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Pentacyclic Aromatic Bislactam-based Conjugated Polymers: Constructed by Beckmann Rearrangement and Application in Organic Field-Effect Transistor

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A Beckmann rearrangement was applied to construct the pentacyclic aromatic bislactam thieno[2',3':4,5]pyrido[2,3-*g*]thieno[3,2-*c*]quinoline-4,10(5*H*,11*H*)-dione (**TPT**) from diketone in two steps under mild condition. Two conjugated polymers **P1** and **P2** based on **TPT** unit were developed through a Stille coupling polymerization. Their photophysical and electrochemical properties were investigated. **P1** exhibited hole mobility up to 0.58 cm^2 V^{-1} s^{-1}, whereas **P2** showed slightly lower mobility of 0.15 cm^2 V^{-1} s^{-1}. The better device performance of **P1** was attributed to the ordered molecular packing in thin film. Our result indicates that **TPT** moiety is a good building block in polymeric semiconductors and the Beckmann rearrangement is a powerful tool in constructing lactam-containing molecules for organic electronic applications.

Introduction

As the promising candidate materials for the next generation of electronics, polymeric semiconducting materials have attracted increasing interest from both industry and academia due to their intriguing flexible, low-cost, and light-weight features.[1] Constructing alternating donor-acceptor (D-A) conjugated polymers is a common design strategy to achieve high-performance materials for organic photovoltaic (OPV) and organic field-effect transistor (OFET) applications.[2] The photophysical and electronic properties of alternating D-A copolymers can be feasibly modulated by adjusting the relative strength of donor and acceptor moieties in conjugated backbones.[3] As the development of acceptors significantly lagged behind that of donors, it has been an intensive research topic to develop novel electron-deficient moieties.

Aromatic lactams widely exist in electron-deficient building blocks including some star molecules such as diketopyrrolopyrrole (**DPP**), isoindigo (**IID**) and benzodifurandione-based PPV (**BDPPV**).[4] Incorporating strong electron-withdrawing amide groups into conjugated backbones is an efficient strategy to lower the LUMO levels of the resulting polymers. Meanwhile, the aromatic lactam structure covalently fixes the conjugated backbones which significantly increase rigidity and lower the reorganization energy of the molecular skeleton, thus enhancing the intrinsic charge mobility.[5] Moreover, the simplicity in obtaining *N*-substituted lactams is very meaningful to obtain solution-processable semiconducting materials with excellent device performances, since side-chains not only improve solubility of materials but also strongly affect intermolecular interactions and molecular packing, resulting in quite different device performances.[6] Recently, some semiconducting polymers based on six-membered-ring lactams were developed for OPV and OFET applications.[7]

The Beckmann rearrangement is a classical reaction which has been proved to be an efficient tool in constructing amides and lactams,[8] thus providing a possibility to efficiently synthesize electron-deficient lactams from corresponding ketones as acceptors in D-A conjugated polymers. To the best of our knowledge, the Beckmann rearrangement reaction has not been employed in the synthesis of organic semiconductors. In our previous work, we demonstrated that polymers with centrosymmetric backbones have more ordered and denser packing in thin films to facilitate charge transport.[9] Therefore, constructing centrosymmetric building blocks is important to develop high-performance polymers for OFET applications.

Herein, the Beckmann rearrangement is applied to construct a pentacyclic aromatic lactam, thieno[2',3':4,5]pyrido[2,3-*g*]thieno[3,2-*c*]quinoline-4,10(5*H*,11*H*)-dione (**TPT**), as an acceptor unit for semiconducting polymers. **TPT**-based conjugated polymers **P1** and **P2** containing different donors are obtained via Stille coupling polymerization. Hole mobility up to 0.58 cm^2 V^{-1} s^{-1} is achieved for **P1**-based FET device whereas **P2** shows lower mobility of 0.15 cm^2 V^{-1} s^{-1}. The better device performance of **P1** is attributed to its ordered molecular packing in thin film.

