Electronic Supplementary Information (ESI)

High Photovoltage All-Polymer Solar Cells based on a Diketopyrrolopyrrole-Isoindigo Acceptor Polymer

Zhaojun Li, Xiaofeng Xu,* Wei Zhang, Zewdneh Genene, Wendimagegn Mammo, Arkady Yartsev, Mats R. Andersson, René A. J. Janssen,* and Ergang Wang*

* Corresponding authors: X. Xu, e-mail: xixu@chalmers.se
R. A. J. Janssen, e-mail: r.a.j.janssen@tue.nl
E. Wang, e-mail: ergang@chalmers.se

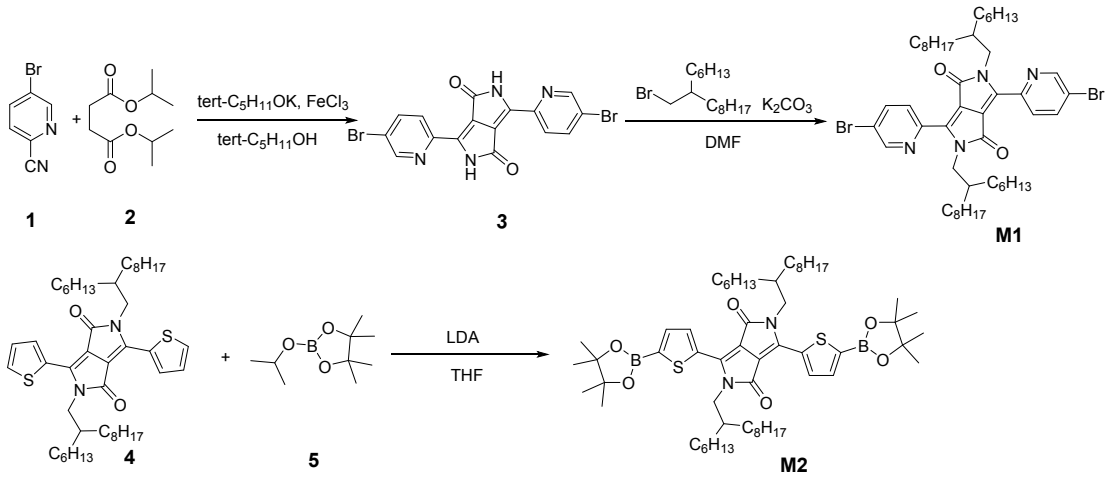
Table of Contents

1. Synthesis

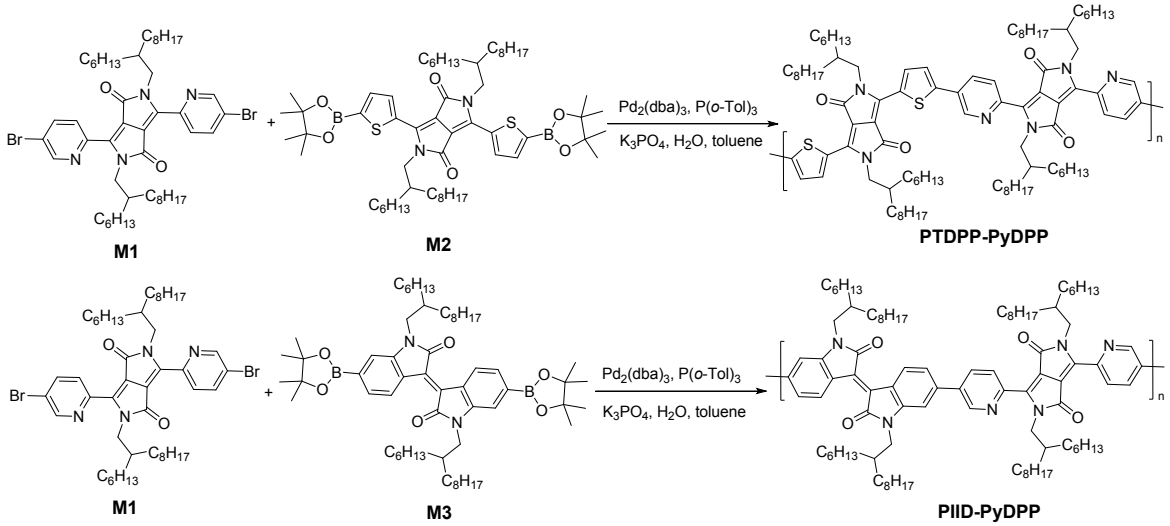
All starting materials, reagents and the donor polymer PTB7-Th were purchased from commercial sources and used without further purification. The synthesis of the donor polymer PBDTTS-FTAZ was described in our previous work.[1] Monomer 3,6-bis(5-bromopyridin-2-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M1**) and monomer 2,5-bis(2-hexyldecyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M2**) were prepared according to literature procedures and were recrystallized twice to high purity.[2, 3] The synthesis of the monomer (E)-1,1'-bis(2-hexyldecyl)-6,6'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[3,3'-biindolinylidene]-2,2'-dione (**M3**) was described in our previous work.[4]

