Supporting Information

Expert-assisted and sub-unit-based molecular description enabling accurate prediction of the energy levels of non-fullerene acceptors in organic solar cells.

This supporting information presents the following contents.

Table S1. Examples of differences between DFT calculated and CV measured energy levels.

Material	$LUMO_{(DFT)}$	$LUMO_{(CV)}$	ΔEv(LUMO)	$HOMO_{(DFT)}$	$HOMO_{(CV)}$	ΔEv(HOMO)
ITIC[1]	-3.41	-4.02	0.61	-5.55	-5.61	0.06
IT-M[1]	-3.35	-3.98	0.63	-5.5	-5.58	0.08
IT-DM[1]	-3.29	-3.93	0.64	-5.45	-5.56	0.11
Y6[2]	-3.52	-4.07	0.55	-5.55	-5.74	0.19
L8-BO[2]	-3.49	-3.9	0.41	-5.53	-5.68	0.15
L8-OD[2]	-3.49	-3.91	0.42	-5.55	-5.71	0.16
L8-HD[2]	-3.5	-3.9	0.4	-5.54	-5.71	0.17
DTPC-IC[3]	-3.29	-3.97	0.68	-5.03	-5.21	0.18
DTPC-DFIC[3]	-3.44	-4.1	0.66	-5.14	-5.31	0.17
		average	0.56		average	0.14

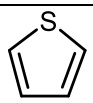
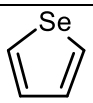
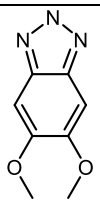
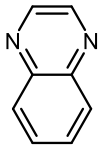
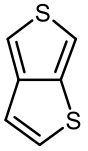
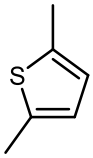
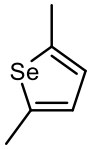
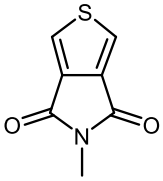
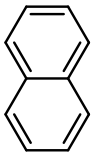
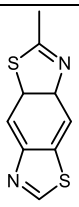
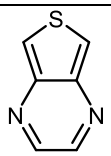
Table S2. Variation of CV measured energy level between different research groups for the same material.

Material/Y6	Ref. [2]	Ref. [4]	Ref. [5]	Ref. [6]	Max - Min	SD
$LUMO_{(CV)}$	-4.07	-4.04	-4.08	-3.89	0.19	0.088
$HOMO_{(CV)}$	-5.74	-5.56	-5.70	-5.71	0.18	0.080
Material/PM6	Ref. [7]	Ref. [2]	Ref. [8]	Ref. [9]	Max - Min	SD
$LUMO_{(CV)}$	-3.64	-3.47	-3.68	-3.60	0.21	0.091
$HOMO_{(CV)}$	-5.74	-5.56	-5.70	-5.71	0.18	0.080

Table S3. Variation of Voc and bandgap of Y6 measured between different research groups for the same active layer composition.

Active Layer/ PM6:Y6	Ref. [2]	Ref. [4]	Ref. [5]	Ref. [6]	Ref. [7]	Ref. [8]	Ref. [9]	Max - Min	SD
Voc	0.84	0.82	0.86	0.82	0.84	0.85	0.82	0.04	0.015
Y6 Bandgap	1.33	1.35	1.33	1.33	1.33	1.32	1.35	0.03	0.010

Table S4. Computed HOMO/LUMO energy values for common aromatic building blocks used in non-fullerene acceptors of organic solar cells.

