Journal Name

COMMUNICATION

N-Fused BDOPV: A Tetralactam Derivative as Building Block for Polymer Field-Effect Transistors

Yue Cao, Jing-Song Yuan, Xu Zhou, Xiao-Ye Wang, Fang-Dong Zhuang, Jie-Yu Wang, and Jian Pei*

N-fused BDOPV derivative, *N*BDOPV, was designed and synthesized. The photophysical and electrochemical properties of *N*BDOPV were systematically investigated. *N*BDOPV-based conjugated polymer PITET shows a large hole mobility of 1.92 cm² V⁻¹ s⁻¹.

The increasing interest in π-conjugated polymers is driven by their potential applications in flexible and low-cost optoelectronic devices.[1] As the photophysical and electronic properties of polymers can be feasibly modulated by adjusting the building blocks in conjugated backbones, the development of building blocks is of great importance for increasing the diversity of polymer semiconductors and providing more flexibility in material design.[2] Moreover, the structure–property relationship investigation will further promote the development of polymer semiconductors. It has been an intriguing research topic to develop novel building blocks for conjugated polymer synthesis and applications.

Owing to the excellent device performances of isoindigo-based polymers in organic photovoltaics (OPVs) and organic field-effect transistors (OFETs),[3] much effort has been devoted to developing isoindigo-type structures by replacing the central double bond between two lactam rings in isoindigo with different π-conjugated bridges.[4] But the derivatives which contain flexible π-bridge did not exhibit comparable mobility in OFET devices. It is possibly due to the change of molecular rigidity which has great effect on reorganization energy, resulting in a decrease of intrinsic mobility. By inserting a benzodifurandione moiety between two indolin-2-one units in isoindigo structure, **BDOPV**, which contains rigid conjugated backbone enforced by intramolecular hydrogen bonds, was developed.[4a,4b] Due to the limited solubility of **BDOPV**, **BDOPV**-based polymer could achieve large mobility only when some specific alkyl chains were incorporated.[4b] Compared to lactone, incorporating lactam[5] will not only retains the fixed backbone by the four intramolecular hydrogen bonds but also improves the solubility by additional *N*-substituted alkyl chains. On the other hand, the additional side-chains may also provide more opportunity for material engineering.[6]

Herein, an electron-deficient π-extended isoindigo-type structure, (3*E*,7*E*)-3,7-bis(6-bromo-2-oxoindolin-3-ylidene)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1*H*,3*H*)-dione (*N*BDOPV), is designed and synthesized (Fig. 1a). *N*BDOPV has a rigid planar skeleton which is fixed by four intramolecular hydrogen bonds. Furthermore, by incorporating a benzodipyrroledione structure between the two indolin-2-one units, the solubility of *N*BDOPV is enhanced due to the additional alkyl chains introduced at *N*–positions. The photophysical and electrochemical properties of *N*BDOPV were systematically investigated. Moreover, the *N*BDOPV-based copolymer **PITET** exhibits a large hole mobility up to 1.92 cm² V⁻¹ s⁻¹.

