Supplementary Information (SI) for EES Solar.
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Supporting Information

Porphyrin–Thieno[3,2-b]thiophene Hole-Transport Materials Enabling Long-Lived Radical Ion Pairs and High-Performance Perovskite Solar Cells

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1. Experimental Section:

1.1 Materials and methods

Some materials are purchased from commercially available sources and used without any additional purification. All the reaction solvents were distilled and dried by well-known methods and stored over molecular sieves. ^{1}H-NMR characterizations were performed with different advanced spectrometers (300, 400, and 500 MHz), with tetramethylsilane (TMS) as an internal standard. The matrix-assisted laser desorption/ionization (MALDI-TOF) technique was used to measure the mass of intermediates and the final molecule. The American PE2400 II CHNS/O elemental analyzer was used to analyze the C, H, N, S, and O of the final compound.

1.2 Optical spectral measurement

The UV-visible spectral measurements were carried out with a Jasco V-770 double monochromator UV-visible spectrophotometer. The fluorescence emission was monitored using a Horiba Yvon Nanolog coupled with time-correlated single photon counting with nanoLED excitation sources. A right-angle detection method was used.

1.3 Electrochemical experiments

Differential pulse and cyclic voltammograms were recorded on an EG&G potentiostat using a three-electrode system. A platinum button electrode was used as the working electrode. A platinum wire served as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements using argon gas.

A spectroelectrochemical study was performed by using a cell assembly (SEC-C) supplied by ALS Co., Ltd. (Tokyo, Japan). This assembly comprised a Pt counter electrode, a 6 mm Pt Gauze working electrode, and an Ag/AgCl reference electrode in a 1.0 mm path length quartz cell. The optical transmission was limited to 6 mm covering the Pt Gauze working electrode. Spectra were recorded by applying a potential of 100 mV past the potential of a given oxidation or reduction process and continuing until no additional changes were observed.

1.4 Rehm-Weller analysis

The free energy change for charge separation (ΔG_{CS}) from the singlet excited state of the donor-acceptor system was calculated using spectroscopic, computational, and electrochemical data following eqn (1)– (3)

$$\Delta G_{CR} = E_{ox} - E_{red} + \Delta G_S \qquad (1)$$

$$-\Delta G_{CS} = E_{00} - (-\Delta G_{CR}) \qquad (2)$$

$$\Delta G_S = e^2/4\pi\varepsilon\ [(1/2R_{+} + 1/2R_{-})\Delta(1/\varepsilon_R) - 1/R_{CC}\varepsilon_R] \qquad (3)$$

where E_{00} and ΔG_{CS} correspond to the energy of the excited singlet state and electrostatic energy, respectively. The *Eox* and *Ered* represent the oxidation and reduction potentials of the donor-acceptor system. The term ΔGs refers to the static Coulombic energy, calculated by using the “dielectric continuum model” according to eqn (3). The symbols ε_0, and ε_R represent the vacuum permittivity and dielectric constant of the solvent used for photochemical and electrochemical studies, respectively. R_{CC} is the center-to-center distance between pull-pull entities from computational data. R_+ and R_- are the ionic radii of the donor and acceptor.

1.5 Computational analysis

All the theoretical calculations were carried out in Gaussian 16 employing the CAM-B3LYP functional and 6-311+g(d,p)basis set at the DFT level of theory.4 Vertical excitation energies and oscillator strengths were calculated employing time-dependent DFT (TD-DFT) at the CAM-B3LYP /6-311+g(d,p) level of theory.

1.6 Femtosecond transient absorption (fs-TA) measurement

Femtosecond transient studies were performed using an Ultrafast Femtosecond Laser Source (Astrella) by Coherent, which incorporates a diode, mode-locked Ti: Sapphire laser (Vitara), and diode-pumped intracavity doubled Nd: YLF laser (Revolution) to generate a fundamental compressed laser of 800 nm and power output of 5.24 W. For optical detection, a Helios transient absorption spectrometer, coupled with a femtosecond harmonics generator, both provided by Ultrafast Systems LLC, will be used. The source for the pump pulse is derived from the fundamental output of Astrella (compressed output 5.24 W, pulse width 91 fs, 800nm at a repetition rate of 1 kHz) by introducing 95% of the beam into the HG or OPA, while the other 5% is sent to the delay line and white light generating crystal. The beam sent through the HG or OPA is termed the pump beam as it is used to excite the sample. The beam sent through the delay line and crystal is termed the probe beam, as it shows what spectral changes occur in the sample with time. The OPA takes the 800 nm fundamental and converts it into a specific wavelength in the range of 400 – 2200 nm, which allows the excitation wavelength to be selected.

