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Effects of pyridyl group orientations on the optoelectronic π -

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Abstract

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Two novel regio-isomeric π -conjugated polymers consisting of the pyridyl unit flanked diketopyrrolopyrrole as the electron-accepting unit and 2,5-bis(3-hexylthiophen-2vl)thieno[3,2-b]thiophene as the electron-donating unit were designed and synthesized. The comparison of the optical and electrochemical properties indicated that the copolymer based on the nitrogen atom proximal to the central diketopyrrolopyrrole unit (p-PDBPy) exhibited bathochromic shifted absorption spectra and narrower bandgaps than the counterpart copolymer (*d*-PDBPy) with the distal oriented nitrogen atom, which can be correlated to the stronger intermolecular aggregations of the former as a result of the different intrinsic molecular geometry of the polymer backbone. Of particular interests is that the copolymer *p*-PDBPy exhibited a moderate hole mobility of 0.35 cm² V⁻¹ s⁻¹, which is about three orders of magnitude higher than the hole mobility of 3.2×10^{-4} cm² V⁻¹ s⁻¹ obtained based on the counterpart copolymer *d*-PDBPy, as measured by organic field-effect transistors. These results demonstrated that the delicate control of the pyridyl orientations along the polymer backbone is of vital importance for the molecular design of π -conjugated polymers for high-performance organic electronic devices.

Keywords: Donor-acceptor conjugated polymers, regioisomer, diketopyrrolopyrrole, organic field effect transistors

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The orientation of N-atom in the pyridyl groups shows pronounced effects on the molecular geometry and charge transport property.



Introduction

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Solution processable π -conjugated polymers have gained much attention due to their specific advantages of light-weight, low-cost processing techniques and great potential for the mass-production of large-area flexible organic electronic products.¹⁻³ Over the past decades, significant progress has been achieved in developing high-performance π -conjugated polymers through rational molecular design along with device engineering.⁴⁺⁹ In particular, π -conjugated polymers based on the alternating connected electron-rich (donor, D) unit and electron-deficient (acceptor, A) unit, along the backbone have been extensively investigated.¹⁰⁻¹⁴ The exceptional merit of this molecular framework is that it allows for the delicate modification of both D and A units, which can lead to well-controlled frontier molecular orbital levels, finely tailored supramolecular stacking, associated with appropriate optoelectronic properties.^{15,16} However, it is worth concerning the subject of stereo-regularity when the involved unit of either D or A unit is asymmetric, since the regiore gularity of π -conjugated polymers can significantly affect the optoelectronic properties.^{17,18}

As a well-studied species, diketopyrrolopyrrole (DPP) moiety has been extensively used for the construction of high-performance organic semicoductors for organic photovoltaics and organic field-effect transistors.^{15, 19-21} Regarding to the synthetic procedures, the DPP derivatives typically comprising of two flanked aromatic groups, such as the thienyl¹⁵, selenophenyl²², furyl²³, thiazolyl²⁴, and phenyl²⁵ units, etc. In conjugated polymers, these units may form non-covalent interactions with the central DPP unit or the adjacent species, which can potentially influence the backbone

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co-planarity, energy levels, crystallinity, and π - π stacking in thin films. Of particultar corresponses interests is the recently emerged Py-DPP unit that consists of two flanked 2-pyridyl units. The strong electronegativity of the amine group (C=N) in pyridyl can effectively withdraw electrons and lead to simultaneously decreased highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, thus imparting the resultant polymers n-type properties with outstanding electron mobilities.²⁶⁻²⁹ Additionally, since the nitrogen-atom is proximal to the central DPP unit, the lack of hydrogen in the nitrogen atom adjacent to the DPP unit can significantly reduce the repulsive interaction between the central DPP unit and the flanked 2-pyridyl unit, and thus lead to nearly co-planar architecture. However, it is worth noting that the hydrogen atoms in the 3,5-position of the pyridyl unit may also give rise to the steric interactions with adjacent species.

Given the asymmetric molecular structures of the 2-pyridyl unit, in this manuscript, we introduced a novel Py-DPP derivative based on the isomer of 3-pyridyl unit, which has the nitrogen atom oriented distal to the central DPP unit. Despite the existence of hydrogen atoms adjacent to the central DPP is unfavorable for the effective conjugation, the lack of hydrogen atom in 3-position of the nitrogen atom is beneficial for the formation of co-planar structure. The 2,5-bis(3-hexylthiophen-2-yl)thieno[3,2*b*]thiophene was used as donors, since it can promote intermolecular π - π stacking that can facilitate charge transportation. ³⁰⁻³⁵ The constructed regio-isomeric Py-DPP conjugated polymers provide an interesting platform to study the effects of the orientation of nitrogen unit on the molecular structures and optoelectronic properties.

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Results and discussion

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Synthesis and characterizations

Scheme 1 shows the synthesis of monomers and polymers. The compound 2,5-bis(3hexylthiophen-2-yl)thion[3,2-b]thiophene (1) was synthesized via a palladium catalyzed Stille coupling reaction of 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene 2-bromo-3-hexylthiophene. The 5-bis(3-hexyl-5and compound (trimethylstannyl)thiophen-2-yl)thiophene (2, TT2T-Sn₂) was prepared by treating (1) with *n*-butyllithium at -78 $^{\circ}$ C followed by treating with trimethyltin chloride in a relatively high yield of 80%. The alkylation 3,6-bis(5-bromopyridin-2yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3) by using 1-bromo-2-octyldodecyl gives the dibromo-monomer 3,6-bis(5-bromopyridin-2-yl)-2,5-bis(2octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (4) in a yield of 41%. It is worth noting that the nitrogen-atom in (4) is proximal to the central DPP unit.

