Supporting Information

Solution-Processable Cu(II) Phthalocyanine Derivative as Dopant-Free Hole Transport Layer for Efficient and Low-Cost Rutile TiO_2 Array-Based Perovskite Solar Cells

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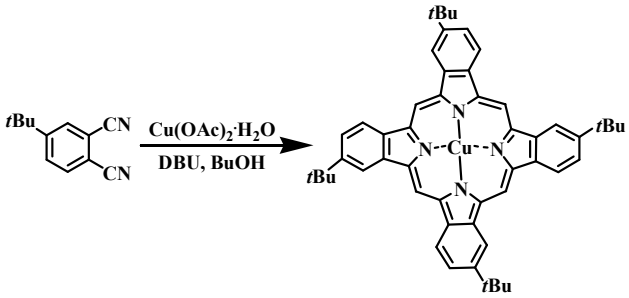

Figure S1. Synthetic route of CuPc(tBu)$_4$.

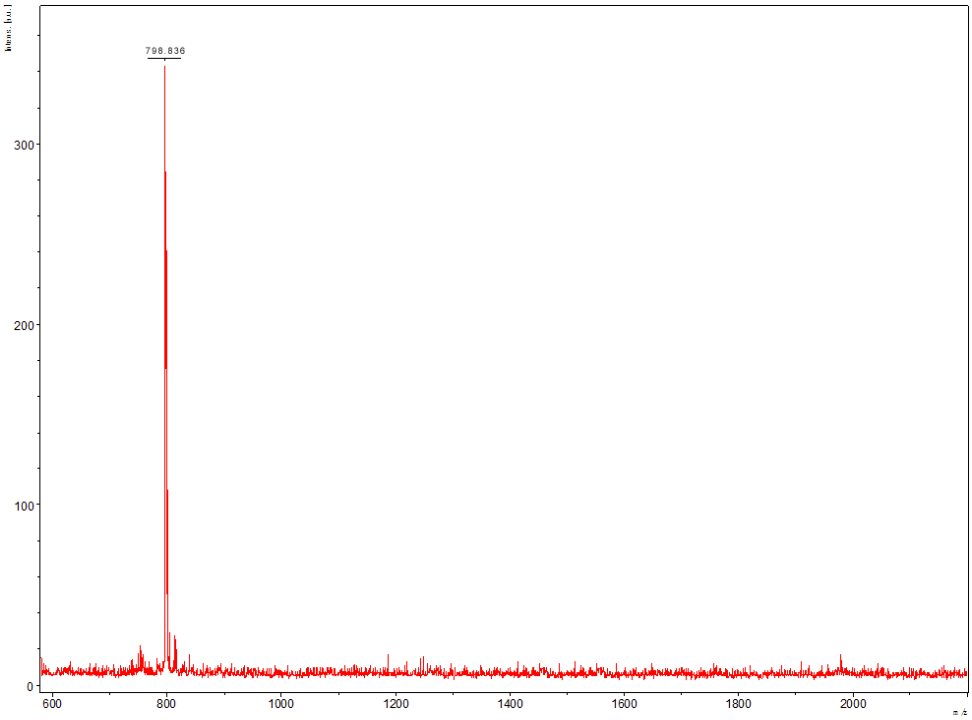

Figure S2. MALDI-TOF mass spectrum of molecular ion of CuPc(tBu)$_4$.

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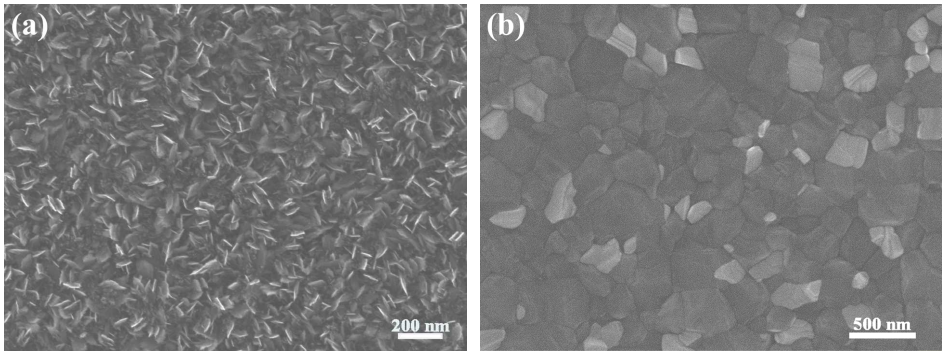

Figure S3. Top-view FESEM images of the RTA (a) and perovskite/RTA (b) films.

