

Supporting Information to

Spectroelectrochemically Determined Energy Levels of PM6:Y6 Blends and their Relevance to Solar Cell Performance

David Neusser,^a Bowen Sun,^b Wen Liang Tan,^c Lars Thomsen,^d Thorsten Schultz,^e Lorena Perdigón-Toro,^f Norbert Koch,^e Safa Shoaee,^b Christopher R. McNeill,^c Dieter Neher^{f,*} and Sabine Ludwigs^{a,*}

^a IPOC – Functional Polymers, Institute of Polymer Chemistry, University of Stuttgart, Germany

^b Optoelectronics of Disordered Semiconductors, Institute of Physics and Astronomy, University of Potsdam, Germany

^c Department of Materials Science and Engineering, Monash University, Wellington Road, Clayton, Victoria, 3800 Australia

^d Australian Synchrotron, ANSTO, 800 Blackburn Road, Clayton, Victoria 3168, Australia

^e Helmholtz-Zentrum Berlin für Materialien und Energie GmbH 12489 Berlin, Germany

^f Soft Matter Physics and Optoelectronics, Institute of Physics and Astronomy, University of Potsdam, Germany

*sabine.ludwigs@ipoc.uni-stuttgart.de

*neher@uni-potsdam.de

Table S1: Published HOMO and LUMO levels of PM6 and Y6 in the literature, determined by various experimental techniques from recent years. Electrochemical band gaps as well as the transport energy is given as well. If known, the correction factor for transferring the CV onset into the energy scale is given in brackets. Measurements performed on blend films are marked with an asterix.

PM6			Y6			$\Delta E_{HOMO} /$ eV	$E_{tr} /$ eV	method	Ref.
HOMO / eV	LUMO / eV	E_g^{EC} / eV	HOMO / eV	LUMO / eV	E_g^{EC} / eV				
-5.30	-3.05	2.25	-5.64	-3.92	1.72	0.34	1.38	spectroelectro-	our work
-5.30*	-3.06*	2.24*	-5.63*	-3.90*	1.73*	0.33*	1.40*	chemistry (4.8 eV)	
-5.56	-3.50	2.06	-5.65	-4.10	1.55	0.09	1.46	CV (4.36 eV)	1
-5.05	-3.59	1.46	-5.61	-4.10	1.51	0.56	0.95	CV (4.73 eV)	2
-5.45	-3.20	2.25	-	-	-	-	-	CV (4.8 eV)	3
-5.18	-	-	-	-	-	-	-	PESA	3
-5.54	-3.65	1.89	-5.62	-4.11	1.51	0.08	1.43	CV	4
-5.13	-3.28	-	-5.66	-4.29	-	0.53	0.84	UPS + opt. band gap CV	5
-5.45	-3.65	1.80	-	-	-	-	-	(4.71 eV) + opt. band gap CV	6
-5.50	-3.61	1.89	-	-	-	-	-	(4.29 eV)	7
-5.10	-3.10	-	-5.81	-4.10	-	0.71	1.00	UPS + IPES	8
-5.43	-3.47	1.96	-5.69	-3.96	1.73	0.26	1.47	CV	9
-5.53*	-	-	-	-3.92*	-	-	1.61*	CV	9
-5.50	-3.50	2.00	-	-	-	-	-	CV	10
-5.56	-3.48	2.08	-5.67	-4.08	1.59	0.11	1.48	CV (4.44 eV)	11
-	-	-	-5.65	-4.10	1.55	-	-	CV	12

