Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

π-Conjugated Polymers and Molecules Enabling Small Photon Energy Loss Simultaneously with High Efficiency in Organic Photovoltaics

Masahiko Saito[1,2], Hideo Ohkita[3*], and Itaru Osaka[1,2*]

[1] *Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan*

[2] *Department of Applied Chemistry, Graduate School of Advanced Science and Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan*

[3] *Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*

E-mail address: ohkita@photo.polym.kyoto-u.ac.jp, iosaka@hiroshima-u.ac.jp

Table S1. E_g, V_{OC}, $E_g - qV_{OC}$, EQE_{max}, and PCE for solar cells summarized in Figure 2.

System	Blend	E_g (eV)	V_{OC} (V)	$E_g - qV_{OC}$ (eV)	EQE_{max} (%)	PCE (%)	Ref
Polymer /Fullerene	P3HT/PCBM	1.9	0.58	1.30	65	3.9	1
	P3HT/bis-PCBM	1.9	0.73	1.15	70	4.5	2
	P3HT/ICMA	1.9	0.63	1.25	–	3.9	3
	P3HT/ICBA	1.9	0.84	1.04	62	5.4	3
	P3HT/SIMEF	1.9	0.67	1.23	63	3.2	4
	PCDTBT/PCBM	1.88	0.88	1.00	–	6.1	5
	PBTI3T/PCBM	1.81	0.86	0.95	75	8.66	6
	PM6/PCBM	1.80	0.98	0.82	78	9.2	7
	PTB7-Th/PCBM/ICBA	1.58	0.83	0.69	78	10.5	8
	PBDTTPD/PCBM	1.73	0.97	0.76	72	8.5	9
	PNNT/PCBM	1.68	0.82	0.86	72	8.2	10
	PTB7/PCBM	1.65	0.74	0.91	68	7.4	11
	PffBT4T-2OD/PCBM	1.65	0.77	0.88	82	10.5	12
	TBTIT/PCBM	1.6	0.72	0.88	75	9.1	13
	PBDT-TS1/PCBM	1.51	0.80	0.71	73	9.48	14
	P3TI/PCBM	1.50	0.70	0.80	66	6.3	15
	PTI-1/PCBM	1.6	0.91	0.69	42	4.5	16
	PIPCP /PCBM	1.47	0.86	0.61	62	6.15	17
	PDPP2TzT/PCBM	1.44	0.96	0.48	5	1.1	18
	PDPP2TzBDT/PCBM	1.53	0.98	0.55	25	3.2	18
	PDPP2Tz2T/PCBM	1.47	0.92	0.55	40	5.1	18
	PDPP2TzDTP/PCBM	1.28	0.69	0.59	52	5.6	18
	PSBTBT/PCBM	1.45	0.68	0.77	46	5.1	19
	PCPDTBT/PCBM	1.46	0.62	0.84	–	5.5	20
	PDPP3T*alt*TPT/PCBM	1.43	0.75	0.68	58	8.0	21
	PDPP3T/PCBM	1.33	0.67	0.66	52	7.1	21
	PDPT-DFBT/PCBM	1.38	0.70	0.68	61	8.0	22
	PBDTDPP/PCBM	1.31	0.82	0.49	54	5.16	23
	PDTTDPP/PCBM	1.22	0.66	0.56	64	6.05	24
	PDTP-DTDPP/PCBM	1.13	0.38	0.75	38	2.71	25

	TTV2/PCBM	1.1	0.42	0.68	62	4.99	26
	PNTz4T/PCBM	1.56	0.71	0.85	79	10.1	27
	PNTz4TF2/PCBM	1.60	0.82	0.78	82	10.5	28
	PNTz4TF4/PCBM	1.62	0.93	0.69	51	6.5	28
	PFN4T/PCBM	1.46	0.73	0.73	71	9.6	29
	PFN4TF2/PCBM	1.53	0.84	0.69	73	10.8	29
	PBDTT-SF-TT/PCBM	1.59	1.00	0.59	82	9.1	30
	PNOz4T/PCBM	1.52	0.96	0.56	65	8.9	31
	PSiNO/PCBM	1.56	0.90	0.66	62	8.4	32
	PisoBBT4T /PCBM	1.40	0.81	0.59	68	10.3	33
Polymer /NFA	PffBT-T3(1,2)-2/TPE-PDI4	1.63	1.04	0.60	54	6.0	34
	PffBT4T-DT/diPDI	1.65	0.84	0.81	55	5.4	35
	SF-PDI2/PffBT4T-DT	1.65	0.98	0.67	51	6.3	35
	P3TEA/SF-PDI2	1.72	1.11	0.61	66	9.5	36
	PffBT-T3(1,2)-2/TPC-PDI4	1.63	1.04	0.59	46	4.7	34
	PffBT-T3(1,2)-2/TPE-PDI4	1.63	1.03	0.60	54	6.0	34
	PffBT-T3(1,2)-2/TPPz-PDI4	1.63	0.99	0.64	61	7.1	34
	P3TEA/FTTB-PDI4	1.72	1.13	0.53	68	10.6	37
	PffBT4T-DT/FBR	1.61	1.12	0.49	57	7.8	38
	PCE10/IDTBR/IDFBR	1.58	1.04	0.54	83	11.4	38
	J61/ITIC	1.57	0.89	0.68	77	9.5	39
	PDCBT-2F/IT-M	1.59	1.13	0.46	48	6.6	40
	PBQ0F/ITIC	1.57	0.69	0.88	76	6.70	41
	PBQ-QF/ITIC	1.57	0.83	0.74	80	8.90	41
	PBQ4F/ITIC	1.57	0.95	0.62	82	11.3	41
	PTB7-Th/IDTIDT-IC	1.53	0.94	0.59	62	6.5	42
	PBDB-T/ITIC	1.59	0.90	0.69	75	11.2	43
	J61/m-ITIC	1.58	0.91	0.67	80	11.8	44
	PBDB-T/IT-M	1.58	0.94	0.64	78	11.6	45
	FTAZ/INIC3	1.48	0.86	0.62	76	11.5	46
	J71/ITIC	1.58	0.94	0.64	74	11.4	47
	PTFBDT-BZS/IDIC	1.65	0.91	0.74	69	11.0	48