Experimental

General

Chemical reagents were purchased and used as received. All air and water sensitive reactions were performed under nitrogen atmosphere. Toluene and tetrahydrofuran (THF) were distilled from sodium. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-400 (400 MHz). All chemical shifts were reported in parts per million (ppm). HRMS were recorded on Bruker BIFLEX III mass spectrometer (Bruker Daltonics, Billerica, MA, USA). Absorption spectra were recorded on PerkinElmer Lambda 750 UV-*vis* Spectrometer. Cyclic voltammetry was performed using BASI Epsilon workstation. Elemental analyses were performed using German Vario EL III elemental analyzer. Thermal gravity analyses (TGA) were carried out on TA Instrument Q600 analyzer and differential scanning calorimetry analyses (DSC) were performed on METTLER TOLEDO Instrument DSC822 calorimeter. High-temperature GPC was performed on Viscotek HT-GPC with RI monitor using 1,2,4-trichlorobenzene (TCB) as eluent (140 °C). Atomic force microscopy (AFM) studies were performed with Bruker Dimension Icon microscope. All experiments were carried out in tapping mode at ambient temperature. The X-ray diffraction data were obtained at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF).

Device fabrication

Top-contact/bottom-gate OFET devices were fabricated using n^{++}-Si/SiO$_2$ substrates where n^{++}-Si and SiO$_2$ were used as the gate electrode and gate dielectric, respectively. The substrates were subjected to cleaning using ultrasonication in acetone, cleaning agent, deionized water (twice), and *iso*-propanol. The cleaned substrates were dried under vacuum at 80 ^{o}C. The substrates were then treated with plasma for 15 min and transferred into a glove box. The substrates were modified with octadecyltrimethoxysilane (OTMS) to form a SAM monolayer according to the literature reported by Bao and coworkers.[11] Thin films of the polymers were deposited on the treated substrates by spin coating using a polymer solution (6 mg/mL) in trichloroethylene (TCE), optionally followed by thermal annealing at 200 °C, 180 °C or 160 °C under nitrogen. After polymer thin film deposition, about 30 nm thick gold was deposited as source and drain contacts using a shadow mask. The OFET devices have a channel length (L) of 60 μm and a channel width (W) of 2.4 mm. The evaluations of the OFETs were carried out in ambient atmosphere using a Keithley 4200 parameter analyzer on a probe stage. The carrier mobility, μ, was calculated from the data in the saturated regime according to the equation $I_{SD} = (W/2L)C_i\mu(V_G - V_T)^2$, where I_{SD} is the drain current in the saturated regime. W and L are, respectively, the semiconductor channel width and length, C_i (C_i = 11 nF) is the capacitance per unit area of the gate dielectric layer, and V_G and V_T are the gate voltage and threshold voltage. V_G -V_T of the device was determined from the relationship between the square root of I_{SD} and V_G at the saturated regime.

Synthesis

s-Indaceno[1,2-*b*:5,6-*b′*]dithiophene-4,9-dione dioxime (2)

In a 250 mL round bottle, *s*-indaceno[1,2-*b*:5,6-*b′*]dithiophene-4,9-dione (**1**) (1.00 g, 3.40 mmol), hydroxylamine hydrochloride (4.73 g, 68.0 mmol) and triethylamine (8.10 g, 80 mmol) were added in 150 mL of ethanol and refluxed for 6 h. After cooled to room temperature, the mixture was poured into 300 mL of water and filtered. The red powder (1.03 g, 94%) was dried in vacuum and used directly in next step.

5,11-Bis(2-decyltetradecyl)thieno[2',3':4,5]pyrido[2,3-*g*]thieno[3,2-*c*]quinoline-4,10(5*H*,11*H*)-dione (4)

Cyanuric chloride (0.57 g, 3.10 mmol) was added to DMF (2 mL) at room temperature and stirred for 0.5 h. After the formation of a white solid, *s*-indaceno[1,2-*b*:5,6-*b′*]dithiophene-4,9-dione dioxime (**2**) (0.50 g, 1.54 mmol) in DMF (10 mL) was added. The mixture was stirred at room temperature overnight. Then 100 mL of water was added. The mixture was filtered and dried in vacuum to afford the bislactam as a red solid (0.44 g, 88%). In a 100 mL round bottle, bislactam (0.40 g, 0.81 mmol), 11-(bromomethyl)tricosane (1.80 g, 2.43 mmol), potassium carbonate (0.45 g, 3.24 mmol) and 30 mL of DMF were added and stirred at 100 ^{o}C overnight. Then the solvents were removed under reduced pressure. The residue was purified by silica gel chromatography with eluent (PE:DCM = 20:1) to give 5,11-bis(2-decyltetradecyl)thieno[2',3':4,5]pyrido[2,3-*g*]thieno[3,2-*c*]quinoline-4,10(5*H*,11*H*)-dione (**4**) as a red oil (0.54 g, 44%). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) δ: 7.63 (s, 2H), 7.41 (d, J = 4.8 Hz, 2H), 7.21 (d, J = 4.8 Hz, 2H), 4.31 (d, J = 5.6 Hz, 4H), 1.88-1.82 (m, 2H), 1.47-1.23 (m, 80H), 0.89-0.83 (m, 12H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 148.7, 148.3, 139.1, 135.7, 135.0, 127.4, 124.9, 113.0, 37.9, 31.9, 29.6, 29.4, 29.3, 28.8, 22.7, 14.1. ESI-HRMS: Calcd. for [M]$^+$: 997.7612. Found: 997.7638.