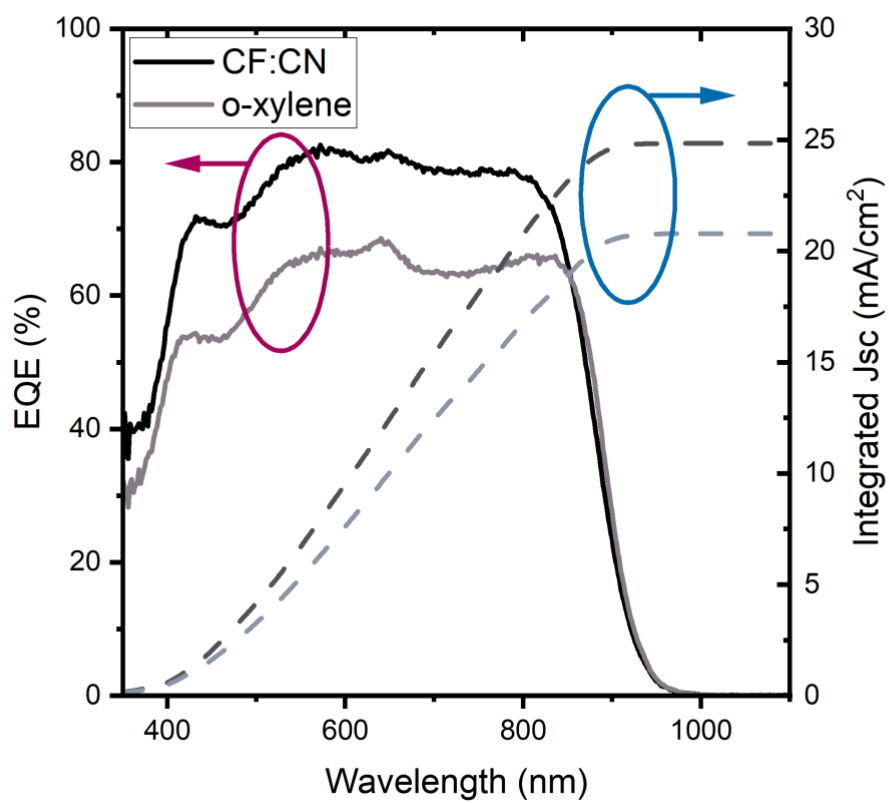


Figure S1: External quantum efficiency (EQE) spectrum of PM6:Y6 devices fabricated with CF:CN and o-xylene as the solvent for the active layer.

