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Ambient Stable, Hydrophobic electrically conductive Porphyrin Hole-Extracting Materials for Printable Perovskite Solar Cells

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Supporting information

1. Theoretical calculations

D-π-D porphyrin molecular systems (ZPPHT, HPPHT) designed and optimized with density functional theory (Gaussian 09 program package)[1]. By using the optimized structures, HOMO-LUMO energy levels calculated and generated with B3LYP 6-31g (d,p) level theory. Here, we run the DFT with a methyl group instead of bulky octyl-chain both phenothiazine firmed D-π-D porphyrin molecular systems.

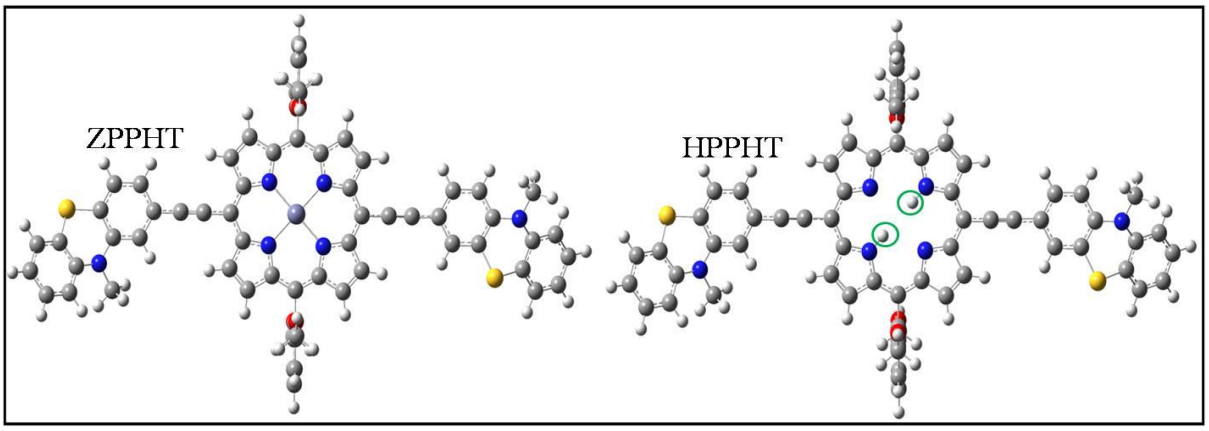
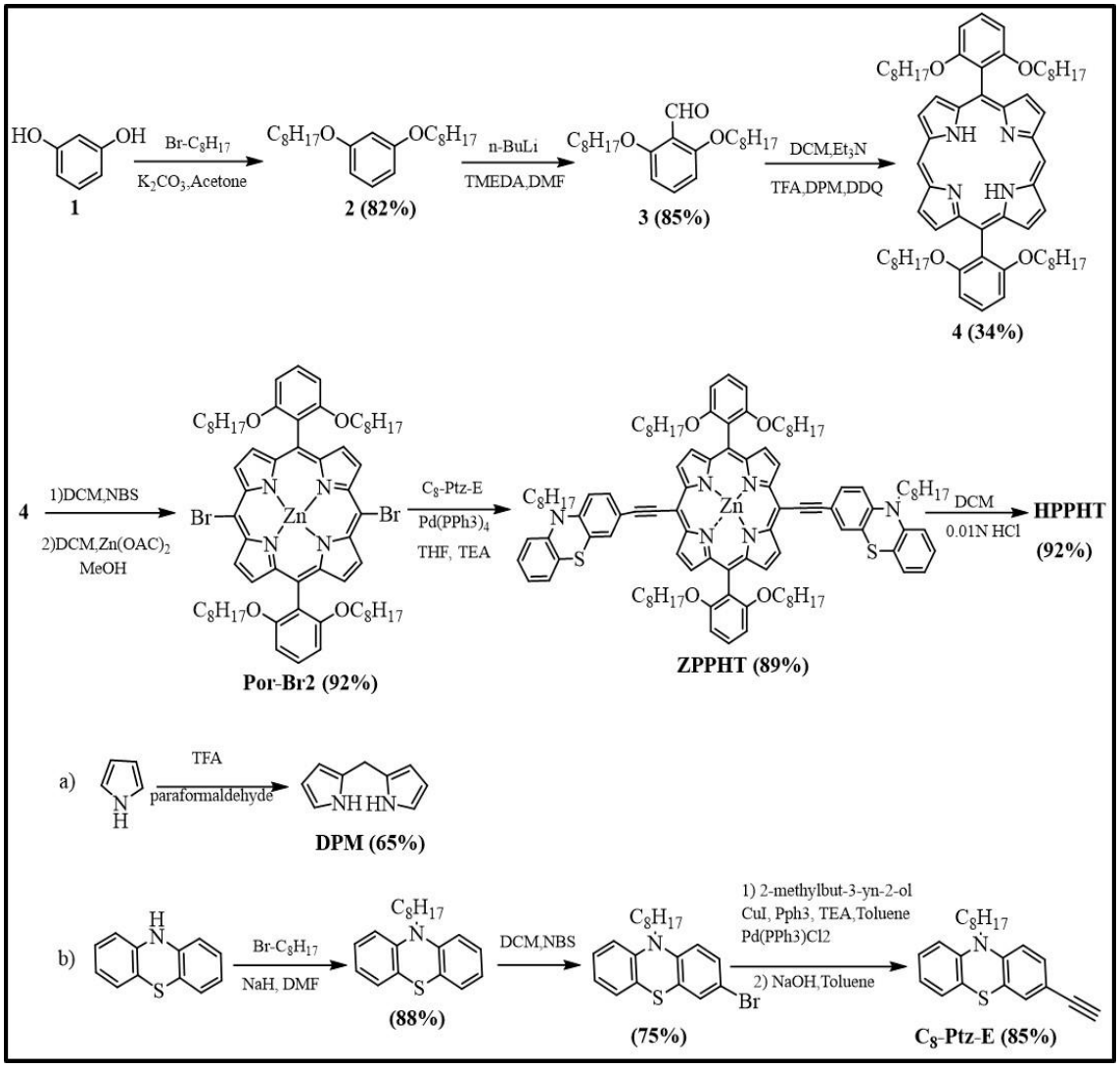


Figure S1. Optimized geometries of the ZPPHT/HPPHT at B3LYP 6-31g (d.p) level.

