Electronic Supplementary Information

for

Fragment-LEGO Strategy toward Seven-Ring-Fused Acceptors for Organic Solar Cells

*Yuqian Cai,† Rui Zhu,† Lina Yin, Zhangyuan Wang, and Hongguang Liu**

College of Chemistry and Materials Science, Jinan University, 601 Huang-Pu Avenue West, Guangzhou 510632, China.

† These authors contribute equally to this work.

* E-mail: hongguang_liu@jnu.edu.cn

Computational details

The Generalized Mulliken-Hush model is used to calculate the charge-transfer integral (V_{DA}):[1]

$$V_{DA} = \frac{\mu_{tr}\Delta E}{\sqrt{(\Delta\mu)^2 + 4(\mu_{tr})^2}} \#(S1)$$

where ΔE is the energy difference between the initial state and the final state; μ_{tr} is the transition dipole moment; $\Delta\mu$ denotes the change of dipole moment, which is calculated by using the Hellmann-Feynman theorem.[2]

The total charge reorganization energy (λ) is composed of the internal reorganization energy (λ_{in}) and the external reorganization energy (λ_{ext}):

$$\lambda = \lambda_{in} + \lambda_{ext} \#(S2)$$

λ_{in} refers to the energy change caused by the structural relaxation when an electron is added to or removed from the molecule; λ_{ext} accounts for the energy change induced by the structural relaxation in the surrounding media due to polarization effects. The λ_{in} is calculated using the following equations:[3]

$$\lambda_{in} = \lambda_{in}(A) + \lambda_{in}(D) \#(S3)$$

$$\lambda_{in}(A) = E(A^-) - E(A) \#(S4)$$

$$\lambda_{in}(D) = E(D) - E(D^+) \quad (S5)_{\mathrm{W}}$$

here $\lambda_{in}(A)$ and $\lambda_{in}(D)$ denote the internal reorganization energies for the acceptor and the donor, respectively; $E(A^-)$ and $E(A)$ represent the neutral-state energies of the acceptor at the optimized anionic structure and the optimized neutral structure, respectively; $E(D)$ and $E(D^+)$ represent the cationic-state energies of the donor at the optimized neutral structure and the optimized cationic structure, respectively. It is worthy to note that using quantum mechanical method to compute λ_{ext} is still challenging and λ_{ext} can be best estimated only when the material solid-state structure is available. Therefore, in line with the study carried out by Kuss-Petermann et al. on D-A systems,[4] we treat λ_{ext} as a constant (λ_{ext} = 1.1 eV) in this work.

The change of the Gibbs free energy in the charge recombination process (ΔG_{CR}) can be estimated by the following formula:[5]

$$\Delta G_{CR} = E_{IP}(D) - E_{EA}(A) \#(S6)$$

where $E_{IP}(D)$ is the ionization potential of the donor, and $E_{EA}(A)$ represents the electron affinity of the acceptor. The change of the Gibbs free energy in the charge separation process (ΔG_{CS}) can be calculated by the Rehm-Weller equation:[6]

$$\Delta G_{CS} = -\Delta G_{CR} - E_{S1} - E_b^{DA} \#(S7)$$

where E_{S1} is the first excited state energy of the free donor-based polymer; The exciton binding energy (E_b^{DA}) at the lowest ICT of acceptor is calculated by the following formula:[7]

$$E_b^{DA} = E_{IP} - E_{EA} - E_{opt} \#(S8)$$

where E_{IP} is the ionization potential, E_{EA} is the electron affinity, and E_{opt} is the optical energy gap of a D-A pair.

Table. S1 Experimental and RR-predicted (in parenthesis) parameters for collected 144 binary OSC

Number	Donor	Acceptor	PCE (%)	J_{SC} ($mA.cm^{-2}$)	V_{OC} (V)	FF (%)	Reference
1	PM6	ITIC	10.30 (10.2)	15.60 (16.24)	1.01 (0.97)	66 (64.54)	Adv. Energy Mater. 2018, 8, 1802131
2	PBDBT	ITIC	8.37 (9.64)	15.28 (15.61)	0.85 (0.94)	63 (65.56)	J. Mater. Chem. A 2018, 6, 395-403
3	PBDBT	IO-4F	8.06 (11.46)	12.20 (17.79)	1.05 (0.89)	63 (71.23)	J. Phys. Chem. C 2020, 124, 7691-7698
4	PM6	ITCPTC	12.30 (11.76)	17.10 (17.88)	0.97 (0.94)	74 (70.09)	Energy Environ. Sci. 2018, 11, 3275-3282
5	PM6	ITC-2Cl	13.60 (11.56)	20.10 (17.82)	0.91 (0.94)	74 (68.99)	Adv. Energy Mater. 2019, 9, 1900041
6	PM6	ITC-2Br_2	13.10 (11.48)	19.80 (17.77)	0.90 (0.94)	74 (68.99)	Nano Energy 2019, 66, 104146
7	PM6	MeIC	13.00 (11.61)	18.50 (17.63)	0.99 (0.96)	71 (68.62)	Energy Environ. Sci. 2018, 11, 3275-3282
8	PBDBT	ITCT-DM	10.60 (10.42)	17.40 (16.52)	0.90 (0.92)	65 (67.83)	Adv. Energy Mater. 2018, 8, 1800204
9	PBDBT	IDTC	11.10 (10.68)	16.10 (16.63)	1.00 (0.93)	69 (69.01)	Nanoscale 2020, 12, 12928-12941
10	PM6	ITC-2Br	10.90 (11.11)	15.40 (17.04)	1.03 (0.96)	69 (68.16)	Nano Energy 2019, 66, 104146
11	PM6	ITC-2Brl	11.90 (11.28)	16.60 (17.24)	1.01 (0.96)	71 (68.49)	Nano Energy 2019, 66, 104146
12	PBDBT	IDTTC	13.50	18.30	1.01	73	Nanoscale 2020,

