Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Impact of Backbone Linkage Positions on the Molecular Aggregation Behavior of Polymer Photovoltaic Materials

Jinyue Zhu,[a, #] Yanfang Liu,[c,#] Shaohua Huang,[d, #] Shuguang Wen,[e] Xichang Bao,[e] Mian Cai,[b, **] Jingwen Li [a, *]

[a] *College of Science, State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao 266580, China*

[b] *Research and Development Center of Aluminum-ion Battery, College of Electronic Engineering and Automation, Shandong University of Science and Technology, Qingdao 266590, China*

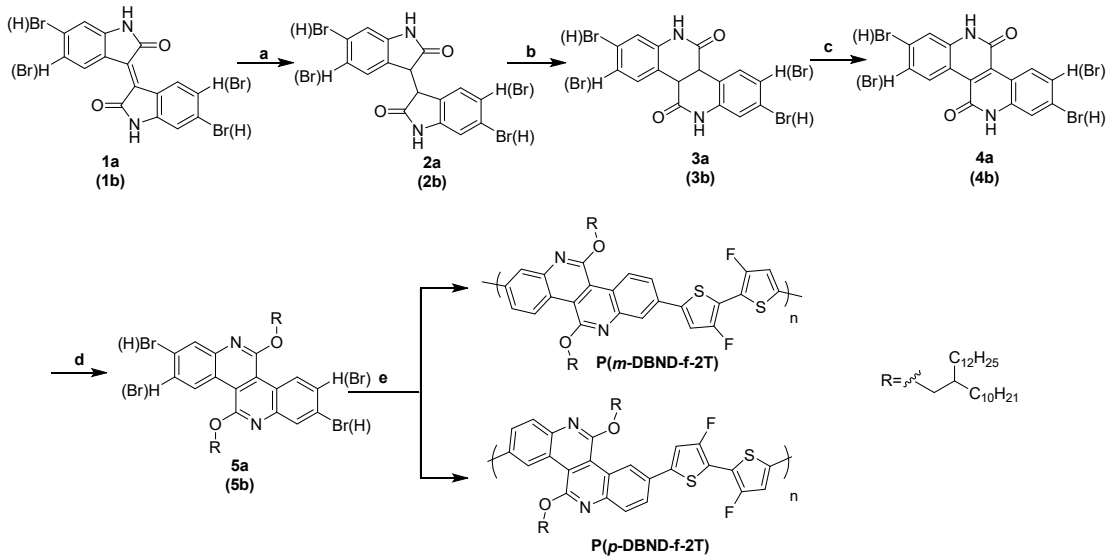
[c] *National & Local Joint Engineering Research Center for Mineral Salt Deep Utilization, Key Laboratory for Palygorskite Science and Applied Technology of Jiangsu Province, Huaiyin Institute of Technology, Huaian 223003, China*

[d] *Institute of Drug Discovery Technology, Ningbo University, Ningbo 315211, China*

[e] *Qingdao Institute of Bioenergy & Bioprocess Technology, Chinese Academy of Sciences, 189 Songling Road, Qingdao 266101, China*

[#] These authors contributed equally to this work.

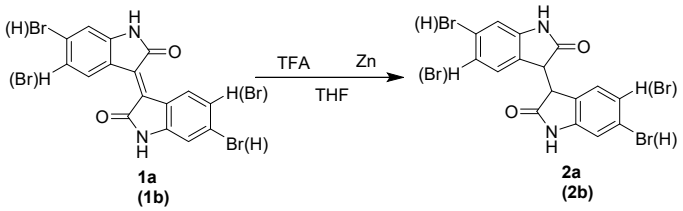
Scheme S1. Synthesis of DBND based polymers.



