Electronic Supplementary Information

Ultrafast-Response and High-Detectivity Self-Powered Perovskite Photodetector Based on Triazine-derived Star-shaped Small Molecule as Dopant-free Hole Transporting Layer†

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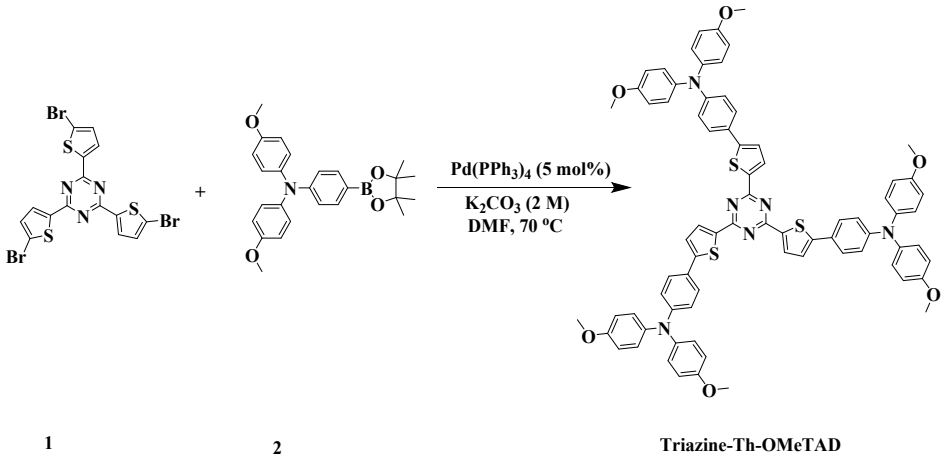
Synthesis and Photophysical and Electrochemical Properties

Under N_2 condition, compound 1 (282.1 mg, 0.50 mmol), compound 2 (1.08 g, 2.50 mmol), degassed aqueous K_2CO_3 (2 M, 2 mL), dry DMF (50 mL) and $Pd(PPh_3)_4$ (144 mg, 0.12 mmol) were filled in a 100 ml three-necked flask and the mixture was stirred at 70 °C for 48 h. After cooling down to room temperature and the mixture was extracted with DCM (50 mL) for three times. After combination, the organic layer was washed with brine for several times, dried over anhydrous $MgSO_4$. After removal of solvent, the residue was purified by chromatography with petroleum ether/CH_2Cl_2 (1:5, v:v) to get a yellow solid Triazine-Th-OMeTAD (599 mg, 96%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, J=3.8 Hz, 3H), 7.53 (d, J=8.6 Hz, 6H), 7.28 (d, J=2.6 Hz, 3H), 7.10 (d, J=8.7 Hz, 12H), 6.94 (d, J=8.5 Hz, 6H), 6.86 (d, J=8.8 Hz, 12H), 3.82 (s, 18H). ^{13}CNMR (101 MHz, $CDCl_3$) ppm 167.21, 156.36,151.40, 149.13, 140.37, 138.83, 132.72, 126.97, 122.88, 119.96, 114.84, 55.54. Elemental Analysis: C, 72.79; H, 4.89; N, 6.55; S, 7.45. found: C, 72.77; H, 5.03; N, 6.55; S, 7.45.

UPS is usually used to determine the Fermi level (E_F) and the valence band maximum (E_V) with respect to vacuum level (E_{VAC}).[1, 2] For a photoelectron to escape the sample surface and be collected, it has to have sufficient energy to overcome the sum of the binding energy (with respect to E_F) of its initial level and the work function (Φ), where $\Phi = E_{VAC} - E_F$. Therefore, for a fixed incident photon energy of 21.20 eV, the secondary electron cut-off (high binding energy edge) represents photoelectrons with zero kinetic energy when they escape from the sample surface. The work function Φ is determined by the difference between the incident photon energy (21.20 eV) and the binding energy of the secondary electron cut-off. The difference between E_F and E_V is determined by the intersection of the

linear portion of the spectra near the Fermi edge (low binding energy region) with the baseline.