Scheme 1 illustrates the synthetic route to *N*BDOPV and the corresponding copolymer **PITET**. The alkylation of 6-bromoisatin
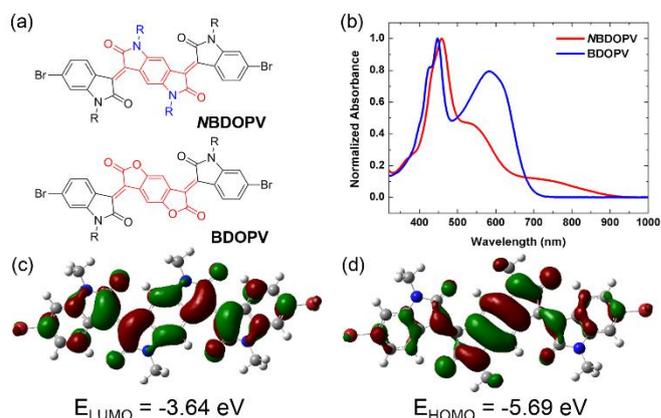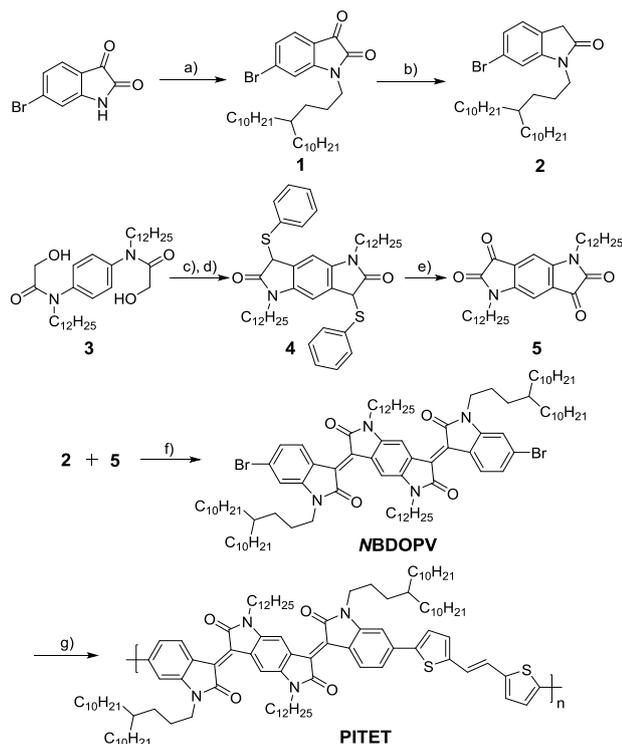

Fig. 1 (a) Chemical structures and (b) normalized absorption spectra of *N*BDOPV and **BDOPV**. Calculated frontier orbital distribution and energy levels of *N*BDOPV (c, d)

Scheme 1 Synthetic route to *N*BDOPV and polymer **PITET**: a) K$_2$CO$_3$, 11-(3-iodopropyl)-henicosane, DMF, THF, 70 ºC, 12 h, 70%; b) N$_2$H$_4$•H$_2$O, reflux, 24 h, 67%; c) (COCl)$_2$, DMSO, Et$_3$N, DCM, -78 ºC 2 h; d) PhSH, (CF$_3$CO)$_2$O, BF$_3$•Et$_2$O, DCM, 20 ºC, 19 h; e) (NH$_4$)$_2$Ce(NO$_3$)$_6$, THF, H$_2$O, 20 ºC, 16 h, 22% for three steps; f) AcOH, TsOH, P$_2$O$_5$, 110 ºC, 12 h, 40%; g) Pd$_2$(dba)$_3$, P(*o*-tol)$_3$, (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethane, toluene, 110 ºC, 36 h, 89%.

gave compound **1** in 70% yield. After refluxed in hydrazine monohydrate for 24 h, *N*-alkylated indolin-2-one **2** was obtained in 67% yield. **4** was prepared by using a connective Pummerer-type cyclization as previously developed by Procter *et al*.[7] Through oxidation with ceric ammonium nitrate, **4** was converted to the key intermediate **5**. The overall yield from **3** to **5** is 22%. An acid-catalyzed aldol condensation between **2** and **5** was carried out in AcOH, providing *N*BDOPV in 40% yield. *N*BDOPV exhibits good solubility in common organic solvents including CH$_2$Cl$_2$, CHCl$_3$ and THF. Afterwards, a copolymer **PITET** was prepared through the Stille-coupling polymerization between *N*BDOPV and (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethane using Pd$_2$(dba)$_3$ and P(*o*-tol)$_3$ as catalyst. The as-synthesized polymer was purified by Soxhlet extraction to afford a dark solid. The polymer exhibits good solubility in CHCl$_3$, trichloroethylene, chlorobenzene, and dichlorobenzene. The molecular weight of **PITET** was evaluated by high temperature gel permeation chromatography at 150 ℃ using 1,2,4-tricholorobenzene as the eluent. **PITET** displays a high molecular weight with M_n of 37.6 kDa and PDI of 2.38. The polymer shows excellent thermal stability with high decomposition temperature of 385 ℃ (ESI).

