstrate that the optoelectronic properties of PDPP1-DPP2 are mainly determined by the DPP1 component.

The charge carrier transport of the new copolymer PDPP1-DPP2 was studied in field-effect transistors based on a bottom-gate, bottom-contact (BG-BC) architecture. The 200 nm thick SiO_2 dielectric was functionalized with hexamethyldisilazane (HMDS) to minimize interfacial trapping sites. The polymer film was drop-cast on the FET substrates from 10 mg/mL chloroform solution in nitrogen atmosphere, followed by annealing at 120 °C for 1 h. The polymer PDPP1-DPP2 exhibits an ambipolar transport with values up to 0.02 (± 0.005) $\text{cm}^2/(\text{V s})$ for holes and electrons indicating a balanced transport (Figure 3). These values are 2–3 orders of magnitude higher than those of a DPP1-based “homo”-polymer reported in literature.³³ They are also compared with results for another DPP1 “homo”-polymer containing triethylene glycol side chains, which has mobilities of $\sim 0.01 \text{ cm}^2/(\text{V s})$ for both charges in a BG-BC transistor.¹⁷ It has to be emphasized that the transfer plots quite clearly indicate ambipolarity, whereby the output curves, especially for the electron accumulation

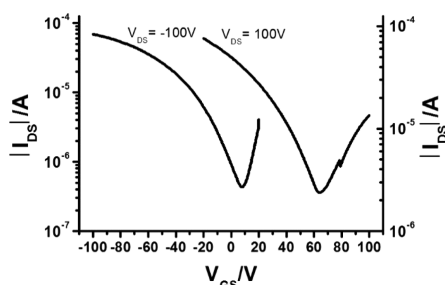


Figure 3. Transistor transfer curves for PDPP1-DPP2 determined for $V_{SD} = 100$ V.

mode (see Figure S4 in the Supporting Information), suggest serious trapping of the negative carriers.

To correlate the device performance with the organization of the polymers, we used X-ray techniques to investigate the structure of PDPP1-DPP2 both in bulk and on surface. For the bulk organization, two-dimensional wide-angle X-ray scattering (2D-WAXS) on macroscopically extruded fibers was exploited. The corresponding pattern is shown in Figure 4a. The small-

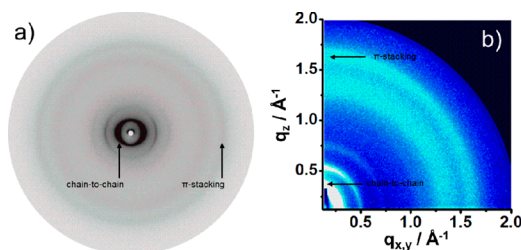


Figure 4. (a) 2D-WAXS pattern of bulk and (b) GIWAXS pattern of thin film for PDPP1-DPP2 (reflections related to the chain-to-chain and π -stacking spacings are indicated in both patterns).

angle equatorial reflection corresponds to the chain-to-chain distance between the lamellar stacks of 2.59 nm for PDPP1-DPP2, while the scattering intensity in the wide-angle region in the same plane is related to the π -stacking reflection of 0.38 nm. This observation is in agreement with the absorption data of the thin films. To further investigate the surface order in the thin film, grazing incidence WAXS (GIWAXS) was performed. The polymer arranges predominantly edge-on toward the surface as indicated by the meridional (along q_z at $q_{x,y} = 0 \text{ Å}^{-1}$) small-angle reflections (Figure 4b) which are in agreement to the chain-to-chain spacing observed for the bulk. Additionally the same π -stacking distance of 0.38 nm is found as for the fiber sample. Nevertheless, the rather isotropic intensity distribution of the reflections implies pronounced misalignment of the domains toward the surface. Despite this random organization of the polymer chains on the dielectric, a decent charge carrier transport is observed because of good order and quite close packing distance of PDPP1-DPP2 allowing even a sufficient electron migration.

In conclusion, we have presented a novel ambipolar copolymer PDPP1-DPP2 derived from two DPP isomers. It was found that the DPP1 moiety played a main role in determination of the optoelectronic behaviors of PDPP1-DPP2 so that this polymer possessed similar absorption band edges and energy levels as PDPP1. Interestingly, the polymer containing two DPP isomers afforded good order and quite close packing distance in the solid state, as indicated by the thin-film absorption spectra and X-ray investigation. This led to