To construct the regioisomeric copolymers of compound (4) that comprising the nitrogen-atom distal to the central DPP core unit, our initial efforts were carried out based on the condensation reaction of the nitrile with succinic acid ester by using 6-bromonicotinonitrile and diisopropyl succinate as the starting materials. However, this reaction gave complex products while failed to give the target regioisomeric intermediate corresponding to (3). Thus, we switch the synthetic strategy by incorporating an alkylthiophene unit to the nicotinonitrile moiety. The synthesis of the intermediate compound 6-(4-hexylthiophen-2-yl)nicotinonitrile (5) is performed

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through a Stille coupling reaction of tributyl(4-hexylthiophen-2-yl)stannane^{Dol:10,1029/C6TC00051G} bromonicotinonitrile, which can be successfully reacted with disopropyl succinate through condensation reaction in 2-methylbutan-2-ol solution to give the target intermediate compound 3,6-bis(6-(4-hexylthiophen-2-yl)pyridin-3-yl)pyrrolo[3,4c]pyrrole-1,4(2H,5H)-dione (6) in a moderate yield of 50%. Compound (6) was directly used for the alkylation with 1-bromo-2-octyldodecyl without purification, giving the intermediate 3,6-bis(6-(4-hexylthiophen-2-yl)pyridin-3-yl)-2,5-bis(2compound octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (7) in a moderate yield of 39%. The target dibromo-monomer 3,6-bis(6-(5-bromo-4-hexylthiophen-2-yl)pyridin-3-yl)-2,5-bis(2-octyldodecyl)pyrrol o[3,4-c]pyrrole-1,4(2H,5H)-dione (8) can be afforded by bromination of intermediate compound (7) with N-bromosuccinimide (NBS) in chloroform solution. The molecular structures of all intermediates, monomers and polymers are confirmed by nuclear magnetic resonance (NMR) spectroscopy (see the Supporting Information, SI).

The palladium-catalyzed Stille polymerization of the bis-stannylled monomer (2) with dibromo-monomer (4) gives the copolymer *p*-**PDBPy**, where the "*p*" represents that the N-atom in the pyridyl unit is proximal to the central DPP unit. Based on similar procedure, the palladium-catalyzed Stille polymerization of the 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene and dibromo-monomer (8) gives the copolymer *d*-**PDBPy**, where the "*d*" denotes that the N-atom in the pyridyl unit is distal to the central DPP unit. After polymerization, the solids were precipitated in methanol and collected by filtration. The purification of these copolymers was carried out by

Soxhlet extraction using methanol, acetone and hexane successively to remove the successively to remove the sing small-molecule and catalyst residues. Then the copolymers were collected by using hexane for *d*-PDBPy and dichloromethane for *p*-PDBPy followed by re-precipitation and filtration in methanol. Both of the two resultant copolymers can be readily dissolved in common organic solvents, such as chloroform (CF), tetrahydrofuran (THF), chlorobenzene (CB) owing to the tethered bulky 2-octyldodecyl side groups on the DPP unit and hexyl side groups on the thiophene units. The number average molecular weight (M_n) and polydispersity indices (PDIs) of these polymers were evaluated by gel permeation chromatography (GPC) using THF as the eluent and polystyrene as the standard. The estimated M_n are 37.7 and 21.4 kDa with PDI of 2.5 and 3.1 for *d*-PDBPy and *p*-PDBPy, respectively.



⁽i)Pd(PPh 3), toluene, 110 °C, 8 h. (ii) & BuLi, trimethyttin chloride, THF, -78 °C. (iii) K2C03, DMF, 130 °C, 12 h. (vi) Pd(PPh 3), xylene, MW 180 °C, 45 min. (v) sodium, FeCl 3, 2-methylbutan-2-ol, AcOH, 90 °C, 20h. (vi) NBS, chloroform, 25 °C, overnight.

Scheme 1 Synthetic route of pyridine-bridged DPP polymers.

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Thermal properties

Thermal properties of two copolymers were investigated by thermogravimetric analysis (TGA) at a heating rate of 20 °C min⁻¹ and differential scanning calorimetry (DSC) at a scanning speed of 10 °C min⁻¹ under a nitrogen atmosphere. As shown in Fig. S1a (see the Supporting Information, SI), both copolymers exhibited good thermal stability with 5% mass loss temperature higher than 400 °C. Copolymer *p*-PDBPy exhibited an obvious glass transition temperature (T_g) of about 120 °C, indicating good thermal property of the copolymer. In contrast, no discernable glass transition temperature can be realized for copolymer *d*-PDBPy up to 250 °C (Fig. S1b in the SI). The different T_g of these copolymers might be correlated to the different intermolecular interactions.^{29, 36, 37} Detailed molecular weight and thermal analysis data are summarized in Table S1 (see the SI).

