

Supplementary Information for:

Dopant-Free Small-Molecule Hole-Transport Material for Low-Cost and Efficient Perovskite Solar Cell

S1. Experimental

All starting materials were purchased from Aldrich Chemical and Merck Companies and used without further purification. ^1H NMR spectra were recorded on Bruker Advance 250 MHz spectrometers with CDCl_3 and $\text{D}_6\text{-DMSO}$ as solvents. Chemical shifts were calibrated against TMS as an internal standard. UV/Vis and emission spectra were measured using an Ultraspec 3100 pro spectrophotometer, and AvaSpec-125 spectrophotometer in CHCl_3 solution. E_{0-0} was obtained using interception of absorption and emission spectra. The Electrochemical studies were accomplished by using SAMA500 potentiostat electrochemical analyzer with a conventional three electrode cell, and a Pt disk as the working electrode, a Pt wire as the counter electrode. Ag/AgCl was used as the reference electrode and the supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAP) in DMF. For conductive measurement, glass substrates without conductive layer were cleaned carefully with detergents, deionized water, acetone, and ethanol, respectively. Then to remove the remaining organic residues, the substrates were sintered at 500 °C. A thin layer of nanoporous TiO_2 was coated on the glass substrates by spin-coating with a diluted TiO_2 paste (PST-20T) with ethanol (1: 3, mass ratio). After that, TiO_2 film was sintered in the oven at 500 °C. Then a solution of HTM in chlorobenzene (concentrations similar to photovoltaic devices) was deposited by spin-coating on the TiO_2 layer. Finally, an Au layer was deposited on top of the HTM layer by thermal evaporation.

The current density–voltage (J–V) curves were measured using a solar simulator (Newport, Oriel Class A, 91195A) with a source meter (Keithley 2420) under 100 mA cm^{-2} illumination (AM 1.5G) and a calibrated Si-reference cell certificated by NREL. The J–V curves of all devices were measured by masking the active area with a metal mask of area 0.096 cm^2 .

Synthesis of new HTMs (1) and (2)

HTMs (**1**) were prepared according to the procedure reported in the literature¹. In brief, a mixture of terephthalaldehyde (0.136 g), 9,10 phenanthrene (0.21 g), ammonium acetate (3.85 g), and 10 ml of acetic acid was heated to reflux for 24 hours under N₂ atmosphere. After cooling to ambient temperature, the organic was extracted by using CHCl₃ and H₂O. The combined organic phases were dried over anhydrous MgSO₄ and the solvent was evaporated and washed with ethanol three times to remove residuals. The synthesis procedure of (**2**) is the same as (**1**), except 3-phenyl propanal (0.13 g) was used instead of terephthalaldehyde as the precursor of the imidazole derivative. The products did not need any purification by chromatography methods.

Analysis data for (**1**): ¹HNMR (250. 13MHz, DMSO-d₆, 25°C, TMS, ppm) δ= 7/62 (2H, m), 7/68 (2H, m), 7/96 (2H, d), 8/04 (2H, d), 8/11 (2H, d), 8/98 (2H, d), 9/89 (1H, s), 12/81 (2H,s). FT-IR (KBr): ν= 3428(w) (N-H), 3067(w), 2849(w), 1698(m), 1660(s) (C=N), 1606(s), 1455(m), 1427-(m), 1213(m) (C-H), 1117(m), 960(w), 839(s), 754(s), 724(s), 668(m), 462(m), 427(s), 416(s). CHN: Anal. calcd. For C₂₃H₁₆N₂ (%): C, 86.228; H, 5.032; N, 8.745 Found (%): C, 86.222; H, 5.038; N, 8.741 ESI-MS: m/z 319.40, [M-H]⁺.