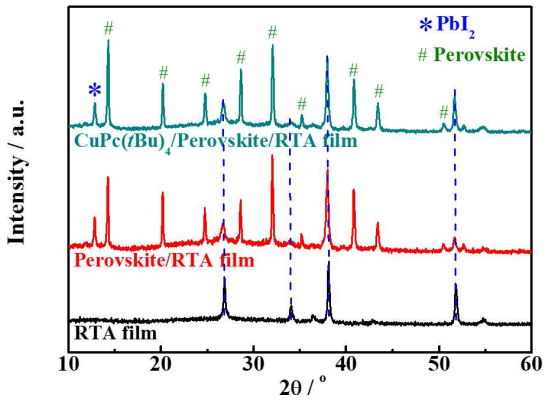

Figure S4. X-ray diffraction (XRD) patterns of RTA, perovskite/RTA and CuPc(tBu)$_4$/perovskite/RTA films.

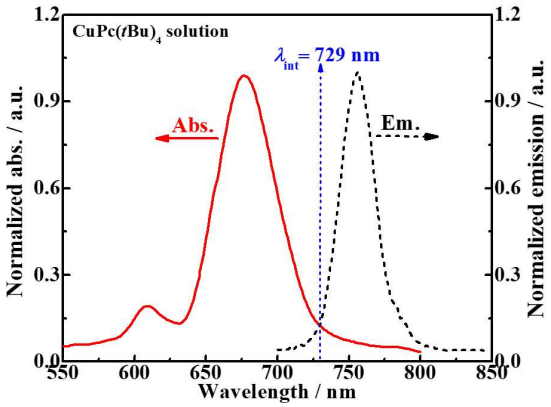

Figure S5. Normalized UV-vis absorption and PL spectra of 1.0×10^{-3} M CuPc(tBu)$_4$ DMF solution.

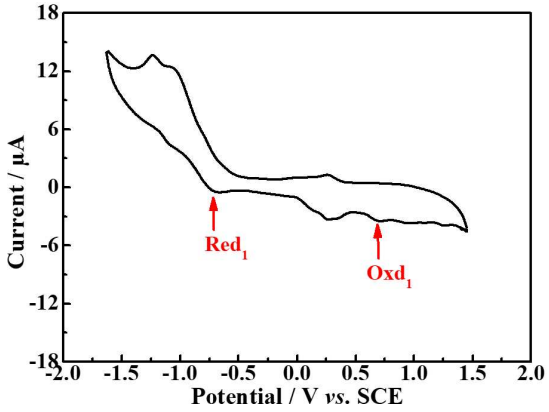

Figure S6. Cyclic voltammogram (CV) curve of CuPc(*t*Bu)$_4$ solution.

Table S1. Calculated Data of Optical and Electrochemical Properties of CuPc(*t*Bu)$_4$

Dye	$E_{1/2}$ /V *vs.* SCE		$E_{0\text{-}0}$	E_{HOMO} [a]	E_{LUMO} [b]
	Ox	Red	/eV	/eV	/eV
CuPc(*t*Bu)$_4$	0.49	-0.92	1.70	-5.20	-3.50

[a] Calculated with the equation $E_{HOMO} = -(E_{ox}+4.71)$ eV, [b] Calculated with the equation $E_{LUMO} = (E_{HOMO} + E_{0\text{-}0})$ eV.

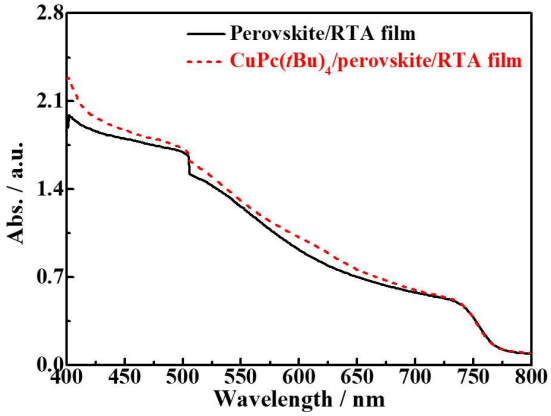

Figure S7. UV-Vis diffuse reflectance absorption spectra (DRS) of perovskite/RTA and CuPc(*t*Bu)$_4$/perovskite/RTA films.

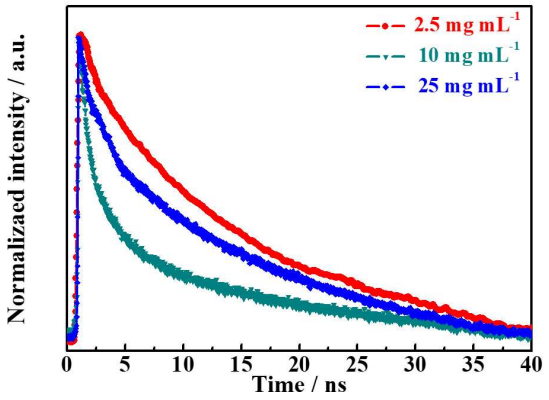

Figure S8. Time-revolved photoluminescence (TRPL) spectra of the PSCs with CuPc(*t*Bu)$_4$ as HTLs that were spin-coated using CuPc(*t*Bu)$_4$ solutions with different concentrations.