1.7 Nanosecond Transient Absorption Measurement (ns-TA)

The compounds studied were excited by an Opolette HE 355 LD pumped by a high-energy Nd: YAG laser with second and third harmonics OPO (tuning range 410-2200 nm, pulse repetition rate 20 Hz, pulse length 7 ns) with the powers of 1.0 to 3 mJ per pulse. The transient absorption measurements were performed using a Proteus UV-Vis-NIR flash photolysis spectrometer (Ultrafast Systems, Sarasota, FL) with a fibre optic delivered white probe light and either a fast rise Si photodiode detector covering the 200-1000 nm range or an InGaAs photodiode detector covering 900-1600 nm range. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing Tektronix oscilloscope. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems.

2. Perovskite fabrication process

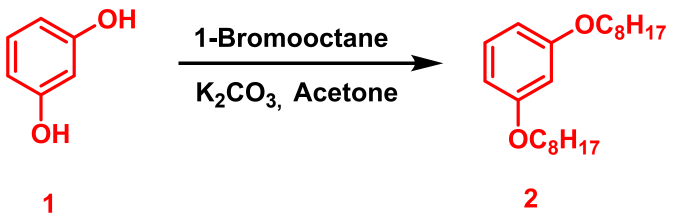
2.1. Materials

All the purchased materials were directly used for the device fabrication method without any additional modifications. Lead (II) iodide (PbI_2, 99.999%), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine) cobalt (III) tris (bis (trifluoromethyl sulfonyl) imide) (FK209), and bis(trifluoromethane) sulfonimide lithium salt (Li-TFSI), were purchased from TCI. 2,2′,7,7′-tetrakis-(N, N-di-p-methoxyphenylamine)-9,9-spirobifluorene (Spiro-OMeTAD) was obtained from Lumtec (Taiwan). Methylammonium iodide (MAI, 99.99%) was received from Dyesol (Australia) and Tin (IV) oxide (SnO_2) (15% in H_2O) was purchased from Alfa Aesar. The organic solvents including dimethyl sulfoxide (DMSO), acetonitrile (ACN), toluene, isopropanol (IPA), dimethylformamide (DMF), 4-tert-butylpyridine (^{t}BP) and chlorobenzene (CB) were purchased from Sigma-Aldrich. fluorine-doped tin oxide (FTO) glass substrates were purchased from TEC 8, Pilkington.

2.2. Fabrication process of $MAPbI_3$ solar cells

The FTO plates were sequentially cleaned with soap, distilled water, ethanol, and isopropanol by sonication for 15-20 min each. These substrates were cleansed with N_2 gas and dried at 70 °C for 4 h, then placed under the ultraviolet-ozone atmosphere for 20 min before electron transport layer (ETL) deposition. The ETL solution was prepared by diluting SnO_2 in isopropanol and deionizing H_2O with a volume/volume ratio of 1:3:3 v/v respectively. Then ETL was formed by spin coating SnO_2 solution at 4000 rpm for 30 s followed by annealing on hot plate at 100 °C and 180 °C for 10 min and 30 min, respectively. The 1M $MAPbI_3$ perovskite solution was prepared from PbI_2 and MAI materials and dissolved in 4:1 ratio of DMF and DMSO. Next, the SPS-PPY-TT (110 mg/mL in chlorobenzene) or spiro-OMeTAD (73 mg/mL in chlorobenzene) were coated at 3000 rpm for 30 s. Finally, Au (80 nm) electrode was thermally evaporated under high vacuum level using a shadow mask to obtain Glass/FTO/SnO_2/$MAPbI_3$//(SPS-PPY-TT/Spiro-OMeTAD)/Au structured PSCs device (active area of 0.22 cm^2).

