Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A
This journal is © The Royal Society of Chemistry 2013

Supporting Information

Significant Improvement of Photovoltaic Performance by Embedding Thiophene in Solution-Processed Star-Shaped TPA—DPP Backbone

Ailing Tang, [a,d,†] Liangjie Li, [b,c,†] Zhenhuan Lu,[a] Jianhua Huang,[a] Hui Jia,[a] Chuanlang Zhan, [a,*] Zhan'ao Tan, [b,c,*] Yongfang Li, [b] Jiannian Yao[a,*]

[a]Beijing National Laboratory of Molecular Science, CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing, P. R. China. Fax: (+86)-10-82616517; E-mail: (C.Z.) clzhan@iccas.ac.cn, (J.Y.) jnyao@iccas.ac.cn.

[b]CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, , Beijing, PR China.

[c]State Key Laboratory of Alternate Electrical Power System with Renewable Energy Sources, The New and Renewable Energy of Beijing Key Laboratory, North China Electric Power University, Beijing, China. Email: (Z.T.) tanzhanao@ncepu.edu.cn.

[d]Graduate School, Chinese Academy of Sciences, Beijing 100039, People's Republic of China.

[†] These authors do the equal contributions.

Contents:

1. Synthesis of TDPP-Br

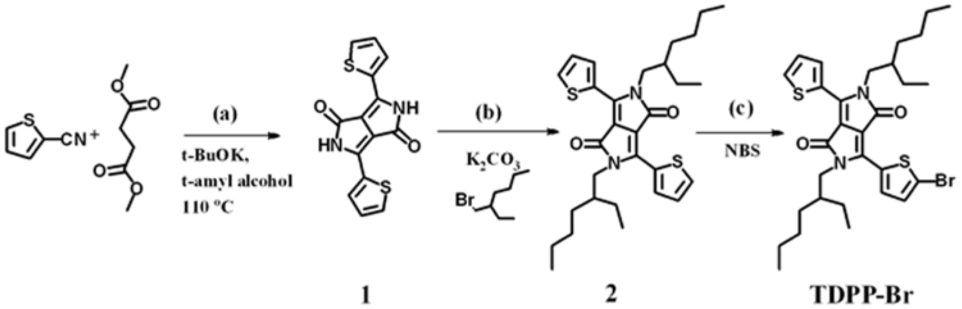
1.1 Materials.

All reagents were purchased from Sigma-Aldrich, Acros, Alfa Aesar or TCI, **,** and used as received.

1.2 Measurements and characterizations.

The ^{1}H NMR spectra were obtained using a Bruker AVANCE 400 MHz spectrometer with tetramethylsilane (TMS; δ = 0 ppm) as an internal standard.