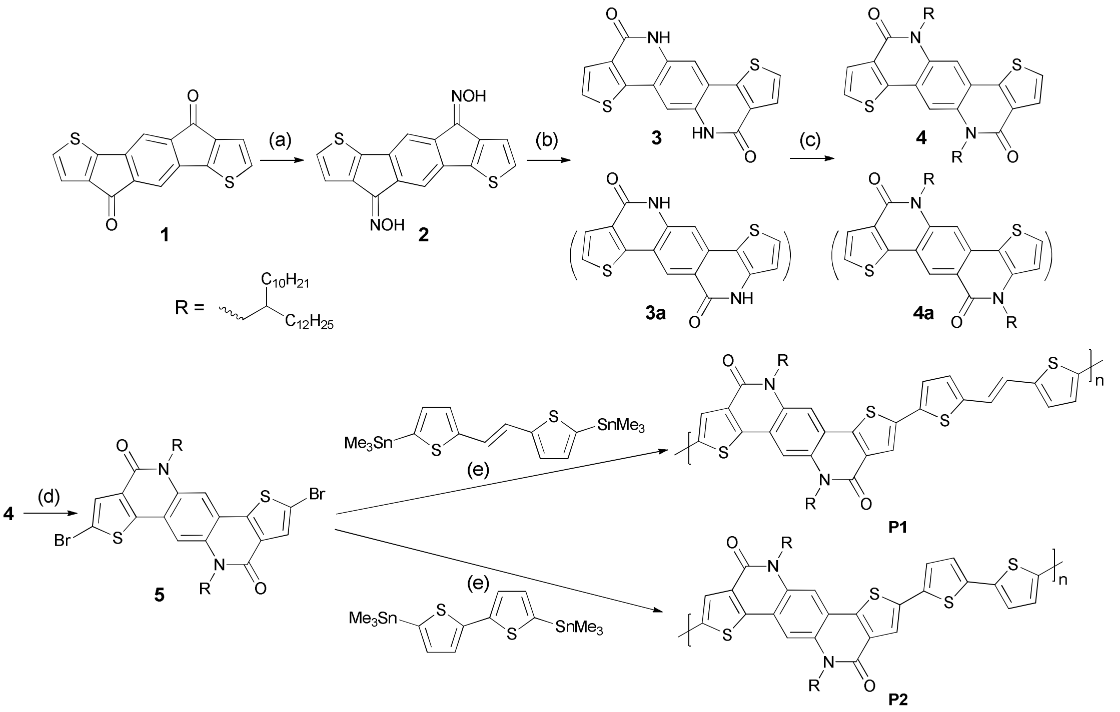
2,8-Dibromo-5,11-bis(2-decyltetradecyl)thieno[2',3':4,5] pyrido[2,3-*g*]thieno[3,2-*c*]quinoline-4,10(5*H*,11*H*)-dione (5)

4 (0.25 g, 0.25 mmol) was dissolved in 20 mL of THF, *N*-bromosuccinimide (0.09 g, 0.51 mmol) was added. The mixture was stirred at room temperature overnight. Then the solvents were removed under reduced pressure. The residue was purified by silica gel chromatography with eluent (PE:DCM = 50:1) to give 2,8-dibromo-5,11-bis(2-decyltetradecyl)thieno[2',3':4,5]pyrido [2,3-*g*]thieno[3,2-*c*]quinoline-4,10(5*H*,11*H*)-dione (**5**) as a red oil (0.26 g, 90%). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) δ: 7.45 (s, 2H), 7.33 (s, 2H), 4.30 (d, J = 6 Hz, 4H), 1.88-1.81 (m, 2H), 1.43-1.23 (m, 80H), 0.89-0.84 (m, 12H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 148.3, 147.5, 137.8, 134.8, 134.4, 127.5, 113.8, 112.8, 37.9, 32.0, 31.4, 30.0, 29.7, 29.4, 28.8, 22.7, 14.1. ESI-HRMS: Calcd. for [M]$^+$: 1153.5822. Found: 1153.5807.