			(11.08)	(17.00)	(0.93)	(69.68)	12, 12928-12941
13	PBDBT	IDTTTC	6.46 (9.91)	14.50 (16.26)	1.03 (0.93)	43 (64.68)	Nanoscale 2020, 12, 12928-12941
14	PM6	ITTBC	6.83 (10.06)	12.50 (16.23)	0.86 (0.93)	63 (66.49)	Dyes Pigm. 2020, 180, 108452
15	PBDBT	IDTTIC	11.20 (9.85)	17.30 (16.08)	0.92 (0.92)	70 (65.98)	Adv. Funct. Mater. 2018, 28, 1802895
16	PM6	POIT-IC	10.10 (10.51)	16.10 (16.79)	1.04 (0.97)	60 (64.18)	Sol. RRL 2019, 3, 1900169
17	PBDBT	ITIC-OE	8.50 (9.4)	14.80 (15.67)	0.85 (0.91)	67 (65.48)	J. Mater. Chem. A 2018, 6, 395-403
18	PBDBT	m-ITIC-O-H	9.55 (9.58)	16.00 (15.87)	0.85 (0.91)	70 (65.98)	Adv. Energy Mater. 2019, 9, 1900044
19	PBDBT	m-ITIC-O-EH	9.77 (9.61)	15.90 (15.85)	0.88 (0.92)	68 (65.65)	Adv. Energy Mater. 2019, 9, 1900044
20	PBDBT	m-F-ITIC	8.98 (9.47)	15.80 (15.83)	0.88 (0.92)	64 (64.98)	J. Mater. Chem. A 2019, 7, 18468-18479
21	PBDBT	o-F-ITIC	11.10 (9.84)	18.10 (16.2)	0.92 (0.92)	67 (65.48)	J. Mater. Chem. A 2019, 7, 18468-18479
22	PBDBT	ITC6-IC	10.90 (9.64)	16.20 (15.61)	0.94 (0.94)	71 (65.56)	J. Mater. Chem. A 2020, 8, 22907-22917
23	PM6	POIT-IC2F	12.40 (11.62)	18.60 (18.03)	0.97 (0.95)	69 (67.86)	Sol. RRL 2019, 3, 1900169
24	PM6	POIT-IC4F	13.80 (12.33)	20.90 (19.15)	0.91 (0.92)	73 (69.85)	Sol. RRL 2019, 3, 1900169
25	PM6	ITThBC	7.59 (9.6)	13.40 (15.95)	0.87 (0.91)	65 (65.92)	Dyes Pigm. 2020, 180, 108452
26	PM6	ITzN-C9	9.51 (10.55)	14.10 (16.74)	1.05 (0.95)	64 (66.63)	Proc. Natl. Acad. Sci. U. S. A. 2018, 115, E8341-E8348
27	PM6	ITzN-F4	10.90 (10.78)	17.50 (17.3)	0.92 (0.93)	68 (67.3)	Adv. Energy Mater. 2020, 10, 2000635.
28	PM6	ITN-C9	9.33 (9.88)	15.70 (16.4)	0.92 (0.93)	65 (65.3)	Proc. Natl. Acad. Sci. U. S. A. 2018, 115, E8341-E8348.
29	PM6	ITN-F4	10.70	19.60	0.82	67	Adv. Energy

			(10.91)	(18.11)	(0.91)	(67.04)	Mater. 2020, 10, 2000635.
30	PBDBT	IDTT-OBH	10.90 (9.86)	17.50 (17.3)	0.87 (0.89)	72 (67.65)	J. Mater. Chem. A 2018, 6, 8586-8594
31	PBDBT	ITC-4F	10.50 (11.12)	18.60 (18.3)	0.78 (0.86)	73 (70.58)	J. Mater. Chem. A 2020, 8, 22907-22917
32	PM6	IM-4F	14.20 (13.29)	22.10 (20.79)	0.88 (0.9)	73 (70.83)	Chem. Mater. 2020, 32, 1297-1307
33	PM6	IOM-4F	13.40 (13.15)	21.70 (20.72)	0.86 (0.9)	72 (70.66)	Chem. Mater. 2020, 32, 1297-1307
34	PM6	SeTIC	7.46 (10.37)	15.50 (17.35)	0.95 (0.94)	51 (64.02)	ACS Energy Lett. 2018, 3, 2967-2976
35	PM6	BDSeIC	7.10 (9.30)	14.00 (15.76)	0.97 (0.94)	52 (62.55)	Sol. RRL 2018, 1800250
36	PBDBT	BPIC	10.70 (9.82)	17.90 (17.03)	0.88 (0.9)	68 (63.99)	Sol. RRL 2019, 3, 1900262
37	PBDBT	BDTIC	12.10 (11.20)	20.00 (18.9)	0.88 (0.89)	68 (66.44)	Chin. J. Polym. Sci. 2021, 39, 35-42
38	PBDBT	DBTIC	9.66 (9.98)	15.50 (16.87)	1.00 (0.94)	62 (63)	J. Mater. Chem. A 2019, 7, 9609-9617
39	PBDBT	Y1	13.40 (11.97)	22.40 (20.2)	0.87 (0.9)	69 (65.95)	Nat. Commun. 2019, 10, 570
40	PBDBT	Y16	13.00 (11.63)	21.30 (20.53)	0.91 (0.87)	67 (65.3)	J. Mater. Chem. A 2019, 7, 7843-7851
41	PBDBT	Y9	13.30 (12.67)	23.30 (21.77)	0.90 (0.88)	63 (65.57)	. J. Energy Chem. 2020, 42, 169-173
42	PBDBT	Y5	14.10 (12.38)	22.80 (20.91)	0.88 (0.87)	70 (67.12)	Adv. Mater. 2019, 31, 1807577
43	PM6	BTP	8.85 (13.18)	16.30 (22.04)	0.96 (0.91)	57 (65.13)	Appl. Mater. Interfaces 2020, 12, 50541-50549
44	PM6	Y6	14.87 (15.00)	24.91 (24.4)	0.84 (0.86)	71 (70.8)	Appl. Mater. Interfaces 2020, 12, 50541-50549
45	PM6	Y6-C3	13.80 (14.20)	24.10 (23.63)	0.83 (0.84)	67 (70.36)	Sci. China: Chem. 2020, 63, 361-369

46	PM6	BTP-PhC6	11.10 (13.92)	21.30 (23.2)	0.84 (0.86)	62 (69.44)	Org. Electron. 2020, 87, 105963
47	PM6	DTY6	16.30 (14.79)	25.30 (23.87)	0.86 (0.86)	75 (71.6)	Joule 2020, 4, 2004-2016
48	PM6	BTPD-4F	16.20 (14.74)	24.80 (23.96)	0.82 (0.84)	76 (71.54)	J. Mater. Chem. A 2020, 8, 23239-23247
49	PM6	BTP-PhC6	16.70 (14.98)	25.00 (23.98)	0.87 (0.86)	77 (72.28)	Nano Energy 2020, 76, 105087
50	PM6	BTP-C6Ph	15.50 (14.78)	24.30 (23.86)	0.84 (0.85)	76 (72.12)	Nano Energy 2020, 76, 105087
51	PM6	N-C1BTP-C12-4Cl	12.90 (14.02)	21.50 (22.81)	0.85 (0.85)	71 (71.74)	Joule 2019, 3, 3020-3033
52	PM6	BTP-Cl	16.50 (14.70)	25.40 (24.33)	0.87 (0.85)	75 (70.72)	Nat. Commun. 2019, 10, 2515
53	PM6	BTIC-Cl2-Cl	11.40 (13.72)	19.80 (22.9)	0.84 (0.85)	68 (70.37)	J. Mater. Chem. A 2020, 8, 8903-8912
54	PM6	BTPS-4Cl	13.50 (14.44)	24.00 (23.9)	0.8 (0.83)	68 (71.46)	J. Mater. Chem. A 2020, 8, 23239-23247
55	PM6	BT_6IC-BO-4Cl	14.40 (14.61)	23.60 (23.99)	0.84 (0.83)	73 (73.05)	ACS Appl. Mater. Interfaces 2020, 12, 28329-28336
56	PM6	BT_6IC-HD-4Cl	14.90 (14.37)	23.40 (23.43)	0.88 (0.84)	73 (72.72)	ACS Appl. Mater. Interfaces 2020, 12, 28329-28336
57	PM6	BT_6IC-OD-4Cl	9.60 (12.56)	18.60 (21.67)	0.89 (0.84)	58 (68.48)	ACS Appl. Mater. Interfaces 2020, 12, 28329-28336
58	PM6	BTIC-4Br	12.20 (13.79)	20.70 (23.27)	0.85 (0.86)	70 (68.64)	Adv. Sci. 2020, 7, 1903784
59	PM6	BTPC-BO-4Br	14.00 (14.74)	24.10 (24.17)	0.86 (0.86)	68 (71.23)	Adv. Sci. 2020, 7, 1903784.
60	PM6	BTPOC-2Br-5	14.00 (14.11)	22.90 (23.12)	0.90 (0.89)	68 (68.49)	J. Mater. Chem. A 2020, 8, 25101-25108
61	PM6	BTPOC-2Br-6	15.00 (14.28)	24.10 (23.32)	0.87 (0.88)	71 (68.99)	J. Mater. Chem. A 2020, 8, 25101-25108
62	PM6	LY-Cl-1	14.40 (13.70)	24.30 (22.73)	0.91 (0.89)	65 (67.45)	Energy Environ. Sci. 2020, 13, 5028-5038
63	PM6	LY-Cl-2	15.20	24.20	0.88	71	Energy Environ.