Reagents and conditions: (a) Zn, CF_3COOH, THF, r.t. 1h; (b) HCl (conc.):THF (1:2), 100 °C, 8h; (c) K_2CO_3, DMF, bubbling air, r.t., 48h; (d) K_2CO_3, 11-(bromomethyl)tricosane, DMF, 100 °C, 24h; (e) $Pd_2(dba)_3$, P(o-tol)$_3$, (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane), toluene, 110 °C, 72h.

1. Synthetic procedures

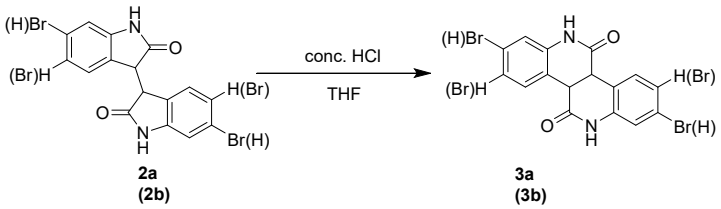
The starting materials of 1a and 1b are synthesized according to the literature.[1]



TFA (4.7 ml, 60 mmol) was added dropwise to a cooled (0°C) suspension of **1a (1b)** (1 g, 2.39 mmol) and activated Zn dust (940 mg, 14.5 mmol) in THF (125 ml) solution. The mixture was stirred at r.t. for 1 hour. Then the mixture was precipitated into a stirring H_2O (500 ml). The white solid **2a (2b)** obtained were collected on a filter, washed with H_2O, and dried under reduced pressure. (1.03 g, quantitative).

2a: ^{1}H-NMR (DMSO-d_6, 600 MHz) δ: 10.51 (s, 2H), 7.09 (d, J = 8.02 Hz, 2H), 6.95 (s, 2H), 6.75 (d, J =8.02 Hz, 2H), 4.19 (s, 2H). ^{13}C-NMR (DMSO-d_6, 150 MHz) δ: 176.33, 145.45, 126.83, 125.72, 124.47, 121.46, 112.71, 45.70.

2b: ^{1}H-NMR (DMSO-d_6, 600 MHz) δ: 10.53 (s, 2H), 7.39 (d, J = 8.28 Hz, 2H), 6.93 (s, 2H), 6.79 (d, J =8.28 Hz, 2H), 4.28 (s, 2H). isomer: δ: 10.85 (s, 2H), 7.29 (d, J = 8.28 Hz, 2H), 7.08 (s, 2H), 6.74 (d, J =8.28 Hz, 2H), 4.21 (s, 2H). ^{13}C-NMR with isomer (DMSO-d_6, 150 MHz) δ: 176.99, 175.97, 143.15, 142.61, 131.61, 131.53, 129.98, 126.78, 126.41, 113.47, 113.35, 111.92, 111.79, 46.07, 46.05.

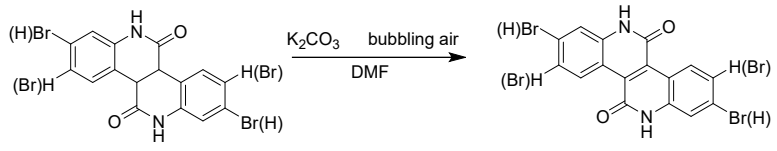


A suspension of **2a (2b)** (1 g, 2.38 mmol) in conc. HCl (10 ml) and THF (20 ml) was added to a Schlenk tube. The mixture was stirred for 10 hours at 100 °C. The mixture was then cooled down to r.t. The precipitate was collected on a filter and washed with water, ethanol, and ethyl acetate to give a white solid **3a (3b),** which was pure enough to carry out on next step (609 mg, 61%).