	PDCBT/ITIC	1.58	0.94	0.64	72	10.2	49
	PBDB-T-SF/IT-F4	1.55	0.88	0.66	83	13.1	50
	PvBDTTAZ/O-IDTBR	1.63	1.08	0.55	71	11.6	51
	PBDT-T/NFBDT	1.56	0.87	0.69	74	10.4	52
	PTB7-Th/ATT-2	1.32	0.73	0.59	71	9.6	53
	PBDTTT-EFT/IEICO-F4	1.24	0.74	0.50	74	10.0	54
	J52/IEICO-F4	1.24	0.73	0.51	72	9.4	54
	PTB7-Th/DTPC-DFIC	1.21	0.76	0.45	69	10.2	55
	PTB7-Th/DTPC-IC	1.28	0.86	0.42	28	3.1	55
	PDBD-T/NCBDT	1.45	0.84	0.61	73	12.1	56
	FTAZ/IOIC2	1.55	0.90	0.65	83	12.3	57
	FTAZ/IHIC2	1.67	0.78	0.89	79	7.3	57
	PTB7-Th/IEICO-4Cl	1.23	0.73	0.50	72	10.3	58
	PTQ10/DF-PCIC	1.59	1.04	0.55	35	3.50	59
	PTQ10/HC-PCIC	1.48	0.94	0.54	68	10.4	59
	PBDB-TF/HC-PCIC	1.48	0.89	0.59	63	11.7	59
	PBDB-T/DF-PCIC	1.59	0.89	0.70	66	8.40	59
	PBDB-T/FO-PCIC	1.59	0.90	0.69	69	8.30	59
	PBDB-T/HC-PCIC	1.48	0.73	0.75	78	9.00	59
	PBDB-T/Y5	1.38	0.88	0.50	75	14.1	60
	PBDB-TF/BTP-0F	-	0.96	~0.51	48	8.2	61
	PBDB-TF/BTP-2F	-	0.89	~0.54	76	14.1	61
	PBDB-TF/BTP-4F	-	0.85	~0.55	81	16.7	61
	PBDB-TF/BTP-6F	-	0.81	~0.57	82	15.3	61
	PBDB-TF/Y11	1.31	0.85	0.46	79	16.5	62
	PBDB-TF/ANT-4F	1.67	0.93	0.74	78	13.1	63
	PBDB-T/IT-M/BisPC$_{71}$BM	1.59	0.95	0.64	76	12.2	64
	J-52/ITIC/IEICO	1.34	0.85	0.49	80	11.1	65
	PTB7-Th/ COi8DFIC	1.18	0.69	0.49	75	10.5	66
	PTB7-Th/COi8DFIC/PCBM	1.18	0.73	0.45	85	14.6	66
	PM6/Y6	1.40	0.83	0.57	83	15.6	67
	PM6/BTP-4Cl	1.40	0.87	0.53	85	16.5	68
	PBDB-T2Cl/IT-4F	1.55	0.86	0.69	82	14.4	69

	PBDT-TDZ/ITIC	1.57	1.01	0.56	77	11.7	70
	PBDTS-TDZ/ITIC	1.57	1.10	0.47	79	12.8	70
	PBDT-ODZ/ITIC	1.57	1.08	0.50	75	11.6	71
	L1/Y6	1.40	0.80	0.60	79	14.4	72
	L2/Y6	1.40	0.87	0.53	68	12.6	72
	D16/Y6	1.40	0.83	0.57	83	16.0	73
	D18/Y6	1.40	0.86	0.54	86	18.2	74
	PTQ10/IDIC	1.57	0.97	0.60	78	12.7	75
	PTQ11/TPT10	1.36	0.88	0.48	86	16.3	76
Polymer /Polymer	PTB7-Th/PBNBP-T	1.58	1.12	0.46	50	2.3	77
	PiI-2T/P(TP)	1.65	1.04	0.61	37	4.4	78
	PTB7-Th/N2200	1.45	0.81	0.64	66	5.7	79
	PTB7-Th/PTPD[2F]T-HD	1.58	1.10	0.51	50	4.4	80
	PTB7-Th/P-BNBP-fBT	1.58	1.07	0.51	58	6.3	81
	PTB7-Th/BTI2-50TPD	1.58	1.05	0.53	68	8.3	82
	TQ-FF/N2200	1.45	0.94	0.51	69	4.1	83
	PBDT-DFQX1/N2200	1.45	0.89	0.56	56	6.7	84
	PTzBI-Si/N2200	1.45	0.86	0.59	70	11.0	85
	PBDB-T/BSS10	1.45	0.86	0.59	85	10.1	86
	PM6/PN1	1.55	1.00	0.55	62	10.5	87
	PBDB-TF/PFBDT-IDTIC	1.68	0.96	0.72	68	10.3	88
	PBDB-T/PZ1	1.55	0.83	0.72	67	9.2	89
	J50/N2200	1.45	0.60	0.85	74	4.9	90
	J51/N2200	1.45	0.83	0.62	69	8.3	90
	PDPP5T/N2200	1.45	0.68	0.77	23	1.7	91
	PDPP2TBDT/N2200	1.44	0.80	0.64	16	1.5	91
	P1/N2200	1.45	0.63	0.82	70	2.6	92
	P2/N2200	1.45	0.72	0.73	63	5.0	92
	P3/N2200	1.45	0.79	0.66	52	6.4	92
	PJ1/PBDB-T	1.40	0.90	0.51	80	14.4	93

Supplementary references

1. G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nat. Mater.*, 2005, **4**, 864–868.
2. M. Lenes, G.-J. A. H. Wetzelaer, F. B. Kooistra, S. C. Veenstra, J. C. Hummelen and P. W. M. Blom, *Adv. Mater.*, 2008, **20**, 2116–2119.
3. Y. He, H.-Y. Chen, J. Hou and Y. Li, *J. Am. Chem. Soc.*, 2010, **132**, 1377–1382.
4. Y. Matsuo, A. Ozu, N. Obata, N. Fukuda, H. Tanaka and E. Nakamura, *Chem. Commun.*, 2012, **48**, 3878–3880.
5. N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletête, G. Durocher, Y. Tao and M. Leclerc, *J. Am. Chem. Soc.*, 2008, **130**, 732–742.
6. X. Guo, N. Zhou, S. J. Lou, J. Smith, D. B. Tice, J. W. Hennek, R. P. Ortiz, J. T. L. Navarrete, S. Li, J. Strzalka, L. X. Chen, R. P. H. Chang, A. Facchetti and T. J. Marks, *Nat. Photon.*, 2013, **7**, 825–833.
7. M. Zhang, X. Guo, W. Ma, H. Ade and J. Hou, *Adv. Mater.*, 2015, **27**, 4655–4660.
8. P. Cheng, C. Yan, Y. Wu, J. Wang, M. Qin, Q. An, J. Cao, L. Huo, F. Zhang, L. Ding, Y. Sun, W. Ma and X. Zhan, *Adv. Mater.*, 2016, **28**, 8021–8028.
9. C. Cabanetos, A. El Labban, J. A. Bartelt, J. D. Douglas, W. R. Mateker, J. M. J. Fréchet, M. D. McGehee and P. M. Beaujuge, *J. Am. Chem. Soc.*, 2013, **135**, 4656–4659.
10. I. Osaka, T. Kakara, N. Takemura, T. Koganezawa and K. Takimiya, *J. Am. Chem. Soc.*, 2013, **135**, 8834–8837.
11. Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, *Adv. Mater.*, 2010, **22**, E135–E138.
12. Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade and H. Yan, *Nat. Commun.*, 2014, **5**, 5293.
13. W. Yue, R. S. Ashraf, C. B. Nielsen, E. Collado-Fregoso, M. R. Niazi, S. A. Yousaf, M. Kirkus, H.-Y. Chen, A. Amassian, J. R. Durrant and I. McCulloch, *Adv. Mater.*, 2015, **27**, 4702–4707.
14. L. Ye, S. Zhang, W. Zhao, H. Yao and J. Hou, *Chem. Mater.*, 2014, **26**, 3603–3605.
15. E. Wang, Z. Ma, Z. Zhang, K. Vandewal, P. Henriksson, O. Inganäs, F. Zhang and M. R. Andersson, *J. Am. Chem. Soc.*, 2011, **133**, 14244–14247.
16. Z. Ma, E. Wang, K. Vandewal, M. R. Andersson and F. Zhang, *Appl. Phys. Lett.*, 2011, **99**, 143302.
17. M. Wang, H. Wang, T. Yokoyama, X. Liu, Y. Huang, Y. Zhang, T.-Q. Nguyen, S. Aramaki and G. C. Bazan, *J. Am. Chem. Soc.*, 2014, **136**, 12576–12579.
18. W. Li, K. H. Hendriks, A. Furlan, M. M. Wienk and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2015, **137**, 2231–2234.