2. Synthesis of D-π-D porphyrin molecular systems

Detailed synthetic pathway for **ZPPHT** and **HPPHT** follows a Sonogashira cross-coupling and demetallation. However, other intermediates were synthesized as previous reports with slight modification[2,3,4,5,6]. Synthetic routes and yields were shown in Scheme S1.[1]H-NMR andMALDI-TOF spectra were recorded on a 400MHz INOVA spectrometer and Shimadzu Biotech Axima Performance mass spectrometer respectively.



Scheme S1. Synthetic scheme for D-π-D porphyrin molecular systems.

2.1 3,3'-((10,20-bis(2,6-bis(octyloxy)phenyl)porphyrin-5,15-diyl)bis(ethyne-2,1-diyl))bis(10-octyl-10H-phenothiazine)-Zn(II) (ZPPHT): under N_2 atmosphere Por-Br_2 (1.00g) was dissolved in 10ml Triethyle amine (TEA) and 10 ml of dry Tetrahydrofuran (THF) in 50 ml RB. Resulting solution fudged with N_2 gas for about 20 min followed by CuI (0.023g), Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) (0.14g) were added and heated to 50^{o}C-60^{o}C. Next, 3-ethyl-10octyl-10H-phenothiazine (C_8-Ptz-E (0.84g)) was dissolved in 5ml THF and added slowly with the help of syringe, spontaneous colour change (brown to green) was observed. Monitoring the TLC until starting materials were consumed. Then, cool the reaction mixture to RT and remove the solvent with rotatory evaporator and workup with DCM filtered and dried over Na_2SO_4. Further, reaction mixture purified by column chromatography using Hexane: DCM (3:1 v/v) and recrystalized with methanol/DCM yielded 89% as green powdered. Anal.Calcd. For $C_{108}H_{130}N_6O_4S_2Zn$% (1702.89): C,76.05; H,7.68; N,4.93; Found C,76.10; H,7.58; N,4.88. MALDI-TOF: m/z $[M]^+$calcd (1702.89): For $C_{108}H_{130}N_6O_4S_2$; found, 1702.96. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (d, *J* = 4.6 Hz, 4H), 8.84 (d, *J* = 4.6 Hz, 4H), 7.72 (dt, *J* = 23.1, 8.4 Hz, 6H), 7.19 (t, *J* = 7.1 Hz, 4H), 7.01 – 6.91 (m, 10H), 3.94 (t, *J* = 7.2 Hz, 4H), 3.84 (t, *J* = 6.4 Hz, 8H), 1.49 (s, 16H), 1.25 (s, 8H), 1.02 – 0.93 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 8H), 0.84 – 0.75 (m, 8H), 0.60 (dt, *J* = 14.6, 7.1 Hz, 8H), 0.50 (t, *J* = 7.3 Hz, 26H), 0.46 – 0.40 (m, 8H). FT–IR ($CHCl_3$ cm-1): 2930, 2864, 1736, 1586, 1465, 1251, 1103.