Optical properties

The UV-Vis absorption spectra of the copolymers *d*-PDBPy and *p*-PDBPy in dilution chlorobenzene (CB) solution with concentration of 1×10^{-5} g mL⁻¹ and as thin films are shown in Fig. 1. Copolymer *p*-PDBPy based on 2-pyridyl as the flanked unit exhibited much broader and bathochromic-shifted absorption spectra both in CB solution and as thin film than that of *d*-PDBPy based on 3-pyridyl moiety as the flanked unit. In addition, both in solution and as thin films, these copolymers exhibit dual absorption bands, which are characteristic absorption profiles for the donor-acceptor type of conjugated polymers. The relatively weak absorption band located at 350-450 nm can

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be ascribed to the delocalized π - π^* transition, and the intense absorption bands at 500^{-12} $corrections at 500^{-12}$ $corrections at 500^{-12}$ corrections corrections

The absorption profiles of *d*-PDBPy in CB solution and as thin film are quite analogous to a maximal absorption (λ_{max}) of about 570 nm, which are distinctly hypsochromic shift with respect to those for *p***-PDBPy**. One notes that there is a sharp absorption signal emerged at 693 nm, which can be correlated to the formation of strong intermolecular aggregation of the *p*-PDBPy in thin film. It is also worth noting that there is a relatively weak shoulder peak for the absorption profile of *p*-PDBPy in CB solution, which is supposed to be attributed to the existence of aggregation. This is understandable since for copolymer *d*-PDBPy, one notes that there are the two hydrogen atoms in the pyridal unit that are adjacent to the central DPP unit, which would lead to steric hindrance with less favorable aggregation tendency. In contrast, since there is only one hydrogen atom in the pyridal unit that is adjacent to the central DPP unit, thus segments comprising of Py-DPP-Py may have strong tendency to aggregate. This assumption can be confirmed by the UV-vis absorption spectra of copolymers at raised temperatures (Fig. 1c and d). As can be seen in Fig. 1c, the absorption spectra of *d*-PDBPy showed trivial variations upon raised temperature from

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28 to 130 °C, which is understandable since the lack of strong aggregation in the CB^{//CGTCOOD51G} solution. In contrast, for the UV-vis spectra of copolymer *p*-PDBPy, it was realized that the shoulder peak located at about 690 nm gradually disappeared, while the λ_{max} progressively hyposchromic shift from 626 nm to about 590 nm, which can be ascribed to the breakup of aggregations. These observations clearly indicated that the strong aggregation can only be formed in solution of *p*-PDBPy, implying that the 2-pyridyl unit can facilitate the formation of co-planar geometry that is favorable for the overlap of π -orbitals along the polymeric chain.

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Fig. 1 UV-vis absorption spectra of the copolymers in CB solution with concentration of 1×10^{-5} g mL⁻¹ (a) and as thin films (b); temperature-dependent UV-vis absorption spectra of copolymers in chlorobenzene (CB) solution with concentration of 1×10^{-5} g mL⁻¹ for *d*-PDBPy (c) and *p*-PDBPy (d).

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polymer	λ_{\max} (nm)		λ_{onset}^{b}	$E_{g}^{opt c}$	Еномо	$E_{\rm LUMO}$	$E_{g}^{cv d}$
	in solution ^a	as films ^b	(nm)	(eV)	(eV)	(eV)	(eV)
d-PDBPy	576	570	672	1.84	-5.44	-3.01	2.43
<i>p</i> -PDBPy	626	635, 693	765	1.62	-5.32	-3.09	2.23

Table 1 Optical and electrochemical properties of copolymers

a. Measured in chlorobenzene solution;

b. Measured as thin film spin-coated from chlorobenzene solution;

c. Calculated from the UV-vis absorption band edge of the copolymers film by the equation, $E_g^{opt} = 1240/\lambda_{onset}$;

d. Estimated by cyclic voltammetry.

Electrochemical properties

Cyclic voltammetry (CV) measurements were performed to evaluate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of these copolymers. The characteristics of CV curves were recorded under an inert atmosphere at a scan rate of 100 mV s⁻¹, with relevant curves shown in Fig. 2 and relevant data summarized in Table 1. Here the ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as the standard for the measurement, which was assumed to have an absolute energy level of –4.8 eV of the redox potential relative to vacuum.³⁸ Under exactly the same conditions for the measurements of samples, the potential of Fc/Fc⁺ was measured as 0.39 V relative to the saturated calomel electrode. Thus, the HOMO energy levels and the LUMO energy levels of the copolymers can be calculated according to the equation of HOMO = $-e(E_{ax} + 4.41)$ (eV) and LUMO = $-e(E_{red} + 4.41)$ (eV), where the E_{ax} and E_{red} represent the onset of oxidation and reduction, respectively.

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The calculated HOMO/LUMO energy levels are -5.44/-3.01 eV and -5.32/-3.09 eV/C6TC00051G for *d*-PDBPy and *p*-PDBPy, respectively. Relative to the copolymer *d*-PDBPy, the HOMO energy level of *p*-PDBPy slightly increased while the LUMO energy level slightly decreased. The combination of these factors leads to reduced electrochemical band gaps (E_g^{cv}) of 2.23 eV for *p*-PDBPy relative to that of 2.43 eV for *d*-PDBPy.