19. J. Hou, H.-Y. Chen, S. Zhang, G. Li and Y. Yang, *J. Am. Chem. Soc.*, 2008, **130**, 16144–16145.

20. J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger and G. C. Bazan, *Nat. Mater.*, 2007, **6**, 497–500.

21. K. H. Hendriks, G. H. L. Heintges, V. S. Gevaerts, M. M. Wienk and R. A. J. Janssen, *Angew. Chem. Int. Ed.*, 2013, **52**, 8341–8344.

22. L. Dou, C.-C. Chen, K. Yoshimura, K. Ohya, W.-H. Chang, J. Gao, Y. Liu, E. Richard and Y. Yang, *Macromolecules*, 2013, **46**, 3384–3390.

23. J. Woong Jung, J. Woong Jo, F. Liu, T. P. Russell and W. Ho Jo, *Chem. Commun.*, 2012, **48**, 6933–6935.

24. J. W. Jung, F. Liu, T. P. Russell and W. H. Jo, *Energy Environ. Sci.*, 2012, **5**, 6857–6861.

25. E. Zhou, Q. Wei, S. Yamakawa, Y. Zhang, K. Tajima, C. Yang and K. Hashimoto, *Macromolecules*, 2010, **43**, 821–826.

26. E. Zhou, J. Cong, K. Hashimoto and K. Tajima, *Energy Environ. Sci.*, 2012, **5**, 9756–9759.

27. V. Vohra, K. Kawashima, T. Kakara, T. Koganezawa, I. Osaka, K. Takimiya and H. Murata, *Nat. Photon.*, 2015, **9**, 403.

28. K. Kawashima, T. Fukuhara, Y. Suda, Y. Suzuki, T. Koganezawa, H. Yoshida, H. Ohkita, I. Osaka and K. Takimiya, *J. Am. Chem. Soc.*, 2016, **138**, 10265–10275.

29. M. Saito, T. Fukuhara, S. Kamimura, H. Ichikawa, H. Yoshida, T. Koganezawa, Y. Ie, Y. Tamai, H. D. Kim, H. Ohkita and I. Osaka, *Adv. Energy Mater.*, 2020, **10**, 1903278.

30. Z. Du, X. Bao, Y. Li, D. Liu, J. Wang, C. Yang, R. Wimmer, L. W. Städe, R. Yang and D. Yu, *Adv. Energy Mater.*, 2017, **8**, 1701471.

31. K. Kawashima, Y. Tamai, H. Ohkita, I. Osaka and K. Takimiya, *Nat. Commun.*, 2015, **6**, 10085.

32. Z. Zhang, F. Lin, H.-C. Chen, H.-C. Wu, C.-L. Chung, C. Lu, S.-H. Liu, S.-H. Tung, W.-C. Chen, K.-T. Wong and P.-T. Chou, *Energy Environ. Sci.*, 2015, **8**, 552–557.

33. L. Bianchi, X. Zhang, Z. Chen, P. Chen, X. Zhou, Y. Tang, B. Liu, X. Guo and A. Facchetti, *Chem. Mater.*, 2019, **31**, 6519–6529.

34. H. Lin, S. Chen, H. Hu, L. Zhang, T. Ma, J. Y. L. Lai, Z. Li, A. Qin, X. Huang, B. Tang and H. Yan, *Adv. Mater.*, 2016, **28**, 8546–8551.

35. J. Zhao, Y. Li, H. Lin, Y. Liu, K. Jiang, C. Mu, T. Ma, J. Y. Lin Lai, H. Hu, D. Yu and H. Yan, *Energy Environ. Sci.*, 2015, **8**, 520–525.

36. J. Liu, S. Chen, D. Qian, B. Gautam, G. Yang, J. Zhao, J. Bergqvist, F. Zhang, W. Ma, H. Ade, O. Inganäs, K. Gundogdu, F. Gao and H. Yan, *Nat. Energy*, 2016, **1**, 16089.

37. J. Zhang, Y. Li, J. Huang, H. Hu, G. Zhang, T. Ma, P. C. Y. Chow, H. Ade, D. Pan and H. Yan, *J. Am. Chem. Soc.*, 2017, **139**, 16092–16095.

38. D. Baran, R. S. Ashraf, D. A. Hanifi, M. Abdelsamie, N. Gasparini, J. A. Röhr, S. Holliday, A.

Wadsworth, S. Lockett, M. Neophytou, C. J. M. Emmott, J. Nelson, C. J. Brabec, A. Amassian, A. Salleo, T. Kirchartz, J. R. Durrant and I. McCulloch, *Nat. Mater.*, 2016, **16**, 363.