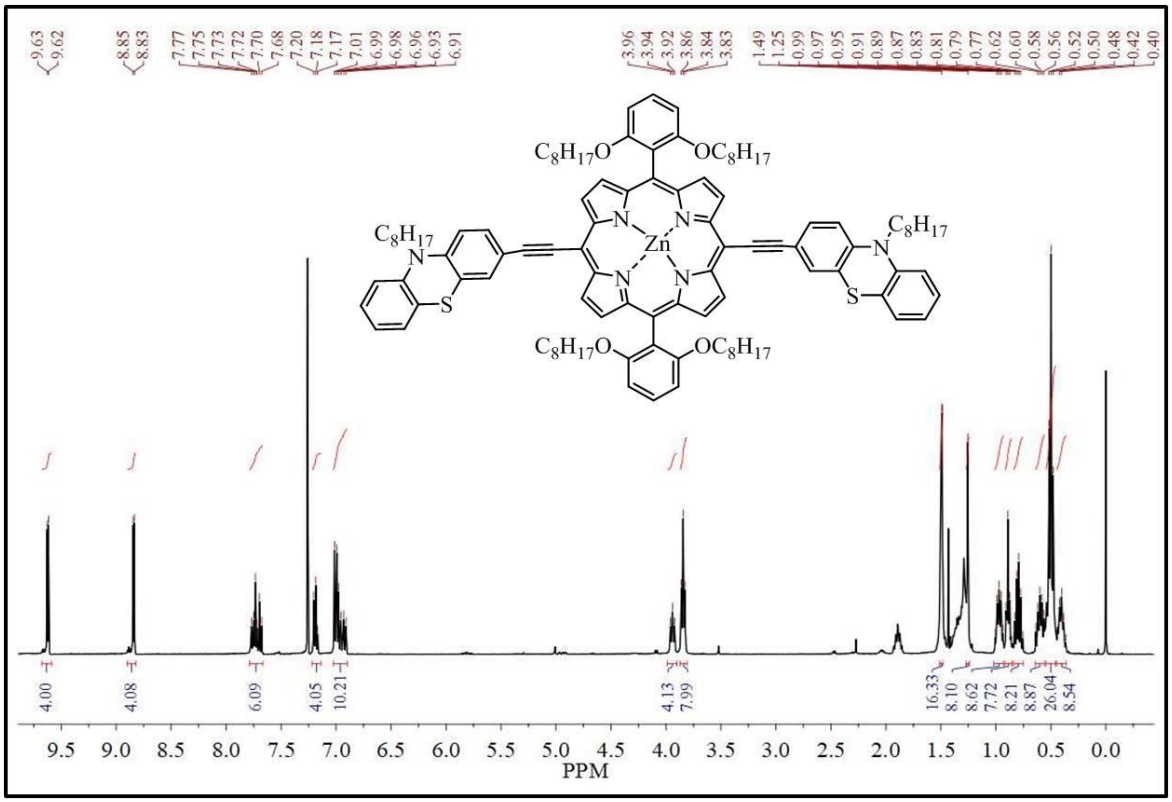


Figure S2.[1]H NMR spectra of ZPPHT.

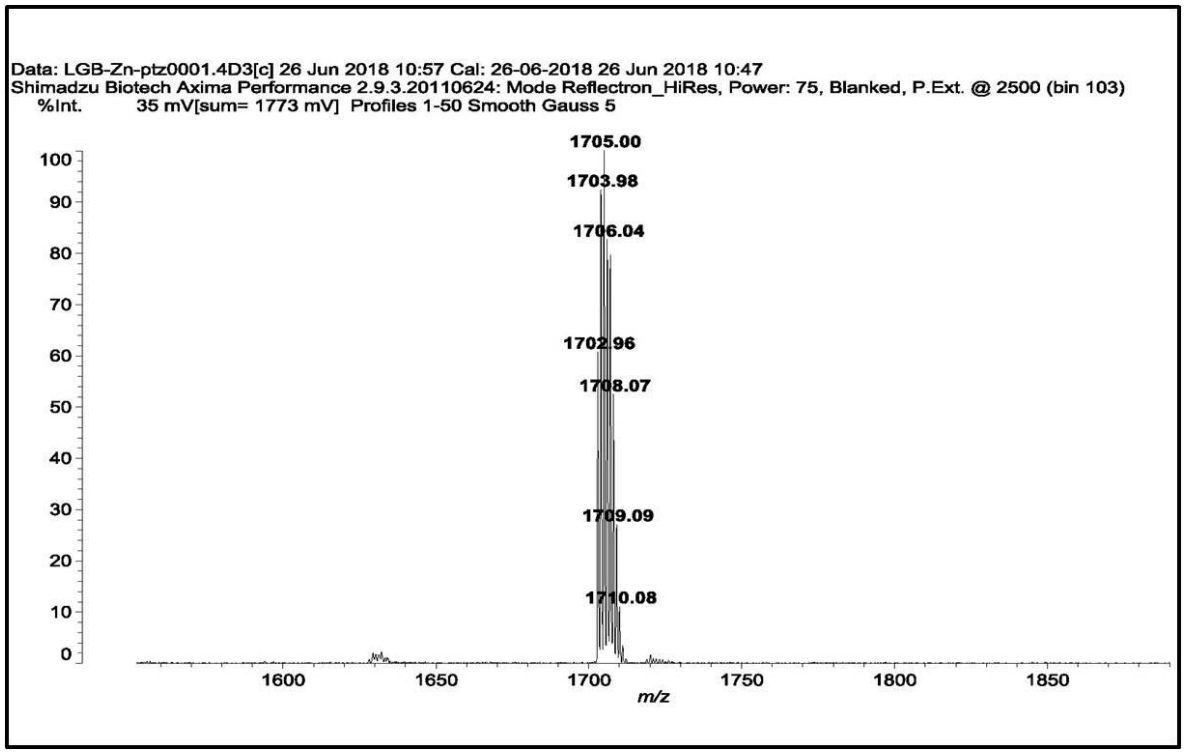


Figure S3. MALDI-TOF of the ZPPHT.

2.2 3,3'-((10,20-bis(2,6-bis(octyloxy)phenyl)porphyrin-5,15-diyl)bis(ethyne-2,1-diyl))bis(10-octyl-10H phenothiazine)(HPPHT): Here, we synthesized free-based porphyrin from ZPPHT by demetallation. In 25 ml of 0.5g of ZPPHT was dissolved in DCM added aqueous 0.01N HCl dropwise and monitor the TLC until ZPPHT spot disappears then after quenched with water, dried over rotatory evaporator and recrystalize with Methanol and Dichloromethane HPPHT obtained dark green solid yielded as 92%. Anal.Calcd. For $C_{108}H_{132}N_6O_4S_2$ % (1641.98): C, 78.98; H,8.10; N,5.12. Found;C, 79.13; H, 8.39; N,4.93. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (d, *J* = 4.5 Hz, 4H), 8.74 (d, *J* = 4.3 Hz, 4H), 7.76 – 7.67 (m, 6H), 7.20 – 7.18 (m, 4H), 7.01 – 6.91 (m, 10H), 3.94 (t, *J* = 7.1 Hz, 4H), 3.84 (t, *J* = 6.3 Hz, 8H), 1.55 (s, 16H), 1.26 (s, 12H), 1.02 – 0.94 (m, 10H), 0.89 (s, 10H), 0.82 (dt, *J* = 14.9, 7.3 Hz, 10H), 0.64 (dt, *J* = 14.1, 7.2 Hz, 10H), 0.56 (s, 8H), 0.50 (dd, *J* = 14.8, 7.3 Hz, 16H), -1.80 (s, 2H).MALDI-TOF: m/z [M]+calcd. For $C_{108}H_{132}N_6O_4S_2$,1641.98; found, 1641.97. FT–IR ($CHCl_3$ cm-1): 2925, 2859, 1588, 1464, 1384, 1339, 1250, 1102, 804, 756.