Scheme S1. Synthesis of Triazine-Th-OMeTAD

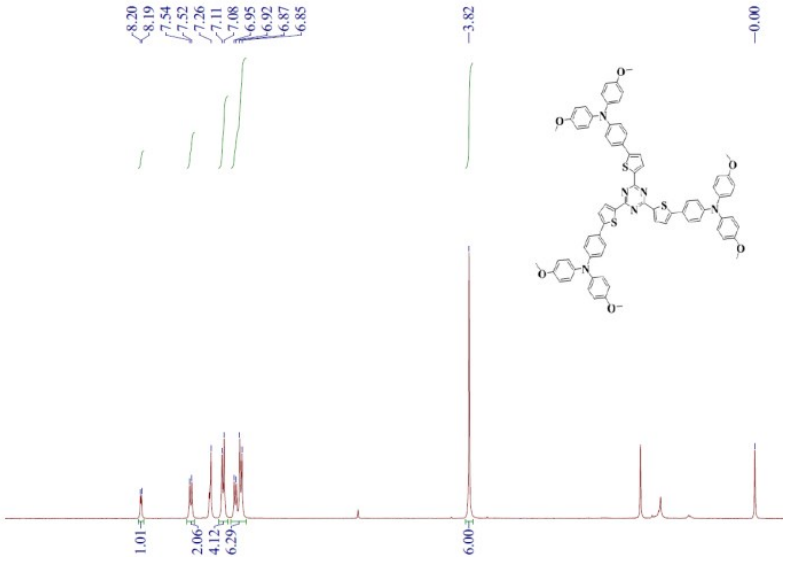


Figure S1. The ^{1}HNMR spectrum of Triazine-Th-OMeTAD

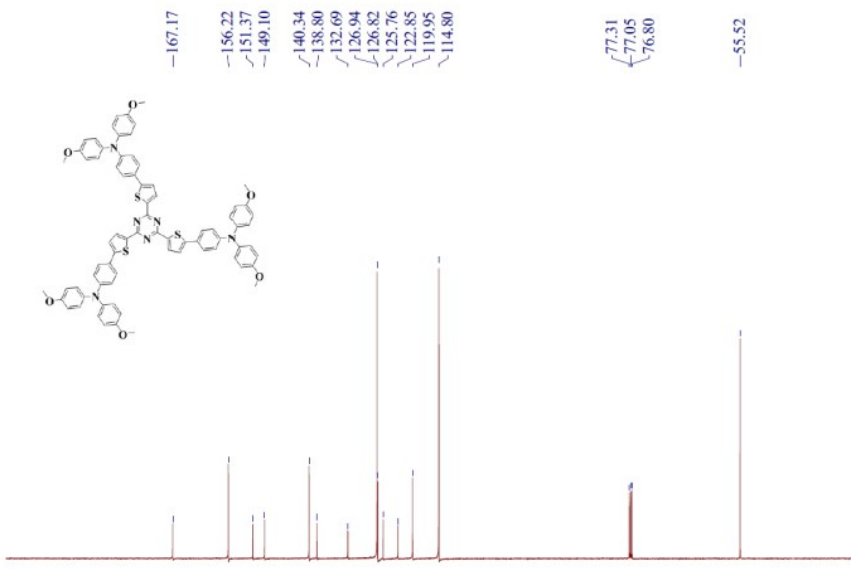


Figure S2. The ^{13}CNMR spectrum of Triazine-Th-OMeTAD

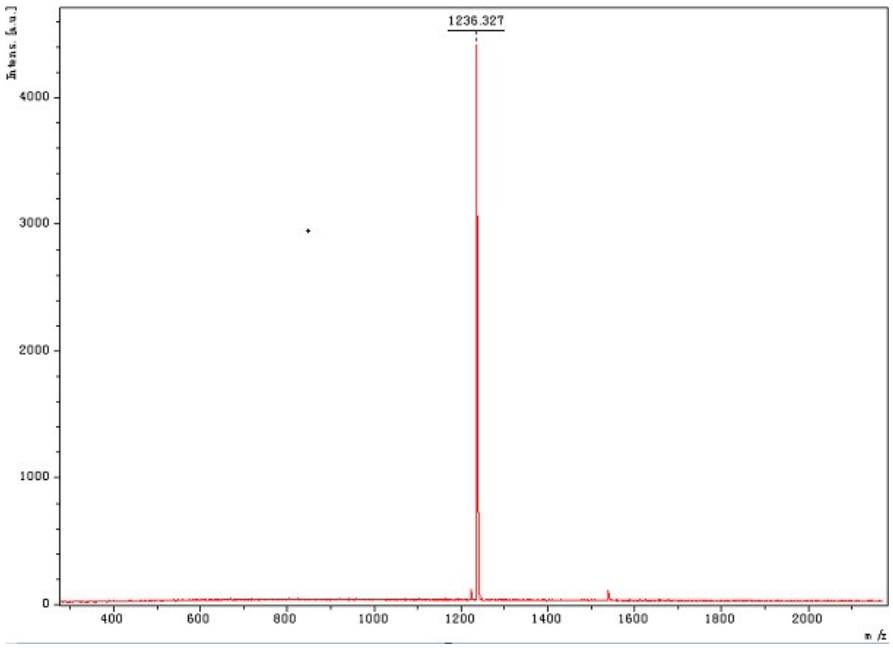