39. H. Bin, Z.-G. Zhang, L. Gao, S. Chen, L. Zhong, L. Xue, C. Yang and Y. Li, *J. Am. Chem. Soc.*, 2016, **138**, 4657–4664.
40. H. Zhang, S. Li, B. Xu, H. Yao, B. Yang and J. Hou, *J. Mater. Chem. A*, 2016, **4**, 18043–18049.
41. Z. Zheng, O. M. Awartani, B. Gautam, D. Liu, Y. Qin, W. Li, A. Bataller, K. Gundogdu, H. Ade and J. Hou, *Adv. Mater.*, 2016, **29**, 1604241.
42. Y. Li, X. Liu, F.-P. Wu, Y. Zhou, Z.-Q. Jiang, B. Song, Y. Xia, Z.-G. Zhang, F. Gao, O. Inganäs, Y. Li and L.-S. Liao, *J. Mater. Chem. A*, 2016, **4**, 5890–5897.
43. W. Zhao, D. Qian, S. Zhang, S. Li, O. Inganäs, F. Gao and J. Hou, *Adv. Mater.*, 2016, **28**, 4734–4739.
44. Y. Yang, Z.-G. Zhang, H. Bin, S. Chen, L. Gao, L. Xue, C. Yang and Y. Li, *J. Am. Chem. Soc.*, 2016, **138**, 15011–15018.
45. S. Li, L. Ye, W. Zhao, S. Zhang, S. Mukherjee, H. Ade and J. Hou, *Adv. Mater.*, 2016, **28**, 9423–9429.
46. S. Dai, F. Zhao, Q. Zhang, T.-K. Lau, T. Li, K. Liu, Q. Ling, C. Wang, X. Lu, W. You and X. Zhan, *J. Am. Chem. Soc.*, 2017, **139**, 1336–1343.
47. H. Bin, L. Gao, Z.-G. Zhang, Y. Yang, Y. Zhang, C. Zhang, S. Chen, L. Xue, C. Yang, M. Xiao and Y. Li, *Nat. Commun.*, 2016, **7**, 13651.
48. Y. Lin, F. Zhao, Y. Wu, K. Chen, Y. Xia, G. Li, S. K. K. Prasad, J. Zhu, L. Huo, H. Bin, Z.-G. Zhang, X. Guo, M. Zhang, Y. Sun, F. Gao, Z. Wei, W. Ma, C. Wang, J. Hodgkiss, Z. Bo, O. Inganäs, Y. Li and X. Zhan, *Adv. Mater.*, 2016, **29**, 1604155.
49. Y. Qin, M. A. Uddin, Y. Chen, B. Jang, K. Zhao, Z. Zheng, R. Yu, T. J. Shin, H. Y. Woo and J. Hou, *Adv. Mater.*, 2016, **28**, 9416–9422.
50. W. Zhao, S. Li, H. Yao, S. Zhang, Y. Zhang, B. Yang and J. Hou, *J. Am. Chem. Soc.*, 2017, **139**, 7148–7151.
51. S. Chen, Y. Liu, L. Zhang, P. C. Y. Chow, Z. Wang, G. Zhang, W. Ma and H. Yan, *J. Am. Chem. Soc.*, 2017, **139**, 6298–6301.
52. B. Kan, H. Feng, X. Wan, F. Liu, X. Ke, Y. Wang, Y. Wang, H. Zhang, C. Li, J. Hou and Y. Chen, *J. Am. Chem. Soc.*, 2017, **139**, 4929–4934.
53. F. Liu, Z. Zhou, C. Zhang, J. Zhang, Q. Hu, T. Vergote, F. Liu, T. P. Russell and X. Zhu, *Adv. Mater.*, 2017, **29**, 1606574.
54. H. Yao, Y. Cui, R. Yu, B. Gao, H. Zhang and J. Hou, *Angew. Chem. Int. Ed.*, 2017, **56**, 3045–3049.
55. Z. Yao, X. Liao, K. Gao, F. Lin, X. Xu, X. Shi, L. Zuo, F. Liu, Y. Chen and A. K. Y. Jen, *J.*

Am. Chem. Soc., 2018, **140**, 2054–2057.

56. B. Kan, J. Zhang, F. Liu, X. Wan, C. Li, X. Ke, Y. Wang, H. Feng, Y. Zhang, G. Long, R. H. Friend, A. A. Bakulin and Y. Chen, *Adv. Mater.*, 2017, **30**, 1704904.
57. J. Zhu, Z. Ke, Q. Zhang, J. Wang, S. Dai, Y. Wu, Y. Xu, Y. Lin, W. Ma, W. You and X. Zhan, *Adv. Mater.*, 2017, **30**, 1704713.
58. Y. Cui, C. Yang, H. Yao, J. Zhu, Y. Wang, G. Jia, F. Gao and J. Hou, *Adv. Mater.*, 2017, **29**, 1703080.
59. S. Li, L. Zhan, C. Sun, H. Zhu, G. Zhou, W. Yang, M. Shi, C.-Z. Li, J. Hou, Y. Li and H. Chen, *J. Am. Chem. Soc.*, 2019, **141**, 3073–3082.
60. J. Yuan, Y. Zhang, L. Zhou, C. Zhang, T.-K. Lau, G. Zhang, X. Lu, H.-L. Yip, S. K. So, S. Beaupré, M. Mainville, P. A. Johnson, M. Leclerc, H. Chen, H. Peng, Y. Li and Y. Zou, *Adv. Mater.*, 2019, **31**, 1807577.
61. Y. Xu, H. Yao, L. Ma, L. Hong, J. Li, Q. Liao, Y. Zu, J. Wang, M. Gao, L. Ye and J. Hou, *Angew. Chem. Int. Ed.*, 2020, **59**, 9004–9010.
62. S. Liu, J. Yuan, W. Deng, M. Luo, Y. Xie, Q. Liang, Y. Zou, Z. He, H. Wu and Y. Cao, *Nat. Photon.*, 2020, **14**, 300–305.
63. C. Yao, B. Liu, Y. Zhu, L. Hong, J. Miao, J. Hou, F. He and H. Meng, *J. Mater. Chem. A*, 2019, **7**, 10212–10216.
64. W. Zhao, S. Li, S. Zhang, X. Liu and J. Hou, *Adv. Mater.*, 2017, **29**, 1604059.
65. R. Yu, S. Zhang, H. Yao, B. Guo, S. Li, H. Zhang, M. Zhang and J. Hou, *Adv. Mater.*, 2017, **29**, 1700437.
66. Z. Xiao, X. Jia and L. Ding, *Sci. Bull.*, 2017, **62**, 1562–1564.
67. J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. Li and Y. Zou, *Joule*, 2019, **3**, 1140–1151.
68. Y. Cui, H. Yao, J. Zhang, T. Zhang, Y. Wang, L. Hong, K. Xian, B. Xu, S. Zhang, J. Peng, Z. Wei, F. Gao and J. Hou, *Nat. Commun.*, 2019, **10**, 2515.
69. S. Zhang, Y. Qin, J. Zhu and J. Hou, *Adv. Mater.*, 2018, **30**, 1800868.
70. X. Xu, T. Yu, Z. Bi, W. Ma, Y. Li and Q. Peng, *Adv. Mater.*, 2017, **30**, 1703973.
71. X. Xu, Z. Li, Z. Bi, T. Yu, W. Ma, K. Feng, Y. Li and Q. Peng, *Adv. Mater.*, 2018, **30**, 1800737.
72. J. Liu, L. Liu, C. Zuo, Z. Xiao, Y. Zou, Z. Jin and L. Ding, *Sci. Bull.*, 2019, **64**, 1655–1657.
73. J. Xiong, K. Jin, Y. Jiang, J. Qin, T. Wang, J. Liu, Q. Liu, H. Peng, X. Li, A. Sun, X. Meng, L. Zhang, L. Liu, W. Li, Z. Fang, X. Jia, Z. Xiao, Y. Feng, X. Zhang, K. Sun, S. Yang, S. Shi and L. Ding, *Sci. Bull.*, 2019, **64**, 1573–1576.
74. Q. Liu, Y. Jiang, K. Jin, J. Qin, J. Xu, W. Li, J. Xiong, J. Liu, Z. Xiao, K. Sun, S. Yang, X. Zhang and L. Ding, *Sci. Bull.*, 2020, **65**, 272–275.