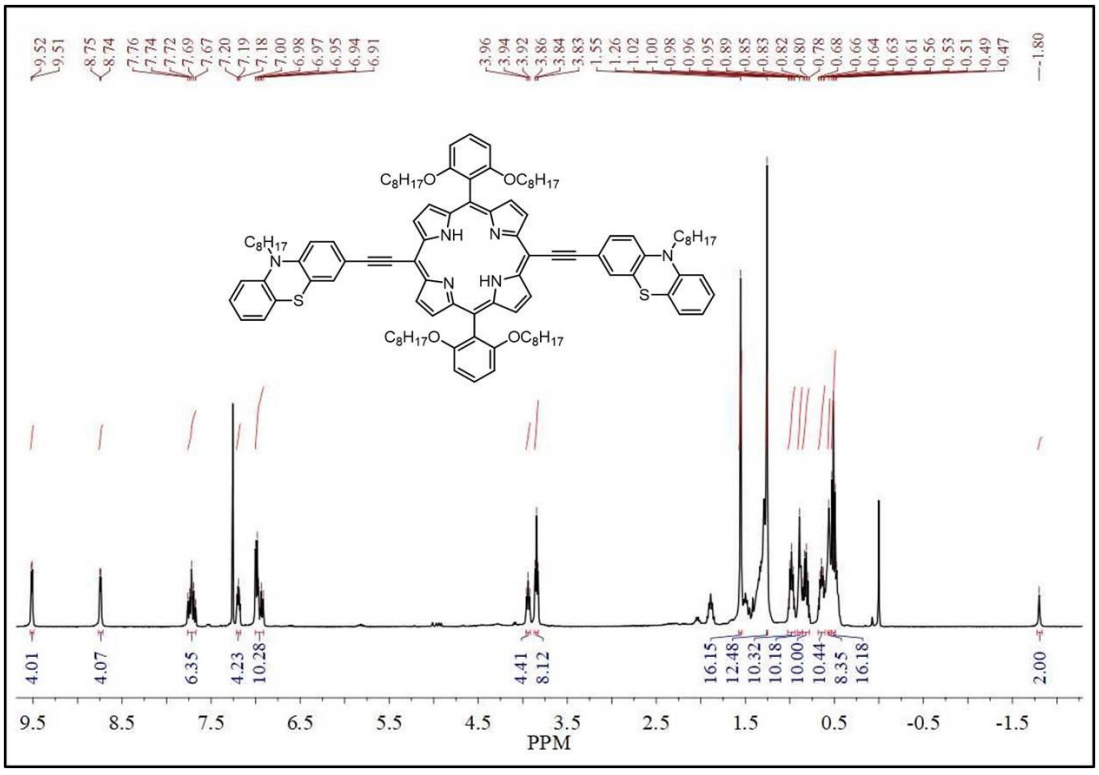


Figure S4.^{1}H NMR spectra of HPPHT.

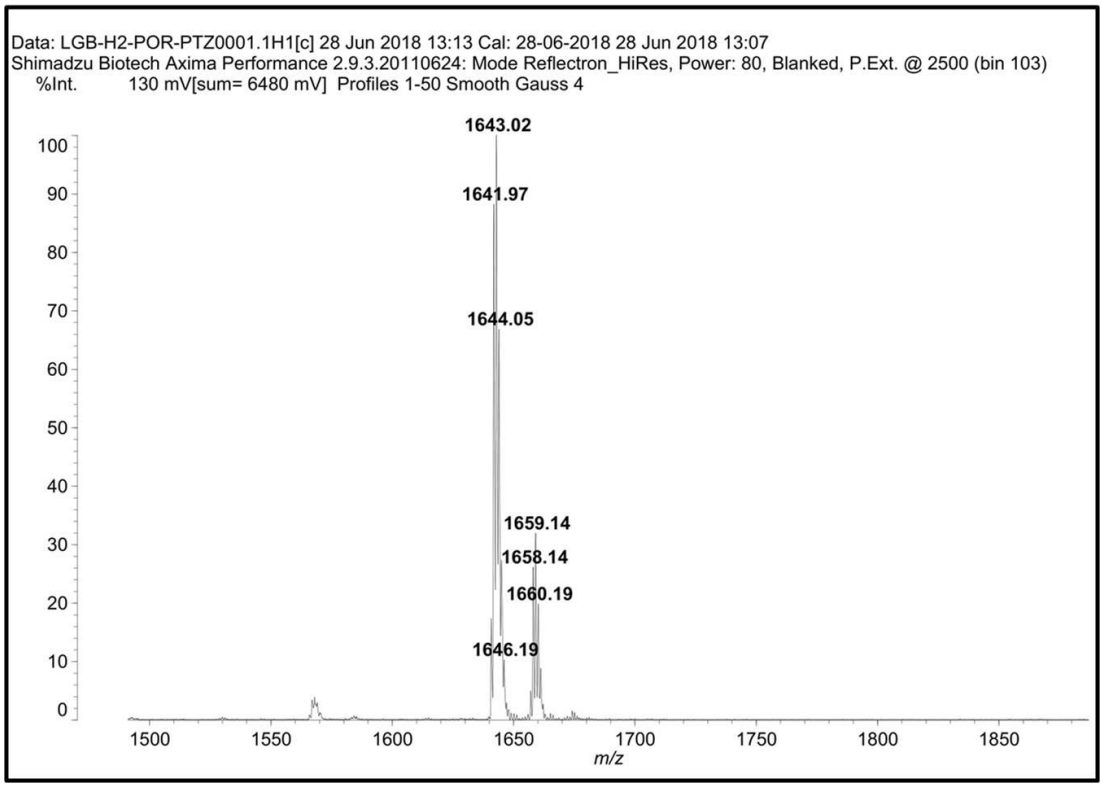


Figure S5.MALDI-TOF of the HPPHT.