3a: ^{1}H-NMR (DMSO-d_6, 600 MHz) δ: 10.58 (s, 2H), 7.20-7.16 (m, 4H), 7.06 (s, 2H), 4.23 (s,

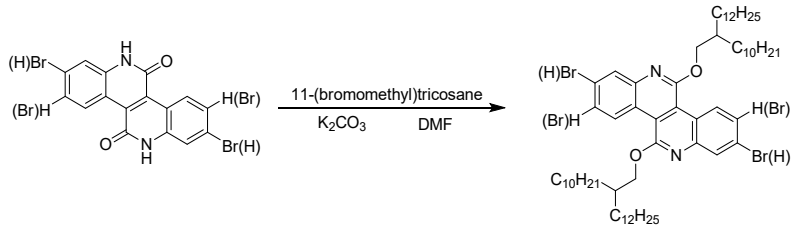
2H). ^{13}C-NMR (DMSO-d_6, 150 MHz) δ: 168.29, 139.53, 132.29, 125.12, 121.28, 120.13, 118.01. 41.78

3b: ^{1}H-NMR (DMSO-d_6, 600 MHz) δ: δ: 10.61 (s, 2H), 7.44 (d, J = 8.41 Hz, 2H), 7.42 (s, 2H), 6.85 (d, J = 8.41 Hz, 2H), 4.24 (s, 2H). ^{13}C-NMR (DMSO-d_6, 150 MHz) δ: 168.16, 137.27, 133.04, 131.53, 123.33, 117.68, 113.98. 41.78



3a (3b) **4a (4b)**

To a solution of **3a** (**3b)** in DMF (0.01 M) was added K_2CO_3 (4 Eq.). The suspension was stirred for 48 hours, with air bubbling into the system. The yellow solid **4a (4b)** (almost quantitative) obtained was filtered and washed with water then THF before drying under reduced pressure, which was to carry out in next step.



4a (4b) **5a (5b)**

To a suspension of K_2CO_3 (995 mg, 7.2 mmol) in DMF (20 ml) was added **4a (4b)** (600 mg, 1.44 mmol) and 11-(bromomethyl)tricosane (2.35 g, 5.76 mmol). The mixture was stirred at 100 ^{o}C for 48 hours before filtration. The filtrate was concentrated under reduced pressure. The obtained crude product was then purified by column chromatography on silica gel eluted with petroleum ether to give a white solid compound **5a (5b)** (1.1 g, 70%), which was then further purified by recrystallization before polymerization.

5a: ^{1}H-NMR ($CDCl_3$, 600 MHz) δ: 9.33 (d, J=9.25 Hz, 2H), 8.13 (s, 2H), 7.61 (d, J=9.25 Hz, 2H), 4.67 (d, J=5.54 Hz, 4H), 2.08 (m, 2H), 1.70-1.20 (m, 80H), 0.90 (m, 12H). ^{13}C-NMR ($CDCl_3$, 150 MHz) δ: 159.59, 145.61, 129.71, 129.28, 128.11, 123.36, 122.72, 119.46, 70.44, 37.59, 31.95, 31.94, 31.93, 30.02, 29.71, 29.69, 29.67, 29.37, 29.37, 26.96, 22.71, 22.70, 14.14.

5b: ^{1}H-NMR ($CDCl_3$, 600 MHz) δ: 9.67 (s, 2H), 7.78 (d, J=8.68 Hz, 2H), 7.73 (d, J=8.68 Hz, 2H), 4.63 (d, J=5.15 Hz, 4H), 1.98 (m, 2H), 1.70-1.00 (m, 80H), 0.79 (m, 12H). ^{13}C-NMR ($CDCl_3$, 150 MHz) δ: 159.26, 143.47, 132.59, 130.54, 128.83, 122.33, 121.83, 118.79, 70.61, 37.94, 32.0,

31.94, 31.92, 30.03, 29.69, 29.66, 29.64, 29.36, 29.35, 27.12, 22.70, 22.69, 14.12.