75. C. Sun, F. Pan, H. Bin, J. Zhang, L. Xue, B. Qiu, Z. Wei, Z.-G. Zhang and Y. Li, *Nat. Commun.*, 2018, **9**, 743.
76. C. Sun, S. Qin, R. Wang, S. Chen, F. Pan, B. Qiu, Z. Shang, L. Meng, C. Zhang, M. Xiao, C. Yang and Y. Li, *J. Am. Chem. Soc.*, 2020, **142**, 1465–1474.
77. Z. Ding, X. Long, C. Dou, J. Liu and L. Wang, *Chem. Sci.*, 2016, **7**, 6197–6202.
78. Y. Zhou, T. Kurosawa, W. Ma, Y. Guo, L. Fang, K. Vandewal, Y. Diao, C. Wang, Q. Yan, J. Reinspach, J. Mei, A. L. Appleton, G. I. Koleilat, Y. Gao, S. C. B. Mannsfeld, A. Salleo, H. Ade, D. Zhao and Z. Bao, *Adv. Mater.*, 2014, **26**, 3767–3772.
79. H. Benten, T. Nishida, D. Mori, H. Xu, H. Ohkita and S. Ito, *Energy Environ. Sci.*, 2016, **9**, 135–140.
80. S. Liu, Z. Kan, S. Thomas, F. Cruciani, J.-L. Brédas and P. M. Beaujuge, *Angew. Chem. Int. Ed.*, 2016, **55**, 12996–13000.
81. X. Long, Z. Ding, C. Dou, J. Zhang, J. Liu and L. Wang, *Adv. Mater.*, 2016, **28**, 6504–6508.
82. H. Sun, B. Liu, C. W. Koh, Y. Zhang, J. Chen, Y. Wang, P. Chen, B. Tu, M. Su, H. Wang, Y. Tang, Y. Shi, H. Y. Woo and X. Guo, *Adv. Funct. Mater.*, 2019, **29**, 1903970.
83. S. Chen, Y. An, G. K. Dutta, Y. Kim, Z.-G. Zhang, Y. Li and C. Yang, *Adv. Funct. Mater.*, 2017, **27**, 1603564.
84. X. Chen, M. Zhao, Z.-g. Zhang, Y. Li, X. Li and H. Wang, *ACS Appl. Energy Mater.*, 2018, **1**, 2350–2357.
85. Z. Li, L. Ying, P. Zhu, W. Zhong, N. Li, F. Liu, F. Huang and Y. Cao, *Energy Environ. Sci.*, 2019, **12**, 157–163.
86. N. B. Kolhe, D. K. Tran, H. Lee, D. Kuzuhara, N. Yoshimoto, T. Koganezawa and S. A. Jenekhe, *ACS Energy Lett.*, 2019, **4**, 1162–1170.
87. G. Wang, F. S. Melkonyan, A. Facchetti and T. J. Marks, *Angew. Chem. Int. Ed.*, 2019, **58**, 4129–4142.
88. H. Yao, F. Bai, H. Hu, L. Arunagiri, J. Zhang, Y. Chen, H. Yu, S. Chen, T. Liu, J. Y. L. Lai, Y. Zou, H. Ade and H. Yan, *ACS Energy Lett.*, 2019, **4**, 417–422.
89. Z.-G. Zhang, Y. Yang, J. Yao, L. Xue, S. Chen, X. Li, W. Morrison, C. Yang and Y. Li, *Angew. Chem. Int. Ed.*, 2017, **56**, 13503–13507.
90. L. Gao, Z.-G. Zhang, L. Xue, J. Min, J. Zhang, Z. Wei and Y. Li, *Adv. Mater.*, 2016, **28**, 1884–1890.
91. C. Li, A. Zhang, Z. Wang, F. Liu, Y. Zhou, T. P. Russell, Y. Li and W. Li, *RSC Adv.*, 2016, **6**, 35677–35683.
92. K. Kranthiraja, S. Kim, C. Lee, K. Gunasekar, V. G. Sree, B. Gautam, K. Gundogdu, S.-H. Jin and B. J. Kim, *Adv. Funct. Mater.*, 2017, **27**, 1701256.

93. T. Jia, J. Zhang, W. Zhong, Y. Liang, K. Zhang, S. Dong, L. Ying, F. Liu, X. Wang, F. Huang and Y. Cao, *Nano Energy*, 2020, **72**, 104718.