1.3 The synthetic route of the compound of TDPP-Br was shown in Scheme1.



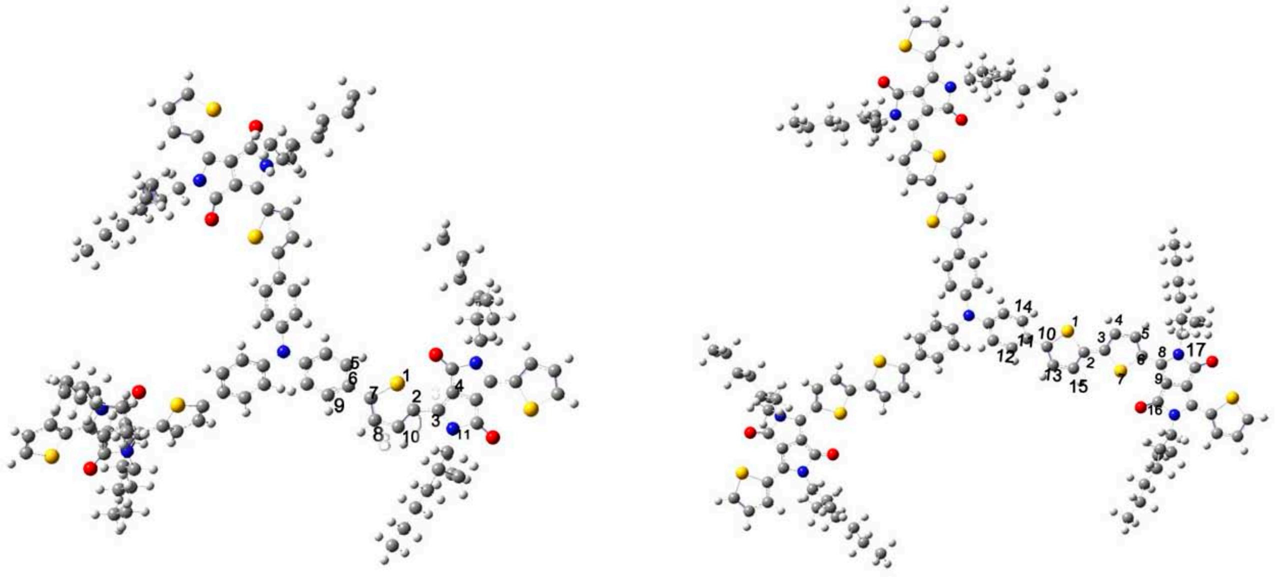
Scheme 1. The synthetic route towards TDPP-Br.

3,6-Dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (1)[1, 2]: Firstly, sodium tert-butylate (10 g, 107 mmol) was added to a two-necked 250 mL round-bottom flask with argon protection. Then 2-thiophenecarbonitrile (8.4 mL, 90 mmol) was dropped by a syringe one portion. The mixture was warmed up to 100–110°C, and a solution of dimethyl succinate (5.4 mL, 90 mmol) in t-amyl alcohol (8 mL) was added dropwise. The reaction mixture was kept 100–110°C for about 12 h. When the mixture was cooled, acetic acid (10 mL) was added to neutralized the remainder sodium tert-butylate. Then the mixture was poured into methanol (200 mL) for 1 h.The suspension was filtered, and washed by methanol and water twice each. The black cake was dried and without further purification (9 g, 70%).

2,5-Diethylhexyl-3,6-dithiophen-2-ylpyrrolo[3,4-c]pyrrole-1,4-dione (2): Compound 1 (1.00 g, 3.3 mmol) and anhydrous potassium carbonate (1.82 g, 13.2 mmol) were added into a two-neck round flask. Then N,N-dimethylformamide (250 mL) was added and heated to 145°C for 1 h, under argon protection. 2-ethylhexylbromide (3.18 g, 2.93 mL, 16.5 mmol) was dropped by a syringe one portion. After the addition was completed, the reaction mixture was stirred for 15 h at 145°C. When the mixture was cooled to room temperature, it was poured into 200 mL of icewater, and the suspension was filtered by vacuum and washed with water and methanol. The crude product was purified by silica gel chromatography with dichloromethane/petroleum ester (1:1) as eluents, giving a purple-black solid (0.64 g, 73.1%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.896–8.884 (d, J = 4, 2 H), 7.631–7.617 (d, J = 8, 2 H), 7.279–7.259 (d, J = 8, 2 H), 4.079–3.970 (m, 4 H), 1.859–845 (m, 2 H), 1.431–1.222 (m, 16 H), 0.892–0.854 (m, 12 H).

3-(5-Bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione:[3] Compound 2 (500 mg, 0.95 mmol) was desolved in $CHCl_3$ (30ml) and stirred at 0°C. Protected from light, NBS (153 mg, 0.85 mmol) in $CHCl_3$ (10 mL) was added to the mixture and kept at 0°C for 3h. Then reaction was warmed to room temperature and stirred overnight. The mixture was partitioned between DCM and water. The organic phase was dried by anhydrous $MgSO_4$, and then the solvent was evaporated under vacuum. The residue was purified by column chromatography on a silica gel (petroleum ester/CH_2Cl_2 = 4 : 1) to afford the title compound as a purple solid (934 mg, 53%). ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 8.906–8.896 (d, *J* = 4, 1 H), 8.634–8.624 (d, *J* = 4, 1 H), 7.648–7.637 (d, *J* = 4, 1 H), 7.279–7.259 (d, *J* = 8, 2 H), 4.035–3.926 (m, 4 H), 1.845–1.835 (m, 2 H), 1.354–1.255 (m, 16 H), 0.906–0.835 (m, 12 H).