Figure S3. MALDI-TOF MS spectra of Triazine-Th-OMeTAD

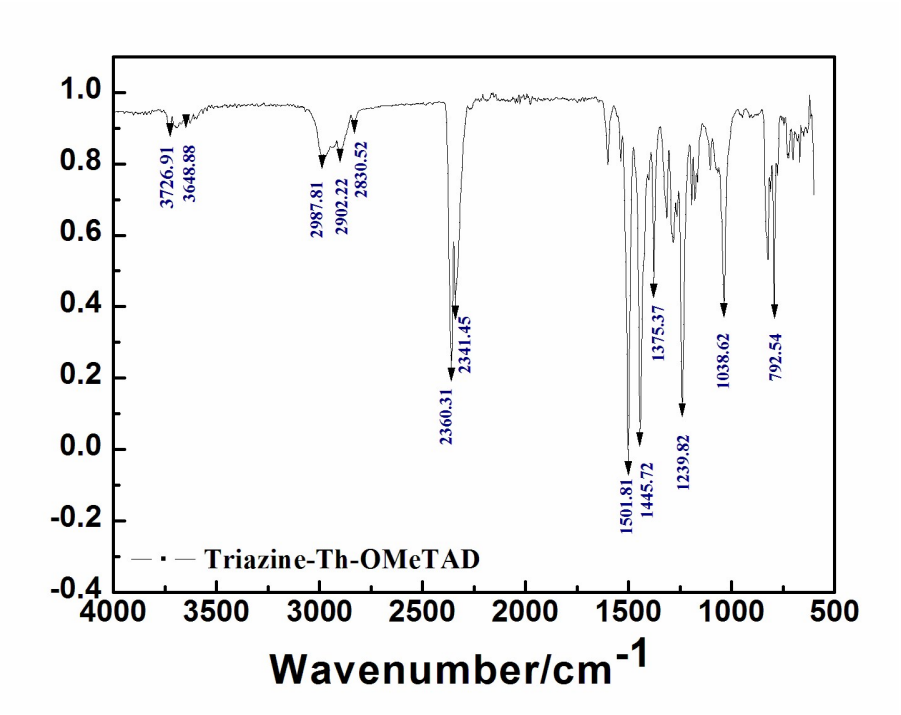


Figure S4. FT-IR spectrum of Triazine-Th-OMeTAD

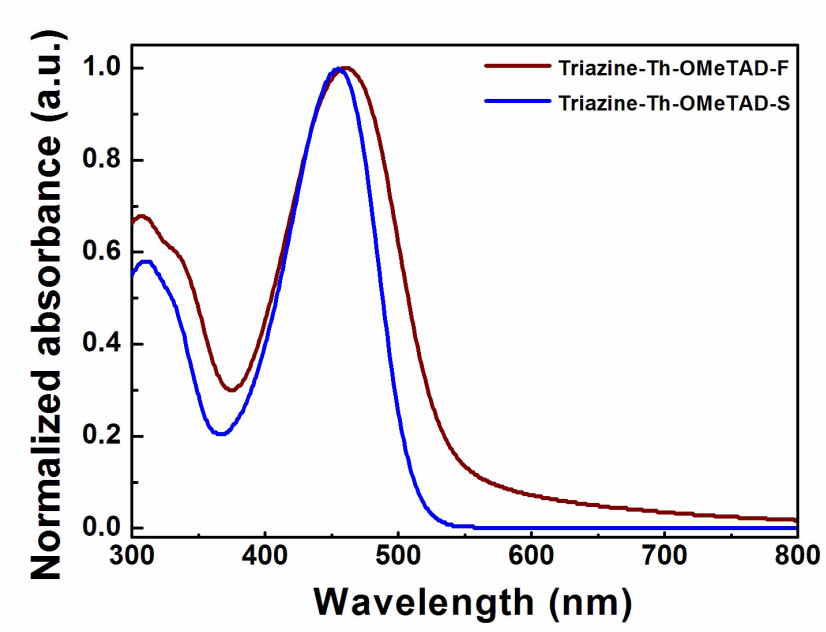


Figure S5. UV-vis absorption spectra of Triazine-Th-OMeTAD in film and $CHCl_3$ solution.