The incorporated lactam structure has strong effect on photophysical and electrochemical properties of *N*BDOPV. The absorption spectra of *N*BDOPV and **BDOPV** in diluted solution are shown in Fig. 1b. **BDOPV** exhibits dual-band absorption feature whereas *N*BDOPV exhibits three absorption bands. Furthermore, the red-shifted absorption onset of *N*BDOPV indicates a relative smaller
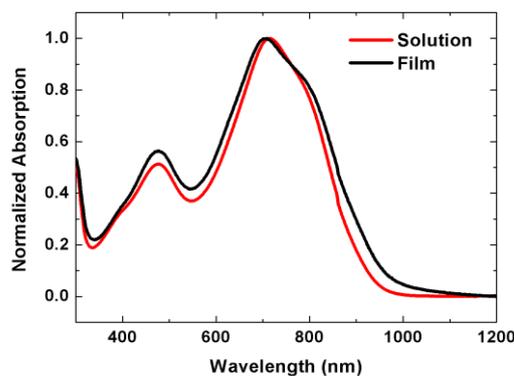

Fig. 2 Normalized absorption spectra of **PITET** in CHCl$_3$ (1 $\times$10^{-5} M) and in thin film (spin-casted from CHCl$_3$ solution, 1 mg/mL).

optical bandgap of 1.36 eV. The HOMO and LUMO energy levels were measured by cyclic voltammetry. **BDOPV** displays HOMO/LUMO levels of -6.08/-4.24 eV, whereas *N*BDOPV exhibits raised HOMO/LUMO levels of -5.55/-3.74 eV (ESI). All data above clearly indicate a different electronic structure of *N*BDOPV.

To further understand the influence of lactam structure on molecular electronic structure from a theoretical view, density functional theory (DFT) calculation was carried out at the B3LYP/6-31G(d) level. Fig. 1c-d illustrate the calculated orbital distribution and energy levels of *N*BDOPV. The long alkyl chains were replaced by methyl groups for simplicity. For *N*BDOPV, the LUMO is well delocalized over the conjugated backbone whereas the HOMO mainly localizes on the benzodipyrroledione core. In contrast, both HOMO and LUMO of **BDOPV** distribute evenly over the entire backbone (ESI). Compared to those of **BDOPV**, the calculated HOMO and LUMO levels of *N*BDOPV are raised by 0.56 eV and 0.34 eV. Both the changing in orbital distribution and raising in energy levels of *N*BDOPV are owing to the conjugated lone pairs of nitrogens in the central benzodipyrroledione core. Take the relatively higher HOMO energy level into consideration, *N*BDOPV could be a good candidate of building block for *p*-type materials.

To explore the potential of *N*BDOPV for building semiconducting polymers, a donor-acceptor polymer **PITET** was developed and characterized. As shown in Fig. 2, **PITET** exhibits dual band absorption features both in dilute solution (1 $\times$ 10^{-5} M in CHCl$_3$) and in thin film. The absorption band from 350 to 580 nm is assigned to the absorption of *N*BDOPV unit, while the band from 580 to 1000 nm is attributed to the intramolecular charge transfer (ICT) absorption. In thin film absorption feature of **PITET**, the slightly blue-shifted absorption maximum λ$_{max}$ indicates the aggregation formed in solution.[8] Moreover, the increased shoulder peak around 800 nm and broadened ICT peak reveal strong intermolecular interactions in solid state. The optical bandgap of **PITET** estimated from the absorption onset of thin film spectrum is 1.27 eV. **PITET** exhibits HOMO/LUMO levels of −5.32/−4.05 eV as estimated from the photoelectron spectroscopy and the optical bandgap (ESI).

The application of **PITET** was explored by fabricating thin film OFET devices in a bottom-gate/top-contact (BGTC) configuration. The active layer was deposited by spin-coating the polymer solution (6 mg/mL in TCE) onto octadecyltrimethoxysilane (OTMS)-treated n^{++}-Si/SiO$_2$ substrate.[9] **PITET** exhibited typical hole-transporting
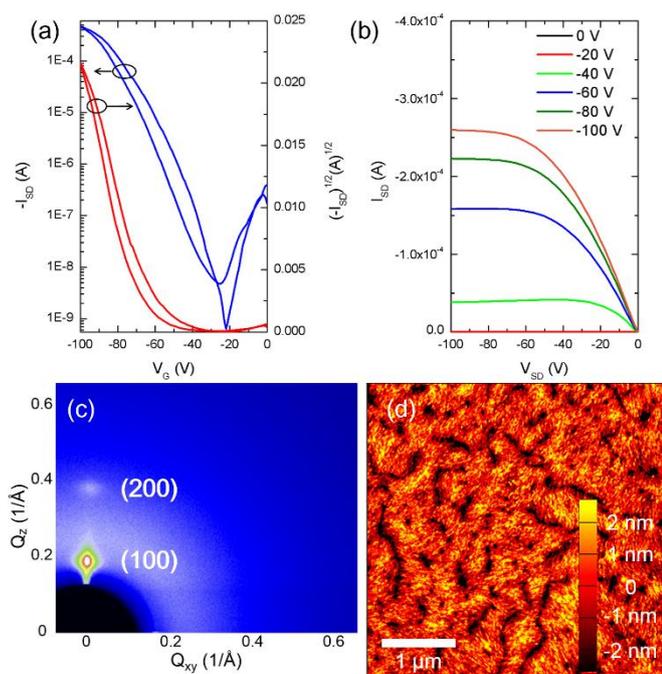
Journal Name