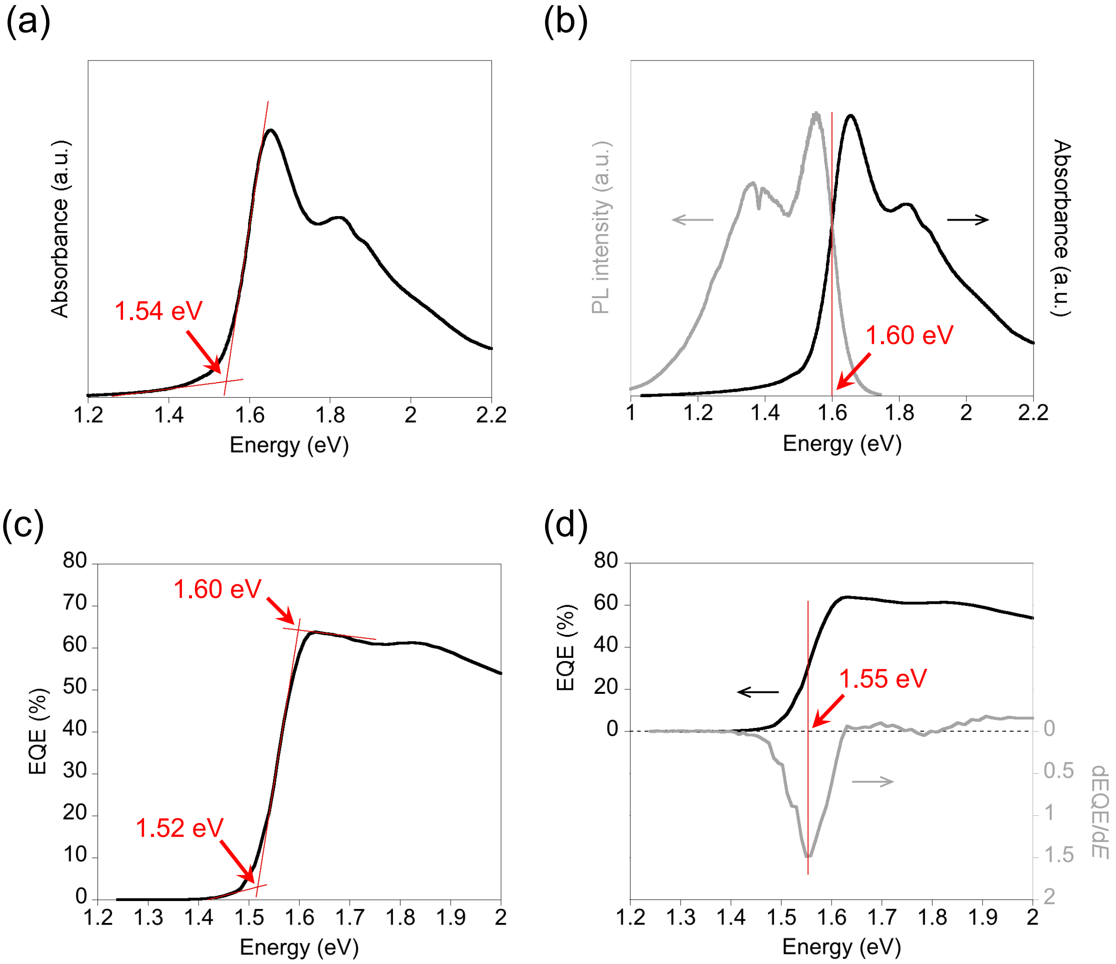

Figure S1. (a) UV–vis absorption spectrum of the PNOz4T neat film. E_g is determined to be 1.54 eV from the absorption onset. (b) Normalized UV–vis absorption and PL spectra of the PNOz4T neat film. E_g is determined to be 1.60 eV from the intersection of these spectra, which corresponds to the method shown in Figure 3b. (c) EQE spectrum of the PNOz4T/PC$_{71}$BM cell. E_g is determined to be 1.52 and 1.60 eV, which corresponds to the methods shown in Figures 3a and 3c, respectively. (d) EQE spectrum (upper) and the corresponding dEQE/dE (lower) of the PNOz4T/PC$_{71}$BM cell. E_g is determined to be 1.55 eV, which corresponds to the methods shown in Figure 3d.

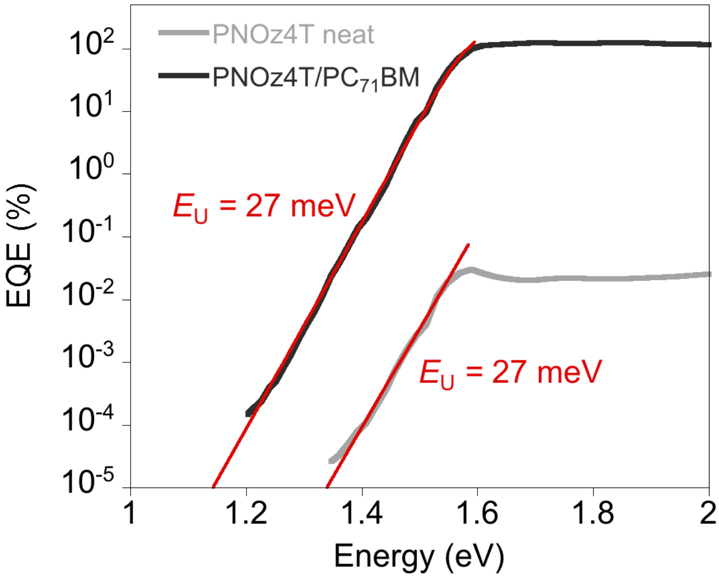

Figure S2. EQE spectra for the photovoltaic cells based on the PNOz4T neat film and the PNOz4T/PC$_{71}$BM blend film.

Radiative recombination loss in organic photovoltaics

We describe how CT state impacts on the photon energy loss (E_{loss}) in organic photovoltaics on the basis of the modified Shockley–Queisser (SQ) theory.94–97) In the SQ theory, the absorptance $\alpha(E)$ is assumed to be a single-step function, which is $\alpha_0 = 1$ for photon energy E above the bandgap energy E_{g} and 0 for photon energy E below the bandgap energy E_{g}. In organic photovoltaics, on the other hand, there is an additional absorption for photon energy above the CT state energy E_{CT} and below E_{g}. Thus, in the modified SQ theory, the CT absorption is considered as an additional step function with an absorptance of α_{CT} (typically $10^{-4} - 10^{-2}$) above E_{CT} and below E_{g} as follows:

$$\alpha(E) = \begin{cases} 0 & \text{for } E < E_{\mathrm{CT}} \\ \alpha_{\mathrm{CT}}\ (10^{-4} - 10^{-2}) & \text{for } E_{\mathrm{CT}} < E < E_{\mathrm{g}} \\ \alpha_0 = 1 & \text{for } E > E_{\mathrm{g}} \end{cases} \tag{1}$$

Here, we consider the relationship between two different photon energy losses based on E_{g} and based on E_{CT} on the basis of the modified SQ theory with two-step functions given by Eq 1. Note that we here focus on the factor for E_{loss} due to the radiative recombination.

First, we consider the radiative energy loss based on E_{g}, $q\Delta V_{\mathrm{rad}}^{\mathrm{Eg}}$: $qV_{\mathrm{OC}} = E_{\mathrm{g}} - q\Delta V_{\mathrm{rad}}^{\mathrm{Eg}}$ where V_{OC} is the open-circuit voltage and q is the elementary charge. In this case, the energy loss due to radiative recombination is given by

$$q\Delta V_{\mathrm{rad}}^{\mathrm{Eg}} = q\Delta V_{\mathrm{r}} + q\Delta V_{\mathrm{SC}} = q\Delta V_{\mathrm{r1}} + q\Delta V_{\mathrm{r2}} + q\Delta V_{\mathrm{SC}} \tag{2}$$

where $q\Delta V_{\mathrm{r1}}$ is the energy loss due to radiative recombination above E_{g}, $q\Delta V_{\mathrm{r2}}$ is the energy loss due to radiative recombination of the CT band above E_{CT} and below E_{g}, and $q\Delta V_{\mathrm{SC}}$ is the energy loss due to the current loss because of the small absorptance of less than unity. Since $q\Delta V_{\mathrm{SC}}$ is typically negligibly small, it is often ignored, as shown in Figure 2c, where $q\Delta V_{\mathrm{rad}}^{\mathrm{Eg}}$ is given by $q\Delta V_{\mathrm{r1}} + q\Delta V_{\mathrm{r2}}$ ($= q\Delta V_{\mathrm{r}}$). In the SQ limit, $q\Delta V_{\mathrm{rad}}^{\mathrm{Eg}} = q\Delta V_{\mathrm{r1}}$ because $q\Delta V_{\mathrm{r2}} = q\Delta V_{\mathrm{SC}} = 0$. Thus, the open-circuit voltage in the SQ limit $qV_{\mathrm{OC,SQ}} = E_{\mathrm{g}} - q\Delta V_{\mathrm{r1}}$ is given by

$$qV_{\mathrm{OC,SQ}} = k_{\mathrm{B}}T\ln\left(\frac{J_{\mathrm{SC,SQ}}}{J_{0,\mathrm{SQ}}}+1\right) \simeq k_{\mathrm{B}}T\ln\left(\frac{J_{\mathrm{SC,SQ}}}{J_{0,\mathrm{SQ}}}\right) \tag{3}$$

where k_{B} is the Boltzmann constant, T is the temperature, $J_{\mathrm{SC,SQ}}$ is the short-circuit current density of the solar cell in the SQ limit, and $J_{0,\mathrm{SQ}}$ is the saturation current density in the SQ limit. As reported previously,[98)] $J_{\mathrm{SC,SQ}}$ and $J_{0,\mathrm{SQ}}$ are given by the following Eqs 4 and 5,

$$J_{\mathrm{SC,SQ}} = q\int_{E_{\mathrm{g}}}^{\infty}\Phi_{\mathrm{sun}}(E)\mathrm{d}E \tag{4}$$

$$J_{0,\mathrm{SQ}} = q\int_{E_{\mathrm{g}}}^{\infty}\Phi_{\mathrm{BB}}(E,300\ \mathrm{K})\mathrm{d}E \tag{5}$$

where $\Phi_{\mathrm{sun}}(E)$ is the solar spectrum and $\Phi_{\mathrm{BB}}(E,T)$ is the black body spectrum at temperature T, which can be simplified to Eq 6.