Analysis data for (**2**): ¹HNMR (250. 13MHz, DMSO-d₆, 25°C, TMS, ppm) δ= 3/9 (1H, s), 4/95 (1H, d), 6/56 (1H, m), 7/24 (4H, d), 7/33 (1H, m), 7/9 (1H, m), 7/47 (1H, m), 7/43 (1H, m), 7/60 (1H, m), 7/69 (1H, m), 7/85 (1H, m), 7/80 (1H, m), 8/00 (1H, d). And FT-IR(KBr) ν= 3400(W) (N-H), 3026(w), 1948(w), 1805(w), 1662(w) (C=N), 1601(w), 1500(w), 1417(w), 1442(w), 1197-(w), 1071(w) (C-N), 1000(w), 965(m), 913(w), 842(w), 736(s), 695(s), 605(w), 500(w). CHN: Anal. calcd. For C₂₂H₁₄N₂O, (%): C, 81.975; H, 4.384; N, 8.692; Found (%): C, 81.971; H, 4.388; N, 8.697; ESI-MS: m/z 321.37, [M-H]⁺.

Fabrication of Cell

Perovskite solar cells were fabricated on fluorine-doped tin oxide (FTO) coated glass substrates. Part of the glass substrate coated with FTO was etched with Zn powder and HCl 2 M ethanol solution. Then, the substrates were washed carefully with distilled water, detergent, acetone, and ethanol, isopropanol and then treated with an ultraviolet/O₃ cleaner for 15 min. On these substrates, a solution of HCl and titanium di-isopropoxide bis(acetylacetonate) in anhydrous ethanol was coated with spin-coating method at 2000 r.p.m. for 30 s. Then, the substrates were heated at 500 °C for 30 minutes and cooled down to room temperature. A mesoporous TiO₂ layer diluted in ethanol was deposited by spin-coating at 2000 r.p.m. for 10 s to achieve a 300-400 nm thick layer.

After that, the substrates were sintered again at 500 °C for 30 minutes. The PbI₂ solution was coated on a mesoporous TiO₂ layer for 5 s at 6500 r.p.m. and dried at 70 °C. The mixed perovskite precursor solution was prepared by dissolving PbI₂ (1.15 M), FAI (1.10 M), PbBr₂ (0.2 M), and MABr (0.2 M) in an anhydrous solvent DMF: DMSO=4:1 (volume ratio). The perovskite solution was spin-coated in a two-step procedure at 1,000 and 6,000 r.p.m. for 10 and 30 s respectively. Chlorobenzene (110 μl) was dropped on the spinning substrate at 20 s in the second step and then films were annealed at 100 °C for 90 min in the glove box. Following this step, the **(1)**, **(2)**, and **(3)** were deposited by spin-coating at 4000 r.p.m. for 20 s. The HTM solutions were prepared by dissolving the HTM in chlorobenzene at a concentration of 78 mM, with the addition of 18 μL LiTFSI (from a stock solution in acetonitrile with a concentration of 1.0 M), 29 μL of tert-butyl pyridine (from a stock solution in chlorobenzene with a concentration of 1.0 M). Finally, an 80 nm Au electrode was deposited by thermal evaporation under a high vacuum.¹⁻³

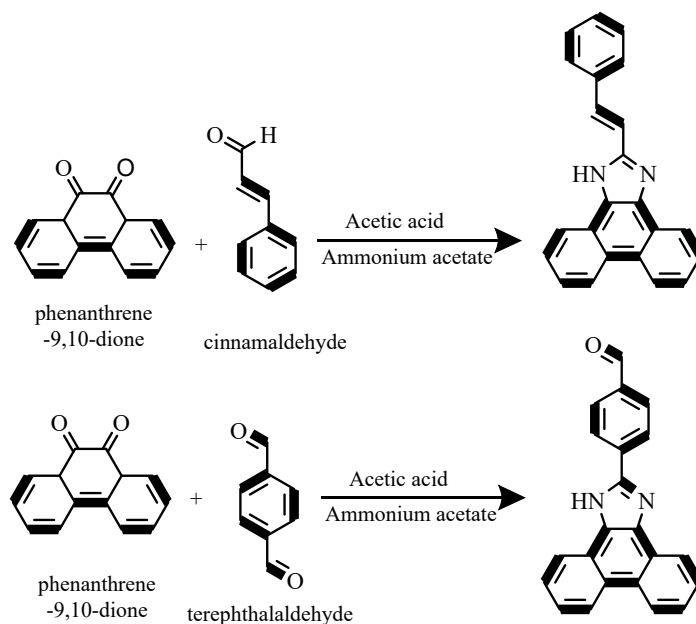


Figure S1. Synthesis reactions and molecular structures of the **(1)**, and **(2)**

