Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2020

Supporting Information

Triple Cation Perovskite Doped with Small Molecule F4TCNQ for High

Efficient Stable Photodetectors

Abbas Ahmad Khan,^a Muhammad Azam, ^b Deborah Eric,^a Guangxing Liang ^{*b} and Zhinong Yu^{*a}

Beijing Engineering Research Center of Mixed Reality and Advanced Display Technology, School of Optics and Photonics, Beijing Institute of Technology, Beijing 100081, China.

E-mail: znyu@bit.edu.cn

Shenzhen Key Laboratory of Advanced Thin Films and Applications ,College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China.

E-mail: lgx@szu.edu.cn





Figure S1. a) Variation in color of perovskite precursors with different incorporating ratios of F4TCNQ. b) Perovskite films spin-coated from control and 5 Vol. % precursors.

Figure S1b shows the color of control and 5 Vol. % films. The color of the film changes from brown to black. It shows that the addition of F4TCNQ has influenced the crystallization process of perovskite film. Therefore, color changes from brown to black.



Figure S2. Ultraviolet photo-electron spectroscopy (UPS) spectra of (a) TiO_2 , (b) Control, and (c) 5 Vol. % films. The inset shows the cut off position of the lower binding energy.



Figure S3. a) Absorption spectra of control, 1 Vol. %, 2 Vol. %, 5 Vol. %,10 Vol. % films. Tauc plot of b) control, c) 1 Vol. %, d) 2 Vol. %, e) 5 Vol. %, and f) 10 Vol. % films.



Figure S4. SEM-EDX elemental mapping of the perovskite film incorporated with 5 Vol. %

F4TCNQ.



Figure S5. XPS spectra of F 1s region for the perovskite film made with/without F4TCNQ.



Figure S6. Fourier transform infrared (FTIR) spectrum of perovskite with and without F4TCNQ doping.



Figure S7. I-V curves of the single layer device a) under dark, and b) under light illumination of 0.1 mW cm⁻² and applied bias of 5 V.



Figure S8. On-Off switching properties of a) 1 Vol. %, b) 2 Vol. %, and c) 10 Vol. % devices. Single cycle rise and decay processes for a) 1 Vol. %, b) 2 Vol. %, and c) 10 Vol. % devices.



Figure S9. (a) I-V characteristics of Control device and the device doped with CB. SEM images of (b) Control film (c) With CB.

Table S1. The lattice constant and Lattice strain of perovskite with different molar ratio ofF4TCNQ.

Sample	a [nm]	Lattice Strain
Control	0.8794	0.000512
1% F4TCNQ	0.8813	0.000508
2% F4TCNQ	0.8820	0.000499
5% F4TCNQ	0.8826	0.000458
10% F4TCNQ	0.8827	0.000498

	I _d [A]	I _L [A]	R [A W ⁻¹]	On/Off	Rise & Decay [s]
Control	1.05×10^{-10}	5.30×10^{-8}	0.88	504	0.96/0.86
1%	7.06×10^{-11}	7.55×10^{-8}	1.25	1078	0.60/0.66
2%	5.13×10^{-11}	1.24×10^{-7}	2.06	2500	0.70/0.79
5%	4.67×10^{-11}	3.24×10^{-7}	5.41	6937	0.53/0.60
10%	6.58×10^{-11}	9.85×10^{-8}	1.64	1496	0.63/0.68

 Table S2. Comparison of all the photodetector devices.

 Table S3. Detailed parameters of device stability.

	I _d [A]	I _L [A]	R [A W ⁻¹]	On/Off
Control	4.57×10^{-10}	3.27×10^{-8}	0.54	72
5 Vol. %	5.13×10^{-11}	2.89 × 10 ⁻⁷	4.81	5621