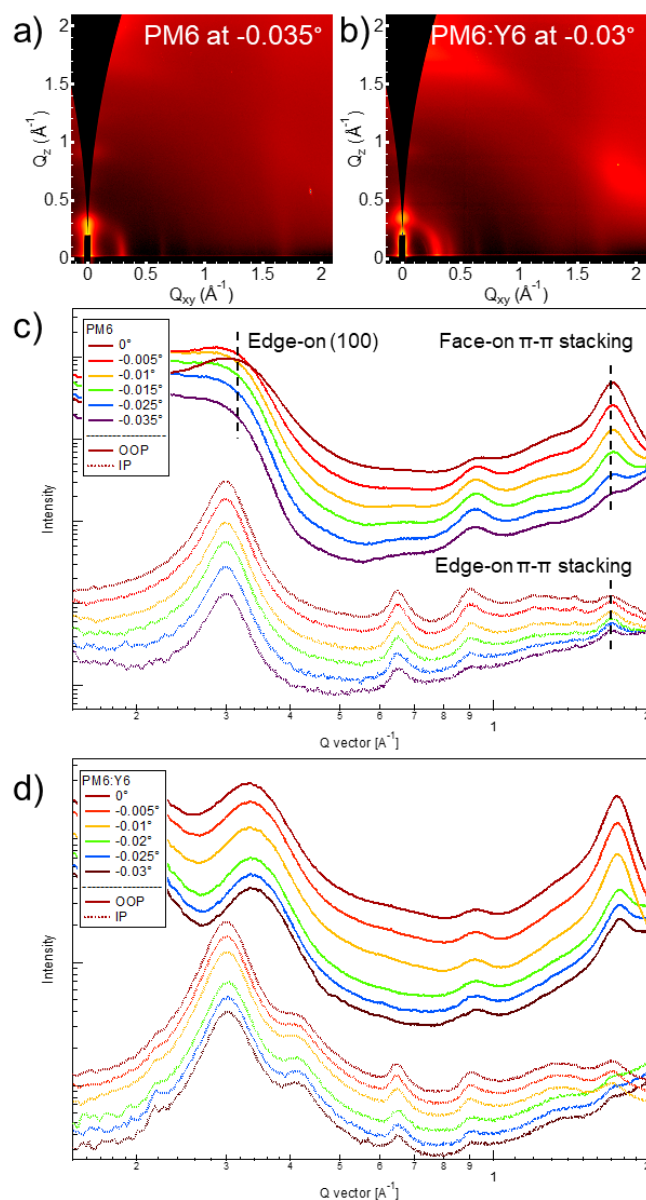


Figure S2: (a-b) 2D GIWAXS patterns and (c-d) the corresponding incident-angle-dependent 1D plots of neat PM6 films and PM6:Y6 blend films (1:1.2 wt%) spin-coated from CF + 0.5 v% CN solvent system. The angles of incidence are labelled relative to critical angle; the 0° data corresponds to the critical angle whereas negative values refer to measurements below the critical angle. In both neat and blend films, GIWAXS data collected at shallower incident angle observed weaker out-of-plane (OOP) π - π stacking peak relative to OOP (100) lamellar stacking peak and in-plane (IP) π - π stacking peak indicating the improved ratio of edge-on oriented PM6 crystallites, which is consistent with the NEXAFS findings. At -0.03° incident angle, the blend film observes stronger OOP π - π stacking peak than that in the neat film due to the π - π stacking order of face-on oriented Y6 crystallites.