2. Procedures for Stille Polymerization and Polymer Purification.

5a (5b) (109.3 mg, 0.1 mmol), (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (52.8 mg, 0.1 mmol), $Pd_2(dba)_3$ (1.1 mg, 1.2 mmol%), P(*o*-tol)$_3$ (2.9 mg, 9.6 mmol%) and 2.5 mL of toluene were added to a Schlenk tube. The tube was charged with argon through a freeze-pump-thaw cycle three times. The mixture was stirred for 72 hours at 110 °C. And then, the mixture was precipitated into methanol (100 mL). The precipitate was filtered and purified via Soxhlet extraction for 8 hours with methanol, 12 hours with hexane, and 12 hours with chloroform, finally it was collected with *o*-DCB. The *o*-DCB solution was then concentrated and precipitated into methanol (100mL) to give a solid (84% for P(*p*-DBND-f-2T) and 65% for P(*m*-DBND-f-2T)).

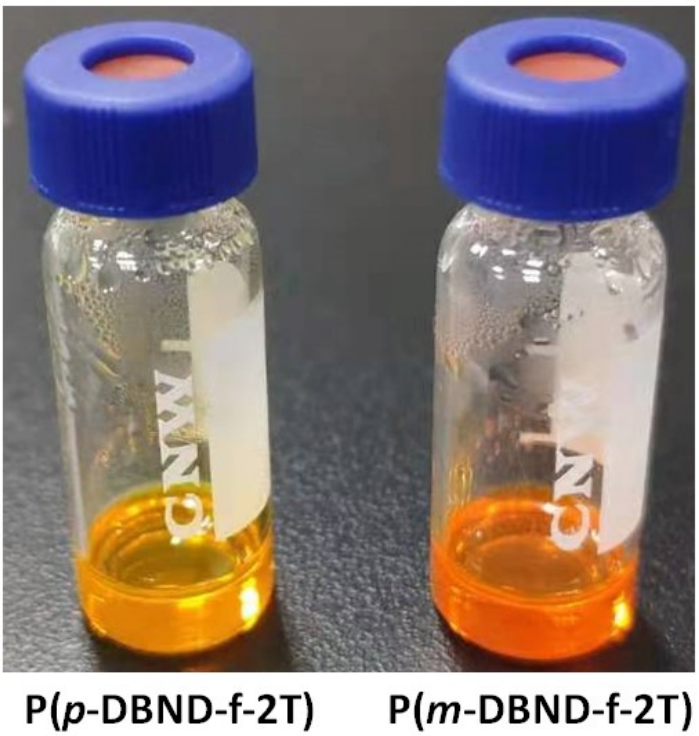


Fig. S1. Polymer solutions in *o*-DCB

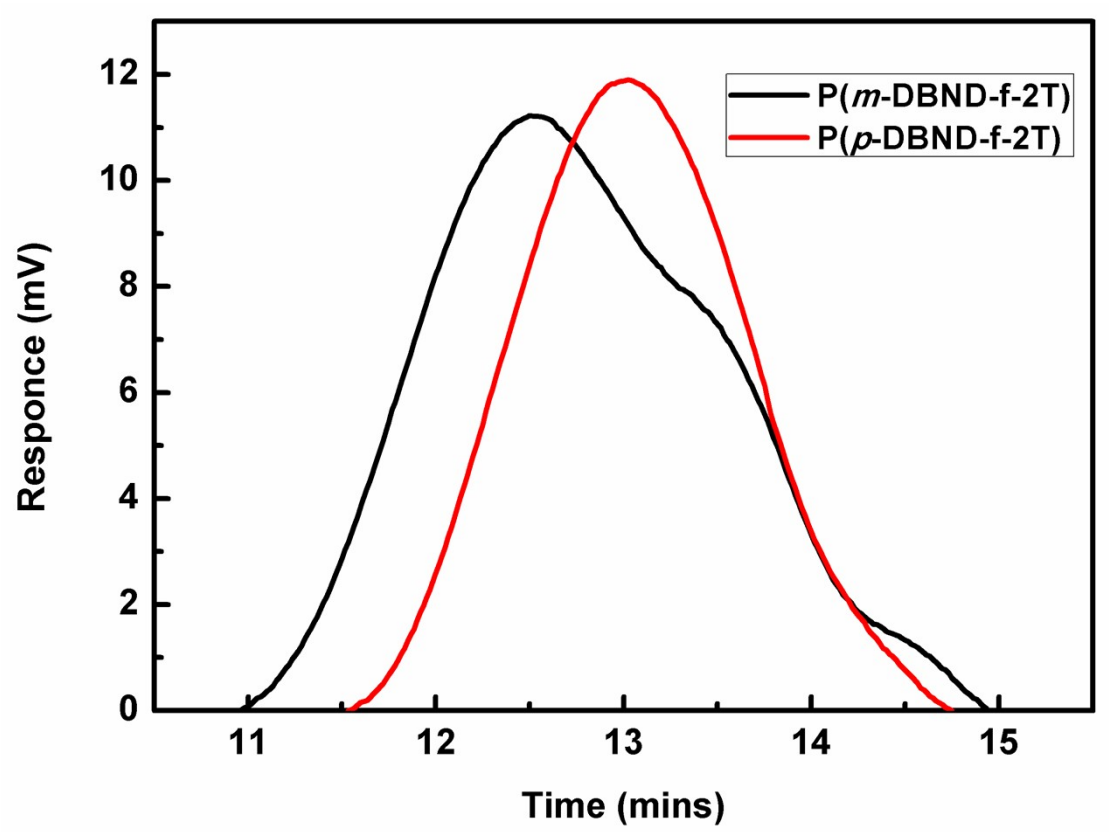


Fig. S2. Gel permeation chromatography (GPC) results of P(*m*-DBND-f-2T) and P(*p*-DBND-f-2T)

