Supporting Information

Efficient Perovskite Solar Cell with Symmetrical Zn(II) Phthalocyanine Infiltrated Buffering Porous Al₂O₃ as Hybrid Interfacial Hole-Transporting Layer

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Synthetic scheme of Sym-HTpCH:

Synthesis of 4-(5-hexylthiophen-2-yl) phthalonitrile (3):

To a stirred solution of 4-iodophthalonitrile 1 (2.5 g 9.84 mmol), 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 2 (3.183 g, 10.82 mmol), water (20 mL) and Sodium bicarbonate (17.36 g, 206.6 mmol) in THF (100 mL). The reaction mixture was degassed with argon for 30 min, after Pd(PPh₃)₄ (1.13 g, 0.984 mmol) was added to the reaction mixture. Then, the reaction mixture was heated at reflux for 12 h under an argon atmosphere. The solvent was removed under vacuum; the crude residue was purified on a silica gel column chromatography by using Hexane/EtOAC (9:1) as an eluent to give the white solid compound 3 (2.3 g, 79.5% yield). ¹H NMR (CDCl₃, 400MHz): δ, ppm 7.92 (d, 1H, J = 1.8 Hz), 7.81 (dd, 1H, J = 1.8, 6.7 Hz), 7.73 (d, 1H, J = 8.5 Hz), 7.31(d, 1H, J = 3.6 Hz), 6.83 (d, 1H, J = 3.6 Hz), 2.8 (t, 2H, J = 7.6 Hz), 1.74 – 1.66 (m, 2H), 1.42-1.25 (m, 6H), 0.89 (t, 3H, J = 7.0 Hz). ESI-MS: m/z Calcd. For C₁₈H₁₈N₂S: 294.1, Found: 293.35 [M⁺].
$^1$H NMR spectrum of Compound 3 in CDCl$_3$

Mass spectrum of Compound 3
Synthesis of Sym-HTPcH:

To a mixture of 4-(5-hexylthiophen-2-yl)phthalonitrile 3 (2.00 g, 6.80 mmol) and zinc acetate (0.596 g, 2.72 mmol) in Pentanol (20 mL). The reaction mixture was warmed to 100 °C at this temp the DBU (1.24 mL, 8.13mmol) was added drop wise to the reaction mixture, then the reaction mixture refluxed for 24 h, after completion of the reaction, the solvent was removed under reduced pressure; the crude residue was purified on a silica gel column chromatography by using DCM / MeOH (99:1) as an eluent to give the green solid and recrystallised from MeOH to afford sym-HTPcH (1.0 g, 11.8 % yield). $^1$H NMR (CDCl$_3$, 400MHz): δ, ppm 7.52 (d, 1H, $J = 8.5$ Hz), 7.35 (d, 1H, $J = 2.0$ Hz), 7.09 (ddd, 1H, $J = 2.4, 5.3, 6.1$ Hz), 6.84 (br. S, 1H), 6.53 (br. S, 1H), 2.72 (br. S, 2H), 1.71 – 1.67 (m, 2H), 1.44-1.25 (m, 6H), 0.89-0.82 (m, 3H) [Not properly integrated]. ESI-MS: m/z Calcd. For C$_{72}$H$_{72}$N$_8$S$_4$Zn:1243.0, Found: 1244.12[M]$^+$. UV-vis:(0.01mM) in THF: $\lambda_{\max}$= 630 ($\varepsilon = 53, 951$), & 700 nm ($\varepsilon = 2, 92, 309$) cm$^{-1}$.
MASS spectrum of Sym-HTPcH

Figure S1. TG/DTG curves of Sym-HTPcH.
Figure S2. DSC curves of Sym-HTPcH.

Figure S3. CV and DPV measurement of Sym-HTPcH with ferrocene as an internal standard and platinum wire as reference electrode.

Solar cells fabrication. Devices were fabricated on fluorine doped tin oxide (FTO) coated glass substrates. The substrates were cleaned sequentially with Hellmanex and isopropano in
ultrasonic bath for 30 min, then washed with acetone and finally with UV/ ozone surface cleaning for 15 min. A 30 nm TiO$_2$ compact layer was deposited on FTO via spray pyrolysis at 450°C from a precursor solution of titanium diisopropoxide bis(acetylacetonate) in anhydrous ethanol. After the spraying, the substrates were left at 450°C for 5 min, then they were left to cool down to room temperature. Mesoporous TiO$_2$ layer was deposited by spin coating for 20 s at 4000 rpm with a ramp of 2000 rpm s$^{-1}$, using 30 nm particle paste (Dyesol) diluted in ethanol to achieve 150 nm thick layer. After the spin coating, the substrate was immediately dried at 100°C for 10 min and then sintered again at 500°C for 30 min, under dry air flow. Upon cooling to room temperature, the perovskite layer was deposited in a nitrogen-filled glovebox by spin coating the perovskite precursor solution. The latter was prepared dissolving a stoichiometric amount (1:1 molar ratio) of lead iodide and methyl ammonium iodide in dimethylsulfoxide at a concentration of 1.1 M of each component. The spin coating program includes two steps, first 1000 rpm for 10 s with a ramp of 200 rpm s$^{-1}$, then 6000 rpm for 30 s with a ramp of 2000 rpm s$^{-1}$. 10 s before the end of the spin-coating program, chlorobenzene was gently dropped on the spinning substrate for 2 s using an automatic dispenser. The substrate was then heated at 100°C for 1 h on a hotplate in the nitrogen-filled glovebox.

For the spiro-OMeTAD, the HTM solution was prepared dissolving the molecule in chlorobenzene at concentration of 70 mM, with the addition of 50 mol\% of bis(trifluoromethanesulfonyl)imide (Aldrich) from a stock solution of 1.8 M in acetonitrile), 330 mol\% of tert-butylpyridine (Aldrich) and 2 mol\% of tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) Tris(trifluoromethylsulfonyl)imide (Dyesol) from a stock solution 0.25 M in acetonitrile. The HTM layer was deposited on the top of the perovskite layer by spin coating from solution at 4000 rpm for 20 s with a ramp of 2000 rpm s$^{-1}$.

For device prepared using HTPcH, we deposited a thin alumina mesoporous layer directly on the top of the perovskite layer. This layer was prepared by spincoating a colloidal dispersion of
< 50 nm Al₂O₃ nanoparticles at 2 wt% in isopropanol at 2000 rpm. The HTPeH solution was prepared dissolving the molecule in chlorobenzene at concentration of used 30 mM, with the same doping composition we used for the spiro-OMeTAD solution. The HTM layer was finally deposited by spin coating from solution at 4000 rpm for 20 s with a ramp of 2000 rpm s⁻¹. Finally, 80 nm of gold was deposited by thermal evaporation under high vacuum, using a shadow masking to pattern the electrodes.

Solar cells characterisation. A ZEISS Merlin HR-SEM was used to characterize the morphology of the device cross-section. Current-voltage characteristics were measured in air under AM 1.5 simulated sunlight with a potentiostat (Keithley). The light intensity was measured for calibration with an NREL certified KG5 filtered Si reference diode. The solar cells were masked with a metal aperture of 0.16 cm² to define the active area. The current-voltage curves were recorded scanning at 0.01 V s⁻¹.