Fig. 2 Cyclic voltammograms (a) and HOMO/LUMO energy levels of copolymers (b).

Theoretical calculation

To get insight into the effects of the position of N atom in pyridine unit on the molecular geometry and the electronic structures, density functional theory (DFT) theoretical calculations were performed at the B3LYP/6-31G (d) basis on the Gaussian 09 package.³⁹ Here the alkyl side chains on the modeling dimer compounds were replaced by methyl groups to simplify the calculation. Fig. 3 illustrated the resulted frontier molecular orbitals and the dihedral angles between the flanked 3-pyridyl or 2-pyridyl unit with the adjacent thiophene unit (φ_2) and the DPP moiety (φ_1). For both dimers

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[*d*-DBPy]₂ and [*p*-DBPy]₂, HOMO orbitals are delocalized over the conjugated ^{View Article Online Dol 10,1039/C6TC00051G} backbone, while the LUMO orbitals more preferentially resided in the DPP unit.

The comparison of these dimers indicated that the dihedral angle of φ_1 significantly reduced from 21.4° for $[d\text{-DBPy}]_2$ to 1.2° for $[p\text{-DBPy}]_2$, which can be attributed to the reduced steric interaction since the lack of hydrogen in the 2-position of the 2-pyridyl moiety. In contrast, due to the potential noncovalent interaction of N···S in $[d\text{-DBPy}]_2$ can promote the formation of coplanar architecture between the adjacent thienyl and pyridyl moieties,⁴⁰ the nearly planar conformation was realized with the dihedral angle of φ_2 is 0.2° for $[d\text{-DBPy}]_2$, which significantly increased to 18.2° due to the repulsion of the adjacent hydrogen atoms for $[p\text{-DBPy}]_2$.



Fig. 3 The frontier molecular orbitals of (d-DBPy)₂ and (p-DBPy)₂ obtained from DFT calculations with a chain length n = 2 at the B3LYP / 6-31G (d) level.

Charge carrier mobility

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To investigate the effects of the orientation of pyridyl groups on the charge transport properties of DPP-based copolymers, bottom-gate and top-contact (BGTC) organic field effect transistors (OFET) with architecture of Al:Nd/AlOx:Nd/ODPA /polymer/Au were fabricated. Here the Al:Nd was used as the gate instead of pure Al, since it can effectively suppress the formation of hillock and can reduce the surface roughness. The Al:Nd film was anodized to produce a layer of AlOx:Nd on the surface of the Al:Nd film as the gate insulator, which was then modified with octadecylphosphonic acid (ODPA, molecular structure shown in Fig. 4a). The DPPbased polymers were spin-coated from chloroform (CF) or chlorobenzene (CB) solution onto ODPA modified AlOx:Nd film. The films were thermally annealed at 100°C in nitrogen atmosphere for 10 min to facilitate the formation of ordered microstructures. Then Au was thermally evaporated onto the polymer film through a shadow mask. The recorded output and transfer characteristics are shown in Fig. 4 (and Fig. S2 in the SI), with relevant parameters summarized in Table 2.

Based on the film spin-casted from CB solution, the copolymer *p*-PDBPy showed a moderate hole mobility (μ_{hole}) of 0.35 cm²·V⁻¹·s⁻¹ with a high on/off ratio ($I_{on/off}$) of 10⁴~10⁵. In contrast, copolymer *d*-PDBPy that is processed under exactly the same conditions exhibited about three orders of magnitude lower hole mobility of about 3.2 × 10⁻⁴ cm² V⁻¹ s⁻¹ with a $I_{on/off}$ of 10²~10³. Similar trend was also realized for the films processed from chloroform (CF) solution, with μ_{hole} of was 0.23 cm²·V⁻¹·s⁻¹ for *p*-PDBPy that is much higher that of 3.7 × 10⁻⁴ cm² V⁻¹ s⁻¹ for *d*-PDBPy. Given that the devices are fabricated under exactly the same conditions, and the molecular weight of

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the two copolymers are quite comparable, thus the difference in charge carrier mobility must be correlated to the orientation of the asymmetric pyridyl unit along with the backbone of the regio-isomeric polymer structures. Since the nitrogen atom in pyridyl unit proximal the adjacent DPP core unit in copolymer *p***-PDBPy**, the 2-pyridyl substituents can effectively reduce the steric interaction with the DPP core unit that resulted in a highly coplanar structure, which may potentially promote close packing of the DPP unit in solid state with obviously increased intermolecular interaction that can offer effective pathways for charge transport. In contrast, despite the nitrogen unit that in 3-pyridyl unit is distal to the central DPP unit can facilitate the formation of co-planar structure with the adjacent thiophene unit, the repulsive interaction of the hydrogen atoms adjacent to the DPP core unit can resulted in increased dihedral angle and thus a larger interchain π - π stacking distance, which would impede both intra- and intermolecular charge transport events. It is also worth mentioning that despite the in hole-mobility can be significantly affected by the pyridyl orientations, one may anticipate such effect of the isomeric structures on the electron-mobility. However. since the resultant polymers in this work do not exhibited apparent *n*-type properties, at the current stage we do not have good explanations on this issue. Nonetheless, these observations clearly indicated that the flanked 2-pyridyl unit that can lead to smaller dihedral angle with the central DPP unit is more promising than 3-pyridyl unit for the attainment of higher hole mobility.