$$\Phi_{\mathrm{BB}}(E,T) = \frac{2\pi E^2}{h^3c^2}\frac{1}{\left[\exp(E/k_{\mathrm{B}}T)-1\right]} \simeq \frac{2\pi E^2}{h^3c^2}\exp\left(-\frac{E}{k_{\mathrm{B}}T}\right) \tag{6}$$

Here, $\Phi_{\mathrm{sun}}(E)$ is assumed to be $\Phi_{\mathrm{BB}}(E,\ 6000\ \mathrm{K})$. The other energy losses $q\Delta V_{\mathrm{r2}}$ and $q\Delta V_{\mathrm{SC}}$ are given by Eqs 7 and 8, respectively,

$$q\Delta V_{\mathrm{r2}} = k_{\mathrm{B}}T\ln\left(\frac{J_{0,\mathrm{rad}}}{J_{0,\mathrm{SQ}}}\right) \tag{7}$$

$$q\Delta V_{\mathrm{SC}} = k_{\mathrm{B}}T\ln\left(\frac{J_{\mathrm{SC,SQ}}}{J_{\mathrm{SC}}}\right) \tag{8}$$

where $J_{0,\mathrm{rad}}$ is the radiative saturation current density and J_{SC} is the short-circuit current density, which are given by Eqs 9 and 10, respectively.

$$J_{0,\mathrm{rad}} = q\int_{0}^{\infty}\alpha(E)\Phi_{\mathrm{BB}}(E,300\ \mathrm{K})\mathrm{d}E \tag{9}$$

$$J_{\mathrm{SC}} = q\int_{0}^{\infty}\alpha(E)\Phi_{\mathrm{BB}}(E,6000\,\mathrm{K})\mathrm{d}E \tag{10}$$

Next, we consider the radiative energy loss based on E_{CT}, $q\Delta V_{\mathrm{rad}}^{\mathrm{CT}}$: $qV_{\mathrm{OC}} = E_{\mathrm{CT}} - q\Delta V_{\mathrm{rad}}^{\mathrm{CT}} = E_{\mathrm{g}}$

$- \Delta E - q\Delta V_{\mathrm{rad}}^{\mathrm{CT}}$ where ΔE is the difference in energy between E_g and E_{CT}. In this case, the energy loss due to radiation recombination is given by

$$q\Delta V_{\mathrm{rad}}^{\mathrm{CT}} = q\Delta V_{\mathrm{r,CT}} + q\Delta V_{\mathrm{SC}} \tag{11}$$

where $q\Delta V_{\mathrm{r,CT}}$ is the energy loss due to radiative recombination above E_{CT} and $q\Delta V_{\mathrm{SC}}$ is the energy loss due to the current loss because of the small absorptance of less than unity as mentioned above. Again since $q\Delta V_{\mathrm{SC}}$ is negligibly small, $q\Delta V_{\mathrm{rad}}^{\mathrm{CT}}$ can be given by $q\Delta V_{\mathrm{r,CT}}$ as shown in Figure 2d. The energy loss $q\Delta V_{\mathrm{r,CT}}$ is given by $q\Delta V_{\mathrm{r,CT}} = E_{\mathrm{CT}} - qV_{\mathrm{OC,SQ'}}$ with the following Eqs 12–14.

$$qV_{\mathrm{OC,SQ'}} = k_{\mathrm{B}}T \ln\left(\frac{J_{\mathrm{SC,SQ'}}}{J_{\mathrm{0,SQ'}}}\right) \tag{12}$$

$$J_{\mathrm{SC,SQ'}} = q\int_{E_{\mathrm{CT}}}^{\infty} \alpha(E)\Phi_{\mathrm{BB}}(E, 6000\,\mathrm{K})\mathrm{d}E \tag{13}$$

$$J_{\mathrm{0,SQ'}} = q\int_{E_{\mathrm{CT}}}^{\infty} \alpha(E)\Phi_{\mathrm{BB}}(E, 300\,\mathrm{K})\mathrm{d}E \tag{14}$$

Note that $J_{\mathrm{SC,SQ'}}$ is the short-circuit current density of the solar cell and $J_{\mathrm{0,SQ'}}$ is the saturation current density not for the one-step absorptance in the SQ limit but for the two-step absorptance given by Eq 1.

Figure S3a shows radiative energy losses from a bandgap of $E_g = 1.5$ eV evaluated on the basis of the modified SQ theory described above. The light blue bars $q\Delta V_{\mathrm{r1}}$ are the radiative energy loss above E_g, which is as large as 0.26 eV. This is an inevitable energy loss even in the SQ limit. The orange bars $q\Delta V_{\mathrm{r2}}$ are the additional radiative energy loss above E_{CT} and below E_g, which is negligibly small for the small energy difference between E_{CT} and E_g (<0.2 eV) but is linearly increased for the large energy difference between E_{CT} and E_g (>0.2 eV). The gray bars $q\Delta V_{\mathrm{SC}}$ are the energy loss due to the current loss because of the small absorptance of less than unity, which is as small as <0.01 V in this case. When $E_{\mathrm{CT}} = E_g = 1.5$ eV, this model results in the SQ theory, where the absorptance is assumed to be a single-step function, and thus both $q\Delta V_{\mathrm{r2}}$ and $q\Delta V_{\mathrm{SC}}$ are 0 eV. However, in the real devices, $q\Delta V_{\mathrm{r2}}$ should not be 0 eV because of the contribution from the additional absorption of

Urbach tail as described in the next section.

Figure S3b shows radiative energy losses from a CT state energy E_{CT} evaluated on the basis of the modified SQ theory described above. Here, E_g is fixed at 1.5 eV and α_{CT} is assumed to be 10^{-4}. The light blue bars ΔE are the energy difference between E_g and E_{CT}, which is linearly increased with decreasing E_{CT}. The orange bars $q\Delta V_{\mathrm{r,CT}}$ are the radiative energy loss above E_{CT}, which is linearly decreased with decreasing E_{CT}. For the small energy difference between E_{CT} and E_g (<0.2 eV), the sum of ΔE and $q\Delta V_{\mathrm{r,CT}}$ is as large as 0.26 eV, which is almost the same as $q\Delta V_{\mathrm{r}}$. For the large energy difference between E_{CT} and E_g (>0.2 eV), $q\Delta V_{\mathrm{r,CT}}$ is negligibly small and hence ΔE is the dominant energy loss. The gray bars $q\Delta V_{\mathrm{SC}}$ are the energy loss due to the current loss because of the small absorptance of less than unity, which is as small as <0.01 V as mentioned above.