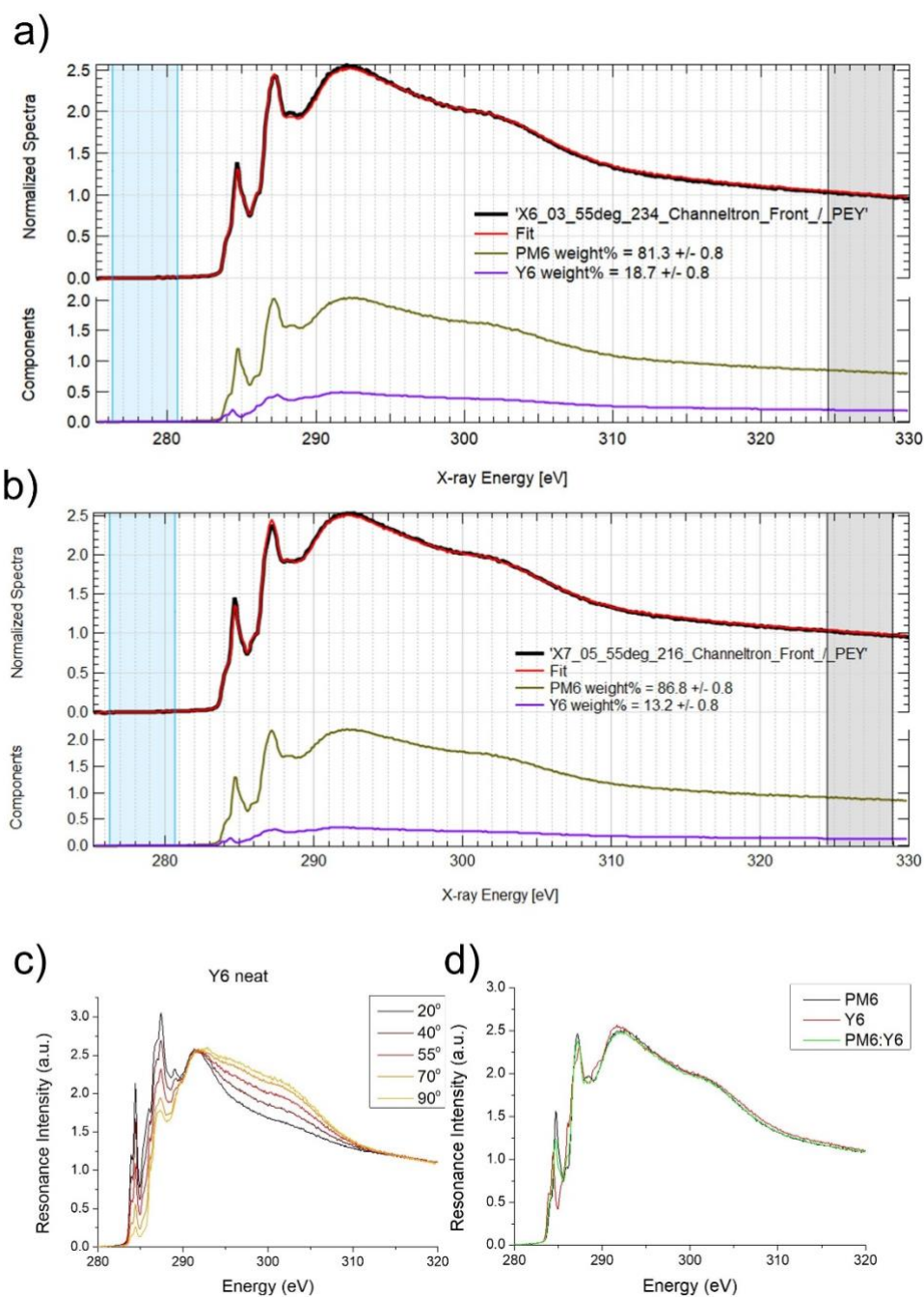


Figure S3: Angle-resolved NEXAFS spectra of PM6:Y6 blend films (1:1.2 wt%, 30 nm) processed from a) CF:CN (CF + 0.5 v% CN) and b) o-xylene solutions. Spectra of the neat compounds are given in c) and d).