2. Supporting figures



TPA-DPP

TPA-T-DPP

Figure S1. The optimal conformations of **TPA-DPP** and **TPA-T-DPP**, respectively. The dihedral angles are shown in the following table.

compound	atom	dihedral angle (θ, °)
TPA-DPP	5-6-7-1	12.05
	9-6-7-8	12.87
	1-2-3-4	-0.027
	10-2-3-11	-0.758
TPA-T-DPP	1-10-11-14	17.82
	12-10-11-13	18.07
	1-2-3-4	0.0923
	15-2-3-7	-0.072
	5-6-8-17	0.009
	7-6-8-19	0.67

Noted: θ(°) is the dihedral angle along the selected atoms.

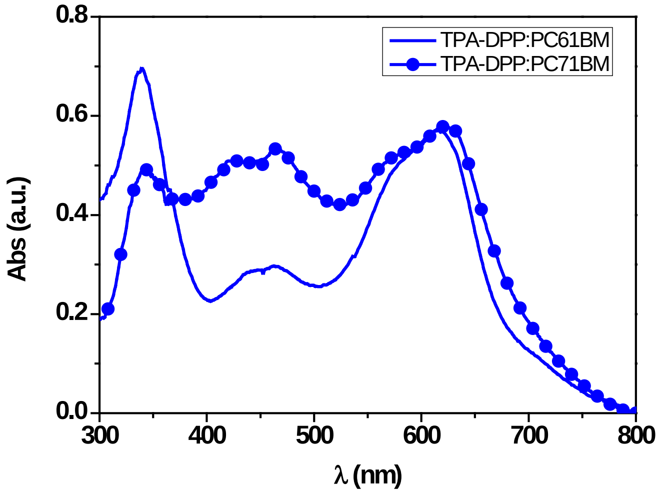


Figure S2. The absorption spectrum of the blended films with **TPA-DPP**: PCBM = 1 : 2

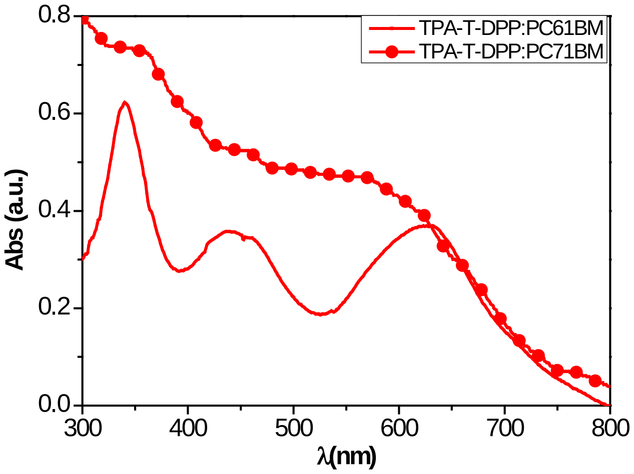


Figure S3. The absorption spectrum of the blended films with **TPA-T-DPP**:PCBM = 1 : 4