3. UV−Vis Absorption and Photoluminescence characterization

A 3 μM solution of $MAPbI_3$, ZPPHT, HPPHT and device configuration of glass/TiO_2/perovskite/HTM, glass/TiO_2/perovskite were characterized using UV−Vis absorption (UV-3600 SHIMADZU UV-VIS spectrophotometer) and photoluminescence (HORIBA JOBN YVON). To analyse the optical absorption and emission for solution and films state. An excitation wavelength of 464 nm was used for measuring the PL, and the light was induced at the side of the glass. A 3 μM solution of ZPPHT, HPPHT was used for analysing lifetime by Time-Correlated Single Photon Counting (TCSPC, HORIBA JOBN YVON).

4. Electrochemical and water Contact angle measurement

Oxidation potentials of HPPHT and ZPPHT were measured using CH instruments electrochemical analyser with the three-electrode system (working electrode (Pt), a counter

electrode (Pt), and the reference electrode ($Hg/HgCl_2$/ 3M KCl). For this 0.1M of $TBAPF_6$in dichloromethane used as supporting electrolyte (100 mV/s). The calibration of the reference electrode was done using ferrocenium/ferrocene redox couple. The device configuration of glass/TiO_2/perovskite, glass/TiO_2/perovskite/HTM, glass/TiO_2/perovskite/HTM/cathode were characterized using water contact analyser (Kruss G10, Germany).

5. Solar Cells Fabrication and Characterization

The D-π-D porphyrin-based perovskite solar cells were fabricated using the screen-printing process and analysed under ambient condition (60 ~ 70% RH, Hyderabad, India). FTO substrates (FTO, Pilkington, TEC8; sheet resistance: 8Ω/□)) used for fabricating perovskite solar cells. Before depositing the electron transport layer, FTO substrate patterned using the zinc dust and 2M HCl solution. The TiO_2 blocking layer was prepared on FTO substrate via screen-printing (ATMA, AT-25 PA) with blocking layer titania paste (MS Code: MS002500, BL-1 Blocking Layer, Greatcell Solar Ltd.) and dried at 125^oC/10 min heating at 500^oC for 30 min[7]. Then, a nanocrystalline TiO_2 layer (MS Code: MS002010, 18NR-T Transparent Titania Paste, Greatcell Solar Ltd.) composed of 20 nm sized particle was deposited similar process and sintered at 500 °C for 30 min. After cooling to room temperature, electrodes were treated in 10 mM aqueous solution of $TiCl_4$ for 1h at 100 °C for minimizing pinhole, rinsed with DI water and finally heat-treated at 500 °C for 30 min. The $MAPbI_3$ absorber layer was prepared using a two-step screen-printing. First, the PbI_2 layer prepared on the nanocrystalline TiO_2 layer and dried at 125 °C/10 min (1M-PbI_2 in DMF). Then, 0.063 M CH_3NH_3I solution in 2-propanol was screen-printed on the PbI_2 film and dried at 125^oC for 20 min. After confirming the chemical structure of our hole-extraction materials (5mM) dissolved in toluene, then deposited on the active layer. After deposition, devices dried at 125^oC for 10 min. Finally, 10 micrometres of carbon nanoparticle-graphene composite layer was deposited on the hole-extraction layer to form the back contact with screen printing and

dried at 125°C for 10 min. The surface and cross-sectional morphologies of perovskite, hole-extraction layer and perovskite solar cells were characterized using the scanning electron microscopy at 25 kV accelerating voltage (JEOL JSM-7610F). The electrical conductivity of $MAPbI_3$, HPPHT and ZPPHT were measured by following the published methods, details can be found in the reference work[7].For the I−V measurement, we use a black metal mask (0.16 to 64 cm^2) above the devices. After 1h, the power conversion efficiencies of the as-fabricated perovskite solar cells measured in the dark and under simulated solar light conditions (Newport, 94043A). All the mentioned solar cell performance values are average of 8 cells.

6. Impedance Measurements

Were performed using IVIUMSTAT electrochemical interface. A dc potential bias was applied and overlaid by a sinusoidal ac potential perturbation of 15 mV over a frequency range of 7 MHz to 0.1 Hz (for the measurements under dark-condition). The applied dc potential bias was changed by ~50 mV steps from 850 to 0 mV. The resulting impedance spectra were fitted using the Z-View software[7].

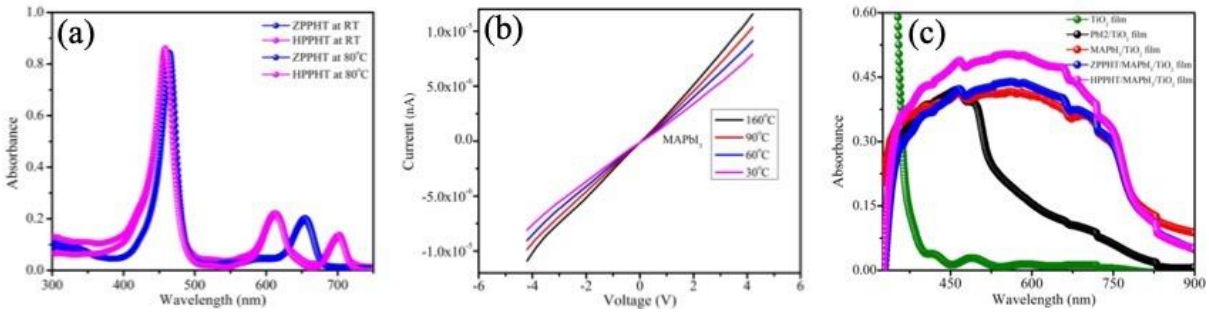


Figure S6. Temperature dependence (a) UV-vis spectra of HPPHT/ZPPHT, (b) Electrical property of $MAPbI_3$ and (c) UV-vis spectra of TiO_2 to HPPHT/ZPPHT layers.