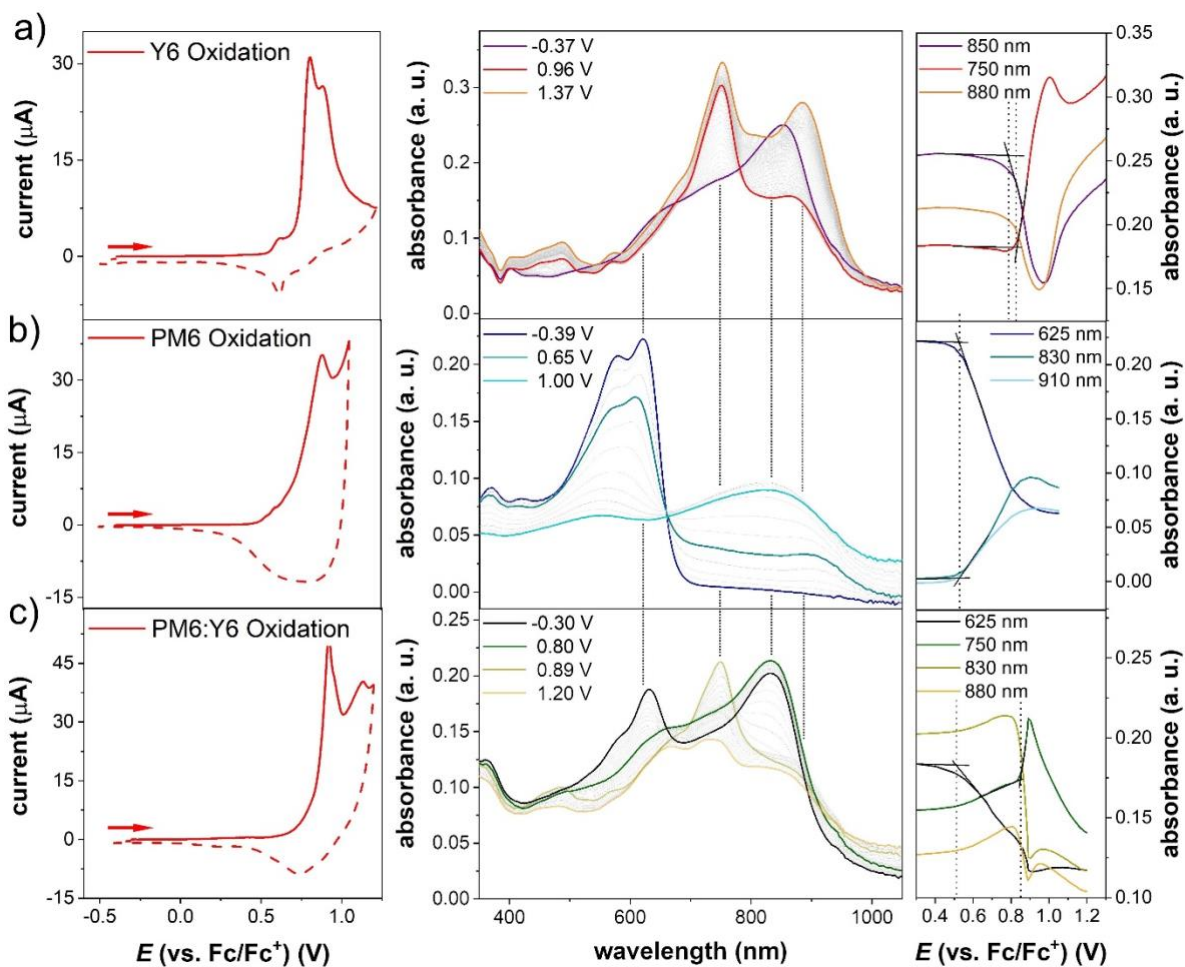


Figure S4: *In situ* CV measurements coupled with UV-vis spectroscopy of a) neat Y6, b) neat PM6 and c) a blend of PM6:Y6 (1:1.2 wt%) films, spin coated and annealed from *o*-xylene solutions. CVs are given on the left, the spectra of the charge half-cycle of the oxidation are presented in the center, completed with peak trends of significant bands on the right side. Spectral onsets of the oxidation are indicated by dotted lines and obtained via tangent method. Underlying CVs (1st cycles) are measured in 0.1 M TBAPF₆/MeCN at 20 mVs⁻¹ on ITO substrates.