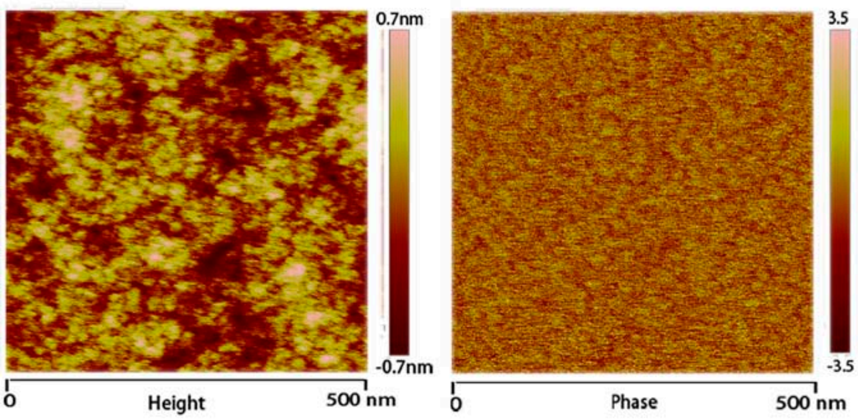


Figure S4. AFM images of blended films: (left) height image and (right) phase image of the blended film with **TPA-T-DPP**/$PC_{61}BM$=1 : 4.

3. Supporting tables

Table S1. Summary of current–voltage parameters of the OSCs based on TPA-T-DPP : PCBM blends with different weight ratio processed from 1,2-chlorobenzene (o-DCB) or chloroform (CF) solvent.

Active layer	D: A radio (w/ w)	V_{OC} (V)	J_{SC} (mA·cm^{-2})	*FF* (%)	*PCE* (%)
TPA-T-DPP: PC61BM (CF)	1:1	0.85	1.91	33.5	0.54
	1:2	0.85	4.42	37.9	1.43
	1:3	0.86	4.48	40.2	1.55
	1:4	0.83	5.60	38.8	1.81
TPA-T-DPP : PC71BM (o-DCB)	2:1	0.75	1.23	24.6	0.23
	1:1	0.80	3.42	26.9	0.74
	1:2	0.82	5.71	31.9	1.49
	1:3	0.83	6.90	33.8	1.94
	1:4	0.81	10.06	36.2	2.95

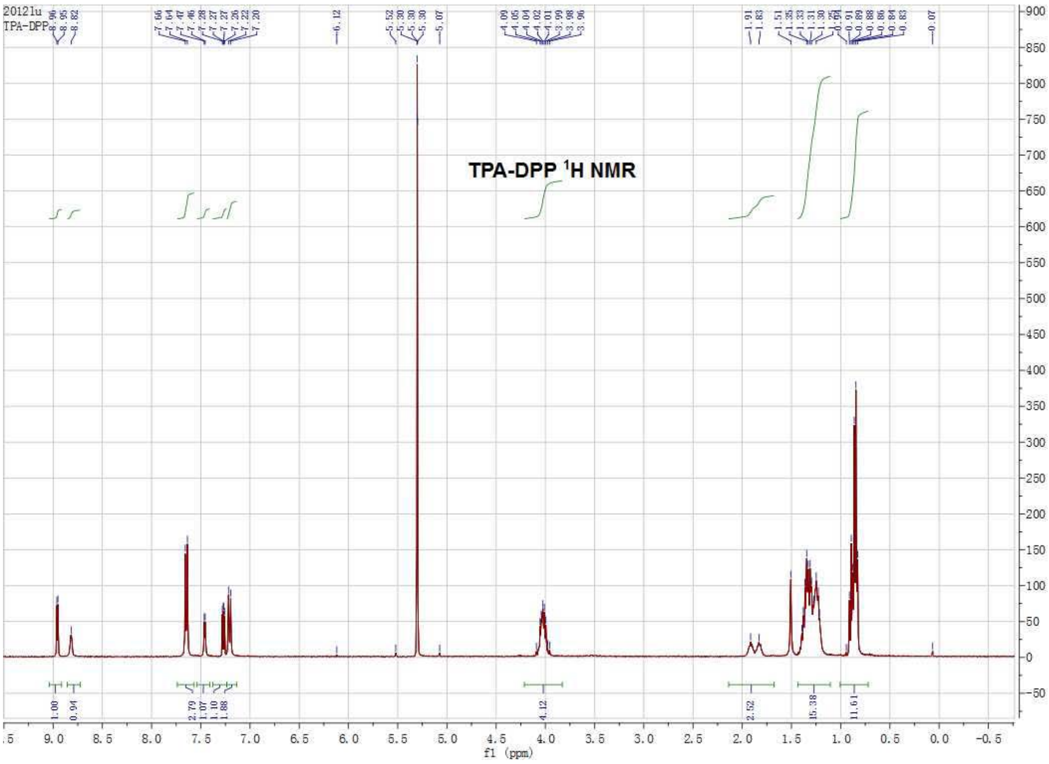
Table S2. XRD diffraction peaks and *d*-spacing of the pristine small molecule films and small molecule/PC71BM blending films and P3HT/**TPA-T-DPP** blending films.