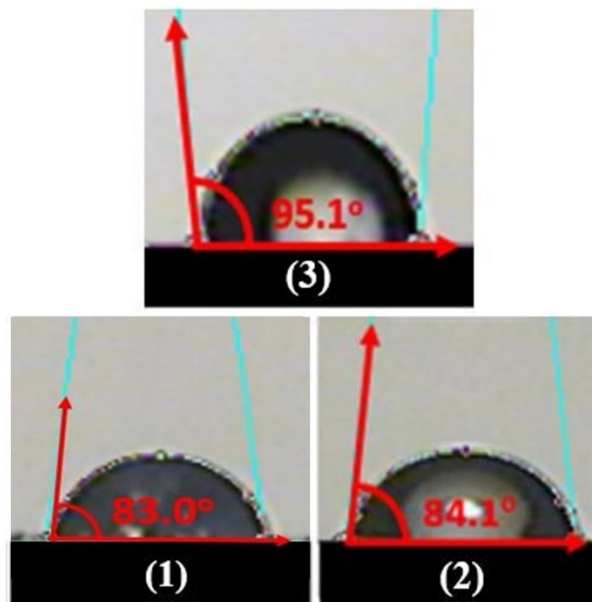


Figure S2. Contact angles of the (1), (2) and (3)

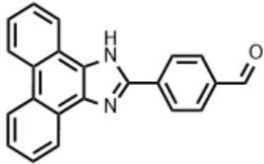
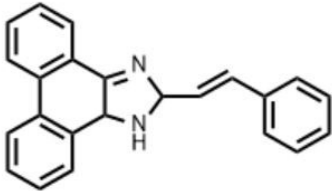
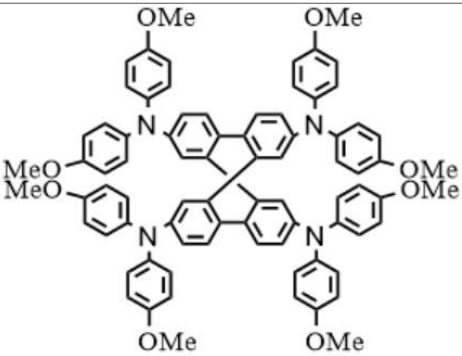
S2. The cost estimation of 1 gram of (1) and (2)

Table S1. The estimation of the cost of 1 gram of (1), and (2) according to the cost models of Pablo et al.⁴ and Osedach et al.⁵ The price of the materials used has been obtained from Merck, Sigma Aldrich, and DeJong companies^{2, 6}.

Component	Chemical name	Weight reagent (g/g)	Weight solvent (g/g)	Price of chemical (\$/kg)	Material cost (\$/gproduct)
(1)	9,10-Phenanthrenequinone	0.21		3410	0.71
	Ammonium acetate	3.85		181	0.69
	Magnesium sulfate	4		208	0.83
	Ammonia		3	447	1.34
	Chloroform		10	94	0.94
	Acetic acid		10	56	0.59
	Terephthalaldehyde	0.068		450	0.03
Total					5.13
(2)	9,10-Phenanthrenequinone	0.21		3410	0.71
	Ammonium acetate	3.85		181	0.69
	Magnesium sulfate	4		208	0.83

(2)	Ammonia	3	447	1.34
	Chloroform	10	94	0.94
	Acetic acid	10	56	0.59
	3Phenylpropionaldehyde	0.13	630	0.08
Total				5.18