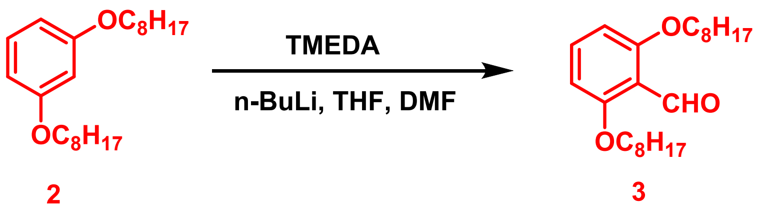
3. Cost calculations



Chemicals/company	Price ($) (Kg or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in mL)	Workup (in g or mL)	
Resorcinol/Hyma	96.06 $/kg	0.500			0.048
1-bromooctane/ TCI	101.7 $/L	2.6			0.264
Potassium Carbonate/ Finar	11.04 $/kg	3.13			0.034
Acetone/Finar	9.01 $/L		30		0.270
Silica gel/Finar	17 $/kg			70 g	1.190
Hexane/Finar	18$/L			200 mL	3.600
Ethyl acetate/Finar	9 $/L			50 mL	0.450
Total					5.856

Moiety 2: Yield, 80%, 1.2 g, 5.856 $

The cost of 1gm is 4.880 $

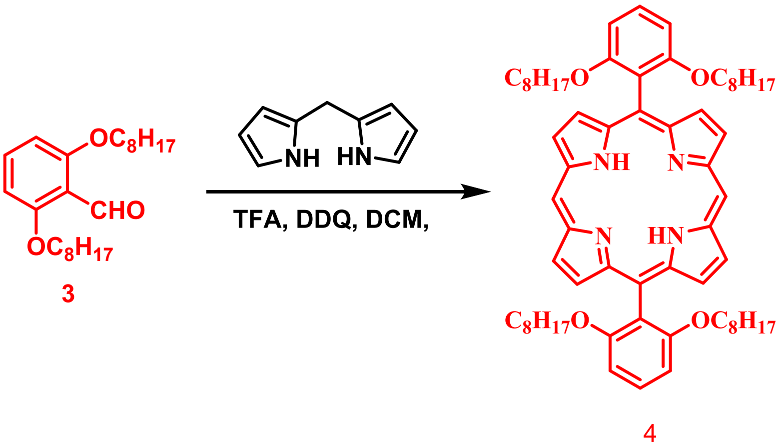


Chemicals/company	Price ($) (Kg or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in mL)	Workup (in g or mL)	
2	4880 $/kg	1.000			4.880

Tetramethylethylenediamine /TCI	51.37 $/kg	0.005			0.002
n-Butyllithium/Hyma	118.35 $/L		3		0.003
THF/Finar	39 $/L		20		0.780
DMF/Finar	11 $/L		2		0.022
Total					5.682