CB

 $\mu(cm^2 \cdot V^{-1} \cdot s^{-1})$

Polymer
d-PDBPy
<i>p</i> -PDBPy
Au
^{10⁻⁹} V _g = (V)
10 ⁻⁹
10 ⁻⁹
0-10
0 -5 -1
(10^{-6}) V = (V)

Table 2. Summary of the device properties of the DPPT-TT OFETs with different/C6TC00051G processing conditions.

Ion/Ioff

CF

Ion/Ioff

 $\mu(cm^2 \cdot V^{-1} \cdot s^{-1})$



Fig. 4 (a) Devices structure of the copolymer OFETs. Output and transfer characteristics of (b and c) d-PDBPy and (d and e) p-PDBPy devices (spin-coated from

CB solutions) at V_{SD}=-30 V (L=70 μ m, W=500 μ m) after thermal annealing at 0.0019 G/C6TC00051G for 10 min.

Morphology

Tapping mode atomic force microscopy (AFM) was used to investigate the film morphology of the isomeric conjugated polymers. The films were processed from the chlorobenzene or chloroform solution on the top of the glass/Al:Nd/AlOx:Nd/ODPA substrate according to the same procedure as that of the OFET device. For copolymer *d*-PDBPy with the nitrogen atom distal to the central DPP unit, one can observe very smooth surface with a root mean square (RMS) values of 0.3 and 0.6 nm for the film spin-casted from CB (Fig. 5a) and CF (Fig. 5c) solution, respectively. In contrast, for copolymer *p*-PDBPy that with the nitrogen atom proximal to the central DPP unit, both films spin-casted from CB (Fig. 5b) and CF (Fig. 5d) showed apparent granular features across the entire film associated with much rougher film morphology with RMS value of 2.0 and 4.6 nm, respectively, indicating the formation of much stronger intermolecular aggregations that is favorable for charge transportation. Given that the only difference in the two films is the intrinsic orientation of pyridyl unit, thus it is rational to surmise that the obviously different film morphology of the regio-isomeric copolymers can be attributed to the discrepancy of the intrinsic orientation of pyridyl unit along polymer backbone. We note that additional film morphology studies may facilitate further understanding of the effects of the orientation of the pyridyl on the microstructures and charge transportations, nonetheless, the current observations clearly indicated that the importance of attaining high co-planarity between the adjacent

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flanked unit with the central DPP unit for the achievement of high mobility.



Fig. 5 AFM topography images $(2 \times 2 \ \mu m^2)$ of (a, c) *d*-PDBPy and (b, d) *p*-PDBPy copolymer thin film. The films were spin-coated from (a, b) CB and (c, d) CF.

Conclusion

In summary, two regio-isomeric π -conjugated polymer consisting of pyridyl flanked diketopyrrolo[3,4-*c*]pyrrole unit have been designed and synthesized, where the nitrogen atom in the pyridyl unit was proximal or distal to the central diketopyrrolopyrrole unit. It was noted that the molecular geometry, absorption spectra, optical band-gaps, frontier molecular orbitals as well as the film morphology of the resulted copolymers can be significantly affected by the orientation of nitrogen atom in the pyridyl unit. Of particular interests is that the copolymer based on proximal oriented nitrogen atom exhibited a moderate field-effect transistor hole mobility for the films processed from both chloroform and chlorobenzene solution, which is about three

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orders of magnitude higher than those obtained based on the counterpart copolymer with distal oriented nitrogen atom. These observations illustrated that the charge transport properties can be significantly affected by the orientation of pyridyl unit along the polymer backbone, which highlighted the importance of the delicate control of molecular structures for the high-performance organic semiconductors.

Experimental section

Materials

All the solvents were purchased from Guangzhou Chemical Reagent Cooperation. Anhydrous THF and xylene were distilled from sodium and benzophenone was used as the indicator. All reagents were purchased from Acros, Strem Chemicals, and were used without further purification. Compound 3,6-bis(5-bromopyridin-2-yl)pyrrolo[3,4c]pyrrole-1,4(2*H*,5*H*)-dione (3) was synthesized according to the reported procedures.

2,5-Bis(3-hexylthiophen-2-yl)thieno[3,2-b]thiophene (1)

In a 100 mL three-necked flask was added compound 2-bromo-3-hexylthiophene (0.80 g, 3.22 mmol) was mixed with 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene (0.60 g, 1.29 mmol) and Pd(PPh₃)₄ (30 mg, 26 µmol) in 50 mL toluene, and then the solution was heated to 110 °C for 8 h under argon protection. After cooling to room temperature, the solvent removed by reduced pressure to give the crude product and purified by column chromatography using petroleum ether as an eluent to obtain compound (1) as a white solid in a yield of 66 % (0.40 g). ¹H NMR (500 MHz, CDCl₃): δ 7.24 (s, 2H),

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7.21 (d, J = 5.2 Hz, 2H), 6.96 (d, J = 5.2 Hz, 2H), 2.79 (t, J = 8 Hz, 4H), 1.65 (dt, J^{32/C6TC00051G}
15.5, 7.6 Hz, 4H), 1.43 – 1.24 (m, 12H), 0.88 (t, J = 7.5 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃): δ 140.43, 139.29, 137.76, 130.87, 130.19, 124.49, 118.20, 31.83, 30.94, 29.40, 22.78, 14.23.