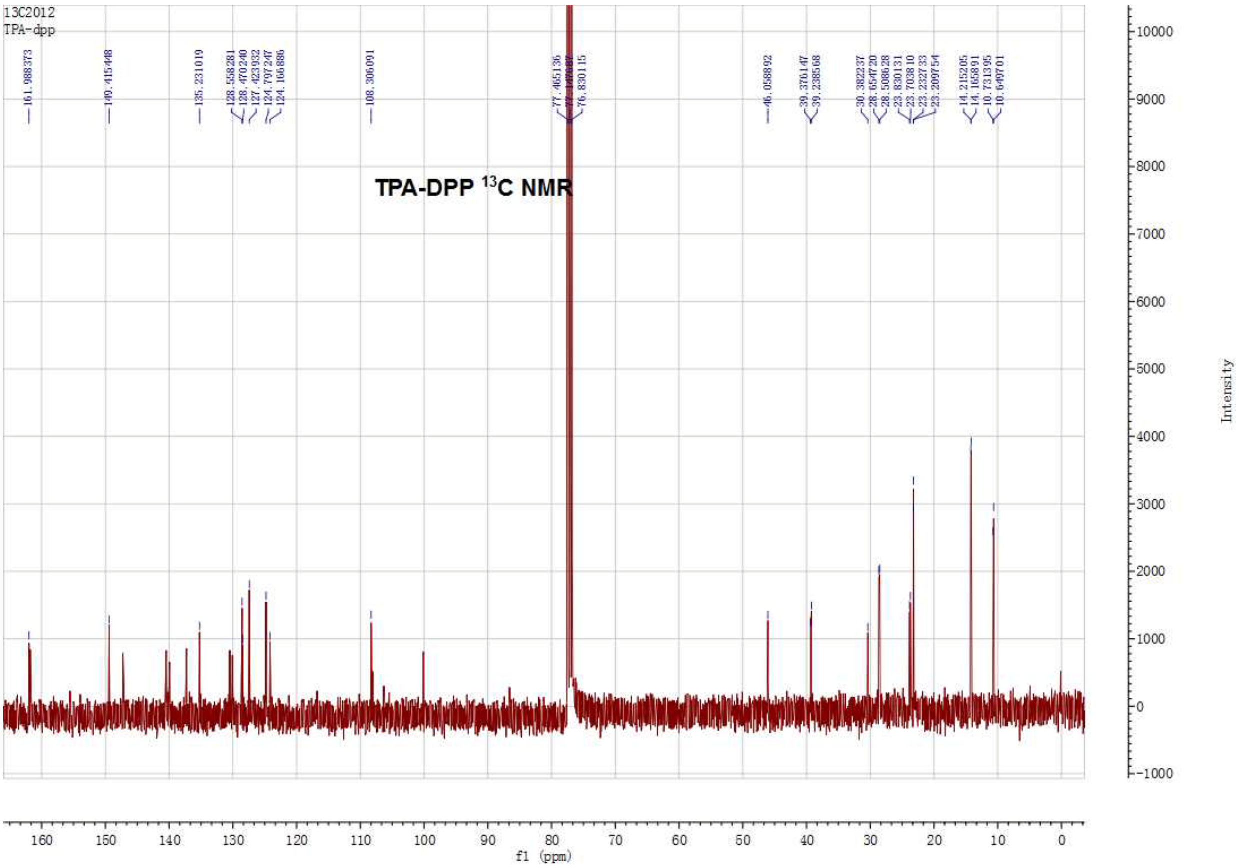
	2θ (°) / d_{100}(Å)	2θ (°) / d_{010}(Å)
TPA-DPP	6.30/14.02	20.11/4.42
TPA-T-DPP	6.05/14.60	21.60/4.11
PC71BM	8.98/9.85	19.25/4.61
P3HT	(d_{100}) 5.42/16.34 (d_{200}) 10.84/8.18	—
TPA-DPP: PC71BM	—	18.89/4.76
TPA-T-DPP : PC71BM	—	18.89/4.76
P3HT: **TPA-T-DPP**	(d_{100}) 5.49/16.10 (d_{200}) 10.98/8.05	—