COMMUNICATION

Fig. 3 (a) Transfer and (b) output characteristics of **PITET**-based FET devices. (c) 2D-GIXD pattern and (d) AFM height image of **PITET** film.

character. The transfer and output curves are shown in Fig. 3a-b. A hole mobility up to 1.92 cm^2 V^{-1} s^{-1} was recorded after thermal annealing at 200 ℃. To the best of our knowledge, this is the largest hole mobility achieved in polymeric semiconductors based on extended-isoindigo-type molecules. The structure of active layer and film morphology have crucial influence on the device performance. Hence, grazing-incident X-ray diffraction (GIXD, data obtained at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility) and tapping-mode atomic force microscopy (AFM) were applied to investigate the molecular packing and morphology of **PITET** thin film. As shown in Fig 3c, the polymer film displays a strong out-of-plane diffraction peak (100) at $2\theta = 2.06°$, corresponding to a d-spacing of 34.5 Å ($\lambda = 1.24$ Å). The diffraction peak corresponding to (200) was also observed, indicating a good lamellar edge-on packing of the polymer chains in the film. In Fig 3d, the AFM height image of **PITET** shows fiber-like intercalating networks with a root mean-square (RMS) roughness of 1.34 nm. Such networks are presumably due to the strong intermolecular π-π interactions.

In conclusion, an electron-deficient π-extended isoindigo-type structure **NBDOPV** was developed. By incorporating a benzodipyrroledione unit, tetralactam **NBDOPV** exhibits good solubility while maintaining skeleton rigidity. Compared to **BDOPV**, **NBDOPV** shows higher HOMO and LUMO energy levels and red-shifted absorption, which results from the differences in electronic structures between lactone and lactam. Based on **NBDOPV**, a conjugated polymer **PITET** was synthesized and characterized, which exhibits a hole mobility up to 1.92 cm^2 V^{-1}s^{-1}. Our result indicates that **NBDOPV** has great potential to be a good building block for polymer semiconductors.

Notes and references

Jian Pei*, Tel: 861062758145 E-mail: jianpei@pku.edu.cn
Beijing National Laboratory for Molecular Sciences, Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, Center of Soft Matter Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing, China