Moiety 3: Yield, 80%, 0.860 g, 5.682 $

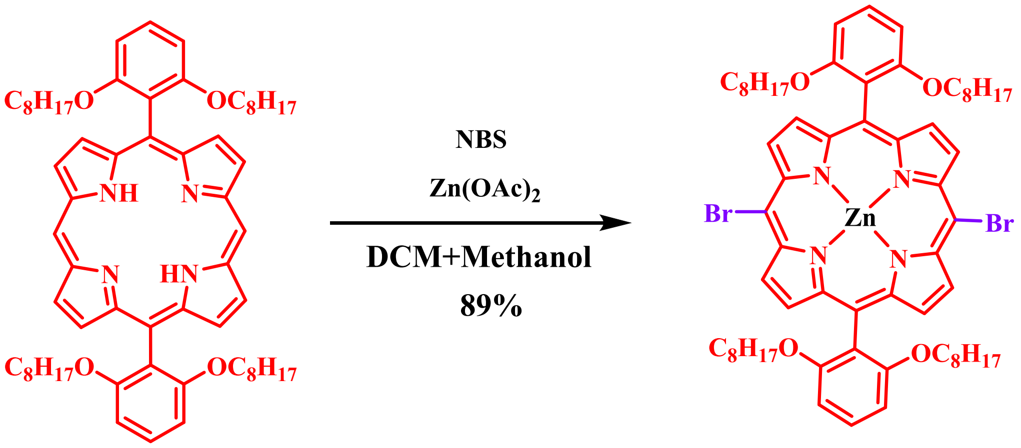
The cost of 1gm is 6.606 $



Chemicals/company	Price ($) (Kg or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in mL)	Workup (in g or mL)	
3	6606 $/kg	1.000			6.606
Dipyrromethane/TCI	92 $/1g	0.402			0.037
Trifluoroacetic acid/ TCI	63.16 $/ L		2		0.006
DDQ/Hyma	451 $/kg	0.936			0.422
DCM/Finar	11 $/L		20		0.220
Silica gel/Finar	17 $/kg			70 g	1.190
Hexane/Finar	18$/L			200 mL	3.600
Ethyl acetate/Finar	9 $/L			50 mL	0.450
Total					12.531

Moiety 4: Yield, 31%, 0.390 g, 12.531 $

The cost of 1gm is 32.130 $



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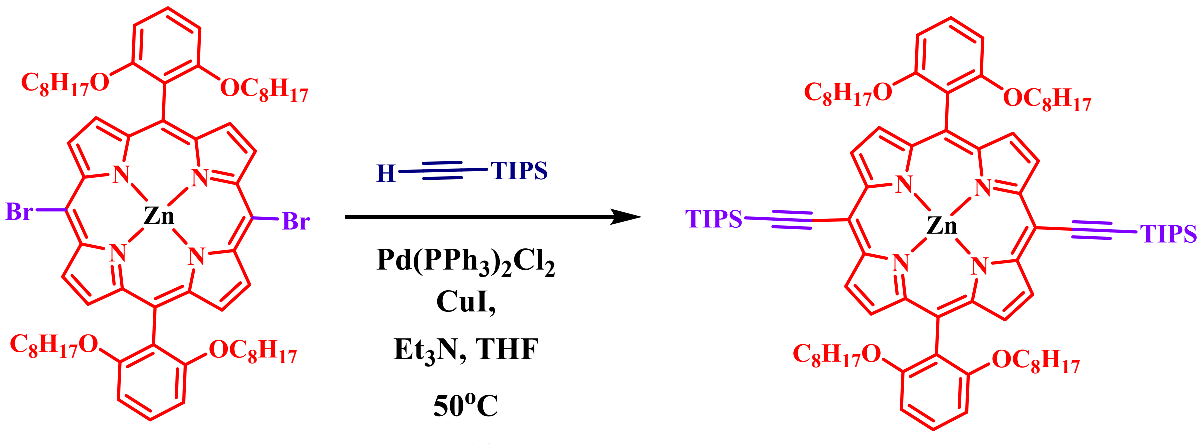
II

Chemicals/company	Price ($) (Kg or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in mL)	Workup (in g or mL)	
4	32.130 $/g	2.000			64.260
N-Bromosuccinimide /Hyma	42.18 $/kg	0.910			0.038
Zinc acetate / TCI	13 $/kg	2.49			0.032
Methanol/Finar	7 $/L		20		0.140
DCM/Finar	11 $/L		20		0.220
Silica gel/Finar	17 $/kg			70 g	1.190
Hexane/Finar	18$/L			200 mL	3.600
Total					69.480