			(14.49)	(23.68)	(0.88)	(69.58)	Sci. 2020, 13, 5028-5038
64	PM6	BTP-ClBr	16.80 (15.37)	23.50 (23.97)	0.91 (0.89)	79 (72.48)	Adv. Energy Mater. 2020, 10, 2002649
65	PM6	BTP-ClBr2	15.50 (15.15)	25.00 (24.22)	0.85 (0.88)	74 (71.65)	Adv. Energy Mater. 2020, 10, 2002649
66	PM6	BTP-IS	12.80 (13.04)	22.60 (22.03)	0.89 (0.87)	64 (67.08)	Appl. Mater. Interfaces 2020, 12, 49659-49665
67	PM6	Y6-2Se	14.60 (14.63)	24.30 (23.86)	0.83 (0.85)	70 (71.12)	J. Mater. Chem. A 2020, 8, 23756-23765
68	PM6	Y1-4F	13.24 (14.35)	24.10 (23.19)	0.81 (0.88)	66 (70.6)	Adv. Mater. 2019, 31, 1904215
69	PM6	Y18	16.02 (14.01)	24.91 (23.52)	0.84 (0.85)	76 (69.95)	Energy Environ. Sci. 2020, 13, 2459-2466
70	PBDBT	Y18-DMO	14.20 (13.15)	24.00 (22.39)	0.81 (0.81)	73 (71.41)	ACS Appl. Energy Mater. 2020, 3, 11981-11991
71	PM6	Y19	12.80 (13.71)	22.40 (23.45)	0.84 (0.83)	68 (69.87)	J. Cent. South Univ. 2020, 27, 3581-3593
72	PM6	Y15	14.10 (14.75)	23.80 (24.69)	0.88 (0.85)	69 (70.13)	Chin. Chem. Lett. 2019, 30, 2343-2346
73	PBDBT	Y2	13.40 (13.53)	23.60 (21.84)	0.82 (0.87)	69 (71.51)	Nat. Commun. 2019, 10, 570
74	PM6	AQx-2	16.60 (14.65)	25.40 (23.51)	0.86 (0.88)	76 (70.59)	Adv. Mater. 2020, 32, 1906324
75	PM6	AQx-1	13.30 (14.10)	22.20 (22.98)	0.89 (0.88)	67 (69.09)	Adv. Mater. 2020, 32, 1906324
76	PM6	BP-4F	13.90 (12.59)	21.60 (20.24)	0.90 (0.89)	72 (69.7)	J. Mater. Chem. A 2019, 7, 24366-24373
77	PM6	HBDT-4Cl	10.40 (11.79)	17.80 (19.58)	0.90 (0.88)	65 (69.4)	J. Mater. Chem. A 2019, 7, 20274-20284
78	PM6	FBDT-4Cl	12.40 (12.09)	19.80 (19.88)	0.89 (0.87)	70 (69.3)	J. Mater. Chem. A 2019, 7, 20274-20284
79	PM6	ClBDT-4Cl	11.70	19.00	0.88	70	J. Mater. Chem. A

			(11.97)	(19.75)	(0.87)	(69.3)	2019, 7, 20274-20284
80	PM6	DPBT-4Cl	11.40 (11.9)	19.20 (19.95)	0.90 (0.87)	66 (68.55)	Nano Energy 2020, 67, 104209
81	PM6	NCBDT-4Cl	12.00 (12.02)	20.10 (19.93)	0.83 (0.86)	72 (69.63)	J. Mater. Chem. C 2020, 8, 15135-15141
82	PM6	POBDT-4Cl	12.60 (12.12)	21.00 (20.08)	0.88 (0.87)	68 (68.97)	Nano Energy 2020, 67, 104209
83	PM6	COBDT-4Cl	13.50 (12.27)	21.8 (20.22)	0.87 (0.87)	71 (69.47)	Nano Energy 2020, 67, 104209
84	PM6	TOBDT	11.30 (11.9)	18.70 (19.7)	0.89 (0.87)	68 (68.97)	Adv. Funct. Mater. 2020, 30, 1909535
85	PBDBT	BPIC-2Cl	12.20 (11.13)	20.70 (18.67)	0.81 (0.91)	72 (68.44)	Sol. RRL 2019, 3, 1900262
86	PM6	BDT_cIC-γCl	7.61 (10.46)	13.80 (17.55)	0.89 (0.89)	62 (65.24)	Mater. Chem. Front. 2021, 5, 1486-1494
87	PBDBT	BTTIC-0M	11.90 (11.45)	19.00 (18.29)	0.86 (0.91)	73 (70.39)	J. Mater. Chem. A 2019, 7, 6809-6817
88	PM6	BDTSF-IC	13.10 (12.24)	20.40 (19.44)	0.90 (0.90)	72 (69.61)	Sol. RRL 2020, 4, 2000071
89	PBDBT	BTTIC-2M	13.20 (11.3)	19.40 (18.05)	0.90 (0.90)	75 (68.92)	J. Mater. Chem. A 2019, 7, 6809-6817
90	PBDBT	BTTIC-4M	9.60 (10.67)	15.70 (17.58)	0.97 (0.90)	64 (67.1)	J. Mater. Chem. A 2019, 7, 6809-6817
91	PBDBT	BTTIC-TT	13.40 (11.7)	19.60 (18.57)	0.92 (0.89)	74 (69.57)	Adv. Funct. Mater. 2019, 29, 1902155
92	PBDBT	BTTIC-Ph	9.14 (11.23)	16.50 (18.41)	0.93 (0.89)	60 (68.07)	Adv. Funct. Mater. 2019, 29, 1902155
93	PBDBT	TOIC	11.00 (11.58)	18.60 (18.64)	0.86 (0.87)	68 (69.69)	Adv. Funct. Mater. 2018, 28, 1803128
94	PBDBT	TOIPC	9.31 (10.82)	15.20 (17.85)	0.88 (0.88)	70 (69.22)	J. Mater. Chem. C 2019, 7, 10111-10118
95	PM6	M36	16.00 (14.17)	24.60 (22.61)	0.90 (0.87)	72 (70.85)	Natl. Sci. Rev. 2020, 7, 1886-