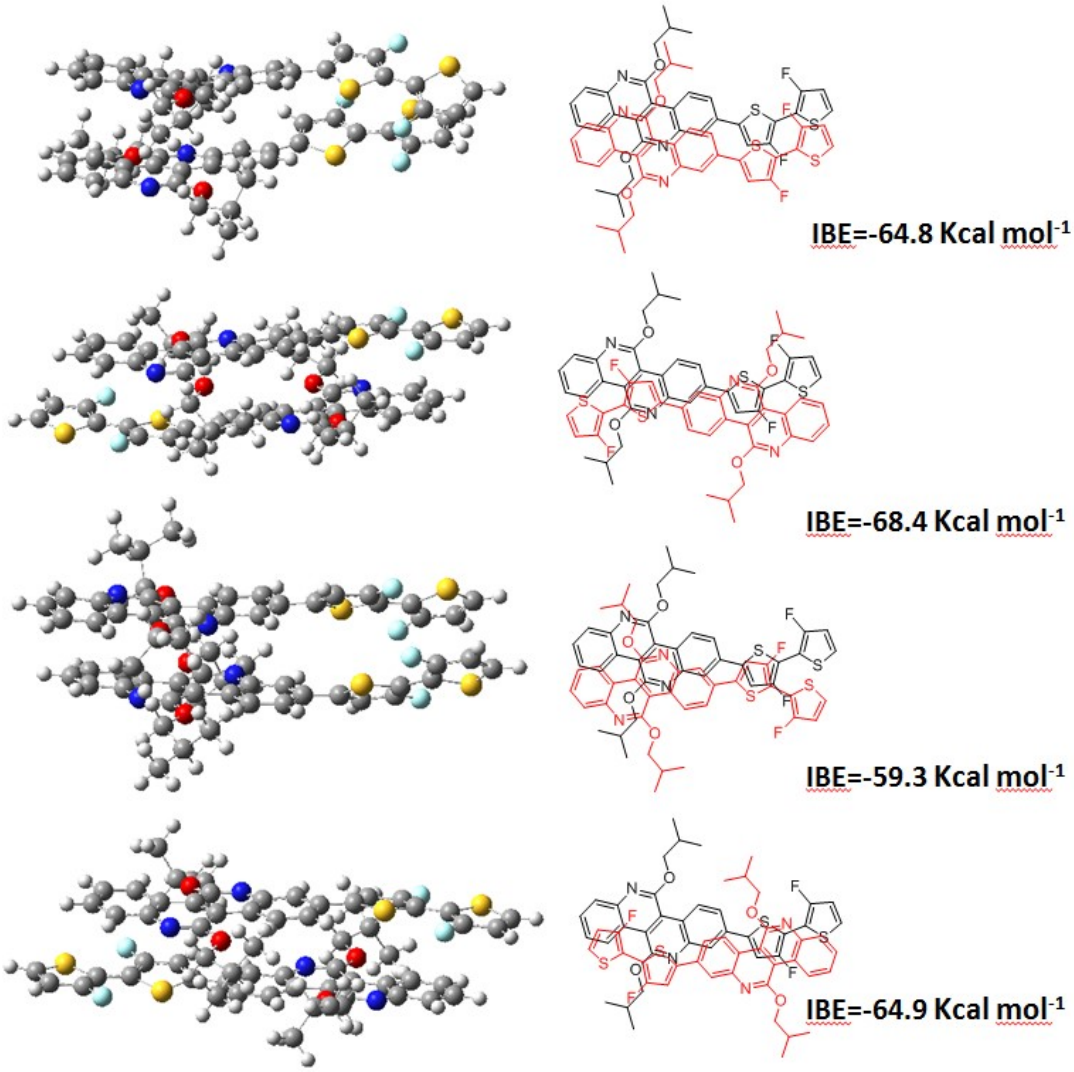


Fig. S3. Local converged intermolecular packing and the binding energy (IBE) of *m*-DBND-f-2T