Synthesis of PTDPP-PyDPP: Monomer **M1** (134.5 mg, 0.15 mmol), **M2** (150.2 mg, 0.15 mmol), tri(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (3 mg) and tri(*o*-tolyl)phosphine ($P(o\text{-tol})_3$) (5 mg) were dissolved in toluene (12 mL) under nitrogen atmosphere. Then 2M K_2CO_3 aqueous solution (2 mL) and Aliquat 336 (2 drops) were added to the mixture. The reaction mixture was heated at 80 °C with vigorous stirring for 12 h. After cooling to room temperature, chloroform (100 mL) was added to the reaction mixture and then the polymer was precipitated by pouring the diluted reaction mixture into acetone (250 mL) and was collected by filtration through a 0.45 μm Teflon filter. Then the polymer was subjected to Soxhlet extraction with acetone, diethyl ether and chloroform. The chloroform fraction was purified by passing through a short silica gel column and then precipitated from acetone. Finally, the polymer was obtained by filtrating through 0.45 μm Teflon filter and dried in the vacuum oven at 40 °C overnight. Yield: 140 mg (90%).

Synthesis of PIID-PyDPP: The polymer was prepared starting from **M1** (134.5 mg, 0.15 mmol) and **M3** (144.5 mg, 0.15 mmol) following a procedure similar to the one described above. Yield: 177 mg (80%).



Scheme S1 Synthetic routes of the monomers M1 and M2.



Scheme S2 Synthetic routes of the acceptor polymers.