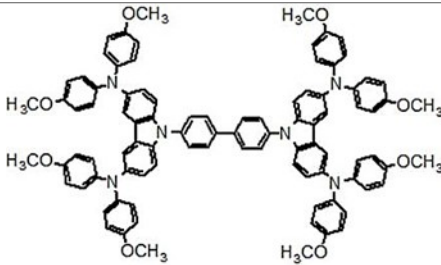
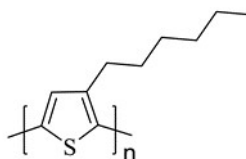
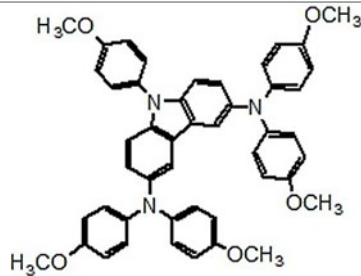
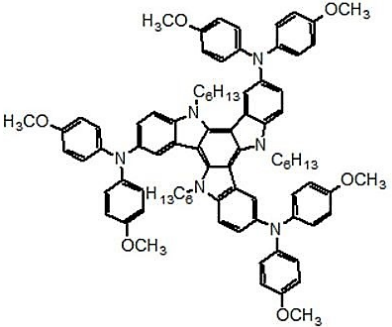
Table S2. Examples of organic HTMs reported in relevant kind of literature, together with the catalysts used for their synthesis; the synthesis cost for 1 g of materials; the photovoltaic characteristics of the corresponding PSCs under AM1.5G illumination.

NO	HTM	Catalyst used for synthesis	Cost per 1 g of HTM (\$/g)	Jsc (mA cm ⁻²)	Voc (V)	FF	η (%)	Ref.
1			5.13	19	1	74	0.92	Current work
2			5.18	8	0.8	55	0.9	Current work
3		t-BuONa Pd ₂ (dba) ₃ P(t-Bu) ₃	273.62	20.7	1.00	0.71	14.9	7

4		Pd(PPh ₃) ₄ K ₂ CO ₃	842.08	20.98	0.97	0.67	13.63	8
5		t-BuONa P(t-Bu) ₃ Pd(OAc) ₂	112.23	23.4	1.13	0.73	19.8	9
6		AlCl ₃ FeCl ₃	367.55	20.6	0.95	0.66	12.8	10
7		Pd(PPh ₃) ₄ K ₂ CO ₃	695.87	21.21	1.09	0.78	18.36	11

8		Pd(PPh ₃) ₄ K ₂ CO ₃	420.22	20.88	0.95	0.62	12.31	6
9		Pd(PPh ₃) ₄ K ₃ PO ₄ NH ₄ Cl	800.49	21.9	1.07	0.77	18.2	12
10		Pd ₂ (dba) ₃ X-Phos t-BuONa	591.57	20.6	1.09	0.77	17.0	9
11		Pd ₂ (dba) ₃ X-Phos t-BuONa	376.30	20.4	1.04	0.72	16.0	9

12		K_2CO_3 $Pd(PPh_3)_4$	633.88	13.8	0.98	0.76	10.3	13
13		K_2CO_3 $Pd(PPh_3)_4$	579.16	17.63	1.02	0.73	13.44	14
14		$Pd(OAc)_2$ Tri- tbutylphos- phine t-BuONa	450.13	20.35	0.99	0.69	13.86	15
15		$Pd(OAc)_2$ Tri- tbutylphos- phine t-BuONa	434.12	20.28	1.02	0.71	14.79	12

16		t-BuONa Pd(OAc) ₂ [(t-Bu) ₃ PH]B F ₄	168.42	21.0	0.92	0.67	12.92	16
17		CuI 1,10-phenanthroline K ₂ CO ₃	216.46	23.2	1.02	0.79	18.6	17
18		t-BuONa P(t-Bu) ₃ Pd ₂ (dba) ₃	148.57	20.4	1.13	0.68	15.8	14
19		t-BuONa Pd(OAc) ₂ P(t-Bu) ₃	245.84	20.6	0.88	0.63	11.54	8