General procedure for the Stille coupling polymerization: To a microwave tube charged with a string bar, compound **5** (100 mg, 0.087 mmol), (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (45 mg, 0.087 mmol), Pd$_2$(dba)$_3$ (1.6 mg), and P(*o*-tol)$_3$ (2.1 mg) were added. The tube was transferred into a glovebox and chlorobenzene (3 mL) was added. After sealed with a snap cap, the tube was put into a microwave reactor and heated to 180 °C for 45 min. After cooling to room temperature, *N,N'*-diethylphenylazothioformamide (20 mg) was added and the mixture was stirred for 3 h to remove residual catalyst before being precipitated into methanol (100 mL). The precipitate was filtered through a nylon filter and purified via Soxhlet extraction for 8 h with methanol, 12 h with hexane, and finally collected with chloroform. The chloroform solution was then concentrated by evaporation, precipitated into methanol (200 mL) and filtered off to afford a dark solid.

P1: 91 mg, yield: 89%. Elemental Anal. Calcd. for $(C_{74}H_{108}N_2O_2S_4)_n$: C, 74.95; H, 9.18; N, 2.36。 Found: C, 77.60; H, 8.85; N, 2.09.

P2: The synthetic procedure is similar as described above (93 mg, 93%). Elemental Anal. Calcd. for $(C_{72}H_{106}N_2O_2S_4)_n$: C, 74.56; H, 9.21; N, 2.42. Found: C, 73.93; H, 9.17; N, 2.30.



Scheme 1 The Synthetic route to monomer **TPT** and **TPT**-based polymers. Reagent and conditions: (a) hydroxylamine hydrochloride, triethylamine, ethanol, reflux, 94%; (b) cyanuric chloride, DMF, room temperature, 88%; (c) 11-(bromomethyl)tricosane, K_2CO_3, DMF, 110 °C, for **4**: 44%; for **4a**: 37%; (d) NBS, THF, room temperature, 90%; (e) $Pd_2(dba)_3$, P(*o*-tol)$_3$, microwave, for **P1**: 89%; for **P2**: 93%.

Results and discussion

Synthesis of monomers and polymers

The synthetic route to monomer **TPT** and **TPT**-based polymers is shown in Scheme 1. The dioxime **2** was obtained via a condensation reaction between diketone **1** and hydroxylamine as a red solid. Afterwards, a Beckmann rearrangement reaction was applied to construct the bislactam **3**. Generally, the Beckmann rearrangement requires high reaction temperature and strong acidic dehydrating media such as sulfuric acid or polyphosphoric acid. Recently, several transition-metal catalysts and organic reagents were utilized in this reaction instead of strong acids.[10] Here, an optimized Beckmann rearrangement condition developed by Giacomelli's group was adopted.[10e] Dioxime **2** underwent the Beckmann rearrangement upon treatment with cyanuric chloride in DMF at room temperature to afford the bislactam as a red solid. Compared to Pd-catalyzed C-H functionalization strategy which is used in the construction of **TPT** and its analogue,[7] the optimized Beckmann rearrangement condition offers some impressive advantages such as simple and easy operability and reproducibility at room temperature, and no need of noble catalyst or inert atmosphere. After introduction of alkyl chains, two isomers of the bislactam (**4** and **4a**) were obtained, indicating that dioxime **2** was a mixture with (*Z*, *Z*) and (*Z*, *E*) configurations. **4** underwent bromination with NBS to give the corresponding monomer **5**. **P1** and **P2** were prepared through the microwave-assisted Stille-coupling polymerizations between **5** and (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethane or 5,5'-bis(trimethylstannyl)-2,2'-bithiophene using $Pd_2(dba)_3$ and P(*o*-tol)$_3$ as the catalyst system. The as-synthesized polymers **P1** and **P2** were purified by Soxhlet extraction (sequentially by methanol, acetone, hexane, and $CHCl_3$) to afford dark green films. Both polymers exhibit good solubility in trichloroethylene (TCE), chlorobenzene, and dichlorobenzene. The molecular weights of both polymers were evaluated by gel permeation chromatography (GPC) using 1,2,4-tricholorobenzene as eluent at 140 °C. The number-average molecular weights (M_n) of **P1** and **P2** were 76.9 kDa and 74.7 kDa with polydispersity index (PDI) of 2.28 and 4.97, respectively. Both polymers exhibit good thermal stability with high decomposition temperatures (302 °C for **P1** and 282 °C for **P2**). No phase transition was observed in the differential scanning calorimetry (DSC) measurement for both polymers before their decomposition (Figures S1 and S2).