Moiety II: Yield, 89%, 2.183 g, 69.480 $

The cost of 1gm is 31.827 $



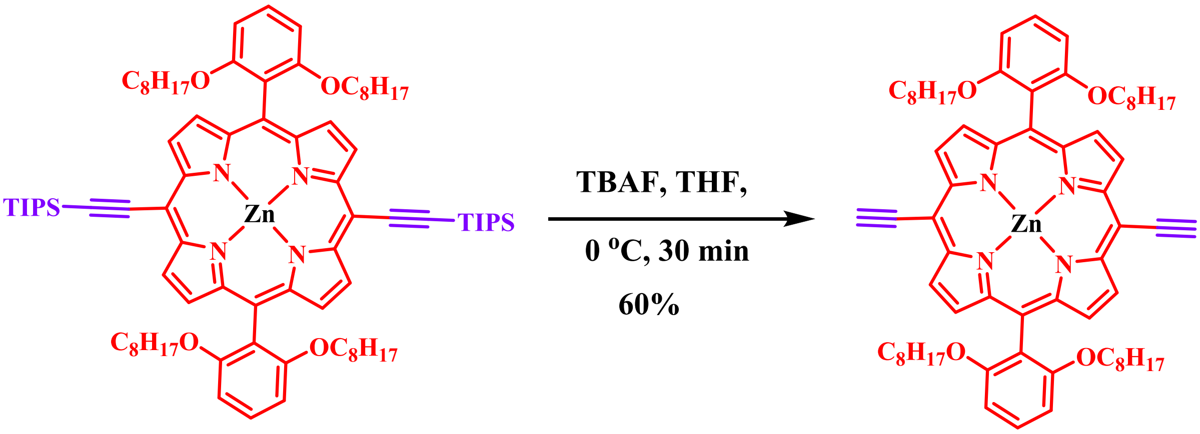
II

III

Chemicals/company	Price ($) (Kg or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in mL)	Workup (in g or mL)	
II	31.82 $/g	2.000			63.640
(Triisopropylsilyl)acetylene/Hyma	57.49 $/5ML		0.75		8.623
Triethylamine/Hyma	16.91 $/L		12		0.203
Copper iodide /TCI	173.25 $/kg	0.025			0.004
$Pd(PPh_3)_2Cl_2$/TCI	31.55 $/g	0.056			1.766
THF/Finar	39 $/L		20		0.780
Silica gel/Finar	17 $/kg			70 g	1.190
Hexane/Finar	18$/L			200 mL	3.600
Ethyl acetate/Finar	9 $/L			50 mL	0.450
Total					80.256

Moiety III: Yield, 60%, 2.090 g, 80.256 $

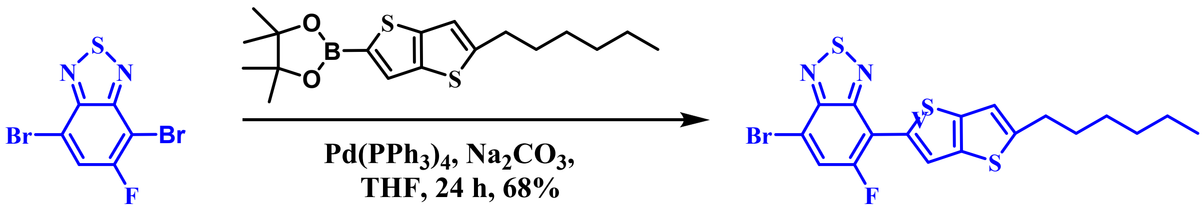
The cost of 1gm is 38.290 $



Chemicals/company	Price ($) (Kg or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in mL)	Workup (in g or mL)	
III	38.290 $/g	0.200			7.658
Tetra-n-butylammonium fluoride	124.73 $/L		0.6		0.074
THF/Finar	39 $/L		20		0.780
Silica gel/Finar	17 $/kg			70 g	1.190
Hexane/Finar	18$/L			200 mL	3.600
Ethyl acetate/Finar	9 $/L			50 mL	0.450
Total					13.752