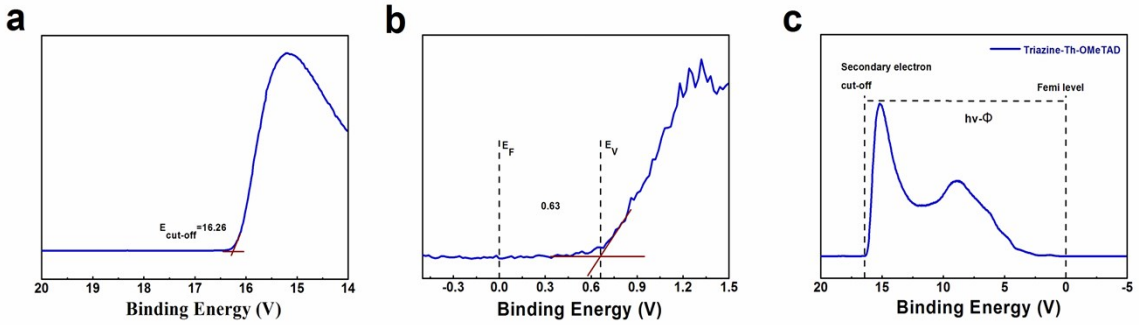


Figure S6. Ultraviolet Photoelectron Spectroscopy of Triazine-Th-OMeTAD

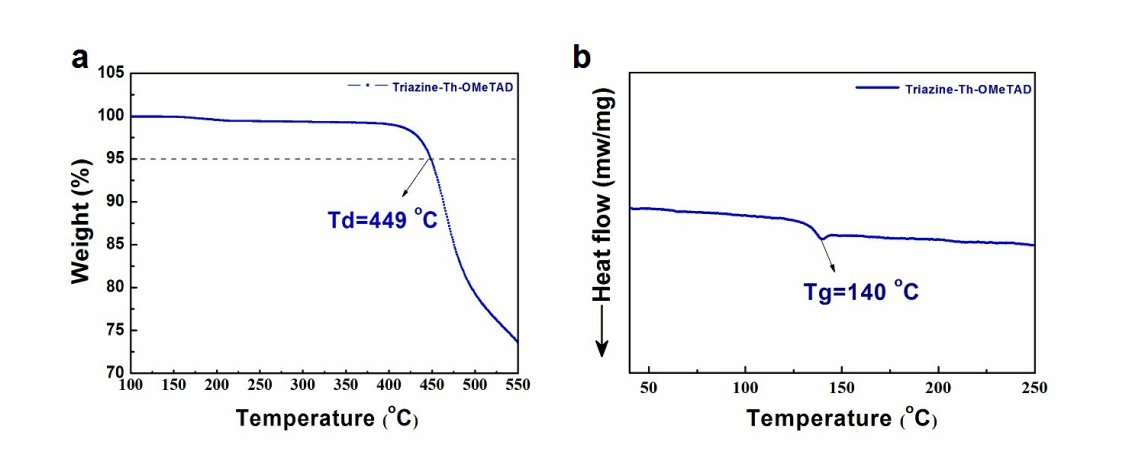


Figure S7. a) Thermogravimetric analysis (TGA) curves; b) differential scanning calorimetry (DSC) trace of Triazine-Th-OMeTAD

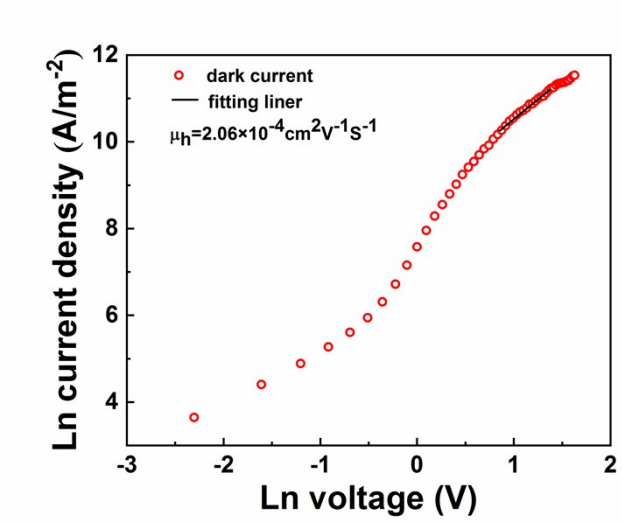


Figure S8. Mobility of Triazine-Th-OMeTAD measured by SCLC and the film thickness of Triazine-Th-OMeTAD is 50.0 nm.