2, 5-Bis(3-hexyl-5-(trimethylstannyl)thiophen-2-yl)thieno[3,2-b]thiophene (2)

In a 50 mL one-necked flask compound (1) (0.2 g, 0.42 mmol) was dissolved in 20 mL THF under argon protection. Then the solution was cooled to -78 °C, to which 0.93 mL n-BuLi (1.48 mmol, 1.6 M in hexanes) was added dropwise. The mixture was kept at -78 °C for 30 minutes and then allowed to warm to 0 °C for another 30 minutes, and then cooled to -78 °C. Then trimethyltin chloride (1.69 mmol, 1 M in THF) was added dropwise. The mixture was stirred overnight at room temperature and poured into water, extracted with hexane, washed with water, dried over MgSO₄. The solvent removed by reduced pressure and to give the product (**2**) as a brown-yellow solid in a yield of 80 % (0.27 g). ¹H NMR (500 MHz, CDCl₃): δ 7.21 (s, 2H), 7.02 (s, 2H), 2.80 (t, *J* = 8.0 Hz, 4H), 1.71 – 1.61 (m, 4H), 1.46 – 1.24 (m, 12H), 0.93 – 0.82 (m, 6H), 0.45 (s, 18H).¹³C NMR (126 MHz, CDCl₃): δ 141.46, 139.28, 138.51, 137.90, 137.36, 136.66, 117.64, 31.84, 31.09, 29.56, 29.34, 22.79, -8.05.

3,6-Bis(5-bromopyridin-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (4)

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In a 250 mL three-necked flask compound 3,6-bis(5-bromopyridin-2-yl)pyrfold $3,4^{22/CETCOODSTC}$ *c*]pyrrole-1,4(2*H*,5*H*)-dione (2.4 g, 5.36 mmol) was mixed with potassium carbonate (2.22 g, 16.07 mmol) and 1-bromo-2-octyldodecyl (5.81 g, 16.07 mmol) in 100 mL DMF under argon. The mixture was poured into 150 mL water after stirred at 130 °C for 12 h. The organic phase was extracted with ethyl acetate, washed with brine, dried over MgSO4. After solvent was evaporated, crude solid was purified by column chromatography using petroleum ether and dichloromethane as an eluent to obtain the target compound (4) as a dark red solid in a yield of 41 % (2.2 g). ¹H NMR (500 MHz, CDCl₃): δ 8.93 (d, *J* = 8.6 Hz, 2H), 8.74 (d, *J* = 2.3 Hz, 2H), 8.01 (dd, *J* = 8.5, 2.4 Hz, 2H), 4.28 (d, *J* = 7.3 Hz, 4H), 1.59 (d, *J* = 16.6 Hz, 2H), 1.40 – 1.01 (m, 64H), 0.87(q, *J* = 7.1 Hz, 12H). ¹³C NMR (126 MHz, CDCl₃): δ 162.63, 150.25, 146.21, 145.11, 139.84, 128.61, 122.73, 111.57, 46.44, 38.36, 32.07, 32.05, 31.59, 30.16, 29.83, 29.81, 29.77, 29.71, 29.51, 29.47, 26.52, 22.84, 22.83, 14.27.

6-(4-Hexylthiophen-2-yl)nicotinonitrile (5)

In a 250 mL three-necked flask compound 6-bromonicotinonitrile (5 g, 27.32 mmol) was mixed with tributyl(4-hexylthiophen-2-yl) stannane (18.74 g, 40.98 mmol) and $Pd(PPh_3)_4$ (0.63 g, 0.55 mmol) in 100 mL toluene, and then the solution was heated to 110 °C for 8 h under argon protection. After the reaction mixture was cooled to room temperature, the solvent removed by reduced pressure to give the crude product and purified by column chromatography using petroleum ether and dichloromethane as an eluent to give the target compound as a white solid in a yield of 93 % (6.90 g). ¹H NMR

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(500 MHz, CDCl₃): δ 8.77 (dd, *J* = 1.9, 1.0 Hz, 1H), 7.89 – 7.87 (m, 1H), 7.67^P(dd, *J*^{32/C6TC00051G} 8.4, 0.6 Hz, 1H), 7.54 (s, 1H), 7.13 (s, 1H), 2.66 – 2.59 (m, 2H), 1.70 – 1.57 (m, 2H), 1.42 – 1.22 (m, 6H), 0.89 (t, *J* = 7 Hz, 3H).¹³C NMR (126 MHz, CDCl₃): δ 155.74, 152.61, 145.17, 142.42, 139.66, 128.71, 125.69, 118.21, 117.17, 106.96, 31.75, 30.60, 30.51, 29.02, 22.70, 14.20.