	**LUMO: -0.23** **HOMO: -6.35**		**LUMO: -0.35** **HOMO: -6.32**
	**LUMO: 0.51** **HOMO: -6.12**		**LUMO: -3.68** **HOMO: -6.78**
	**LUMO: 0.07** **HOMO: -6.72**		**LUMO: -3.27** **HOMO: -5.90**
	**LUMO: -0.38** **HOMO: -5.14**		**LUMO: -2.35** **HOMO: -6.62**
	**LUMO: -1.88** **HOMO: -7.34**		**LUMO: -1.33** **HOMO: -6.06**
	**LUMO: -1.93** **HOMO: -6.70**		**LUMO: -0.90** **HOMO: -5.57**
	**LUMO: 3.90** **HOMO: -8.32**		**LUMO: -0.16** **HOMO: -5.76**
	**LUMO: -2.08** **HOMO: -7.09**		**LUMO: -0.98** **HOMO: -5.80**
	**LUMO: -2.44** **HOMO: -6.47**		**LUMO: -1.81** **HOMO: -5.66**
	**LUMO: -2.28** **HOMO: -6.24**		**LUMO: -1.43** **HOMO: -6.80**

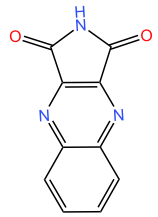
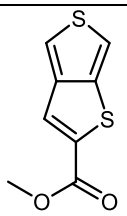
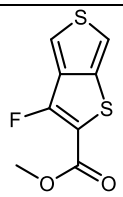
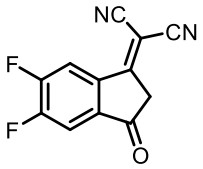
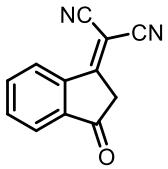
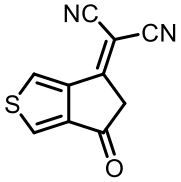
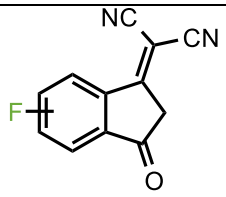
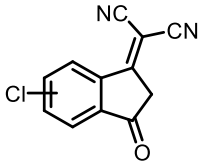
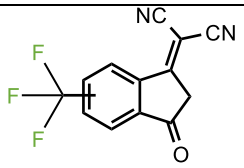
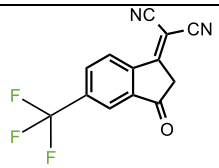
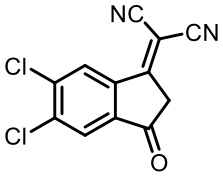
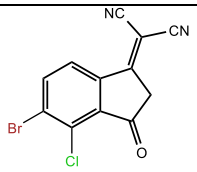
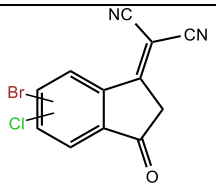
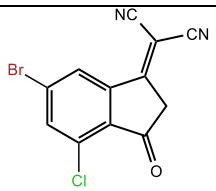
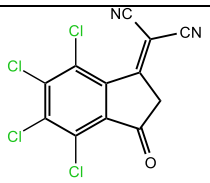
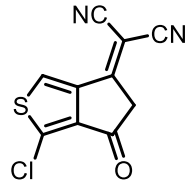
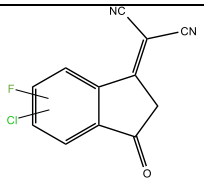
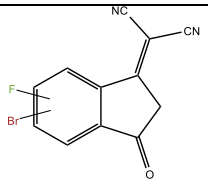
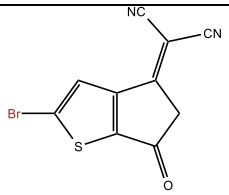
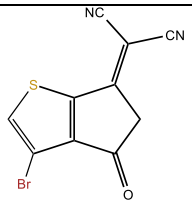
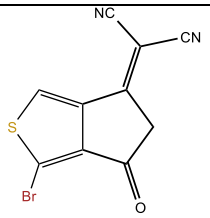
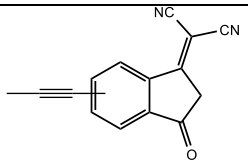
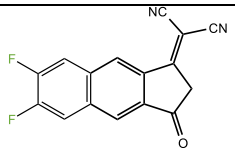
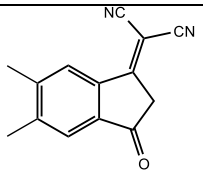
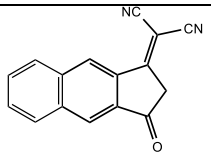
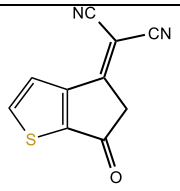
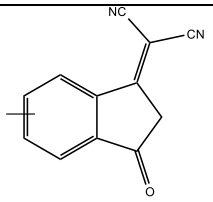