Photophysical properties

The absorption spectra of both polymers are presented in Figure 1. Both in dilute solution (1×10^{-5} M in TCE) and in thin film, **P1** and **P2** exhibit dual band absorption features. The absorption bands from 350 to 400 nm of both polymers are assigned to the

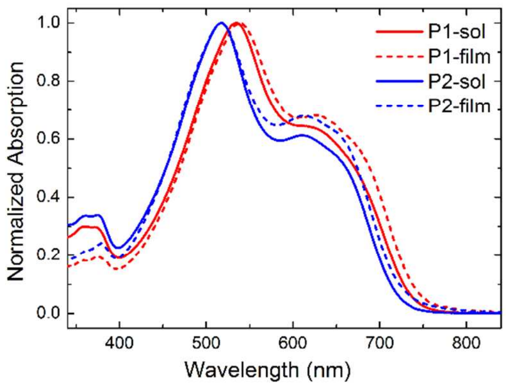


Fig.1 Normalized absorption spectra of **P1** and **P2** in TCE (1×10^{-5} M) and in thin films.

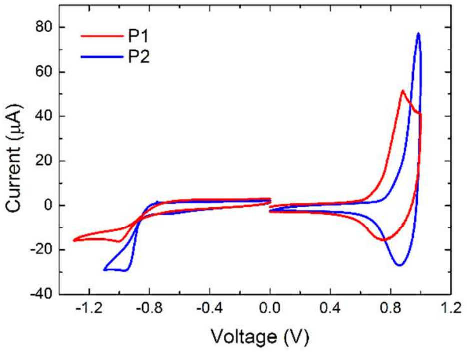


Fig.2 Cyclic voltammograms of **P1** and **P2** in thin films drop-casted on glassy carbon electrodes and tested in *n*-Bu_4NPF_6 /CH_3CN solution.

absorption of **TPT** unit. The bands from 400 to 750 nm are attributed to the intramolecular charge transfer (ICT) absorption. The spectra in solution show absorption maxima at 535 nm for **P1** and 517 nm for **P2**. Owing to the longer effective conjugation length, **P1** exhibits relatively red-shifted absorption. In thin film, the ICT absorption bands red-shift and their intensity increase, indicating that the polymer backbones become more planar in solid state. The optical band gaps of **P1** and **P2** estimated from the absorption onset of thin film spectra are 1.66 eV and 1.70 eV, respectively.

Electrochemical properties

As illustrated in Figure 2, cyclic voltammetry measurements were performed to evaluate the HOMO and LUMO energy levels of two polymers. Estimated from the onset of oxidative peak and reductive peak, the HOMO/LUMO levels of **P1** are -5.14/-3.57 eV, while the HOMO/LUMO levels of **P2** are -5.29/-3.55 eV. Thus the electrochemical band gaps of **P1** and **P2** were calculated to be 1.57 and 1.74 eV, respectively. The relatively higher HOMO level of **P1** is attributed to its more electron-rich donor units. The LUMO levels of **P1** and **P2** are almost same, indicating that the LUMO levels are determined by **TPT** unit. DFT calculations were performed to further understand the electronic structures of both polymers from a theoretical view (Figure S3). **P1** and **P2** exhibit quite similar orbital distribution with both the HOMOs and LUMOs well delocalized along the conjugated backbones, which means that **TPT** is a weak acceptor.