							1895
96	PM6	M38	8.89 (11.82)	18.30 (20.34)	0.87 (0.88)	56 (65.62)	Natl. Sci. Rev. 2020, 7, 1886-1895
97	PM6	M4	14.80 (13.90)	23.40 (22.24)	0.88 (0.83)	72 (70.58)	J. Mater. Chem. A 2020, 8, 24543-24552
98	PBDBT	SRID-4F	13.10 (12.09)	20.20 (19.6)	0.85 (0.85)	75 (73.04)	Chem. Mater. 2019, 31, 6770-6778
99	PBDBT	TRID-4F	12.30 (11.63)	18.50 (19.08)	0.89 (0.85)	75 (70.72)	Chem. Mater. 2019, 31, 6770-6778
100	PM6	TSeIC-4Cl	11.10 (12.35)	20.90 (20.16)	0.74 (0.86)	72 (71.93)	Sol. RRL 2020, 4, 2000212
101	PM6	TSeIC-4Br	11.90 (11.44)	21.30 (10.1)	0.77 (0.87)	72 (69.86)	Sol. RRL 2020, 4, 2000212
102	PM6	SeTIC4Cl	13.30 (11.89)	22.90 (19.64)	0.78 (0.89)	75 (69.61)	ACS Energy Lett. 2018, 3, 2967-2976
103	PM6	TSeTIC	13.70 (12.40)	19.40 (19.51)	0.93 (0.89)	76 (71.9)	J. Mater. Chem. A 2019, 7, 24389-24399
104	PM6	BDSeIC4Br	9.60 (9.91)	16.40 (16.98)	0.85 (0.83)	69 (66.06)	Sol. RRL 2018, 1800250
105	PBDBT	ArSiID-F	9.40 (10.82)	16.80 (18.79)	0.84 (0.85)	65 (66.96)	ACS Appl. Mater. Interfaces 2019, 11, 1125-1134
106	PBDBT	ArSiID-Cl	7.90 (10.52)	16.40 (18.73)	0.79 (0.85)	60 (66.88)	ACS Appl. Mater. Interfaces 2019, 11, 1125-1134
107	PM6	BTP-OE	16.27 (14.78)	27.27 (24.2)	0.81 (0.86)	74 (71.42)	Small, 2023, 19(30): 2302314
108	PM6	Y6BO	17.44 (15.95)	26.93 (25.29)	0.83 (0.87)	79 (73.4)	Small, 2023, 19(30): 2302314
109	PM6	BTP-eC9	19.31 (15.96)	27.88 (25.15)	0.86 (0.89)	80 (74.94)	Nat. Commun. 14, 1760 (2023)
110	PM6	mPh4F-TT	16.46 (15.73)	25.00 (24.73)	0.87 (0.85)	76 (74.28)	Angew. Chem. Int. Ed 2022, 134(46): e202206930
111	PM6	mPh4F-ST	17.30 (15.87)	26.83 (25.03)	0.83 (0.84)	78 (74.61)	Angew. Chem. Int. Ed 2022, 134(46):

							e202206930
112	PM6	mPh4F-TS	17.70 (15.94)	27.93 (25.12)	0.82 (0.84)	78 (74.61)	Angew. Chem. Int. Ed 2022, 134(46): e202206930
113	PM6	BTPIC-4EO-4F	10.64 (13.16)	20.01 (22.39)	0.77 (0.83)	69 (70.1)	ACS Appl. Mater. Interfaces 2021, 13, 5, 6147-6155
114	PM6	BTPIC-4EO-4Cl	11.29 (12.87)	20.59 (22.32)	0.78 (0.82)	70 (70.01)	ACS Appl. Mater. Interfaces 2021, 13, 5, 6147-6155
115	PM6	BTPIC-4EO-4Br	12.41 (11.96)	22.78 (21.26)	0.84 (0.83)	65 (67.94)	ACS Appl. Mater. Interfaces 2021, 13, 5, 6147-6155
116	PM6	YCF3	18.21 (14.92)	27.56 (23.87)	0.86 (0.88)	77 (70.72)	ACS Energy Lett. 2023, 8, 1, 96–106
117	PM6	YCH3	15.53 (14.47)	25.45 (23.52)	0.87 (0.88)	70 (69.59)	ACS Energy Lett. 2023, 8, 1, 96–106
118	PM6	CH-6F	16.77 (15.66)	25.31 (24.17)	0.87 (0.88)	76 (73.09)	Energy Environ. Sci. 2022, 15(8): 3519-3533
119	PM6	CH-4Cl	17.72 (15.36)	26.50 (24.11)	0.87 (0.87)	77 (73.01)	Energy Environ. Sci. 2022, 15(8): 3519-3533
120	PM6	CH-Cl	17.22 (15.36)	26.07 (23.85)	0.87 (0.87)	76 (72.45)	Energy Environ. Sci. 2022, 15(8): 3519-3533
121	PM6	Y6-sch	14.19 (14.44)	22.76 (23.45)	0.84 (0.86)	74 (71.44)	Org. Electron 2023, 114: 10673
122	PM6	Y11	15.27 (15.04)	24.62 (23.75)	0.84 (0.86)	73 (70.22)	Sci. China Chem. 2020, 63: 1159-1168
123	PM6	BT-BO-LIC	9.28 (14.20)	18.41 (23.2)	0.90 (0.88)	56 (69.33)	Adv. Energy Mater. 2022, 12(1): 2102172
124	PM6	BT-BO-L4F	16.17 (15.23)	27.62 (24.91)	0.83 (0.86)	71 (71.06)	Adv. Energy Mater. 2022, 12(1): 2102172
125	PM6	SYSS-Cl	16.73 (15.65)	25.85 (25.23)	0.86 (0.84)	75 (73.31)	Angew. Chem. Int. Ed 2021, 133(35): 19390-19401
126	PM6	S-WSeSe-Cl	16.01 (15.41)	26.35 (24.9)	0.83 (0.83)	73 (73.78)	Angew. Chem. Int. Ed 2021,