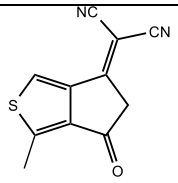
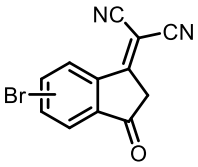
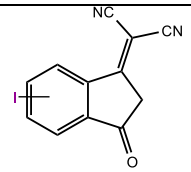
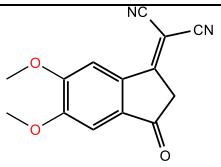
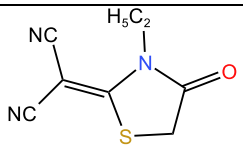
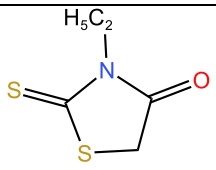
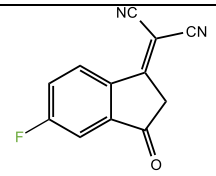
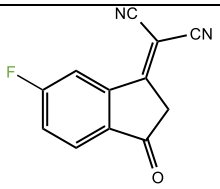
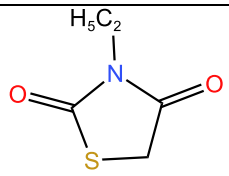
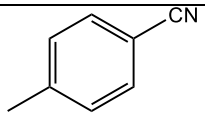
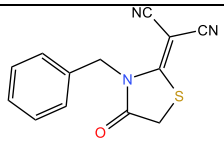
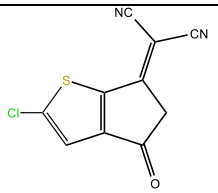
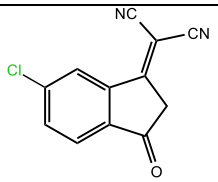
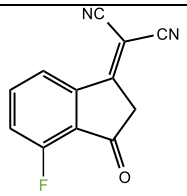
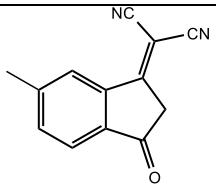
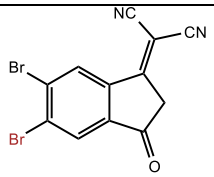
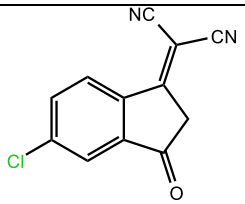
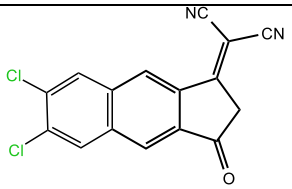
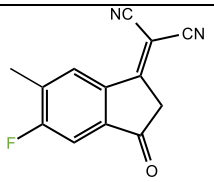
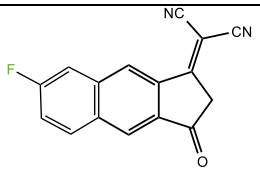
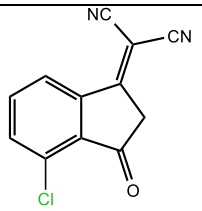
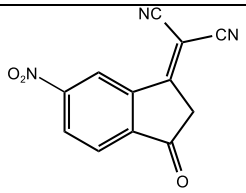
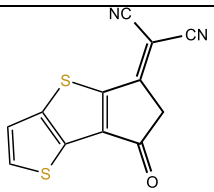
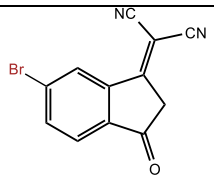
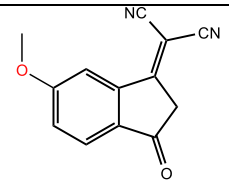
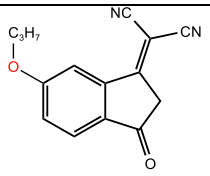
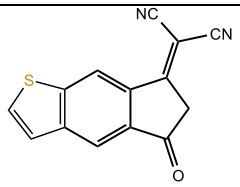
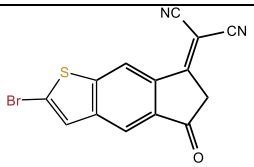
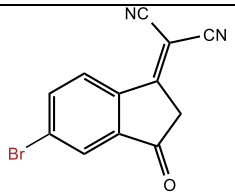
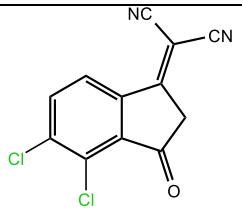
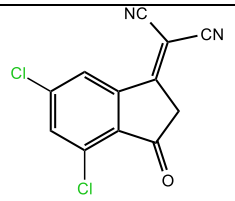
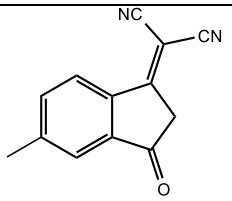
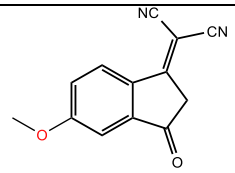
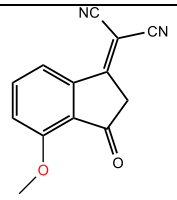
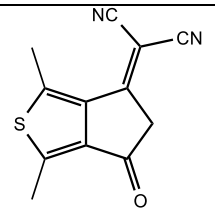
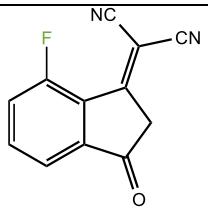
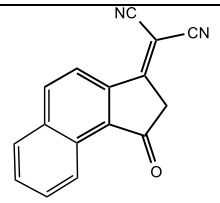
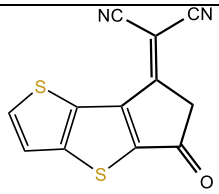
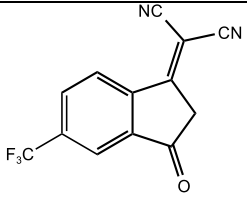
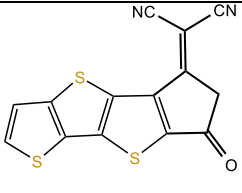
	**LUMO: -2.75** **HOMO: -7.12**		**LUMO: -1.80** **HOMO: -5.80**
	**LUMO: -1.87** **HOMO: -5.89**		