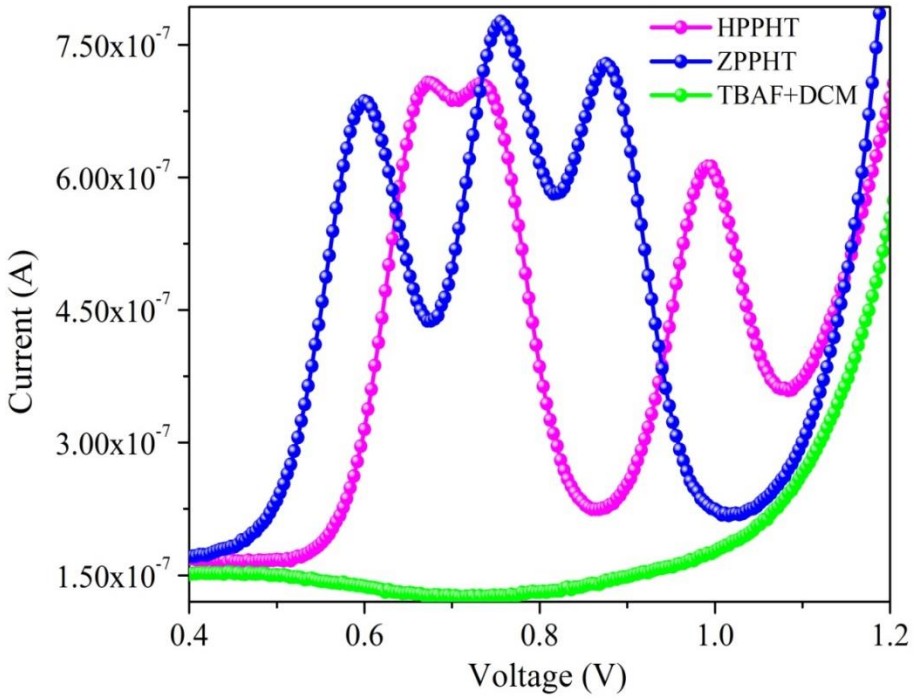


Figure S7. Differential pulsed voltammograms of as prepared HPPHT/ZPPHT in DCM solution containing 0.1M $TBAPF_6$ as the supporting electrolyte at scan rate 100mVs^{-1}.

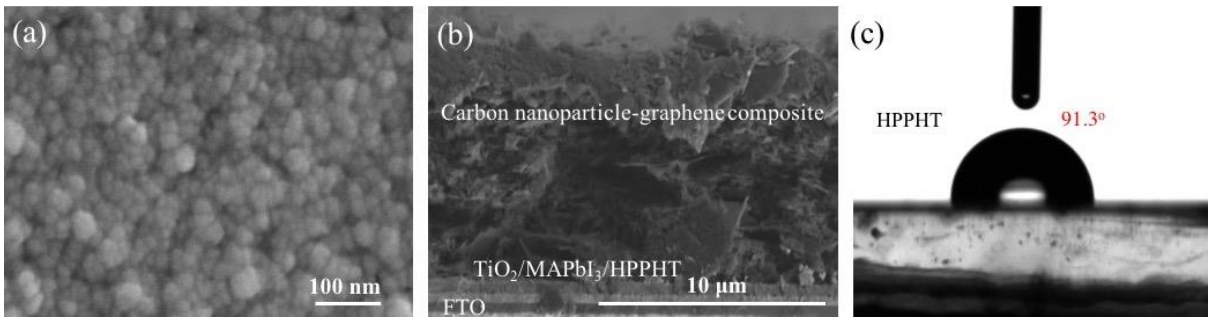


Figure S8. (a) Surface morphology of PbI_2 layer, (b) cross-sectional view of HPPHT with carbon nanoparticle-graphene composite (10-micron thickness), and (c) water contact angle of HPPHT.