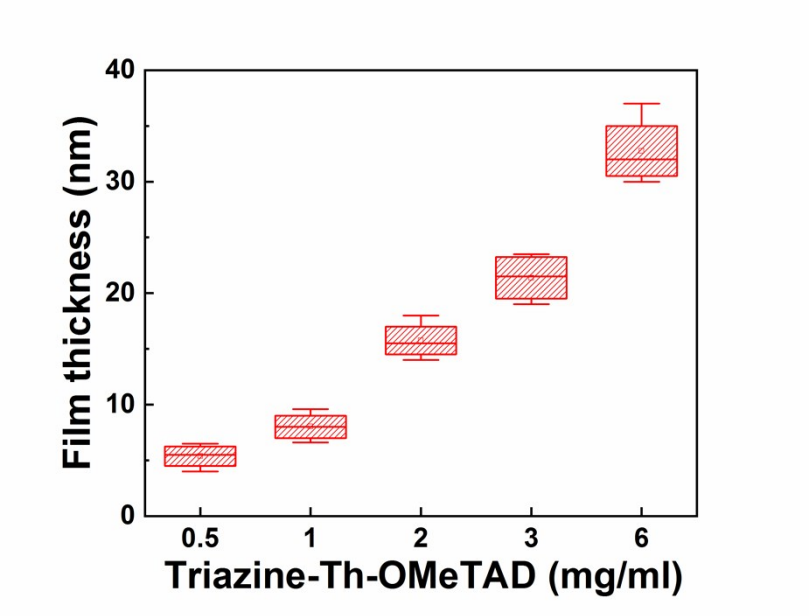


Figure S9. The thickness of Triazine-Th-OMeTAD film obtained from the different concentrations of solution. The average film thickness of 0.5 mg/mL is 5.3 nm, 1 mg/mL is 7.9 nm, 2 mg/mL is 15.8 nm, 3 mg/mL is 21.4 nm and 6 mg/mL is 31.7 nm.

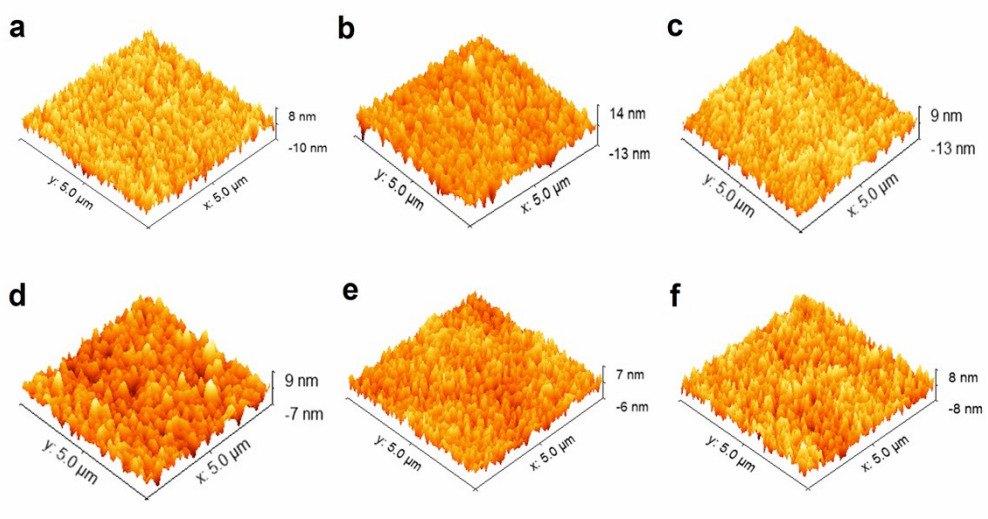


Figure S10. 3D view AFM images of ITO/glass; a) PEDOT:PSS/ITO/glass; b) 0.5 mg/mL Triazine-Th-OMeTAD/ITO/glass; c) 1 mg/mLTriazine-Th-OMeTAD/ITO/glass; d) 2

mg/mLTriazine-Th-OMeTAD/ITO/glass; e) 3 mg/mLTriazine-Th-OMeTAD/ITO/glass; f) 6 mg/mL Triazine-Th-OMeTAD/ITO/glass. The roughness is 1.912, 2.807, 2.551, 1.638, 1.423 and 1.579 nm, respectively.