							133(35): 19390-19401
127	PM6	Y6-4Cl	16.06 (14.50)	25.85 (23.91)	0.84 (0.85)	74 (71.38)	Mater. Chem. Front. 2020, 4(8): 2428-243
128	PM6	N3-4Cl	16.53 (13.90)	25.90 (23.56)	0.85 (0.83)	75 (70.28)	Mater. Chem. Front 2020, 4(8): 2428-243
129	PM6	TPQx-4F	6.78 (13.01)	13.50 (21.53)	0.95 (0.89)	53 (66.67)	Mater. Chem. Front 2020, 4(11): 3310-3318
130	PM6	TPQx-6F	12.10 (13.90)	20.36 (22.67)	0.92 (0.89)	64 (68.55)	Mater. Chem. Front 2020, 4(11): 3310-3318
131	PM6	M3	14.40 (13.41)	22.40 (21.59)	0.89 (0.87)	72 (70.74)	New J Chem. 2024, 48(9): 3974-3983
132	PM6	POR-1N	9.55 (10.30)	15.38 (17.07)	1.07 (0.98)	58 (61.08)	J. Mater. Chem. C 2022, 10(6): 1977-198
133	PM6	POR-2F	15.18 (12.12)	21.25 (19.42)	0.97 (0.93)	73 (66.76)	J. Mater. Chem. C 2022, 10(6): 1977-198
134	PM6	ITOR-IC	9.51 (9.93)	15.41 (16.21)	0.99 (0.96)	62 (63.68)	Sol. Energy 2022, 236: 206-214
135	PM6	ITOR4F-IC	8.09 (9.8)	13.98 (16.06)	0.96 (0.96)	60 (63.48)	Sol. Energy 2022, 236: 206-214
136	PM6	ITOR-IC4F	11.10 (11.75)	18.05 (18.56)	0.90 (0.91)	68 (69.36)	Sol. Energy 2022, 236: 206-214
137	PBDBT	F-2Cl	10.31 (10.72)	18.92 (18.73)	0.74 (0.84)	73 (68.12)	ACS Appl. Mater. Interfaces 2021, 13, 34, 40766-40777
138	PM6	BDTBO-4F	14.83 (13.85)	23.03 (22.26)	0.86 (0.87)	75 (71.35)	ACS Appl. Mater. Interfaces 2020, 12, 46, 51776-51784
139	PM6	BDTBP-4Cl	13.87 (13.55)	23.59 (22.19)	0.83 (0.85)	71 (71.27)	ACS Appl. Mater. Interfaces 2020, 12, 46, 51776-51784
140	PBDBT	IDTTA	10.90 (10.64)	14.90 (16.38)	0.98 (0.92)	69 (68.74)	J. Mater. Chem. A 2020, 8: 1164-1175

141	PBDBT	DTCFO-ICF	6.80 (9.89)	15.52 (17.68)	0.81 (0.87)	54 (63.54)	J. Mater. Chem. C 2021, 9: 3295-3306
142	PBDBT	DTCFO-ICCI	8.55 (9.59)	16.69 (17.62)	0.77 (0.85)	67 (63.45)	J. Mater. Chem. C 2021, 9: 3295-3306
143	PM6	DTCFO-ICF	7.67 (10.45)	15.44 (18.31)	0.99 (0.9)	50 (62.52)	J. Mater. Chem. C 2021, 9: 3295-3306
144	PM6	DTCFO-ICCI	11.03 (10.15)	18.80 (18.25)	0.93 (0.88)	63 (62.43)	J. Mater. Chem. C 2021, 9: 3295-3306