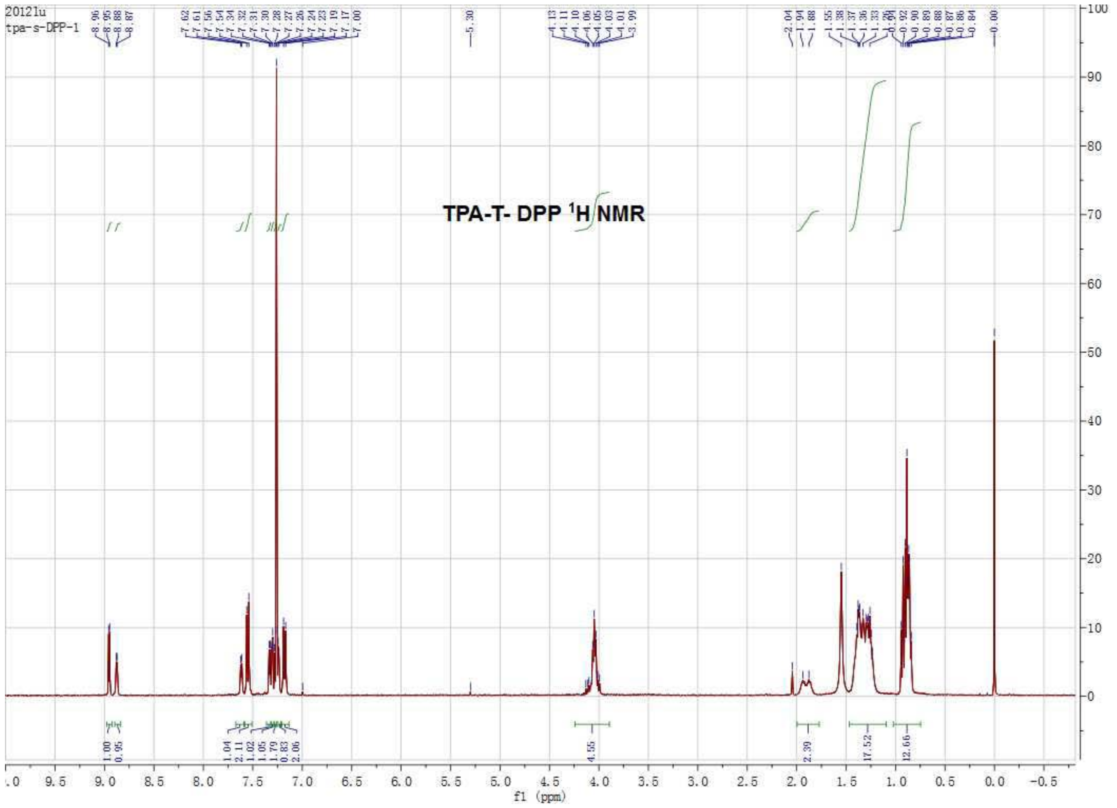
Table S3. Summary of current–voltage parameters of the OSCs based on P3HT: **TPA-T-DPP** blends with different weight ratio processed from different rotate speed.