improved charge carrier transport of the polymer PDPP1-DPP2. Our results demonstrated that the combination of two DPP isomers into one polymer backbone provided a new ambipolar polymer showing balanced hole and electron mobilities of $0.02 \text{ cm}^2/(\text{V s})$ in an OFET. For the future design of conjugated polymers the systematic variation of similar (e.g., isomeric) building blocks as applied in this study holds great promise for comprehensive correlations of electronic and packing properties with the molecular structure.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis, TGA, and CV curves of three polymers, general methods, and experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Guo, X.; Baumgarten, M.; Müllen, K. *Prog. Polym. Sci.* **2013**, *38*, 1832.
- (2) Nielsen, C. B.; Turbiez, M.; McCulloch, I. *Adv. Mater.* **2013**, *25*, 1859.
- (3) Tieke, B.; Rabindranath, A. R.; Zhang, K.; Zhu, Y. *Beilstein J. Org. Chem.* **2010**, *6*, 830.
- (4) Li, Y. N.; Sonar, P.; Murphy, L.; Hong, W. *Energy Environ. Sci.* **2013**, *6*, 1684.
- (5) Guo, X.; Puniredd, S. R.; Baumgarten, M.; Pisula, W.; Müllen, K. *Adv. Mater.* **2013**, *25*, 5467.
- (6) Bürgi, L.; Turbiez, M.; Pfeiffer, R.; Bienewald, F.; Kirner, H.-J.; Winnewisser, C. *Adv. Mater.* **2008**, *20*, 2217.
- (7) Kronemeijer, A. J.; Gili, E.; Shahid, M.; Rivnay, J.; Salleo, A.; Heeney, M.; Sirringhaus, H. *Adv. Mater.* **2012**, *24*, 1558.
- (8) Sonar, P.; Singh, S. P.; Li, Y.; Soh, M. S.; Dodabalapur, A. *Adv. Mater.* **2010**, *22*, 5409.
- (9) Yuen, J. D.; Fan, J.; Seifert, J.; Lim, B.; Hufschmid, R.; Heeger, A. J.; Wudl, F. *J. Am. Chem. Soc.* **2011**, *133*, 20799.
- (10) Cho, S.; Lee, J.; Tong, M. H.; Seo, J. H.; Yang, C. *Adv. Funct. Mater.* **2011**, *21*, 1910.
- (11) Lee, J.; Han, A.-R.; Kim, J.; Kim, Y.; Oh, J. H.; Yang, C. *J. Am. Chem. Soc.* **2012**, *134*, 20713.
- (12) Parnum, D. G.; Mehta, G.; Moore, G. G. I.; Siegal, F. P. *Tetrahedron Lett.* **1974**, *29*, 2549.
- (13) Chen, H. J.; Guo, Y. L.; Yu, G.; Zhao, Y.; Zhang, J.; Gao, D.; Liu, H. T.; Liu, Y. Q. *Adv. Mater.* **2012**, *24*, 4618.
- (14) Lee, J.; Han, A. R.; Yu, H.; Shin, T. J.; Yang, C.; Oh, J. H. *J. Am. Chem. Soc.* **2013**, *135*, 9540.
- (15) Li, J.; Zhao, Y.; Tan, H. S.; Guo, Y. L.; Di, C. A.; Yu, G.; Liu, Y. Q.; Lin, M.; Lim, S. H.; Zhou, Y. H.; Su, H. B.; Ong, B. S. *Sci. Rep.* **2012**, *2*, 754.

- (16) Kang, I.; Yun, H.-J.; Chung, D. S.; Kwon, S.-K.; Kim, Y.-H. *J. Am. Chem. Soc.* **2013**, *135*, 14896.
- (17) Kanimozhi, C.; Yaacobi-Gross, N.; Chou, K. W.; Amassian, A.; Anthopoulos, T. D.; Patil, S. *J. Am. Chem. Soc.* **2012**, *134*, 16532.
- (18) Dou, L. T.; Gao, J.; Richard, E.; You, J. B.; Chen, C. C.; Cha, K. C.; He, Y. J.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2012**, *134*, 10071.
- (19) Langer, P.; Wuckelt, J.; Döring, M. *J. Org. Chem.* **2000**, *65*, 729.
- (20) Wuckelt, J.; Döring, M.; Langer, P.; Görls, H.; Beckert, R. *Tetrahedron Lett.* **1997**, *38*, 5269.
- (21) Song, S.; Ko, S.-J.; Shin, H.; Jin, Y.; Kim, I.; Kim, J. Y.; Suh, H. *Sol. Energy Mater. Sol. Cells* **2013**, *112*, 120.
- (22) Fürstenwerth, H. DE3525109A1 1987.
- (23) Langer, P.; Döring, M. *Eur. J. Org. Chem.* **2002**, *2002*, 221.
- (24) Helmholtz, F.; Schröder, R.; Langer, P. *Synthesis* **2006**, 2507.
- (25) Langer, P.; Helmholtz, F.; Schröder, R. *Syn. Lett.* **2003**, 2389.
- (26) Lu, S.; Facchetti, A.; Yao, Y.; Drees, M.; Yan, H. US2011/0226338 2011.
- (27) Welterlich, I.; Charov, O.; Tieke, B. *Macromolecules* **2012**, *45*, 4511.
- (28) Kirkus, M.; Knippenberg, S.; Beljonne, D.; Cornil, J.; Janssen, R. A. J.; Meskers, S. C. J. *J. Phys. Chem. A* **2013**, *117*, 2782.
- (29) Song, S.; Ko, S.-J.; Shin, H.; Jin, Y.; Kim, I.; Kim, J. Y.; Suh, H. *Syn. Met.* **2013**, *162*, 2288.
- (30) Lu, S.; Drees, M.; Yao, Y.; Boudinet, D.; Yan, H.; Pan, H.; Wang, J.; Li, Y.; Usta, H.; Facchetti, A. *Macromolecules* **2013**, *46*, 3895.
- (31) Zhang, H.; Welterlich, I.; Neudörfl, J.-M.; Tieke, B.; Yang, C.; Chen, X.; Yang, W. *Polym. Chem.* **2013**, *4*, 4682.
- (32) Chandran, D.; Lee, K.-S. *Macromol. Res.* **2013**, *21*, 272.
- (33) Zoombelt, A. P.; Mathijssen, S. G. J.; Turbiez, M. G. R.; Wienk, M. M.; Janssen, R. A. J. *J. Mater. Chem.* **2010**, *20*, 2240.
- (34) Guo, X.; Puniredd, S. R.; Baumgarten, M.; Pisula, W.; Müllen, K. *J. Am. Chem. Soc.* **2012**, *134*, 8404.