3,6-Bis(6-(4-hexylthiophen-2-yl)pyridin-3-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-

dione (6)

In a 500 mL three-necked flask, 150 mL 2-methylbutan-2-ol was added to a mixture of sodium (1.02 g, 44.5 mmol) and FeCl₃ (80 mg, 0.49 mmol), after sodium was completely dissolved by heating the solution at 90 °C protected by argon, cooling the temperature to 50 °C, compound (5) (6.42 g, 23.73 mmol) was added to solution, and then the solution was stirred for 1 h at 90 °C. Diisopropyl succinate (2 g, 9.89 mmol) in 2-methylbutan-2-ol (10 mL) was added drop-wise over 30 min, the resulting black-purple suspension was stirred for another 20 h at 90 °C. After cooling to 60 °C 15 mL acetic acid was added to precipitate the product, and then the solution was refluxed for 1 h. The solution was then cooled to room temperature, and precipitates were filtrated and washed with hot water and methanol until the filtrate remained colorless, and dried at 60 °C in vacuum oven to obtain the target compound (6) as a dark purple solid in a yield of 50 % (3.10 g). The product is insoluble in common NMR solvents and was used in the next step without further purification.

View Article Online 3,6-Bis(6-(4-hexylthiophen-2-yl)pyridin-3-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-

c]pyrrole-1,4(2*H*,5*H*)-dione (7)

In a 250 mL three-necked flask compound (6) (2.54 g, 4.08 mmol) was mixed with potassium carbonate (1.47 g, 10.6 mmol) and 1-Bromo-2-octyldodecyl (3.98 g, 11.01 mmol) in 100 mL DMF under argon. The mixture was poured into 150 mL water after stirred at 130 °C for 12 h. The organic phase was extracted with ethyl acetate, washed with brine, dried over MgSO₄. After solvent was evapoted, crude solid was purified by column chromatography using petroleum ether and dichloromethane as an eluent to obtain the target compound (7) as a bright red solid in a yield of 39 % (1.86 g). ¹H NMR $(500 \text{ MHz}, \text{CDCl}_3)$: δ 8.88 (s, 2H), 8.13 (dd, J = 26.9, 8.3 Hz, 2H), 7.56 (dd, J = 41.7, 8.1 Hz, 2H), 7.37 (d, J = 35.2 Hz, 2H), 7.03 (d, J = 11.2 Hz, 2H), 3.74 (t, J = 8.4 Hz, 4H), 2.59 (dt, J = 12.9, 7.9 Hz, 4H), 1.64 (dd, J = 13.5, 6.8 Hz, 4H), 1.44 - 0.96 (m, 78H), 0.91 (t, J = 6.7 Hz, 6H), 0.85 (dt, J = 10.3, 7.0 Hz, 12H). ¹³C NMR (126 MHz, CDCl₃): δ 162.51, 162.47, 154.21, 154.14, 149.20, 148.99, 145.78, 144.82, 144.76, 143.49, 136.81, 136.61, 127.52, 127.45, 125.41, 124.26, 124.18, 122.44, 122.33, 121.30, 118.30, 118.19, 112.52, 110.42, 110.24, 45.51, 45.37, 37.32, 32.07, 32.02, 31.84, 31.36, 30.71, 30.51, 30.48, 30.05, 29.80, 29.78, 29.73, 29.66, 29.50, 29.44, 29.20, 29.18, 26.21, 26.20, 22.84, 22.80, 22.78, 14.27, 14.26, 14.25.

3,6-Bis(6-(5-bromo-4-hexylthiophen-2-yl)pyridin-3-yl)-2,5-bis(2-octyldodecyl) pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (8)

In a 250 mL one-necked flask compound (7) (1.5 g, 1.27 mmol) was dissolved in

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CHCl₃/AcOH (1:1, 50 mL/50 mL) under argon protection. And then the flask¹⁰ was placed in an ice bath to keep the reaction mixture at 0 °C. N-bromosuccinmide (0.52 g, 2.91 mmol) was added into the solution in small portion and the mixture was stirred for overnight. The reaction mixture was poured into water, extracted with ethyl acetate, washed with water, dried over MgSO₄. The solvent was removed by reduced pressure and the crude product was purified by column chromatography using dichloromethane as an eluent to give the target compound (8) as a bright red solid in a yield of 55 % (0.93 g). ¹H NMR (500 MHz, CDCl₃): δ 8.83 (d, J = 1.7 Hz, 2H), 7.99 (dd, J = 8.3, 1.6Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.09 (s, 2H), 3.69 (d, J = 6.9 Hz, 4H), 2.52 - 2.48(m, 4H), 1.57 (dd, J = 14.4, 6.9 Hz, 4H), 1.39 - 1.04 (m, 78H), 0.91 (t, J = 6.9 Hz, 6H),0.84 (dt, J = 9.9, 7.1 Hz, 12H). ¹³C NMR (126 MHz, CDCl₃): δ 162.34, 153.06, 149.66, 145.66, 143.88, 143.28, 136.32, 126.38, 122.26, 117.31, 114.00, 109.95, 45.06, 37.19, 32.08, 32.02, 31.78, 31.35, 30.04, 29.92, 29.82, 29.79, 29.75, 29.68, 29.52, 29.46, 29.20, 26.17, 22.85, 22.82, 22.77, 14.27, 14.26, 14.25.