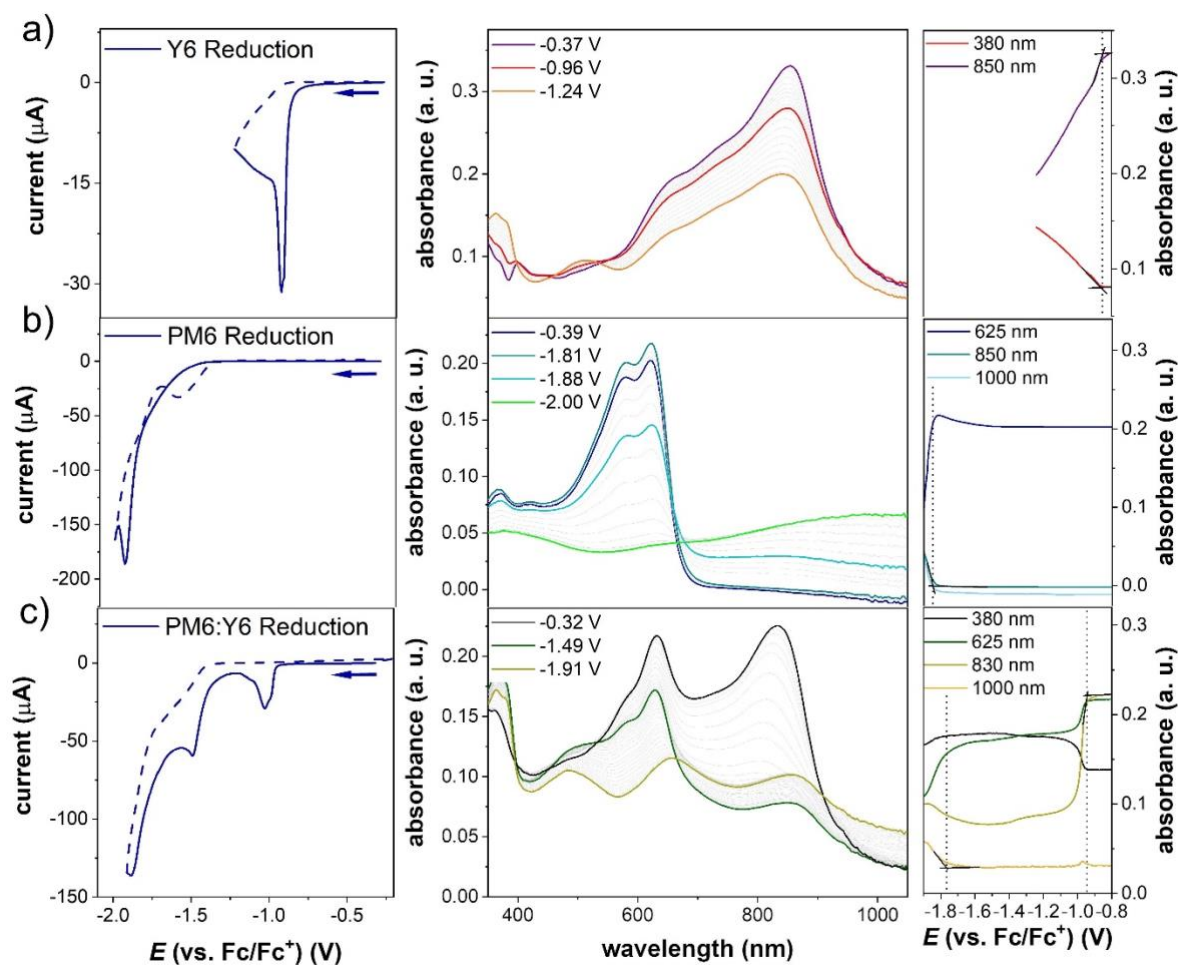


Figure S5: *In situ* CV measurements coupled with UV-vis spectroscopy of a) neat Y6, b) neat PM6 and c) a blend of PM6:Y6 (1:1.2 wt%) films, spin coated and annealed from o-xylene solutions. CVs are given on the left, the spectra of the charge half-cycle of the oxidation are presented in the center, completed with peak trends of significant bands on the right side. Spectral onsets of the reduction are indicated by dotted lines and obtained via tangent method. Underlying CVs (1st cycles) are measured in 0.1 M TBAPF₆/MeCN at 20 mVs⁻¹ on ITO substrates.

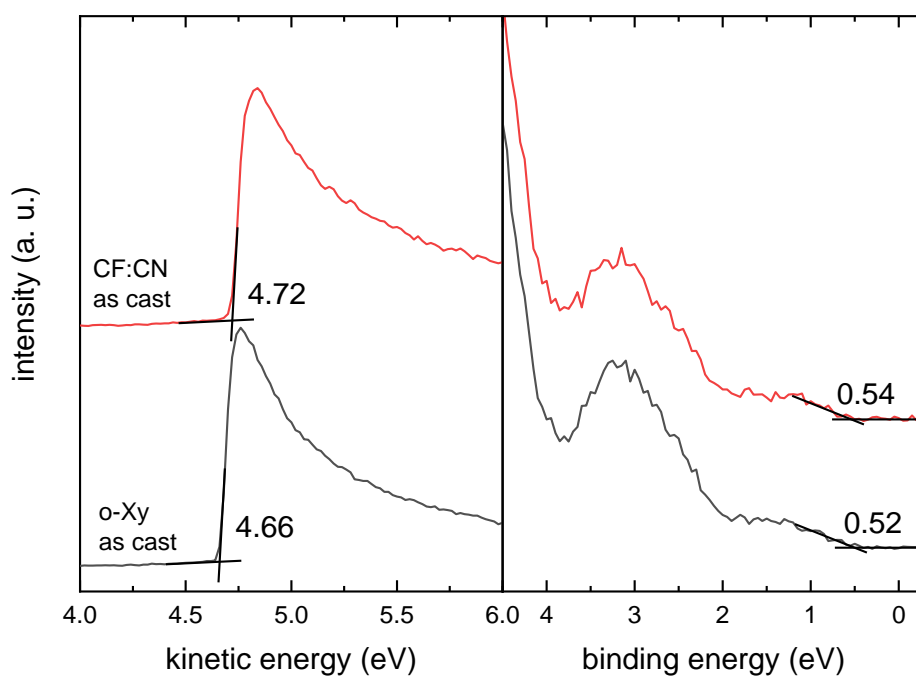


Figure S6: UPS spectra from PM6:Y6 blend films (1:1.2 wt%) processed from different solvent systems. Secondary electron cut-off (SECO) and valence band spectra of PM6:Y6 blend films prepared from CF:CN (0.5 wt%) and o-xylene.