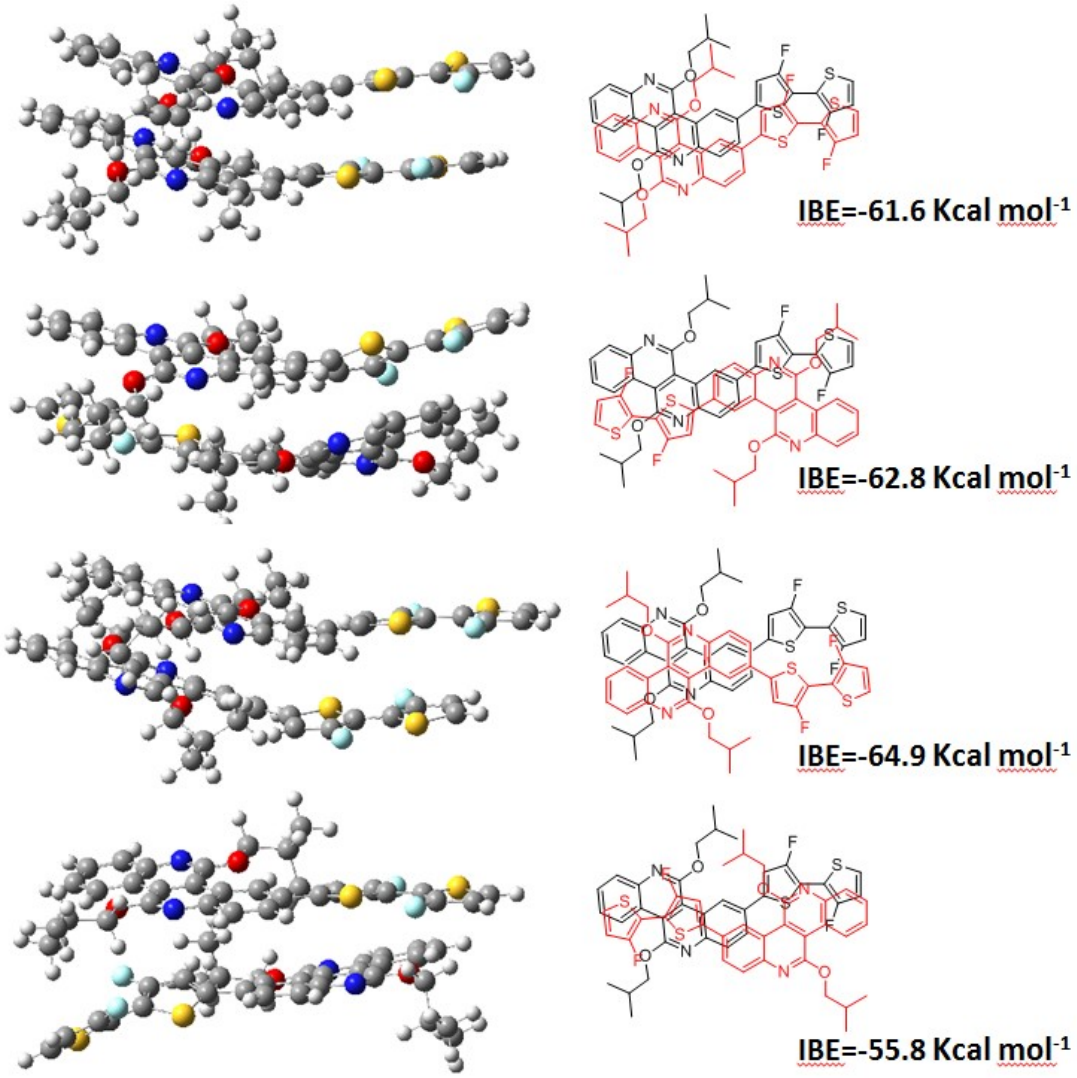


Fig. S4. Local converged intermolecular packing and the binding energy (IBE) of *p*-DBND-f-2T

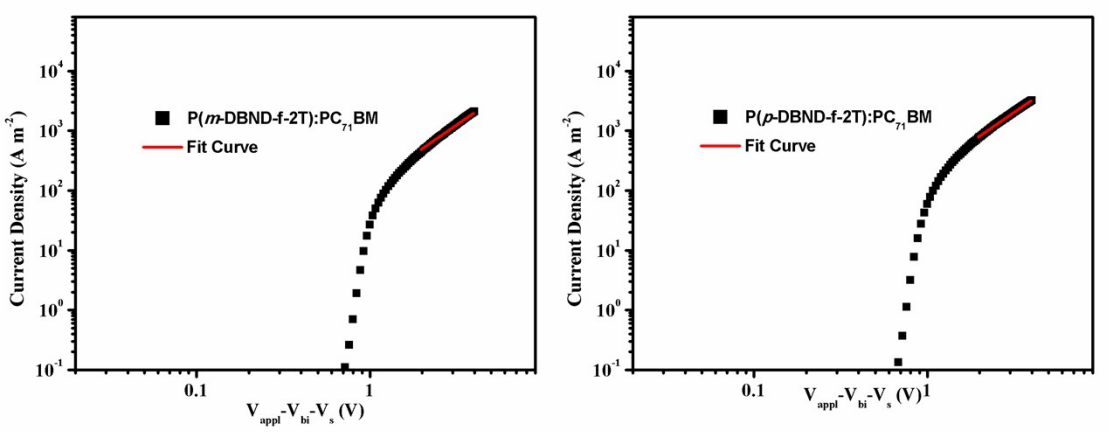


Fig. S5. Space-charge-limited current (SCLC) density-voltage curves of the hole only devices of P(*m*-DBND-f-2T) and P(*p*-DBND-f-2T) blended film (1: 2 with $PC_{71}BM$, w/w).

Reference

1. L. A. Estrada, D. Y. Liu, D. H. Salazar, A. L. Dyer, and J. R. Reynolds, *Macromolecules*, 2012, **45**, 8211−8220.