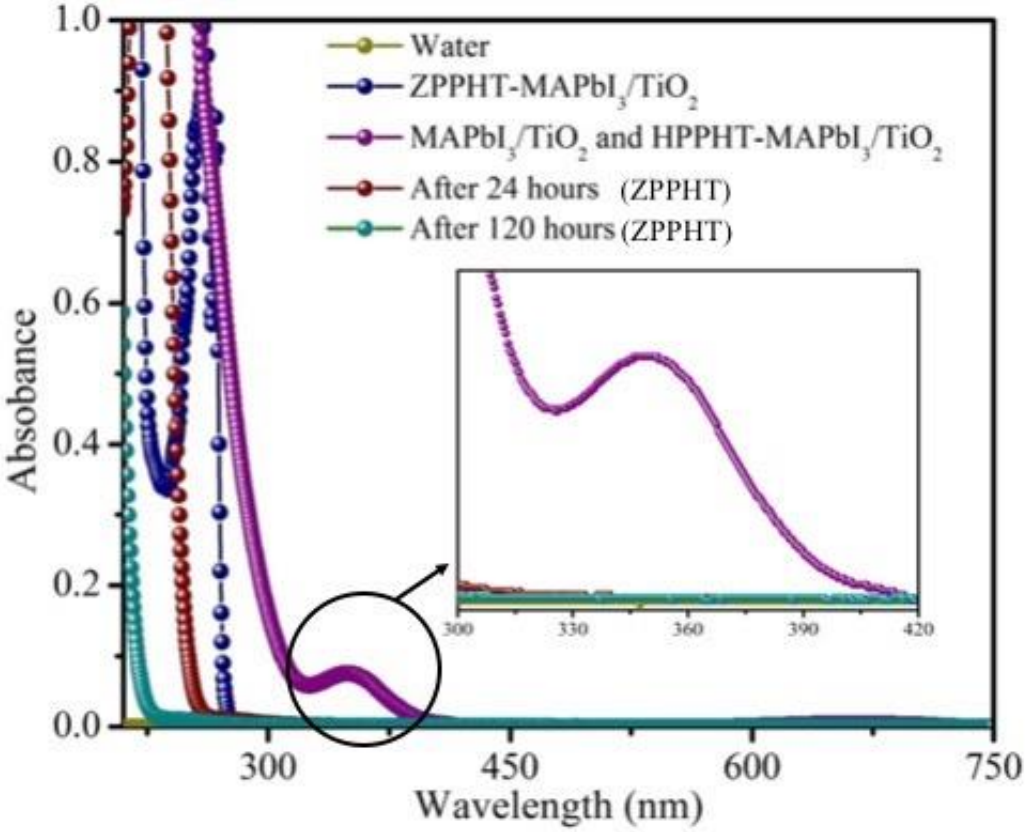


Figure S9. Optical spectra of water; before and after immersion of $MAPbI_3$, HPPHT and ZPPHT perovskite solar cells with different time duration.

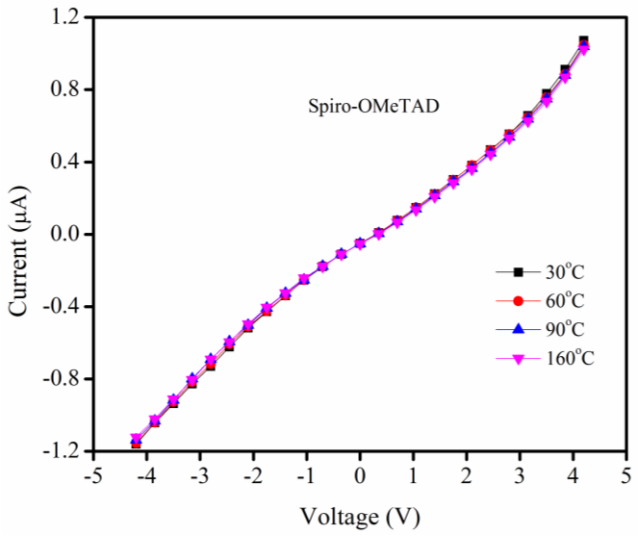


Figure S10. Electrical property of dopant-free Spiro-OMeTAD film with temperature.

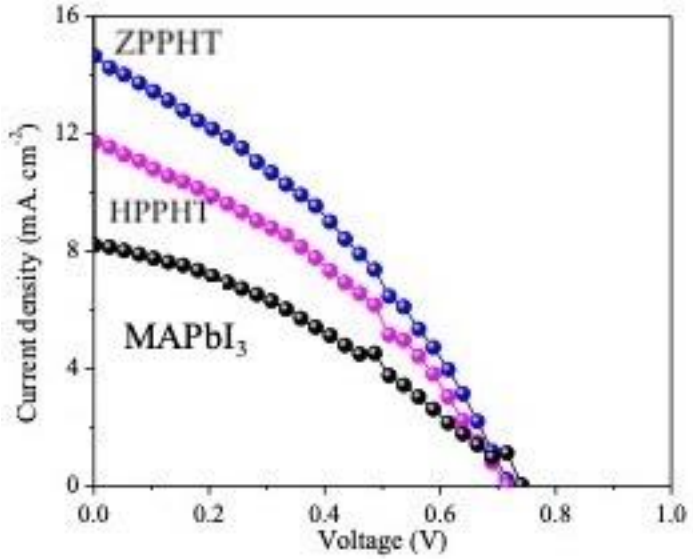


Figure S11.8 X 8 cm^2 Perovskite solar cells fabricated at all−ambient condition (75%, Humidity) of the Current−voltage characteristics.

Table1. Device parameters[a] of all-ambient-processed PSCs under 1sun illumination[b].

Devices	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF	η [%)]
ZPPHT	0.71	14.70	0.34	3.54
HPPHT	0.71	11.77	0.33	2.75
$MAPbI_3$	0.73	8.25	0.35	2.10

[a]*Device active area: 8 X 8 cm^2,* [b]*100 mW/cm^2, Air Mass 1.5G*

7. Estimated Cost for D-π-D porphyrin hole-extracting materials

We estimated synthetic cost of HPPHT/ZPPHT molecular systems, accordingly Osedach's, Petrus and Gratzel's reports[8,9,10].For synthesis of these materials, we used materials of Sigma-Aldrich, Avra Synthesis Private Limited (India), and TCI Chemicals (India) for the cost evaluation. Step by Step usage of reagents, catalysts, reactants, and solvents for obtain 1

gram of HPPHT/ZPPHT (Tables S7.1-7.5). Finally, for a more realistic cost, it was multiplied by a factor of 1.5 for considering the several important parameters, e.g. labour, energy consumption and waste treatment, etc.