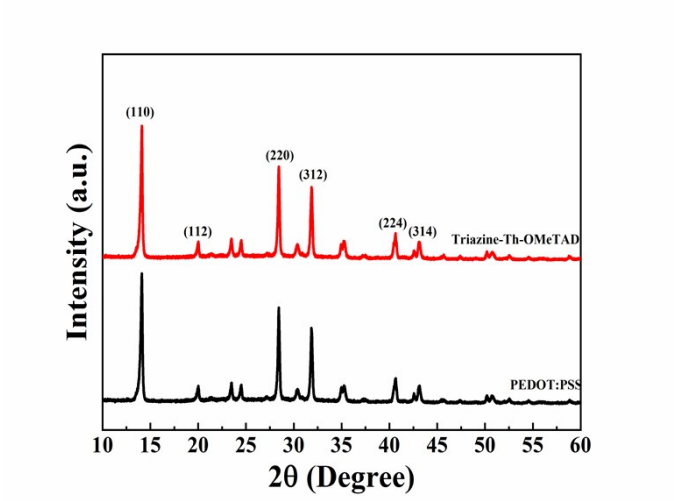


Figure S11. X-ray diffractogram (XRD) of glass/ITO/PEDOT:PSS/perovskite, and glass/ITO/Triazine-Th-OMeTAD (3 mg mL^{-1})/perovskite.

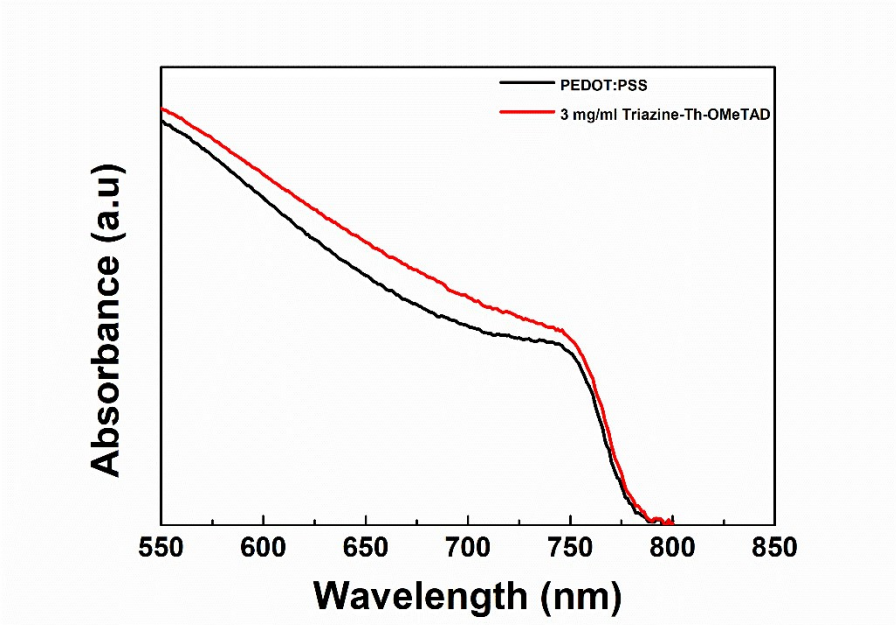


Figure S12. The absorption of perovskite film fabricated on PEDOT:PSS and 3 mg /ml Triazine-Th-OMeTAD.