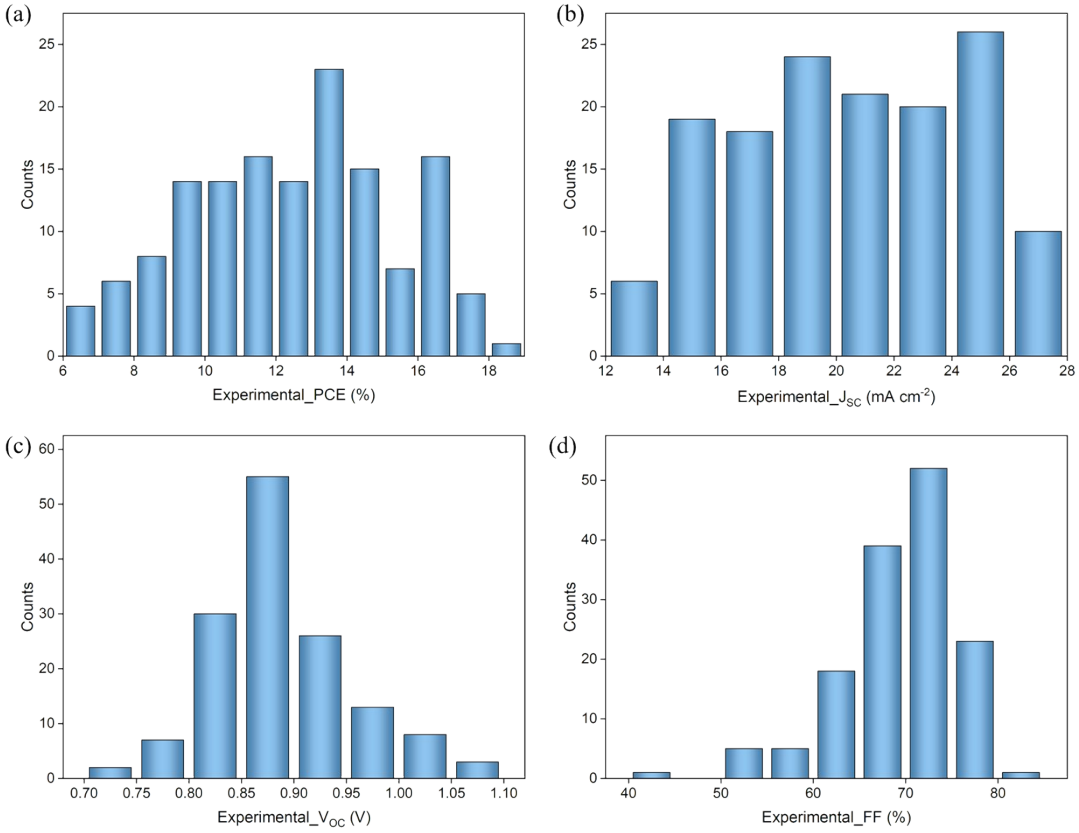


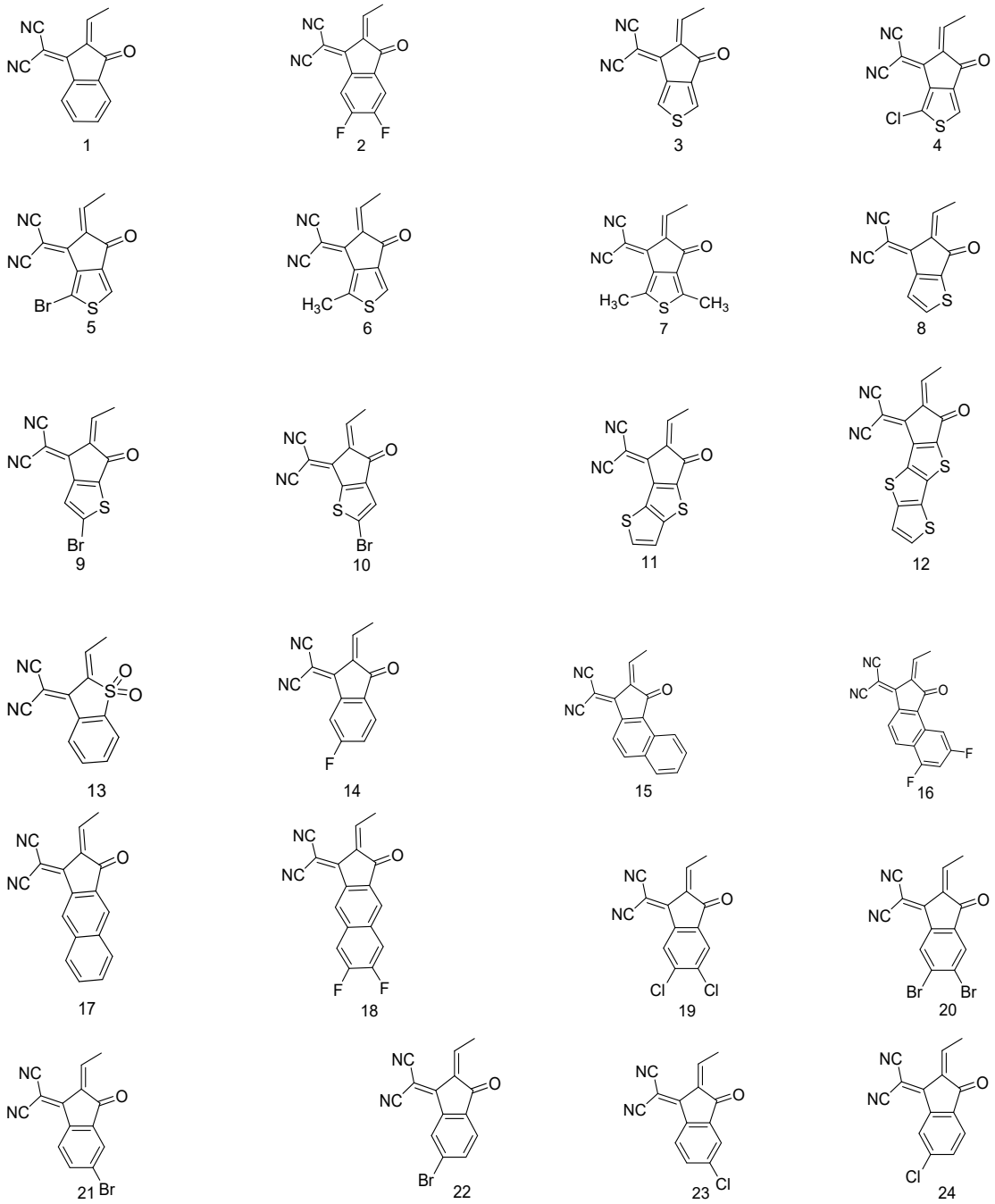
Fig. S1 Data distribution of experimental (a) PCE, (b) J_{SC}, (c) V_{OC} and (d) FF in the original dataset.

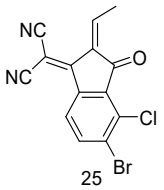
The range (average) of PCE, J_{SC}, V_{OC} and FF are 6.46% ~ 19.31% (12.47%), 12.20 mA.cm^{-2} ~ 27.88 mA.cm^{-2} (20.40 mA.cm^{-2}), 0.74 V ~ 1.07 V (0.88 V) and 43% ~ 80%

(68.87%), respectively.

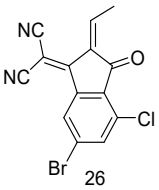
Diagram. S1 Labelled fragments of acceptors in sorted Unit 1/2/3/4 according to the dividing scheme in Fig. 2.