Table S2: Voltage losses for PM6:Y6 devices fabricated with different solvents. The ELQY is measured at 1 sun injection condition ($J_{\text{int}} = J_{\text{SC}, 1 \text{ sun}}$)

Device	$J_{0,rad}$ [A/m^2]	V_{OC}^{rad} [V]	V_{OC} [V]	$\Delta V_{OC,calc}^{non-rad}$ [eV]	ELQY	$\Delta V_{OC,measured}^{non-rad}$ [eV]
PM6:Y6 (CF:CN)	2.81×10^{-16}	1.070	0.83	0.24	1.85×10^{-5}	0.28
PM6:Y6 (o-xylene)	2.36×10^{-16}	1.071	0.77	0.30	2.36×10^{-6}	0.34

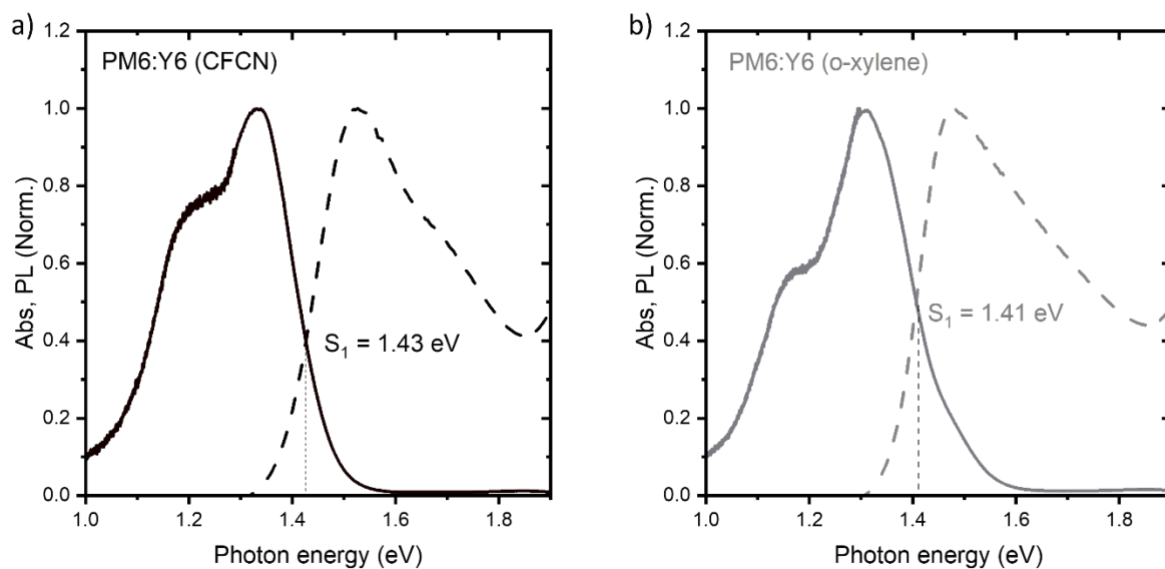


Figure S7: Normalized absorption and photoluminescence (PL) spectra of PM6:Y6 film fabricated with a) CF:CN and b) o-xylene as the solvent.