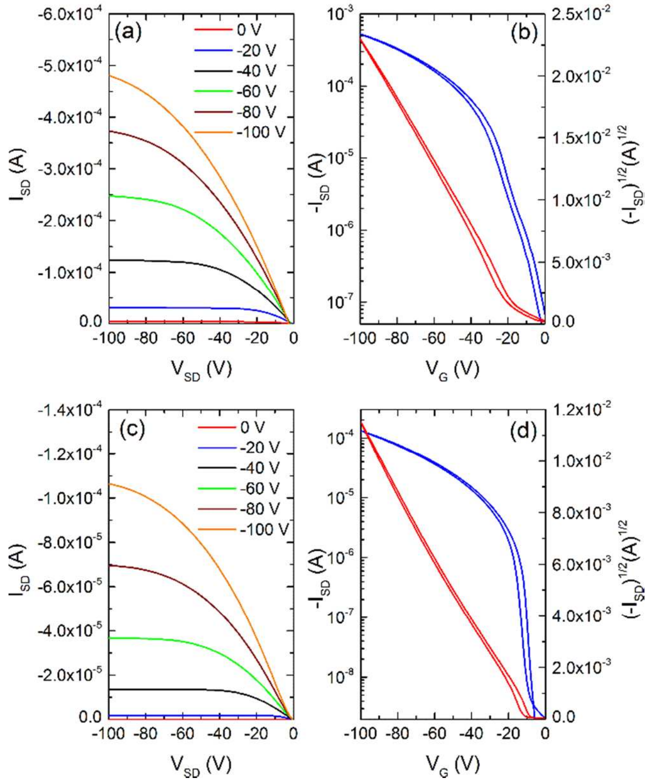


Fig.3 OFET characteristics of two polymers: (a, b) transfer and output curves of a **P1**-based device; (c, d) transfer and output curves of a **P2**-based device.

Table 1 Transistor properties of **P1** and **P2**.

Polymer	Annealing temperature (°C)	Mobility ($cm^2 V^{-1} s^{-1}$)	V_T (V)	I_{on}/I_{off}
P1	200	0.58	-14	10^4
	180	0.28	-11	10^5
	160	0.18	-11	10^5
P2	200	0.12	-7	10^5
	180	0.15	-8	10^6
	160	0.07	-9	10^5

Transistor properties

Thin film OFET devices were fabricated in bottom-gate/top-contact (BGTC) configuration. The active layers were deposited by spin-coating the polymer solutions (6 mg/mL in TCE) onto OTMS-treated n^{++}-Si/SiO_2 substrates.[11] **P1** and **P2** exhibit typical hole-transporting property (summarized in Table 1). The typical transfer and output curves are shown in Figure 3, hole mobility up to 0.58 $cm^2 V^{-1} s^{-1}$ was recorded for **P1**-based device after thermal annealing at 200 °C, whereas **P2**-based device exhibited slightly lower mobility of 0.15 $cm^2 V^{-1} s^{-1}$ after thermal annealing at 180 °C.

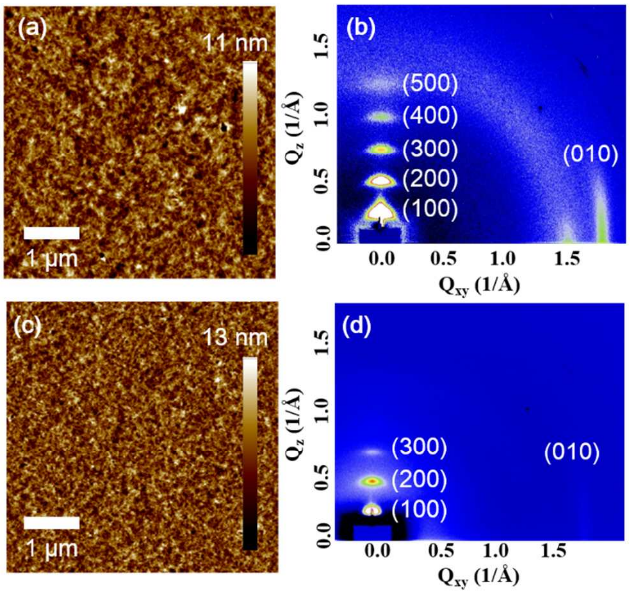


Fig.4 AFM (5 µm × 5 µm) height images (a) (c) and GIXRD patterns (b) (d) of **P1** (a) (b) and **P2** (c) (d) thin films.