$= 58.99 X 1.5 = 88.48/g for ZPPHT

$= 74.70 X 1.5 = 112.05/g for HPPHT

7.1 Cost for the synthesis of Dipyrromethane (DPM)

Reagent	Commercial price in USD (/g or /ml)	Amount of Material (/g or /ml)	Material cost in USD (**$**)
paraformaldehyde	0.0074	1.08	0.0079
Pyrrole	0.14	200.00	27.68
Trifluoroacetic acid	0.076	0.277	0.021
NaOH	0.0041	1.20	0.35
Hexane	1.28	400.00	7.25
Silica gel	0.018	100.00	0.93
Ethyl acetate	0.0068	30.00	0.20
Dichloromethane	0.0062	100.00	0.62
Total cost	$ 37.06		
Amount of Intermediate DPM	4.05gm		
Price per gram	$ 9.15		

7.2 Cost for the synthesis of *3-ethynyl-10-octyl-10H-phenothiazine* (C_8-Ptz-E)

Reagent	Commercial price in USD (/g or /ml)	Amount of Material (/g or /ml)	Material cost in USD (**$**)
Phenothiazine	0.052	2.00	0.10
1-bromooctane	0.047	2.20	0.10
NaH	0.057	0.480	0.027
DMF	0.010	70.00	0.71

NBS	0.030	1.50	0.045
Dichloromethane	0.0062	100.00	0.62
2-methylbut-3-yn-2-ol	0.050	0.80	0.040
CuI	0.20	0.056	0.011
PPh3	0.040	0.076	0.0030
$Pd(PPh_3)Cl_2$	13.84	0.041	0.57
Triethylamine	0.0088	10.00	0.088
Toluene	0.0055	25.00	0.14
NaOH	0.0041	0.205	0.00085
Ethyl acetate	0.0068	80.00	0.54
Hexane	0.018	750.00	13.58
Na2SO4	0.0028	10.00	0.028
Silica gel	0.0093	150.00	1.40
Total cost	$ 18.00		
Amount of Intermediate C_8-Ptz-E	2.00g		
Price per gram	$ 9.00		

7.3 Cost for synthesis of *5,15-bis(2,6-bis(octyloxy)phenyl)-10,20-dibromoporphyrin* (Por-Br_2)

Reagent	Commercial price in USD (/g or /ml)	Amount of Material (/g or /ml)	The material cost in USD (**$**)
Resorcinol	0.031	5.00	0.155
1-Bromooctane	0.047	30.00	1.41
K_2CO_3	0.0099	30.00	0.30
Acetone	0.0048	300.00	1.44
Ethyl acetate	0.0068	150.00	1.02
Silica gel	0.0093	20.00	0.17

Na_2SO_4	0.0028	5.00	0.014
Hexane	0.018	400.00	7.25
Total cost	$11.76		
Amount of Intermediate-2	13g		
Price per gram	$ 0.91		

Reagent	Commercial price in USD (/g or /ml)	Amount of Material (/g or /ml)	The material cost in USD(**$**)
2	0.91	5.00	0.064
TMEDA	0.061	0.80	0.048
THF	0.015	70.00	1.03
n-Butyllithium 2.5M in hexane	0.10	14.30	1.43
Dichloromethane	0.010	4.38	0.045
NH_4Cl	0.0041	2.00	0.0082
Na_2SO_4	0.0028	5.00	0.014
Silica gel	0.0093	60.00	0.56
Hexane	0.018	400.00	7.25
Ethyl acetate	0.0068	100.00	0.68
Total cost of 3	$ 11.13		
Amount of Intermediate-3	3.80g		
Price per gram	$ 2.93		

Reagent	Commercial price in USD (/g or /ml)	Amount of Material (/g or /ml)	Material cost in USD(**$**)
3	2.93	3.72	10.90

Dipyrromethane	9.15	1.50	13.72
Dichloromethane	0.0062	500.00	3.11
DDQ	0.35	3.51	1.24
Trifluoroacetic acid (TFA)	0.076	0.60	0.046
Triethylamine	0.0088	2.00	0.018
Na_2SO_4	0.0028	5.00	0.014
Silica gel	0.0093	100.00	0.93
Hexane	0.018	500.00	9.06
Methanol	0.042	20.00	0.85
Total cost	$ 39.89		
Amount of Intermediate-4	1.6g		
Price per gram	$ 24.93		

Reagent	Commercial price in USD (/g or /ml)	Amount of Material (/g or /ml)	Material cost in USD ($)
Porphyrin (4)	24.93	1.50	37.40
NBS	0.030	0.580	0.017
Dichloromethane	0.0062	800.00	4.98
Zinc acetate dihydrate, 98%	0.010	2.20	1.63
Na_2SO_4	0.0028	10.00	0.023
Hexane	0.018	500.00	9.06
Methanol	0.042	400.00	16.92
Silica gel	0.0093	100.00	0.93
Total cost	$ 70.96		
Amount of Intermediate Por-Br_2	1.4g		

Price per gram	$ 50.68

7.4 Cost for the synthesis of ZPPHT

Reagent	Commercial price in USD (/g or /ml)	Amount of Material (/g or /ml)	Material cost inUSD (**$**)
Por-Br_2	50.68	1.00	50.68
C8-PTZ-E	9.0	0.84	7.56
Tetrakis(triphenylphosphine)palladium(0), 99%	10.19	0.14	1.43
CuI	0.20	0.023	0.0047
THF	0.015	15.00	0.22
Triethylamine	0.0088	10.00	0.088
Silica gel	0.0093	100.00	0.93
Na_2SO_4	0.0028	4.00	0.011
Hexane	0.018	400.00	7.25
Dichloromethane	0.0062	150.00	0.93
Methanol	0.042	40.00	1.69
Total cost	$ 70.79		
Amount of ZPPHT	1.2g		
Price per gram	$ 58.99		

7.5 Cost for the synthesis of HPPHT

Reagent	Commercial price in USD (/g or /ml)	Amount of Material (/g or /ml)	Material cost in USD (**$**)
ZPPHT	58.99	0.50	29.49
HCl	0.0057	0.04	0.00023
Methanol	0.042	40.00	1.69
Dichloromethane	0.0062	150.00	0.93
Na_2SO_4	0.0028	4.00	0.011

Total cost	$ 32.12
Amount of HPPHT	0.430g
Price per gram	$ 74.70

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