Materials	Spectral range [nm]	Power	R [A W ⁻¹]	On/Off ratio	Rise/Decay time	ref
MAPbI ₃	300-800	0.01 mW cm ⁻²	83 (365 nm) 5.5 (780 nm)	324 33	< 0.2 s < 0.1 s	S1
MAPbI ₃ /rGO	-	3.2 mW cm^{-2}	0.073 (520 nm)	168	40.9/28.8 ms	S2
MAPbBr _{3-x} I _x	300-600	2 mW cm^{-2}	0.055	-	$<\!\!20/\!\!<\!\!20\mu_{\rm S}$	S3
MA _{0.5} FA _{0.5} Pb _{0.5} Sn _{0.5} I ₃ / Ascorbic acid	800-950	100 mW cm^{-2}	>0.2	-	-/7.4 μ _s	S4
(FASnI ₃) _{0.6} (MAPbI ₃) _{0.4}	350-900	7.3 mW cm^{-2}	0.4	-	$6.9/9.1 \ \mu_{\rm S}$	85
MAPbI3/PDPP3T	350-950	0.5 mW cm^{-2}	0.010 (365 nm) 0.025 (650 nm) 0.005 (937 nm)	-	-	S6
$FA_{1-x}Cs_xPbI_3$	240-750	0.1 mW cm^{-2}	5.7	6300 (0.5 V) 2100 (3 V)	45/91 ns	S7
MAPbBr ₂ I/graphene	250-700	1.05 nW	6x10 ⁵	1.2	0.12/0.75 s	S8
PCBM-CH ₃ NH ₃ PbI ₃	400-1000	100 mW cm^{-2}	0.01 (0.6 V) 0.27 (10 V)	3000	>0.12/>0.18 s	S9
MAPbI ₃	300-800	5 mW cm^{-2}	0.11	10^{4}	90/120 ms	S10
(CsPbI ₃) _{0.05} [(FAPbI ₃) _{0.83} (MAPbBr ₃) _{0.17}] _{0.95}	400-800	3.5 mW cm^{-2}	1.63 (10 V)	105	19/84 ms	S11
TiO ₂ /MAPbI ₃	400-800	0.5 mW cm^{-2}	0.12	4000	0.49.0.56 s	S12
FA _{0.83} Cs _{0.17} Pb(I _{0.9} Br _{0.1}) ₃ /Dye (Cy ₁ BF ₄ & CyPF ₆)	400-1100	-	0.01-0.02	-	$65/74 \ \mu_{ m S}$	S13
CH ₃ NH ₃ PbI ₃ /RhB	400-800	$500 \ \mu \mathrm{W} \ \mathrm{cm}^{-2}$	0.043	287	60/40 ms	S14
MAPbI _x Cl _{3-x} /Spiro- OMeTAD	300-850	100 mW cm^{-2}	0.10 (550 nm)	69.1	0.2/0.2 s	S15
MAPbBr ₃ /EA/TiO ₂	400-520	0.5 mW cm^{-2}	0.13	2700	0.49/1.17 s	S16
This work	400-800	0.1 mW cm^{-2}	5.41	6937	0.53/0.60 s	-

 Table S4. Performance of photodetector devices based on different perovskite materials.

References

- S1. X. Hu, X. Zhang, L. Liang, J. Bao, S. Li, W. Yang and Y. Xie, Advanced Functional Materials, 2014, 24, 7373-7380.
- S2. M. He, Y. Chen, H. Liu, J. Wang, X. Fang and Z. Liang, *Chem Commun (Camb)*, 2015, 51, 9659-9661.
- S3. F. Wang, J. Mei, Y. Wang, L. Zhang, H. Zhao and D. Zhao, ACS Appl Mater Interfaces, 2016, 8, 2840-2846.
- S4. X. Xu, C.-C. Chueh, P. Jing, Z. Yang, X. Shi, T. Zhao, L. Y. Lin and A. K. Y. Jen, *Advanced Functional Materials*, 2017, **27**.
- S5. W. Wang, D. Zhao, F. Zhang, L. Li, M. Du, C. Wang, Y. Yu, Q. Huang, M. Zhang, L. Li, J. Miao, Z. Lou, G. Shen, Y. Fang and Y. Yan, *Advanced Functional Materials*, 2017, **27**.
- S6. S. Chen, C. Teng, M. Zhang, Y. Li, D. Xie and G. Shi, *Adv Mater*, 2016, **28**, 5969-5974.
- S7. F.-X. Liang, J.-Z. Wang, Z.-X. Zhang, Y.-Y. Wang, Y. Gao and L.-B. Luo, *Advanced Optical Materials*, 2017, **5**.
- S8. Y. Wang, Y. Zhang, Y. Lu, W. Xu, H. Mu, C. Chen, H. Qiao, J. Song, S. Li, B. Sun, Y.-B.
 Cheng and Q. Bao, *Advanced Optical Materials*, 2015, 3, 1389-1396.
- Y. Wang, T. Zhang, P. Zhang, D. Liu, L. Ji, H. Chen, Z. D. Chen, J. Wu and S. Li, Organic Electronics, 2018, 57, 263-268.
- S10. K. C. Kwon, K. Hong, Q. Van Le, S. Y. Lee, J. Choi, K.-B. Kim, S. Y. Kim and H. W. Jang, Advanced Functional Materials, 2016, **26**, 4213-4222.
- S11. T. Zhang, J. Wu, P. Zhang, W. Ahmad, Y. Wang, M. Alqahtani, H. Chen, C. Gao, Z. D.
 Chen, Z. Wang and S. Li, *Advanced Optical Materials*, 2018, 6.
- S12. X. Yi, Z. Ren, N. Chen, C. Li, X. Zhong, S. Yang and J. Wang, Advanced Electronic Materials, 2017, 3.
- S13. Q. Lin, Z. Wang, M. Young, J. B. Patel, R. L. Milot, L. Martinez Maestro, R. R. Lunt, H. J.
 Snaith, M. B. Johnston and L. M. Herz, *Advanced Functional Materials*, 2017, 27.
- S14. C. J. Teng, D. Xie, M. X. Sun, S. Chen, P. Yang and Y. L. Sun, ACS Appl Mater Interfaces, 2016, 8, 31289-31294.
- S15. H. Sun, T. Lei, W. Tian, F. Cao, J. Xiong and L. Li, *Small*, 2017, **13**.
- S16. A. A. Khan, Z. Yu, U. Khan and L. Dong, *Nanoscale Res Lett*, 2018, **13**, 399.