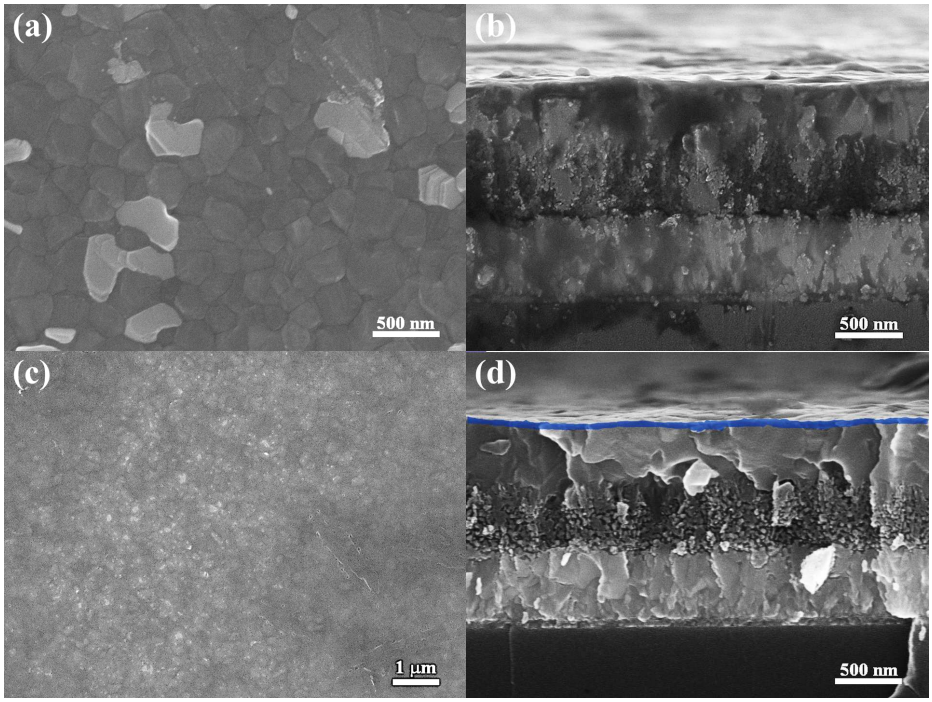

Figure S9. Top-view and cross-sectional FESEM images of the Al_2O_3 layer (a, b) and CuPc(*t*Bu)$_4$/Al_2O_3 layer (c, d) on the perovskite/RTA film. CuPc(*t*Bu)$_4$ HTL was spin-coated by using 20 mg mL^{-1} CuPc(*t*Bu)$_4$ solution.

Table S2. Photovoltaic Performance Parameters of the 15 PSCs Fabricated with CuPc(*t*Bu)$_4$ as HTL by Spin-Coating 10 mg mL^{-1} CuPc(*t*Bu)$_4$ Solution Measured under Forward Scanning Mode

Number	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
1	22.0	1.01	62	13.7
2	22.5	1.03	54	12.5
3	21.7	1.06	57	13.2
4	19.4	1.01	56	10.9
5	20.1	1.02	62	12.8
6	20.8	1.06	53	11.6
7	21.1	1.03	61	13.3
8	19.7	1.04	58	11.8
9	21.4	1.02	58	12.6
10	22.1	1.04	60	13.7
11	20.8	1.04	58	12.5
12	21.2	1.04	57	12.6
13	20.6	1.01	62	12.9
14	21.4	1.05	56	12.7
15	21.8	1.05	58	13.3
Average	21.1 ± 0.9	1.03 ± 0.02	58.1 ± 2.8	12.7 ± 0.8

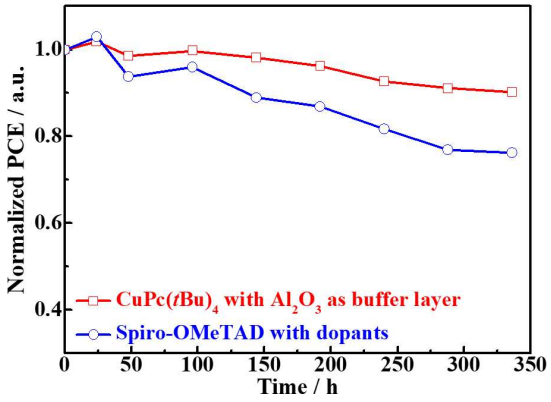

Figure S10. Stability tests for the PSCs fabricated with dopant-free CuPc(tBu)$_4$ and doped spiro-OMeTAD as HTM layer. Those devices without encapsulations were stored at ambient condition in the dark at room temperature with a humidity of ~30%.