2. Optical and electrochemical properties

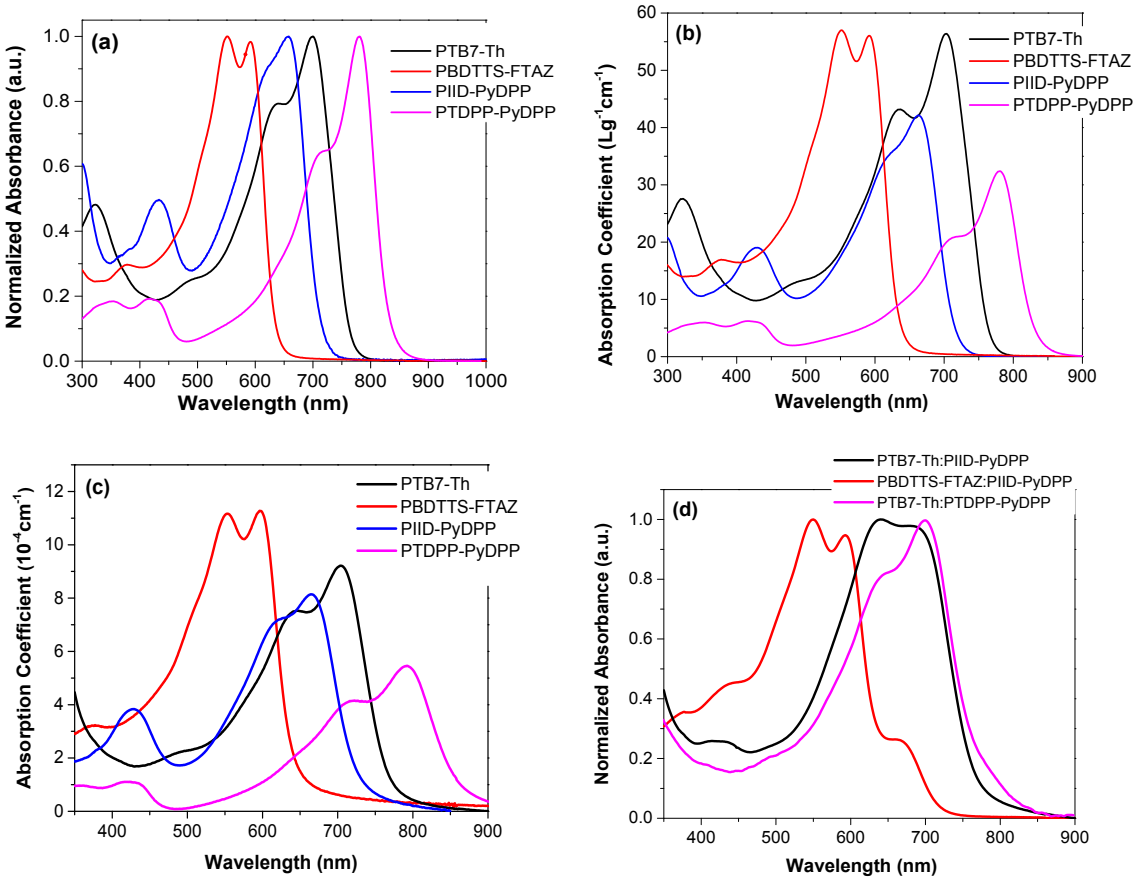


Fig. S1 (a) Normalized UV-Vis-NIR absorption spectra of the polymers in solution. (b) Absorption coefficients of the polymers in chlorobenzene solution and (c) thin films. (d) Normalized UV-Vis-NIR absorption spectra of the polymer:polymer blends (2.5:1, w:w).

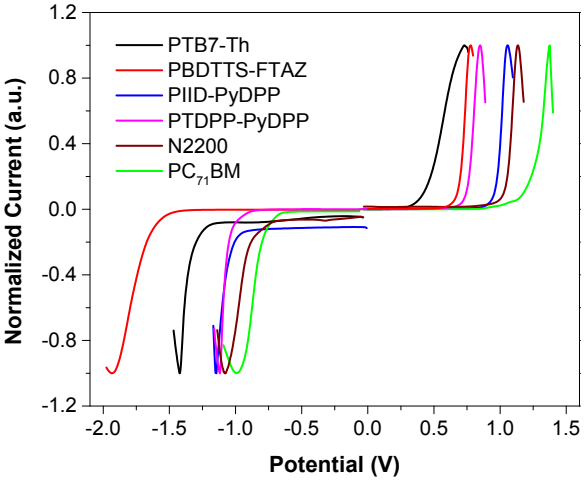


Fig. S2 SWV measurements of the polymers and $PC_{71}BM$.

3. All-PSCs Optimization

Table S1 (a) Photovoltaic parameters of the PIID-PyDPP:$PC_{71}BM$, PTDPP-PyDPP:$PC_{71}BM$ and PTB7-Th: PTDPP-PyDPP solar cells

donor:acceptor	D:A (w:w)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	Thickness (nm)
PIID-PyDPP:$PC_{71}BM$	1:2	0.35	0.26	0.23	0.02	102
PTDPP-PyDPP:$PC_{71}BM$	1:2	0.68	0.95	0.47	0.3	105
PTB7-Th:PTDPP-PyDPP	2.5:1	0.91	0.05	0.32	0.02	85

(b) Photovoltaic parameters of the PTDPP-PyDPP:$PC_{71}BM$ solar cells with different D:A ratio

donor:acceptor	D:A (w:w)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	Thickness (nm)
PTDPP-PyDPP:$PC_{71}BM$	1:1.5	0.66	0.96	0.45	0.28	98
	1:2	0.68	0.95	0.47	0.3	105
	1:2.5	0.66	0.83	0.45	0.24	100

(c) Photovoltaic parameters of the PTB7-Th:PIID-PyDPP solar cells with different D:A ratios

donor:acceptor	D:A (w:w)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	Thickness (nm)
PTB7-Th:PIID-PyDPP	3:1	1.02	5.5	0.34	1.9	96
	2.5:1	1.02	5.9	0.39	2.3	85
	2:1	1.02	4.0	0.34	1.4	84
	1.5:1	1.01	3.1	0.31	1.0	80