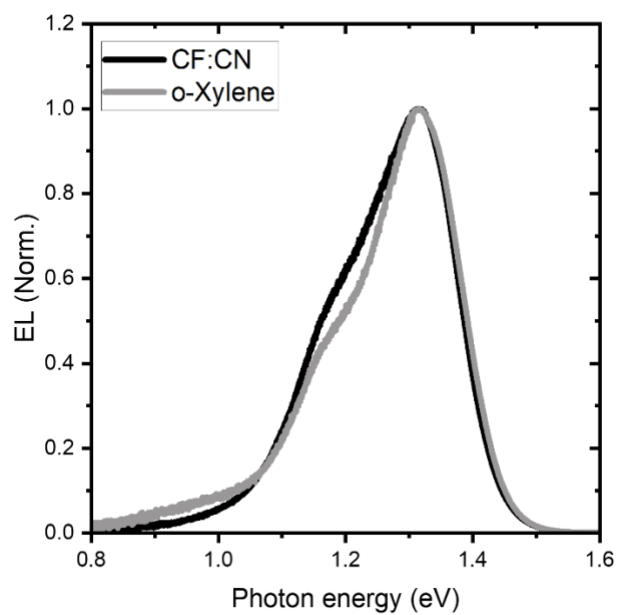


Figure S8: The normalized electroluminescence (EL) spectra of PM6:Y6 devices fabricated with CF:CN and o-xylene as the solvent for the active layer.

References

1. 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.
2. J. Wu, G. Li, J. Fang, X. Guo, L. Zhu, B. Guo, Y. Wang, G. Zhang, L. Arunagiri, F. Liu, H. Yan, M. Zhang and Y. Li, *Nat. Commun.*, 2020, **11**, 4612.
3. W. Peng, Y. Lin, S. Y. Jeong, Z. Genene, A. Magomedov, H. Y. Woo, C. Chen, W. Wahyudi, Q. Tao, J. Deng, Y. Han, V. Getautis, W. Zhu, T. D. Anthopoulos and E. Wang, *Nano Energy*, 2022, **92**.
4. K. Li, Y. Wu, Y. Tang, M. A. Pan, W. Ma, H. Fu, C. Zhan and J. Yao, *Adv. Energy Mater.*, 2019, **9**.
5. M. Zhang, L. Zhu, G. Zhou, T. Hao, C. Qiu, Z. Zhao, Q. Hu, B. W. Larson, H. Zhu, Z. Ma, Z. Tang, W. Feng, Y. Zhang, T. P. Russell and F. Liu, *Nat. Commun.*, 2021, **12**, 309.
6. M. Zhang, X. Guo, W. Ma, H. Ade and J. Hou, *Adv. Mater.*, 2015, **27**, 4655-4660.
7. X. Li, R. Ma, T. Liu, Y. Xiao, G. Chai, X. Lu, H. Yan and Y. Li, *Sci. China Chem.*, 2020, **63**, 1256-1261.
8. S. Karuthedath, J. Gorenflot, Y. Firdaus, N. Chaturvedi, C. S. P. De Castro, G. T. Harrison, J. I. Khan, A. Markina, A. H. Balawi, T. A. D. Pena, W. Liu, R. Z. Liang, A. Sharma, S. H. K. Paleti, W. Zhang, Y. Lin, E. Alarousu, S. Lopatin, D. H. Anjum, P. M. Beaujuge, S. De Wolf, I. McCulloch, T. D. Anthopoulos, D. Baran, D. Andrienko and F. Laquai, *Nat. Mater.*, 2021, **20**, 378-384.
9. J. Wu, J. Lee, Y.-C. Chin, H. Yao, H. Cha, J. Luke, J. Hou, J.-S. Kim and J. R. Durrant, *Energy Environ. Sci.*, 2020, **13**, 2422-2430.
10. T. Liu, R. Ma, Z. Luo, Y. Guo, G. Zhang, Y. Xiao, T. Yang, Y. Chen, G. Li, Y. Yi, X. Lu, H. Yan and B. Tang, *Energy Environ. Sci.*, 2020, **13**, 2115-2123.
11. S. Tu, L. Zhang, X. Lin, L. Xiao, W. Wang and Q. Ling, *J. Mater. Chem. C*, 2022, **10**, 2026-2033.
12. Z. Wang, Z. Peng, Z. Xiao, D. Seyitliyev, K. Gundogdu, L. Ding and H. Ade, *Adv. Mater.*, 2020, **32**, e2005386.