Synthesis of *d*-PDBPy

To a microwave vial was added compound **8** (0.2 g, 0.15 mmol), 2,5bis(trimethylstannyl)thieno[3,2-*b*]thiophene (69.5 mg, 0.15 mmol). Xylenes (3 mL) was added and the solution degassed before addition of $Pd(PPh_3)_4$ (9 mg, 0.05 mmol). The reaction mixture was further degassed and subsequently sealed. The vial was heated in a microwave reactor at 180 °C for 45 min. After cooling to room temperature, the reaction mixture was poured into methanol. The crude product was filtered off and

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purified by subsequent Soxhlet extraction with methanol, acetone and hexane. To the correspondence of the methanol of the maximum sequence of the mixture was added an aqueous solution of sodium diethyldithiocarbamate and the mixture was heated to 60 °C with vigorous stirring for 8 hr. After cooling to room temperature, the organic fraction was extracted with water. The polymer was obtained as dark purple solid (yield 82 %) upon evaporation of the hexane extract and precipitation into methanol. ¹H NMR (500 MHz, CDCl₃): δ 8.85 (br, ArH), 7.96 (br, ArH), 7.14 (br, ArH), 3.92 (br, N-CH₂), 3.45 (br, N-CH₂), 2.76 (br, CH), 1.79 – 1.00 (br, CH₂), 0.88-0.81 (br, CH₃). GPC: M_n = 37.7 kDa, M_w = 94.1 kDa, PDI = 2.5.

Synthesis of *p*-PDBPy

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To a microwave vial was added compound 4 (100.9 mg, 0.1 mmol), compound 2 (79.8 mg, 0.1 mmol). Xylenes (3 mL) was added and the solution degassed before addition of Pd(PPh₃)₄ (9 mg, 0.05 mmol). The reaction mixture was further degassed and subsequently sealed. The vial was heated in a microwave reactor at 180 °C for 45 min. After cooling to room temperature, the reaction mixture was poured into methanol. The crude product was filtered off and purified by subsequent Soxhlet extraction with methanol, acetone, hexane and dichloromethane (CH₂Cl₂). To the CH₂Cl₂ extract was added an aqueous solution of sodium diethyldithiocarbamate and the mixture was heated to 60 °C with vigorous stirring for 8 hr. After cooling to room temperature, the organic fraction was extracted with water. The polymer was obtained as dark green-purple solid (yield 69%) upon evaporation of the hexane extract and precipitation into methanol. ¹H NMR (500 MHz, CDCl₃): δ 9.07 (br, ArH), 8.95 (br, ArH), 8.03 (br, ArH),

7.61 (br, ArH), 7.53 (br, ArH), 7.43 – 7.23 (br, ArH), 4.38 (br, N-CH₂), 2.86 (br, CH), $^{View Article Online View Article Online 1.93 – 1.06 (br, CH₂), 0.96 – 0.82 (br, CH₃). GPC: <math>M_n$ = 21.4 kDa, M_w = 67.5 kDa, PDI = 3.1.

Instruments

¹H NMR and ¹³C NMR spectra were collected on a Bruker AV-500 (500 MHz) in deuterated chloroform with tetramethylsilane as a reference. The molecular weights of polymers were determined by Acquity APC using THF as the eluent. Thermogravimetric analyses (TGA) were performed on a Netzsch TG 209 at a heating rate of 20 °C min⁻¹ under a nitrogen atmosphere. The differential scan calorimetry (DSC) characteristics were measured on a Netzsch DSC 204 under N₂ flow at a heating rate of 10 °C min⁻¹ and cooling rate of 10 °C min⁻¹. UV-vis absorption spectra were obtained with a Shimadzu UV-3600 UV-vis-NIR spectrometer. Cyclic voltammetry (CV) data were measured on a CHI630E electrochemical workstation equipped with a glassy carbon working electrode, a saturated calomel electrode as the reference electrode, and a platinum wire counter electrode, and carried out with anhydrous acetonitrile tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte under an argon atmosphere at a scan rate of 100 mV s⁻¹. The polymers were deposited on the electrode. Potentials were referenced to the ferrocene/ferrocenium couple by using ferrocene as standard. The oxidation potential of ferrocene was set at -4.80 eV with respect to zero vacuum level. The HOMO energy levels were calculated according to the equation of $E_{\text{HOMO}} = -[4.8 + e (E_{\text{OX}} - E_{\text{Fc/Fc}+})]$ (eV).

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Fabrication and Characterization of Organic Field Effect Transistors (OFETs)

For characterization of OFETs performance, the bottom-gate and top-contact (BGTC) device geometry was employed. Firstly, A 150-nm-thick Al:Nd (3 wt%) film was deposited with DC sputtering and patterned with conventional photolithography method. Afterwards, Al:Nd film was anodized for 1.5 h to produce a layer of 200-nmthick AlOx:Nd on the surface of the Al:Nd film as the gate insulator. After plasma treatment, the substrate was immersed in a 2-propanol solution containing 5 mM ODPA (shown in Fig. 4a) molecules at 60 °C for 30 min. The capacitance density (Ci) of the ODPA-treated AlOx:Nd was 42 nF cm⁻². After that, it was removed from the solution, and rinsed thoroughly with 2-propanol, and blown dry with a stream of nitrogen. The copolymer was dissolved in dichlorobenzene (0.5 mg/mL) and spin-coated (2000 rpm) onto ODPA modified AlOx:Nd with a thickness of 20~30 nm. Then a 40-nm-thick Au film was thermally evaporated onto the OSC film through a shadow mask, defining a channel width/length (W/L) of 500/70 μ m. The PTFT characterizations were measured with a semiconductor parameter analyzer (Agilent 4155C) and a probe station at 25°C in air.

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