1   (a) A. J. Heeger, N. S. Sariciftci and E. B. Namdas, S*emiconducting and Metallic Polymers*; Oxford University Press: 2010. (b) H. Klauk, *Organic Electronics: Materials, Manufacturing and Applications*; Wiley-VCH: Weinheim: Germany, 2006. (c) Z. Bao, and J. Locklin, *Organic Field-Effect Transistors*; CRC Press: 2007.
2   (a) Y. Li, *Acc. Chem. Res.,* 2012, **45**, 7233. (b) C. Wang, H. Dong, W. Hu, Y. Liu and D. Zhu, *Chem. Rev.,* 2012, **112**, 2208.
3   (a) T. Lei, Y. Cao, Y. Fan, C.-J. Liu, S.-C. Yuan and J. Pei, *J. Am. Chem. Soc.,* 2011, **133**, 6099. (b) T. Lei, J.-H. Dou, Z.-J. Ma, C.-H. Yao, C.-J. Liu, J.-Y. Wang and J. Pei, *J. Am. Chem. Soc.,* 2012, **134**, 20025. (c) T. Lei, J.-H. Dou, Z.-J. Ma, C.-J. Liu, J.-Y. Wang and J. Pei, *Chem. Sci.,* 2013, **4**, 2447. (d) T. Lei, Y. Cao, X. Zhou, Y. Peng, J. Bian and J. Pei, *Chem. Mater,.* 2012, **24**, 1762. (e) R. Stalder, J. Mei, K. R. Graham, L. A. Estrada and J. R. Reynolds, *Chem. Mater.*, 2014, **26**, 664. (f) E. D. Głowacki, G. Voss and N. S. Sariciftci, *Adv. Mater.*, 2013, **25**, 6783. (g) E. Wang, W. Mammo and M. R. Andersson, *Adv. Mater.*, 2014, **26**, 1801. (h) T. Lei, J.-Y. Wang and J. Pei, *Acc. Chem. Res.,* 2014, **47**, 1117.
4   (a) Z. Yan, B. Sun and Y. Li, *Chem. Commun.,* 2013, **49**, 3790. (b) T. Lei, J.-H. Dou, X.-Y. Cao, J.-Y. Wang and J. Pei, *J. Am. Chem. Soc.,* 2013, **135**, 12168. (c) T. Wu, C. Yu, Y. Guo, H. Liu, G. Yu, Y. Fang and Y. Liu, *J. Phys. Chem. C,* 2012, **116**, 22655. (d) S. Li, Z. Yuan, J. Yuan, P. Deng, Q. Zhang and B. Sun, *J. Mater. Chem. A,* 2014, **2**, 5427. (e) S. Chen, B. Sun, C. Guo, W. Hong, Y. Meng and Y. Li, *Chem. Commun.,* 2014, **50**, 6509. (f) T. Lei, J.-H. Dou, X.-Y. Cao, J.-Y. Wang and J. Pei, *Adv. Mater.,* 2013, **25**, 6589.
5   (a) Z. Liu, G. Zhang, Z. Cai, X. Chen, H. Luo, Y. Li, J. Wang and D. Zhang, *Adv. Mater.,* 2014, **26**, 6965. (b) Y. Cao, Z.-H. Guo, Z.-Y. Chen, J.-S. Yuan, J.-H. Dou, Y.-Q. Zheng, J.-Y. Wang and J. Pei, *Poly. Chem.,* 2014, **5**, 5369.
6   (a) J. Mei, D. H. Kim, A. L. Ayzner, M. F. Toney and Z. Bao, *J. Am. Chem. Soc.,* 2011, **133**, 20130. (b) T. Lei, J.-H. Dou, J. Pei, *Adv. Mater.,* 2012, **24**, 6457. (c) T. Lei, J.-Y. Wang, J. Pei, *Chem. Mater.*, 2014, **26**, 594. (d) Y. Deng, Y. Chen, J. Liu, L. Liu, H. Tian, Z. Xie, Y. Geng and F. Wang, *ACS Appl. Mater. Interfaces,* 2013, **5**, 5741. (e) X.-Y Wang, F.-D. Zhuang, X. Zhou, D.-C. Yang, J.-Y. Wang and J. Pei, *J. Mater. Chem. C,* 2014, **2**, 8152. (f) J.-H. Dou, Y.-Q. Zheng, T. Lei, S.-D. Zhang, Z. Wang, W.-B. Zhang, J.-Y. Wang and J. Pei, *Adv. Func. Mater.,* 2014, **24**, 6270.
7   (a) M. Miller, W. Tsang, A. Merritt and D. J. Procter, *Chem. Commun.,* 2007, **43**, 498. (b) C. Ovens, N. G. Martin and D. J. Procter, *Org. Lett.,* 2008, **10**, 1441. (c) M. Miller, J. C. Vogel, W. Tsang, A. Merritt and D. J. Procter, *Org. Biomol. Chem.,* 2009, **7**, 589. (d) L. H. S. Smith, T. T. Nguyen, H. F. Sneddon and D. J. Procter, *Chem. Commun.,* 2011, **47**, 10821. (e) C. Ovens, J. C. Vogel, N. G. Martin and D. J. Procter, *Chem. Commun.,* 2009, **45**, 3101.
8   W. Yue, T. T. Larsen-Olsen, X. Hu, M. Shi, H. Chen, M. Hinge, P. Fojan, F. C. Krebs and D. Yu, *J. Mater. Chem. A,* 2013, **1**, 1785.
9   Y. Ito, A. A. Virkar, S. Mannsfeld, J. H. Oh, M. Toney, J. Locklin and Z. Bao, *J. Am. Chem. Soc.*, 2009, **131**, 9396.

ChemComm Accepted Manuscript