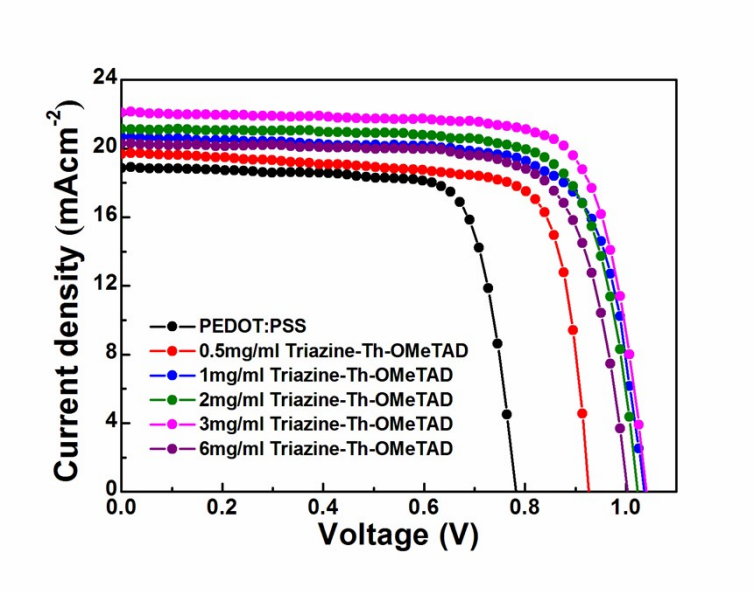


Figure S13. *J-V* characteristics of devices based on PEDOT: PSS and Triazine-Th-OMeTAD with different concentrations.

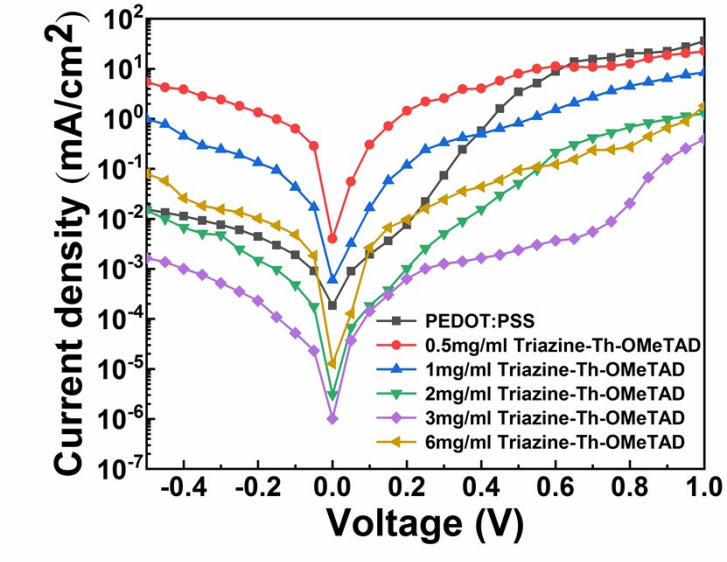


Figure S14. Current density of the devices with various concentrations of Triazine-Th-OMeTAD and PEDOT: PSS under short-circuit and dark condition.

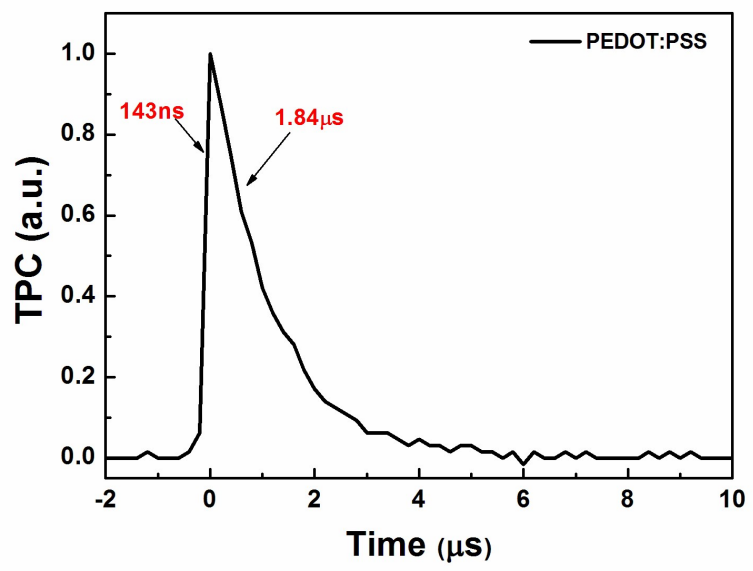


Figure S15. Transient photocurrent response of PEDOT:PSS-based OIHP photodetector.