(d) Photovoltaic parameters of the PBDTTS-FTAZ:PIID-PyDPP solar cells with different D:A ratios

donor:acceptor	D:A (w:w)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	Thickness (nm)
PBDTTS-FTAZ: PIID-PyDPP	3:1	1.07	8.3	0.39	3.5	84
	2.5:1	1.07	9.1	0.43	4.2	85
	2:1	1.07	7.8	0.41	3.4	78

4. Energy loss (E_{loss}) characteristics

Table S2 PCE, V_{oc}, EQE_{max}, E_g and E_{loss} for various all-PSCs

Active layer	PCE (%)	V_{oc} (V)	EQE_{max}	E_g (eV)	E_{loss} (eV)	Reference
J51:N2200	8.27	0.83	0.75	1.48	0.65	5
PTB7-Th:PNDIS-HD	7.73	0.81	0.85	1.59	0.78	6
PTB7-Th:P(NDI2DT-FT2)	6.71	0.81	0.66	1.59	0.78	7
PBDTTPD:PNDIT-HD	6.64	1.06	0.70	1.85	0.79	8
PBDT-TS1:PPDIODT	6.58	0.76	0.75	1.55	0.79	9
PBDTTT-C-T:30PDI	6.29	0.79	0.91	1.55	0.76	10
PTB7-Th:P-BNBP-fBT	6.26	1.07	0.60	1.58	0.51	11
PTB7-Th:PNDIT-HD	5.96	0.79	0.70	1.59	0.80	12
PBDTBDD-T:N2200	5.8	0.87	0.55	1.48	0.60	13
PTB7-Th:N2200	5.73	0.79	0.60	1.48	0.69	14
J51:P(IDT-NDI)	5.33	0.93	0.55	1.51	0.58	15
PTB7-Th: PNDI-TT-TVT(copolymer4)	5.27	0.79	0.61	1.52	0.73	16
PPDT2FBT:N2200	5.1	0.85	0.59	1.48	0.63	17
Ptb7-Th:P-BN-IID	4.95	0.92	0.53	1.59	0.67	18
PSEHTT:PNDIS-HD	4.81	0.76	0.61	1.65	0.89	19
TQ1:N2200	4.4	0.82	0.54	1.48	0.66	20
PTP8:N2200	4.35	0.98	0.46	1.48	0.50	21
Pil-2T-PS5:P(TP)	4.21	1.04	0.46	~1.65	0.61	22
TTV7:PC-NDI	3.68	0.88	0.40	~1.72	0.84	23
PTB7-Th:PDIC8-EB	3.58	0.70	0.49	1.59	0.89	24
PBDTTT-C-T:P(PDI-DTT)	3.45	0.75	0.43	1.46	0.71	25
PSEHTT:PNDIS-HD	3.26	0.76	0.47	1.65	0.89	26
PBDTTT-C-T:PNDIBTOV8	3.14	0.90	0.33	1.46	0.56	27
PTB7-Th:PQP	3.08	0.70	0.40	1.59	0.89	28
PDPP5T:PDPP2TzT	2.9	0.81	0.29	1.44	0.63	29
PTB7:N2200	2.66	0.80	0.27	1.44	0.64	30
PTB7:PCPDT-PDI	2.13	0.7	0.34	1.46	0.76	31

PTB7-Th: PIID-PyDPP	2.3	1.02	0.27	1.59	0.57	This work
PBDTTS-FTAZ: PIID-PyDPP	4.2	1.07	0.58	1.69	0.62	This work