Film structural characterization

To further understand the origination of different device performance of **P1** and **P2**, atomic force microscopy (AFM) and grazing incidence X-ray diffraction (GIXRD) were employed to investigate morphology and molecular packing of both polymer films. Similar morphology and roughness of **P1** and **P2** thin films were observed in AFM images (Figure 4a and 4c). As illustrated in Figure 4, 2D-GIXRD patterns indicate that both **P1** and **P2** display the edge-on lamellar packing in film. **P1** shows a strong out-of-plane diffraction peak at 2.90°, corresponding to a *d*-spacing of 24.3 Å. Other diffraction peaks are attributed to 200, 300, 400, and 500 diffractions. The strong in-plane diffraction peaked at 20.28° corresponds to the π-π distance of 3.57 Å. In the 2D-GIXRD pattern of **P2** film, only three out-of-plane diffraction peaks and a weak in-plane diffraction peak were observed. The *d*-spacing and π-π distance of **P2** are 25.4 Å and 3.60 Å, respectively. The stronger diffraction peaks and shortened *d*-spacing and π-π distance of **P1** indicate that the molecular packing of **P1** in film is more ordered and denser than that of **P2**. The differences in molecular packing and crystallinity may partially explain the different device performance.

Conclusions

In conclusion, the pentacyclic dilactam **TPT** unit has been developed through Beckmann rearrangement from ketones in two steps under mild condition. As an acceptor, **TPT** is incorporated into the construction of conjugated polymers **P1** and **P2** through the Stille coupling polymerization. **P1** exhibits hole mobility up to 0.58 $cm^2 V^{-1} s^{-1}$, whereas **P2** shows slightly lower mobility of 0.15 $cm^2 V^{-1} s^{-1}$. The better device performance of **P1** is attributed to the more ordered molecular packing. Our result indicates that Beckmann rearrangement reaction is a powerful tool to construct lactam structure in the synthesis of organic semiconducting materials, providing new thought to design functional materials. **TPT** presents great potential to be a good building block in polymeric semiconductors.

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† Electronic Supplementary Information (ESI) available: [TGA and DSC traces of both polymers, DFT calculation results and IR spectra of **P1** and **P2**]. See DOI: 10.1039/b000000x/

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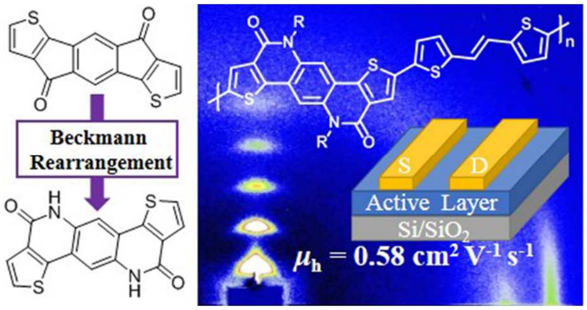
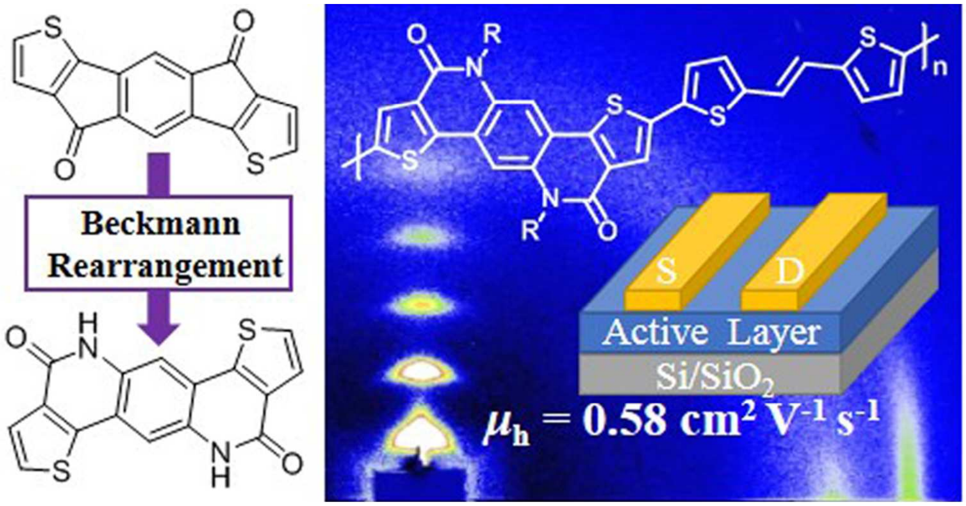
Graphical abstract





Based on the pentacyclic aromatic bislactam constructed through the Beckmann rearrangement, two conjugated polymers were developed, showing high FET performance.
80x39mm (300 x 300 DPI)