Table S5. Computed HOMO/LUMO energy values for common end groups used in non-fullerene acceptors of organic solar cells.

	**IC-2F** **LUMO: -3.40**		**IC** **LUMO: -3.19**
	**IC-Th-1** **LUMO: -3.21**		**IC-F-1** **LUMO: -3.33**
	**IC-Cl-1** **LUMO: -3.38**		**IC-Tf** **LUMO: -3.50**
	**IC-F3** **LUMO: -3.61**		**IC-2Cl** **LUMO: -3.50**
	**IC-ClBr-2** **LUMO: -3.47**		**IC-ClBr-1** **LUMO: -3.48**
	**IC-ClBr-3** **LUMO: -3.52**		**IC-4Cl** **LUMO: -3.71**

	**IC-ThCl-1** **LUMO: -3.22**		**IC-FCl** **LUMO: -3.42**
	**IC-FBr** **LUMO: -3.39**		**IC-ThBr-2** **LUMO: -3.46**
	**IC-ThBr-3** **LUMO: -3.55**		**IC-ThBr-1** **LUMO: -3.19**
	**IC-yle-1** **LUMO: -3.13**		**IC-2FNp-2** **LUMO: -3.25**
	**IC-2Me** **LUMO: -3.02**		**IC-Np** **LUMO: -3.09**
	**IC-Th** **LUMO: -3.20**		**IC-Me** **LUMO: -3.18**
	**IC-ThMe** **LUMO: -2.99**		**IC-Br** **LUMO: -3.37**
	**IC-I** **LUMO: -1.89**		**IC-2MeO** **LUMO: -2.94**
	**Rh-1** **LUMO: -2.84**		**Rh-7** **LUMO: -1.93**