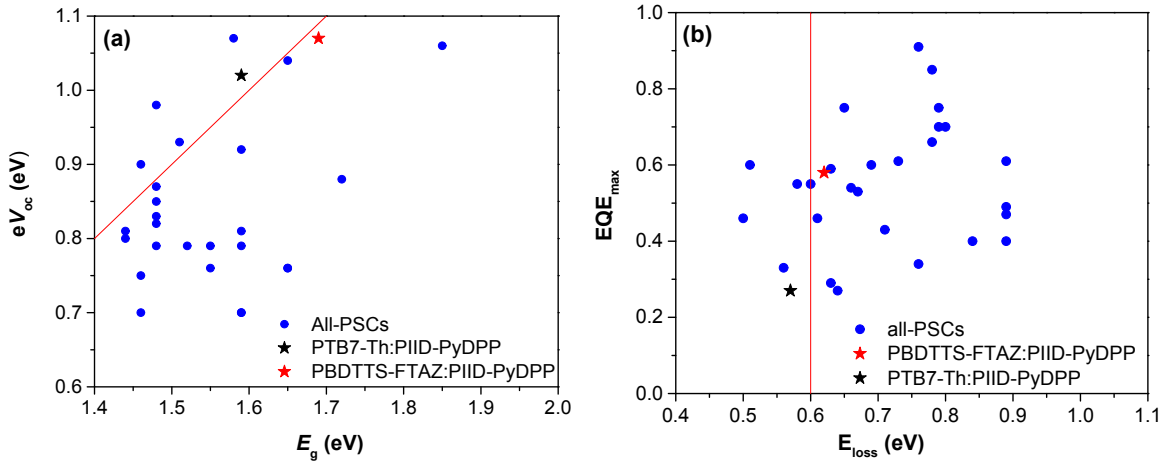
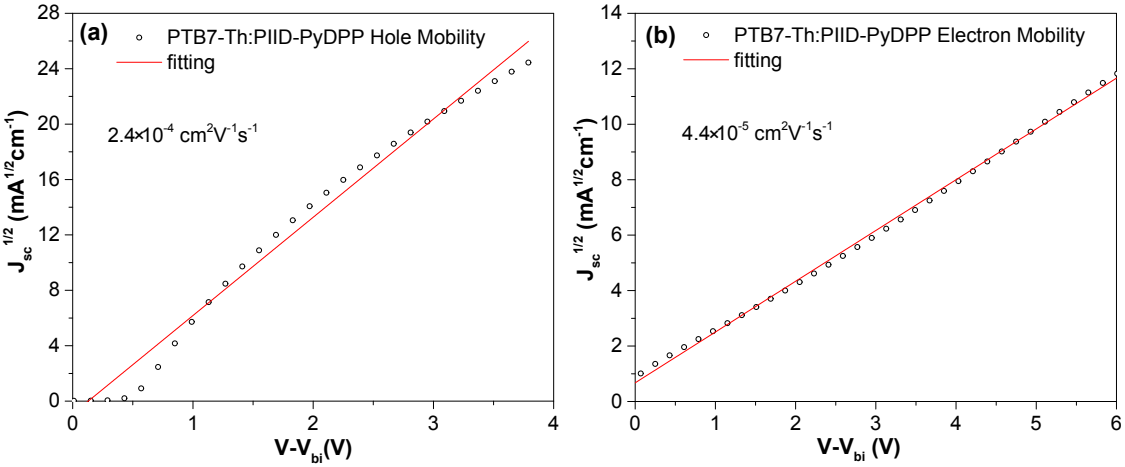


Fig. S3 (a) Plots of V_{oc} against E_g and (b) EQE_{max} against E_{loss} in various all-PSCs. The red line corresponds to E_{loss} = 0.6 eV.

5. Space charge limited current (SCLC) mobilities



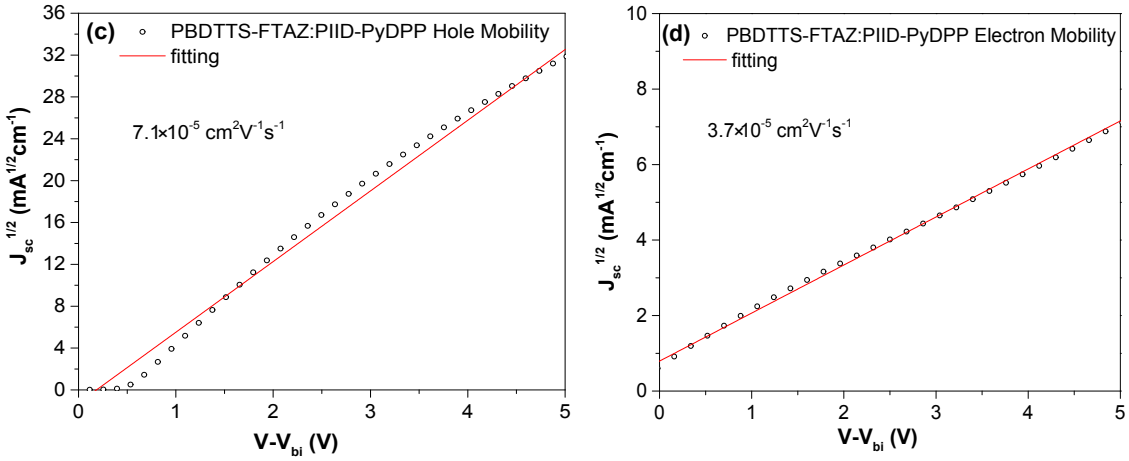


Fig. S4 SCLC fitting curves of the PTB7-Th:PIID-PyDPP and PBDTTS-FTAZ:PIID-PyDPP blend films with the hole-only device structure of ITO/PEDOT:PSS/active layer/Au, and electron-only device structure of ITO/ZnO/active layer/LiF/Al.