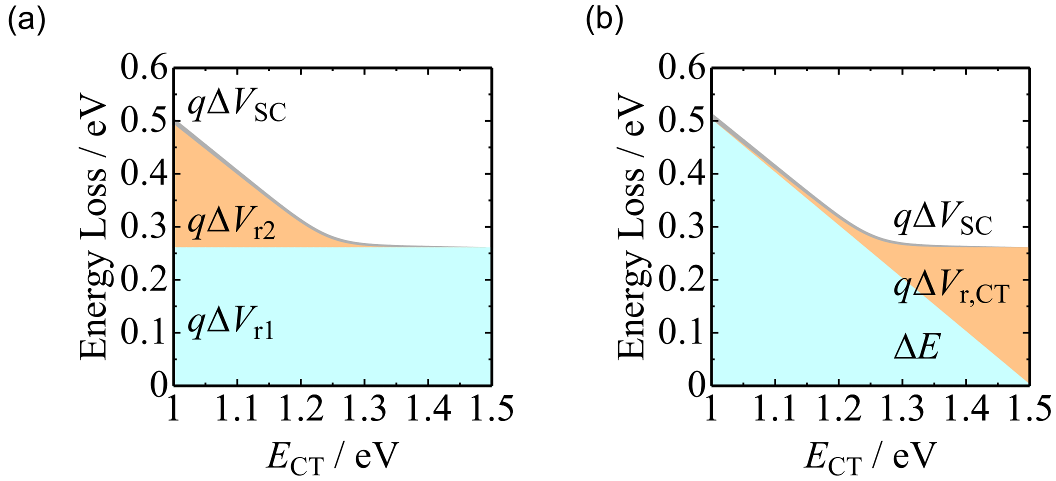

Figure S3. (a) Radiative energy losses from $E_g = 1.5$ eV calculated for the two-step functions with $\alpha_{\mathrm{CT}} = 10^{-4}$: $q\Delta V_{\mathrm{r1}}$ (light blue) is the energy loss due to radiative recombination above E_g, $q\Delta V_{\mathrm{r2}}$ (orange) is the energy loss due to radiative recombination above E_{CT} and below E_g, and $q\Delta V_{\mathrm{SC}}$ (gray) is the energy loss due to the current loss because of the small absorptance of less than unity.
(b) Radiative energy losses from E_{CT} calculated for the two-step functions with $E_g = 1.5$ eV and $\alpha_{\mathrm{CT}} = 10^{-4}$: ΔE (light blue) is the energy difference between E_g and E_{CT}, $q\Delta V_{\mathrm{r,CT}}$ (orange) is the energy loss due to radiative recombination above E_{CT}, and $q\Delta V_{\mathrm{SC}}$ (gray) is the energy loss due to the current loss because of the small absorptance of less than unity.

Energy loss due to Urbach tail

We describe how Urbach tail state impacts on the radiative recombination loss in solar cells on the basis of the modified Shockley–Queisser (SQ) theory. In the SQ theory, as mentioned above, the absorptance $\alpha(E)$ is assumed to be a single-step function, which is $\alpha_0 = 1$ for photon energy E above the bandgap energy E_g and 0 for photon energy E below the bandgap energy E_g. Here, we consider an additional absorption due to Urbach tail as follows:

$$\alpha(E) = \begin{cases} \alpha_0 \exp\left(\dfrac{E - E_\mathrm{g}}{E_\mathrm{U}}\right) & \text{for } E < E_\mathrm{g} \\ \alpha_0 = 1 & \text{for } E > E_\mathrm{g} \end{cases} \tag{15}$$

The energy loss due to the additional Urbach tail $q\Delta V_{\mathrm{r,E_U}}$ is given by

$$q\Delta V_{\mathrm{r,E_U}} = k_\mathrm{B} T \ln\left(\frac{J_{0,\mathrm{rad}}}{J_{0,\mathrm{SQ}}}\right) \tag{16}$$

where the logarithmic term can be calculated with Eqs 5,9, and 15.

Figure S4 shows radiative energy losses due to an additional absorption of Urbach tail ($q\Delta V_{\mathrm{r,E_U}}$) given by Eq 16. As shown in the figure, $q\Delta V_{\mathrm{r,E_U}}$ is as small as 0.06–0.07 eV at E_U = 25 meV (~$k_\mathrm{B}T$) but is steeply increased when E_U exceeds the thermal energy (~25 meV) for all the E_g. Thus, this estimation suggests that it is of particular importance to suppress the Urbach energy to less than the thermal energy (~25 meV) in order to reduce radiative energy losses, specifically $q\Delta V_{\mathrm{r2}}$, in solar cells. Indeed, a recent study has shown small energy losses are accompanied with small Urach energy, which is typically as small as 25–27 meV.[99,100]

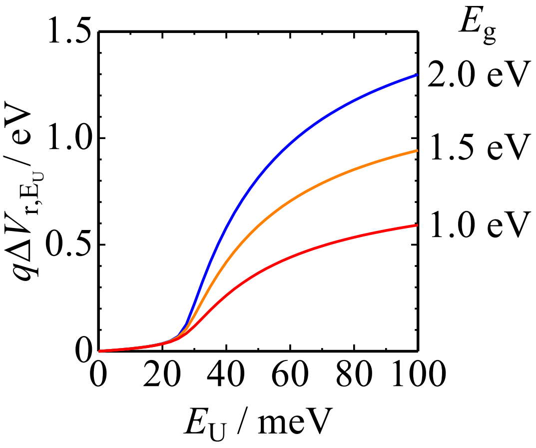

Figure S4. Radiative energy loss due to an additional Urbach tail plotted against Urbach energy E_U with a bandgap energy E_g of 1 eV (red), 1.5 eV (orange), and 2 eV (blue).

Supplementary references

94. N. C. Giebink, G. P. Wiederrecht, M. R. Wasielewski and S. R. Forrest, *Phys. Rev. B*, 2011, **83**, 195326.

95. M. Gruber, J. Wagner, K. Klein, U. Hörmann, A. Opitz, M. Stutzmann and W. Brütting, *Adv. Energy Mater.*, 2012, **2**, 1100–1108.

96. L. J. A. Koster, S. E. Shaheen and J. C. Hummelen, *Adv. Energy Mater.*, 2012, **2**, 1246–1253.

97. R. A. J. Janssen and J. Nelson, *Adv. Mater.*, 2013, **25**, 1847–1858.

98. T. Kirchartz and U. Rau, *Adv. Energy Mater.*, 2018, **8**, 1703385.

99. N. A. Ran, J. A. Love, C. J. Takacs, A. Sadhanala, J. K. Beavers, S. D. Collins, Y. Huang, M. Wang, R. H. Friend, G. C. Bazan and T.-Q. Nguyen, *Adv. Mater.*, 2016, **28**, 1482–1488.

100. S. Liu, J. Yuan, W. Deng, M. Luo, Y. Xie, Q. Liang, Y. Zou, Z. He, H. Wu and Y. Cao, *Nat. Photon.*, 2020, **14**, 300–305.