	**IC-F-2** **LUMO: -3.33**		**IC-F-3** **LUMO: -3.33**
	**Rh-8** **LUMO: -0.92**		**Ph-CN** **LUMO: -1.17**
	**Rh-5** **LUMO: -2.31**		**IC-ThCl-3** **LUMO: -3.55**
	**IC-Cl-1** **LUMO: -3.39**		**IC-F-4** **LUMO: -3.50**
	**IC-Me** **LUMO: -3.27**		**IC-2Br** **LUMO: -3.66**
	**IC-Cl-2** **LUMO: -3.36**		**IC-Ph-2Cl** **LUMO: -3.36**
	**IC-MeF** **LUMO: -3.32**		**IC-NF-1** **LUMO: -3.30**
	**IC-Cl-3** **LUMO: -3.54**		**IC-NO2-1** **LUMO: -4.50**
	**IC-TT-1** **LUMO: -3.23**		**IC-Br-1** **LUMO: -3.37**

	**IC-MeO-1** **LUMO: -3.30**		**IC-MeO-C3H7** **LUMO: -3.27**
	**IC-Ph-T** **LUMO: -3.03**		**IC-TBr** **LUMO: 0**
	**IC-Br-2** **LUMO: -3.36**		**IC-2Cl-1** **LUMO: -3.68**
	**IC-2Cl-2** **LUMO: -3.72**		**IC-Ph-Me-4** **LUMO: -3.25**
	**IC-MeO-4** **LUMO: -3.13**		**IC-MeO-5** **LUMO: -3.24**
	**IC-T2Me** **LUMO: -2.97**		**IC-F-5** **LUMO: -3.42**
	**IC-Ph** **LUMO: -3.44**		**IC-TT-2** **LUMO: -3.23**
	**IC-F3-2** **LUMO: -3.61**		**IC-TTT** **LUMO: -3.15**