6. EQE characteristics under bias light

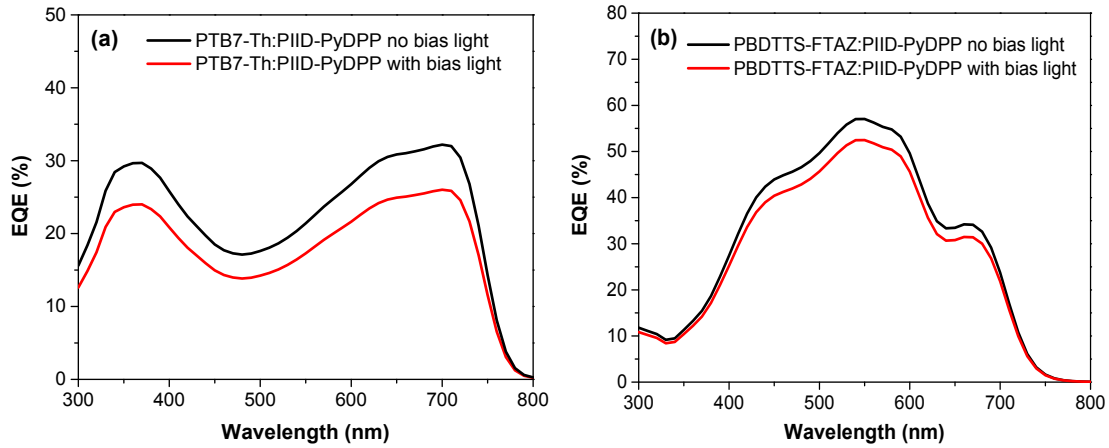


Fig. S5 EQE curves of the (a) PTB7-Th:PIID-PyDPP and (b) PBDTTS-FTAZ:PIID-PyDPP solar cells with and without bias light (530 nm, 100 mW/cm^2).

7. Time resolved photoluminescence (TRPL) parameters

Table S3 Amplitude (A) and lifetime (τ) of the neat polymer and blend films.

Polymer	A_1	τ_1 (ps)	A_2	τ_2 (ps)
PTB7-Th	1	138.7		
PBDTTS-FTAZ	1	310		
PIID-PyDPP	1	102		
PTB7-Th:PIID-PyDPP [a]	0.92	3.6	0.52	69.5
PBDTTS-FTAZ:PIID-PyDPP [a]	0.40	8.7	0.75	70.0

[a] Bi-exponential fit: $I(t)=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)$.

8. Absolute fluorescence quenching yield measurements

Table S4 Summary of absolute fluorescence quantum yield and quenching efficiency

Polymer	fluorescence quantum yield (Φ)	exciton quenching efficiency (η)
PTB7-Th	1.53%	
PBDTTS-FTAZ	4.74%	
PIID-PyDPP	0.39%	
PTB7-Th:PIID-PyDPP	0.34%	
PBDTTS-FTAZ:PIID-PyDPP	0.38%	
η (PTB7-Th) [a]		>70%
η (PBDTTS-FTAZ) [a]		>91%

[a] η is the exciton quenching efficiency of the donor polymer in the blend films.

Absolute fluorescence quantum yield (Φ) is calculated by using the Equation (1),

$$\Phi = \frac{E_c - E_a}{L_a - L_c} \qquad (1)$$

Where E_a is the integrated luminescence from the blank sample, E_c is the integrated luminescence from the samples with direct excitation, L_a is the integrated excitation profile from the blank sample, L_c is the integrated excitation profile when the sample is directly excited by the incident beam.

PL quenching efficiency (η) is calculated by using the Equation (2),

$$\eta_{donor} > 1 - \frac{\Phi_{blend}}{\Phi_{donor} \times R_{donor}} \qquad (2)$$

Where Φ_{blend} is the absolute fluorescence quantum yield of the blend film. Φ_{donor} is the absolute fluorescence quantum yield of the neat donor film. R_{donor} is the absorption contribution of the donor to the blend film at the excitation wavelength.