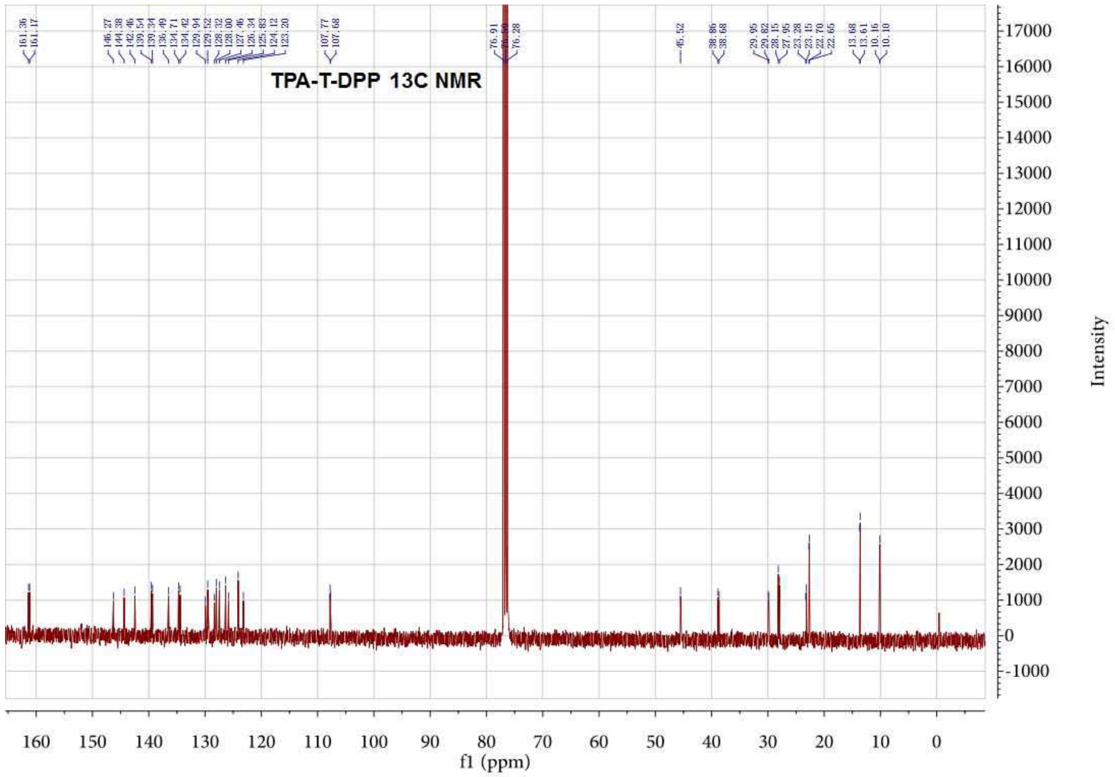
Active layer	D: A radio (w: w)	V_{OC} (V)	J_{SC} (mA·cm^{-2})	*FF* (%)	*PCE* (%)
P3HT: **TPA-T-DPP** (1000rpm)	1:1	1.10	1.28	41.3	0.59
P3HT : **TPA-T-DPP** (2000rpm)	1:1	1.14	1.33	41.4	0.63
P3HT : **TPA-T-DPP** (2000rpm)	3:1	1.14	1.20	33.6	0.46

4. NMR Figures









5. Reference

1. L. Huo, J. Hou, H.-Y. Chen, S. Zhang, Y. Jiang, T. L. Chen and Y. Yang, *Macromolecules*, 2009, **42**, 6564-6571.
2. J. Huang, H. Jia, L. Li, Z. Lu, W. Zhang, W. He, B. Jiang, A. Tang, Z. a. Tan, C. Zhan, Y. Li and J. Yao, *Phys. Chem. Chem. Phys.*, 2012, **14**, 14238-14242.
3. S. Loser, C. J. Bruns, H. Miyauchi, R. o. P. Ortiz, A. Facchetti, S. I. Stupp and T. J. Marks, *J. Am. Chem. Soc.*, 2011, **133**, 8142-8145.