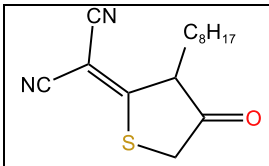
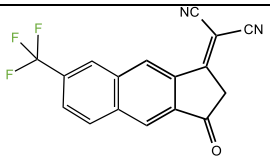
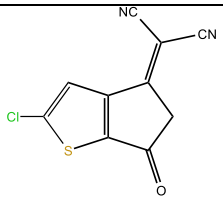
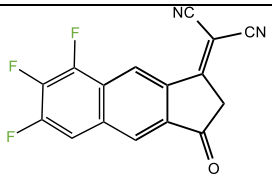
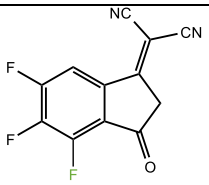
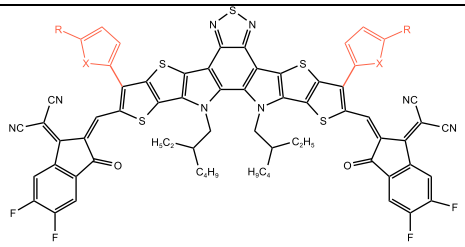
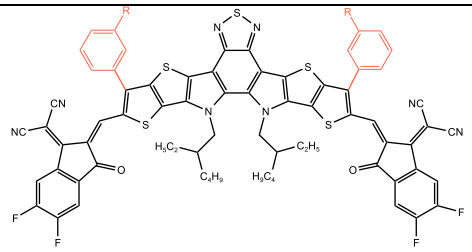
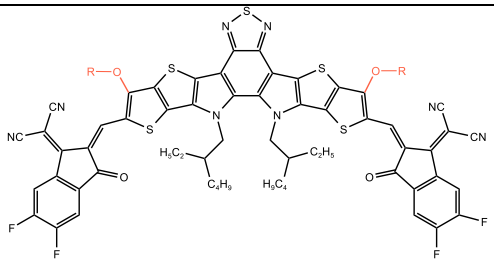
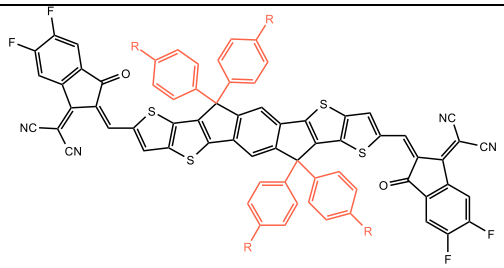
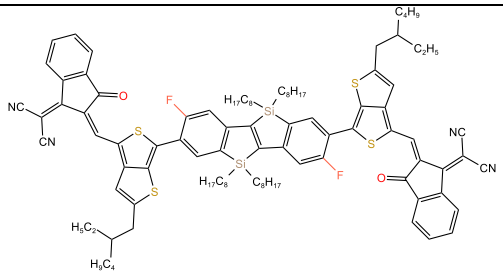
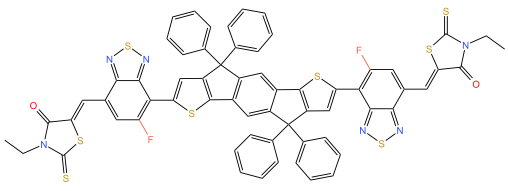
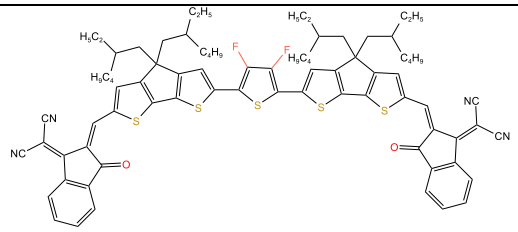
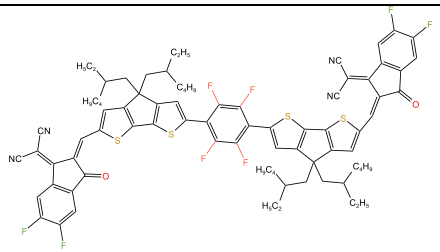
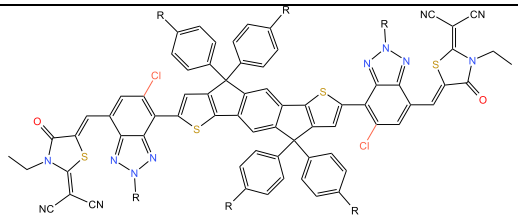
	**Rh-3** **LUMO: -2.28**		**IC-NF3** **LUMO: -3.40**
	**IC-ThCl-2** **LUMO: -3.49**		**IC-N3F** **LUMO: -3.42**
	**IC-3F** **LUMO: -3.70**		

Table S6. Common side chain substitution groups are used in non-fullerene acceptors of organic solar cells.

 **+0.1**	 **+0.1**
 **+0.3**	 **+0.1**
 **-0.1**	 **-0.1**

 **-0.2**	 **-0.1**
 **-0.1**	

Reference

(1) Li, S.; Ye, L.; Zhao, W.; Zhang, S.; Mukherjee, S.; Ade, H.; Hou, J. Energy-Level Modulation of Small-Molecule Electron Acceptors to Achieve over 12% Efficiency in Polymer Solar Cells. *Adv. Mater.* **2016**, *28* (42), 9423–9429.

(2) Li, C.; Zhou, J.; Song, J.; Xu, J.; Zhang, H.; Zhang, X.; Guo, J.; Zhu, L.; Wei, D.; Han, G.; Min, J.; Zhang, Y.; Xie, Z.; Yi, Y.; Yan, H.; Gao, F.; Liu, F.; Sun, Y. Non-Fullerene Acceptors with Branched Side Chains and Improved Molecular Packing to Exceed 18% Efficiency in Organic Solar Cells. *Nat. Energy 2021 66* **2021**, *6* (6), 605–613.