Fragments (28) in Unit 1

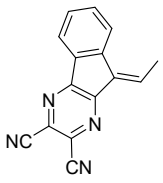




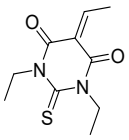
25



26

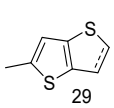


27

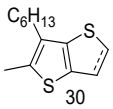


28

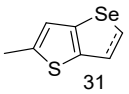
Fragments (25) in Unit 2



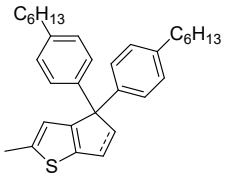
29



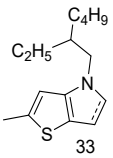
30



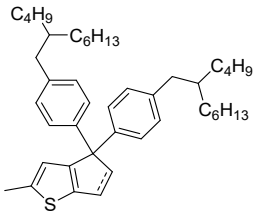
31



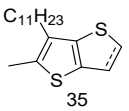
32



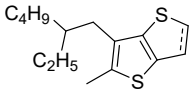
33



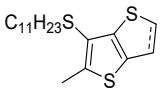
34



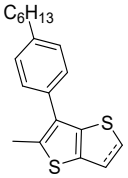
35



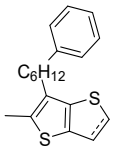
36



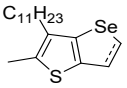
37



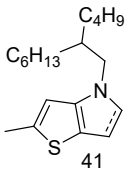
38



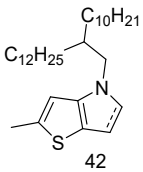
39



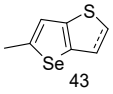
40



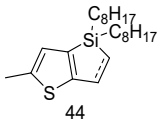
41



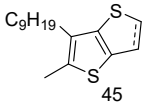
42



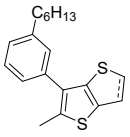
43



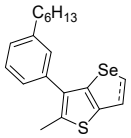
44



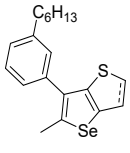
45



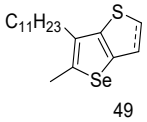
46



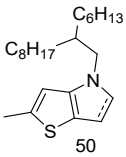
47



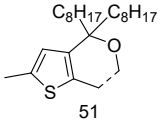
48



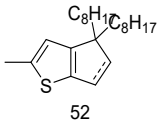
49



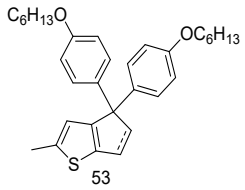
50



51

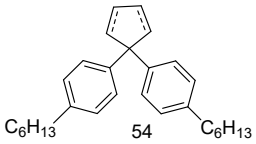


52

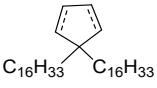


53

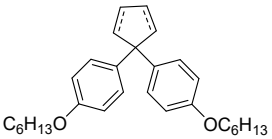
Fragments (30) in Unit 3



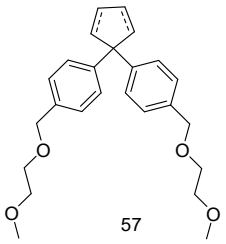
54



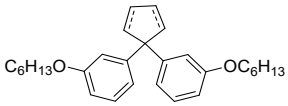
55



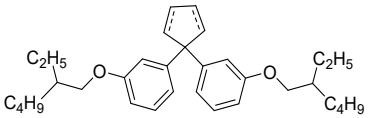
56



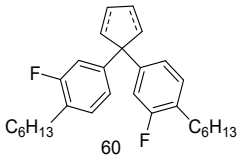
57



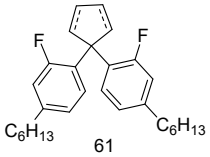
58



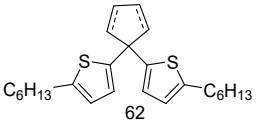
59



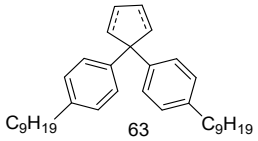
60



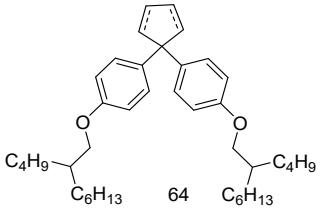
61



62



63

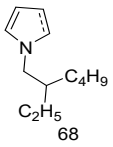


64

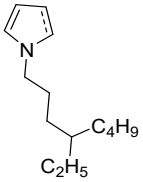
65

66

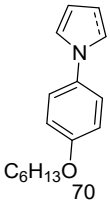

67



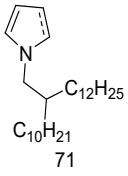
68



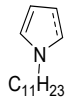
69



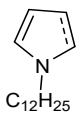
70



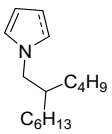
71



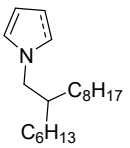
72



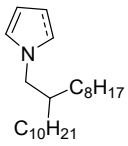
73



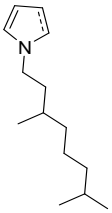
74



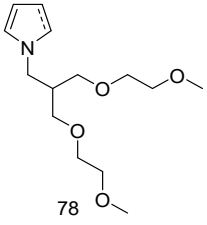
75



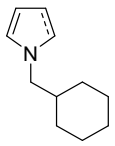
76



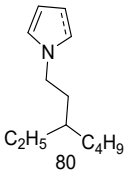
77



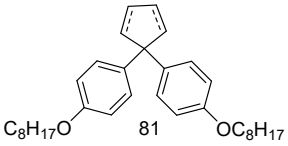
78



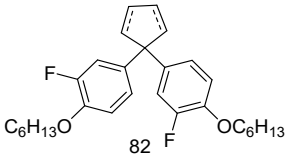
79



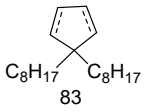
80



81



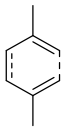
82



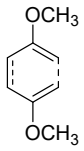
83

Fragments (31) in Unit 4

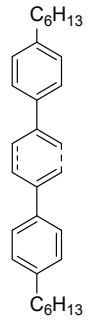
84



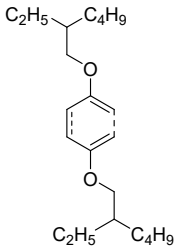
85



86

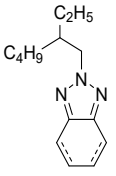


87

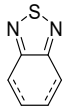


88

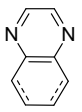
89



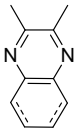
90



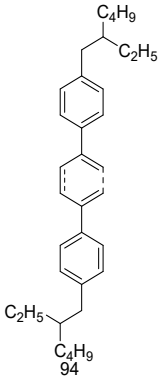
91



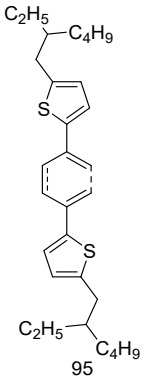
92



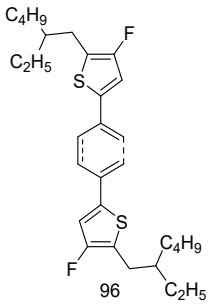
93

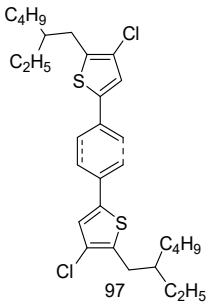


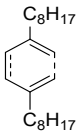
94

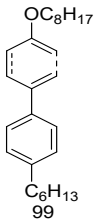


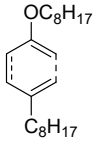
95

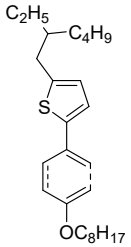

96

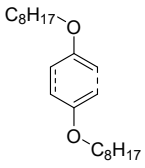

97

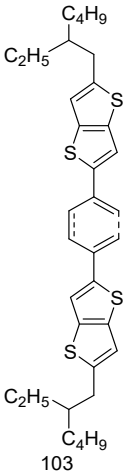

98

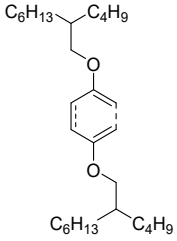

99

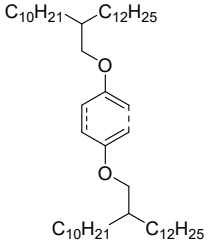