9. Internal quantum efficiency (IQE) parameters

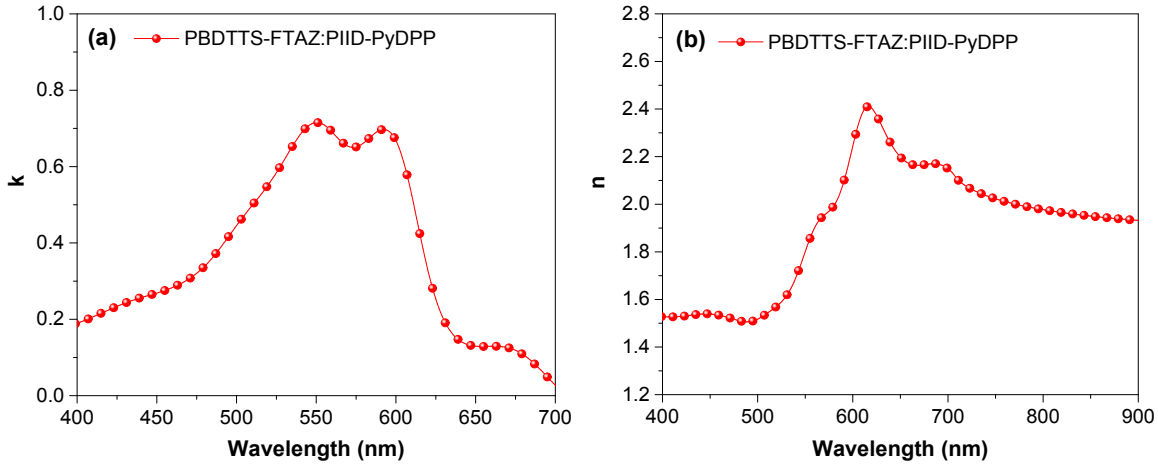


Fig. S6 The optical parameters *k* and *n* curves of the PBDTTS-FTAZ:PIID-PyDPP blend.

Using the transfer matrix formalism (TMF), the fraction of absorbed photons in the active layer was calculated based on a device configuration of glass/SiO_2(20 nm)/ITO(170 nm)/ZnO(40 nm)/active layer (85 nm)/MoO_3(10 nm)/Ag(100 nm). The *n* and *k* values of the glass substrate, ITO, charge transporting layers and electrodes were included as input to simulate the absorption distribution in the all-PSC.

10. References

1. Z. Genene, J. Wang, X. Meng, W. Ma, X. Xu, R. Yang, W. Mammo and E. Wang, *Adv. Electron. Mater.*, 2016, **2**, 1600084.
2. H. Bürckstümmer, A. Weissenstein, D. Bialas and F. Würthner, *J. Org. Chem.*, 2011, **76**, 2426-2432.
3. B. Sun, W. Hong, Z. Yan, H. Aziz and Y. Li, *Adv. Mater.*, 2014, **26**, 2636-2642.
4. W. Sun, Z. Ma, D. Dang, W. Zhu, M. R. Andersson, F. Zhang and E. Wang, *J. Mater. Chem. A*, 2013, **1**, 11141-11144.