References

1. S. Tang, W. Li, F. Shen, D. Liu, B. Yang and Y. Ma, *Journal of Materials Chemistry*, 2012, **22**, 4401.
2. M. Saliba, S. Orlandi, T. Matsui, S. Aghazada, M. Cavazzini, J.-P. Correa-Baena, P. Gao, R. Scopelliti, E. Mosconi and K.-H. Dahmen, *Nature energy*, 2016, **1**, 1.
3. I. Zimmermann, J. Urieta-Mora, P. Gratia, J. Aragón, G. Grancini, A. Molina-Ontoria, E. Ortí, N.

- Martín and M. K. Nazeeruddin, *Advanced Energy Materials*, 2017, **7**, 1601674.
4. M. Petrus, T. Bein, T. Dingemans and P. Docampo, *Journal of Materials Chemistry A*, 2015, **3**, 12159.
 5. T. P. Osedach, T. L. Andrew and V. Bulović, *Energy & Environmental Science*, 2013, **6**, 711.
 6. B. Xu, D. Bi, Y. Hua, P. Liu, M. Cheng, M. Grätzel, L. Kloo, A. Hagfeldt and L. Sun, *Energy & Environmental Science*, 2016, **9**, 873.
 7. N. J. Jeon, H. G. Lee, Y. C. Kim, J. Seo, J. H. Noh, J. Lee and S. I. Seok, *Journal of the American Chemical Society*, 2014, **136**, 7837.
 8. H. Choi, S. Paek, N. Lim, Y. H. Lee, M. K. Nazeeruddin and J. Ko, *Chemistry—A European Journal*, 2014, **20**, 10894.
 9. D. Bi, B. Xu, P. Gao, L. Sun, M. Grätzel and A. Hagfeldt, *Nano Energy*, 2016, **23**, 138.
 10. J. Cao, Y.-M. Liu, X. Jing, J. Yin, J. Li, B. Xu, Y.-Z. Tan and N. Zheng, *Journal of the American Chemical Society*, 2015, **137**, 10914.
 11. K. Rakstys, A. Abate, M. I. Dar, P. Gao, V. Jankauskas, G. n. Jacopin, E. Kamarauskas, S. Kazim, S. Ahmad and M. Grätzel, *Journal of the American Chemical Society*, 2015, **137**, 16172.
 12. A. Molina-Ontoria, I. Zimmermann, I. Garcia-Benito, P. Gratia, C. Roldán-Carmona, S. Aghazada, M. Graetzel, M. K. Nazeeruddin and N. Martín, *Angewandte Chemie International Edition*, 2016, **55**, 6270.
 13. M. Franckevičius, A. Mishra, F. Kreuzer, J. Luo, S. M. Zakeeruddin and M. Grätzel, *Materials Horizons*, 2015, **2**, 613.
 14. P. Ganesan, K. Fu, P. Gao, I. Raabe, K. Schenk, R. Scopelliti, J. Luo, L. H. Wong, M. Grätzel and M. K. Nazeeruddin, *Energy & Environmental Science*, 2015, **8**, 1986.
 15. S. Do Sung, M. S. Kang, I. T. Choi, H. M. Kim, H. Kim, M. Hong, H. K. Kim and W. I. Lee, *Chemical Communications*, 2014, **50**, 14161.
 16. P. Gratia, A. Magomedov, T. Malinauskas, M. Daskeviciene, A. Abate, S. Ahmad, M. Grätzel, V. Getautis and M. K. Nazeeruddin, *Angewandte Chemie International Edition*, 2015, **54**, 11409.
 17. B. Xu, E. Sheibani, P. Liu, J. Zhang, H. Tian, N. Vlachopoulos, G. Boschloo, L. Kloo, A. Hagfeldt and L. Sun, *Advanced materials*, 2014, **26**, 6629.
-