(3) Yao, Z.; Liao, X.; Gao, K.; Lin, F.; Xu, X.; Shi, X.; Zuo, L.; Liu, F.; Chen, Y.; Jen, A. K. Y. Dithienopicenocarbazole-Based Acceptors for Efficient Organic Solar Cells with Optoelectronic Response over 1000 Nm and an Extremely Low Energy Loss. *J. Am. Chem. Soc.* **2018**, *140* (6), 2054–2057.

(4) Zhang, G.; Chen, X. K.; Xiao, J.; Chow, P. C. Y.; Ren, M.; Kupgan, G.; Jiao, X.; Chan, C. C. S.; Du, X.; Xia, R.; Chen, Z.; Yuan, J.; Zhang, Y.; Zhang, S.; Liu, Y.; Zou, Y.; Yan, H.; Wong, K. S.; Coropceanu, V.; Li, N.; Brabec, C. J.; Bredas, J. L.; Yip, H. L.; Cao, Y. Delocalization of Exciton and Electron Wavefunction in Non-Fullerene Acceptor Molecules Enables Efficient Organic Solar Cells. *Nat. Commun. 2020 111* **2020**, *11* (1), 1–10.

(5) Deng, M.; Meng, H.; Xu, X.; Tang, J.; Yu, L.; Li, R.; Peng, Q. Unique W-Shape Y6 Isomer as Effective Solid Additive for High-Performance PM6:Y6 Polymer Solar Cells. *Chem. Eng. J.* **2022**, *440*, 135975.

(6) Chen, Y.; Bai, F.; Peng, Z.; Zhu, L.; Zhang, J.; Zou, X.; Qin, Y.; Kyung Kim, H.; Yuan, J.; Ma, L.-K.; Zhang, J.; Yu, H.; Y Chow, P. C.; Huang, F.; Zou, Y.; Ade, H.; Liu, F.; Yan, H.; Chen, Y.; Bai, F.; Zhang, J.; Zou, X.; Kim, H. K.; Ma, L.; Yu, H.; Y Chow, P. C.; Yan Hong Kong, H.; Yan, H.; Peng, Z.; Qin, Y.; Ade, H.; Zhu, L.; Liu, F.; Yuan, J.; Zou, Y.; Huang, F. Asymmetric Alkoxy and Alkyl Substitution on Nonfullerene Acceptors Enabling High-Performance Organic Solar Cells. *Adv. Energy Mater.* **2021**, *11* (3), 2003141.

(7) Gao, W.; Ma, X.; An, Q.; Gao, J.; Zhong, C.; Zhang, F.; Yang, C. An

Asymmetrical Fused-Ring Electron Acceptor Designed by a Cross-Conceptual Strategy Achieving 15.6% Efficiency. *J. Mater. Chem. A* **2020**, *8* (29), 14583–14591.

(8) Shi, Y.; Chang, Y.; Lu, K.; Chen, Z.; Zhang, J.; Yan, Y.; Qiu, D.; Liu, Y.; Adil, M. A.; Ma, W.; Hao, X.; Zhu, L.; Wei, Z. Small Reorganization Energy Acceptors Enable Low Energy Losses in Non-Fullerene Organic Solar Cells. *Nat. Commun. 2022 131* **2022**, *13* (1), 1–10.

(9) Zhu, C.; Yuan, J.; Cai, F.; Meng, L.; Zhang, H.; Chen, H.; Li, J.; Qiu, B.; Peng, H.; Chen, S.; Hu, Y.; Yang, C.; Gao, F.; Zou, Y.; Li, Y. Tuning the Electron-Deficient Core of a Non-Fullerene Acceptor to Achieve over 17% Efficiency in a Single-Junction Organic Solar Cell. *Energy Environ. Sci.* **2020**, *13* (8), 2459–2466.