5. L. Gao, Z. G. Zhang, L. Xue, J. Min, J. Zhang, Z. Wei and Y. Li, *Adv. Mater.*, 2016, **28**, 1884-1890.
6. Y. J. Hwang, B. A. Courtright, A. S. Ferreira, S. H. Tolbert and S. A. Jenekhe, *Adv. Mater.*, 2015, **27**, 4578-4584.
7. J. W. Jung, J. W. Jo, C. C. Chueh, F. Liu, W. H. Jo, T. P. Russell and A. K. Y. Jen, *Adv. Mater.*, 2015, **27**, 3310-3317.
8. T. Kim, J.-H. Kim, T. E. Kang, C. Lee, H. Kang, M. Shin, C. Wang, B. Ma, U. Jeong and T.-S. Kim, *Nat. Commun.*, 2015, **6**, 8547.
9. S. Li, H. Zhang, W. Zhao, L. Ye, H. Yao, B. Yang, S. Zhang and J. Hou, *Adv. Energy Mater.*, 2015, **6**, 1501991.
10. Y.-J. Hwang, T. Earmme, B. A. Courtright, F. N. Eberle and S. A. Jenekhe, *J. Am. Chem. Soc.*, 2015, **137**, 4424-4434.
11. X. Long, Z. Ding, C. Dou, J. Zhang, J. Liu and L. Wang, *Adv. Mater.*, 2016, **28**, 6504-6508.
12. C. Lee, H. Kang, W. Lee, T. Kim, K. H. Kim, H. Y. Woo, C. Wang and B. J. Kim, *Adv. Mater.*, 2015, **27**, 2466-2471.
13. L. Ye, X. Jiao, M. Zhou, S. Zhang, H. Yao, W. Zhao, A. Xia, H. Ade and J. Hou, *Adv. Mater.*, 2015, **27**, 6046-6054.
14. D. Mori, H. Benten, I. Okada, H. Ohkita and S. Ito, *Energy Environ. Sci.*, 2014, **7**, 2939-2943.
15. L. Xue, Y. Yang, Z.-G. Zhang, X. Dong, L. Gao, H. Bin, J. Zhang, Y. Yang and Y. Li, *J. Mater. Chem. A*, 2016, **4**, 5810-5816.
16. X. Li, P. Sun, Y. Wang, H. Shan, J. Xu, C. You, Z.-x. Xu and Z.-K. Chen, *Polym. Chem.*, 2016, **7**, 2230-2238.
17. H. Kang, M. A. Uddin, C. Lee, K.-H. Kim, T. L. Nguyen, W. Lee, Y. Li, C. Wang, H. Y. Woo and B. J. Kim, *J. Am. Chem. Soc.*, 2015, **137**, 2359-2365.
18. R. Zhao, C. Dou, Z. Xie, J. Liu and L. Wang, *Angew. Chem.*, 2016, **128**, 5399-5403.
19. T. Earmme, Y. J. Hwang, S. Subramaniyan and S. A. Jenekhe, *Adv. Mater.*, 2014, **26**, 6080-6085.
20. Y. Xia, C. Musumeci, J. Bergqvist, W. Ma, F. Gao, Z. Tang, S. Bai, Y. Jin, C. Zhu and R. Kroon, *J. Mater. Chem. A*, 2016, **4**, 3835-3843.
21. J. Yuan and W. Ma, *J. Mater. Chem. A*, 2015, **3**, 7077-7085.
22. Y. Zhou, T. Kurosawa, W. Ma, Y. Guo, L. Fang, K. Vandewal, Y. Diao, C. Wang, Q. Yan and J. Reinspach, *Adv. Mater.*, 2014, **26**, 3767-3772.
23. E. Zhou, J. Cong, K. Hashimoto and K. Tajima, *Adv. Mater.*, 2013, **25**, 6991-6996.
24. S. Nam, S. G. Hahm, H. Han, J. Seo, C. Kim, H. Kim, S. R. Marder, M. Ree and Y. Kim, *ACS Sustainable Chem. Eng.*, 2016, **4**, 767-774.
25. P. Cheng, L. Ye, X. Zhao, J. Hou, Y. Li and X. Zhan, *Energy Environ. Sci.*, 2014, **7**, 1351-1356.
26. T. Earmme, Y.-J. Hwang, N. M. Murari, S. Subramaniyan and S. A. Jenekhe, *J. Am. Chem. Soc.*, 2013, **135**, 14960-14963.
27. F. Liu, H. Li, Y. Wu, C. Gu and H. Fu, *RSC Adv.*, 2015, **5**, 92151-92158.
28. I. H. Jung, D. Zhao, J. Jang, W. Chen, E. S. Landry, L. Lu, D. V. Talapin and L. Yu, *Chem. Mater.*, 2015, **27**, 5941-5948.
29. W. Li, W. Roelofs, M. Turbiez, M. M. Wienk and R. A. Janssen, *Adv. Mater.*, 2014, **26**, 3304-3309.
30. N. Zhou, H. Lin, S. J. Lou, X. Yu, P. Guo, E. F. Manley, S. Loser, P. Hartnett, H. Huang and M. R. Wasielewski, *Adv. Energy Mater.*, 2014, **4**, 1300785.
31. B. Xiao, G. Ding, Z. a. Tan and E. Zhou, *Polym. Chem.*, 2015, **6**, 7594-7602.