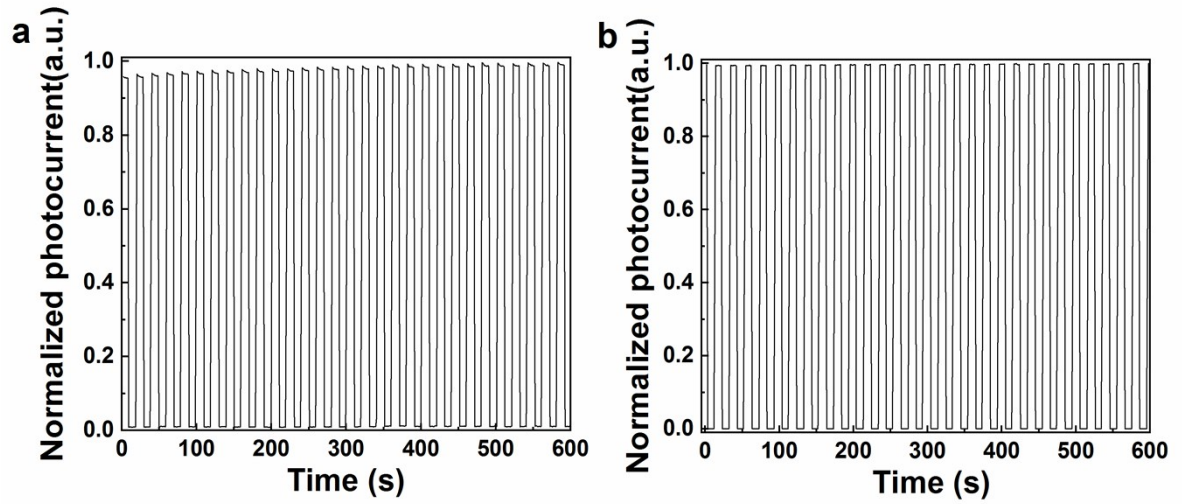


Figure S16. The time-dependent current (*I-t*) curve of device based on Triazine-Th-OMeTAD HTL a) under the -0.1V and b) under self-powered condition.

Table S1. Fitted results of the TRPL spectra with a multiexponential function.

Samples	A_1[a]	τ_1(ns)	A_2[a]	τ_2(ns)	τ_{avg}[b](ns)
PEDOT:PSS/PVK	1.24	5.24	0.77	13.91	10.62
Triazine-Th-OMeTAD/pvk (0.5mg/mL)	2.24	3.52	0.77	10.09	6.78
Triazine-Th-OMeTAD/pvk (1mg/mL)	3.03	2.81	1.12	6.18	4.32
Triazine-Th-OMeTAD/pvk (2mg/mL)	0.80	6.18	3.22	3.06	4.11
Triazine-Th-OMeTAD/pvk (3mg/mL)	0.80	5.85	3.31	2.82	3.83
Triazine-Th-OMeTAD/pvk (6mg/mL)	2.45	3.87	0.58	8.38	5.39

[a]A_1 and A_2 are the relative amplitudes.

[b]Average lifetime $\tau_{avg} = \alpha_1\tau_1 + \alpha_2\tau_2$, where $\alpha_i = A_i\tau_i/\Sigma A_i\tau_i$.

Table S2. Summary of the parameters extracted from capacitor-like devices in which perovskite films deposited on different concentrations of Triazine-Th-OMeTAD or PEDOT:PSS are sandwiched between ITO and Au electrode

HTL	L(nm)[a]	V_{TFL}(V)[b]	n_{trap}(10^{16}cm^{-3})	μ(10^{-4}cm^{-2}V^{-1}S^{-1})
PEDOT:PSS	275	1.76	8.26	2.85
Triazine-Th-OMeTAD (0.5mg/mL)	251	1.361	7.64	2.37
Triazine-Th-OMeTAD (1mg/mL)	251	0.587	4.51	3.30
Triazine-Th-OMeTAD (2mg/mL)	253	0.558	3.08	8.25
Triazine-Th-OMeTAD (3mg/mL)	257	0.332	1.73	11.7
Triazine-Th-OMeTAD (6mg/mL)	254	0.691	3.79	3.98

[a]the thickness of perovskite film based on PEDOT:PSS or different concentration of Triazine-Th-OMeTAD HTL; [b]the trap-filling limit voltage.

References

1. C. H. M. Chuang, P. R. Brown, V. Bulovic and M. G. Bawendi, *Nat. Mater.*, 2014, **13**, 796-801.
2. Z. W. Jin, Q. Zhou, Y. H. Chen, P. Mao, H. Li, H. B. Liu, J. Z. Wang and Y. L. Li, *Adv. Mater.*, 2016, **28**, 3697-3702.