100

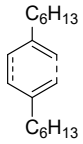

101

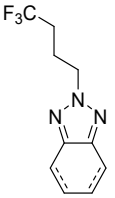

102

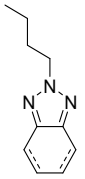

103

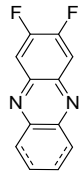

104

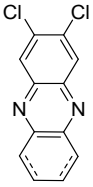

105

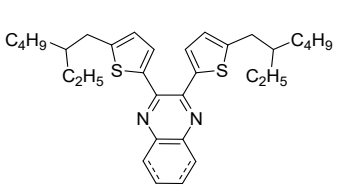

106

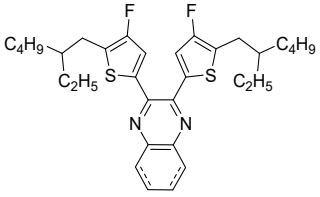

107

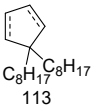

108

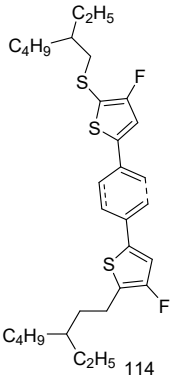

109


110


111


112


113


114

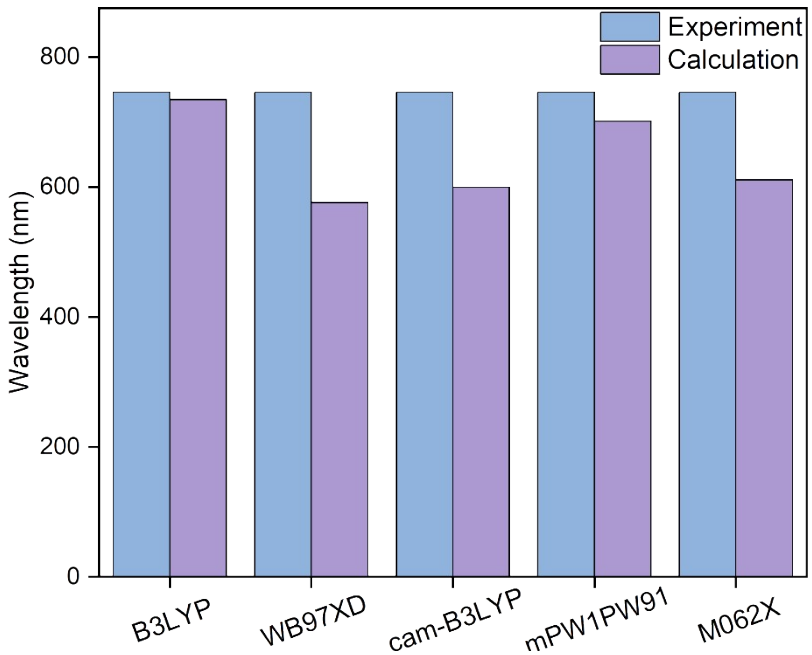
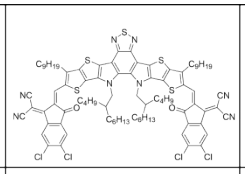
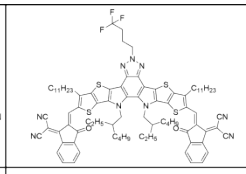
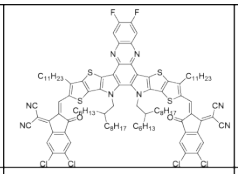
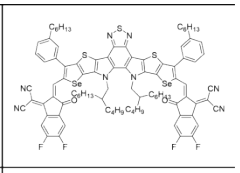
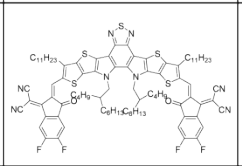
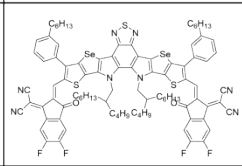
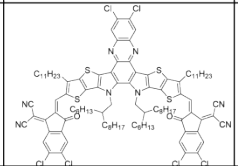
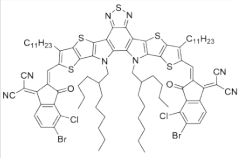
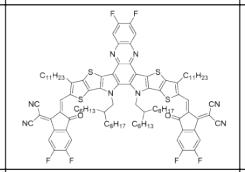
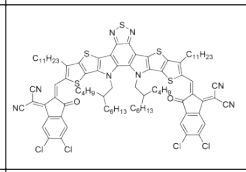
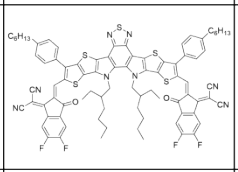
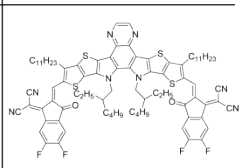
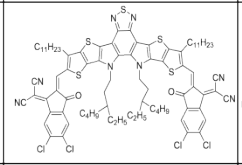
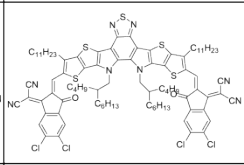
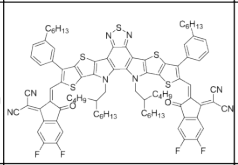
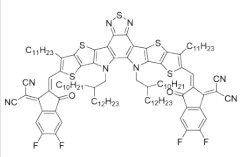
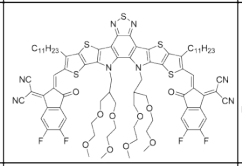
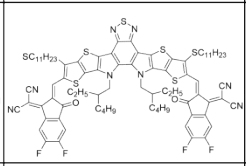
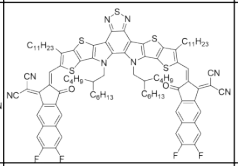
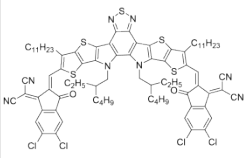
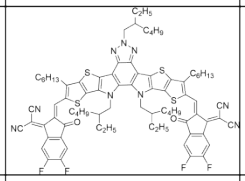
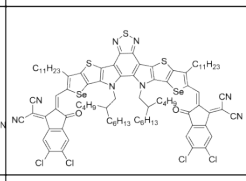
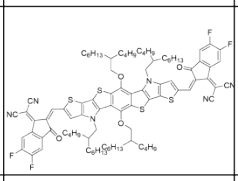
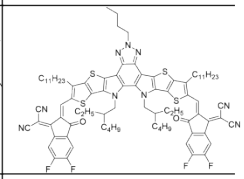
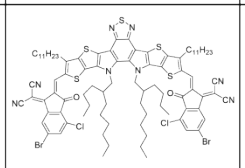
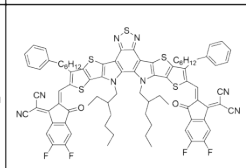
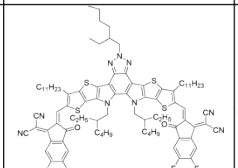
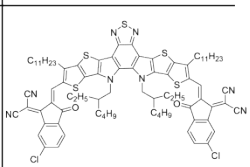
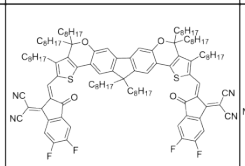
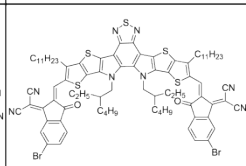
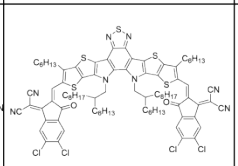


Fig. S2 Maximum absorption wavelength of A7 molecule computed at five standard exchange-correlation functionals with the 6-31G(d,p) basis set.

Table. S2 RR model underestimates the top 20% experimental PCE (in parenthesis) in the original dataset. Note that the donor paired with the acceptor is PM6.

Acceptor				
Predicted PCE (%)	**15.96 (19.31)**	**14.92 (18.21)**	**15.36 (17.72)**	**15.94 (17.7)**
Acceptor				
Predicted PCE (%)	**15.95 (17.44)**	**15.87 (17.3)**	**15.1 (17.22)**	**15.37 (16.8)**
Acceptor				
Predicted PCE (%)	**16.39 (16.77)**	**15.91 (16.73)**	**14.98 (16.7)**	**14.65 (16.6)**
Acceptor				
Predicted PCE (%)	**13.92 (16.53)**	**14.7 (16.5)**	**15.73 (16.46)**	**14.79 (16.3)**
Acceptor				
Predicted PCE (%)	**14.78 (16.27)**	**14.74 (16.2)**	**15.23 (16.17)**	**14.5 (16.06)**
Acceptor				
Predicted PCE (%)	**14.01 (16.02)**	**15.41 (16.01)**	**14.17 (16)**	**14.47 (15.53)**
Acceptor				
Predicted PCE (%)	**14.78 (15.5)**	**15.15 (15.5)**	**15.04 (15.27)**	**14.49 (15.2)**
Acceptor				
Predicted PCE (%)	**12.12 (15.18)**	**14.28 (15)**	**14.37 (14.9)**	

Reference

1. P. Song, Y. Li, F. Ma, T. Pullerits and M. Sun, Chem. Rec., 2016,**16**, 734-753.

2. E. M. Kadilenko and R. Grinis, J. Phys. Chem. A., 2025, **129**, 6694-6702.

3. M. E. Köse, W. J. Mitchell, N. Kopidakis, C. H. Chang, S. E. Shaheen, K. Kim and G. Rumbles, J. Am. Chem. Soc., 2007, **129**, 14257-14270.

4. M. Kuss-Petermann and O. S. Wenger, J. Am. Chem. Soc., 2016, **138**, 1349-1358.

5. T. Caronna, S. Morrocchi and B. M. Vittimberga, J. Am. Chem. Soc., 1986, **108**, 2205-2208.

6. X. Zhang, L. Chi, S. Ji, Y. Wu, P. Song, K. Khan, H. Guo, T. D. James and J. Zhao, J. Am. Chem. Soc., 2009, **131**, 17452-17463.

7. Q. Lu, M. Qiu, M. Zhao, Z. Li and Y. Li, Polymers., 2019, **11**, 958.