Moiety IV: Yield, 60%, 0.093 g, 13.752 $

The cost of 1gm is 147.870 $

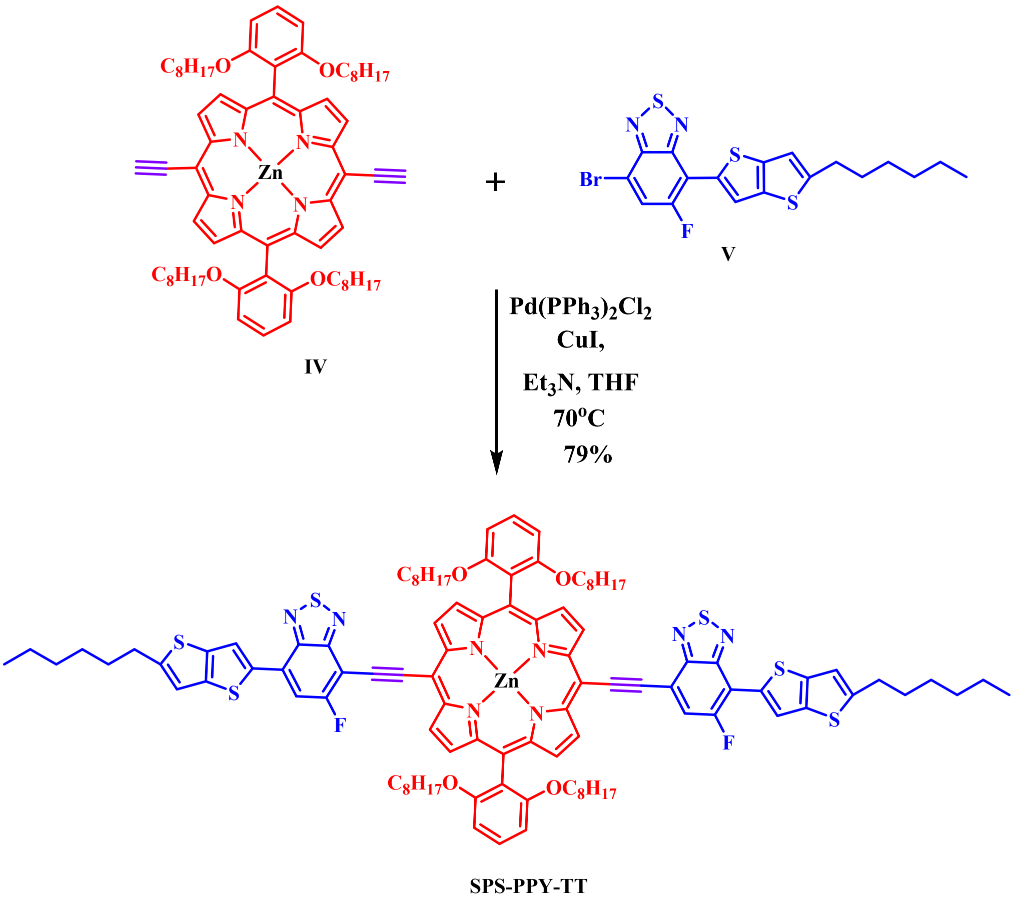


V

Chemicals/company	Price ($) (Kg or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in mL)	Workup (in g or mL)	
4,7-Dibromo-5-fluorobenzo[c]thiadiazole/TCI	110.47 $/g	0.100			11.047
4,4,5,5-Tetramethyl-2-(5-hexylthieno[3,2-b]thiophen-2-yl)-1,3,2-dioxaborolane	25 $/g	0.140			3.500
Tetrakis(triphenylphosphine)palladium(0)/ TCI	39 $/g	0.014			0.546
Sodium carbonate/Hyma	5.86 $/kg	0.190			0.001
THF/Finar	39 $/L		20		0.780
Silica gel/Finar	17 $/kg			35 g	0.595
Hexane/Finar	18$/L			100 mL	1.800
Ethyl acetate/Finar	9 $/L			50 mL	0.450
Total					18.719

Moiety V: Yield, 68%, 0.220 g, 18.719 $

The cost of 1gm is 85.086 $



Chemicals/company	Price ($) (Kg or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in mL)	Workup (in g or mL)	
IV	147.87 $/g	0.100			14.787
V	85.08 $/g	0.077			6.550
Bis(triphenylphosphine)palladium(II) dichloride /TCI	31.55 $/g	0.010			0.315
Copper iodide /TCI	173.25 $/kg	0.020			0.034
Triethylamine/Hyma	16.91 $/L		10		0.169
THF/Finar	39 $/L		20		0.780
Silica gel/Finar	17 $/kg			35 g	0.595
Hexane/Finar	18$/L			100 mL	1.800
Ethyl acetate/Finar	9 $/L			25 mL	0.220

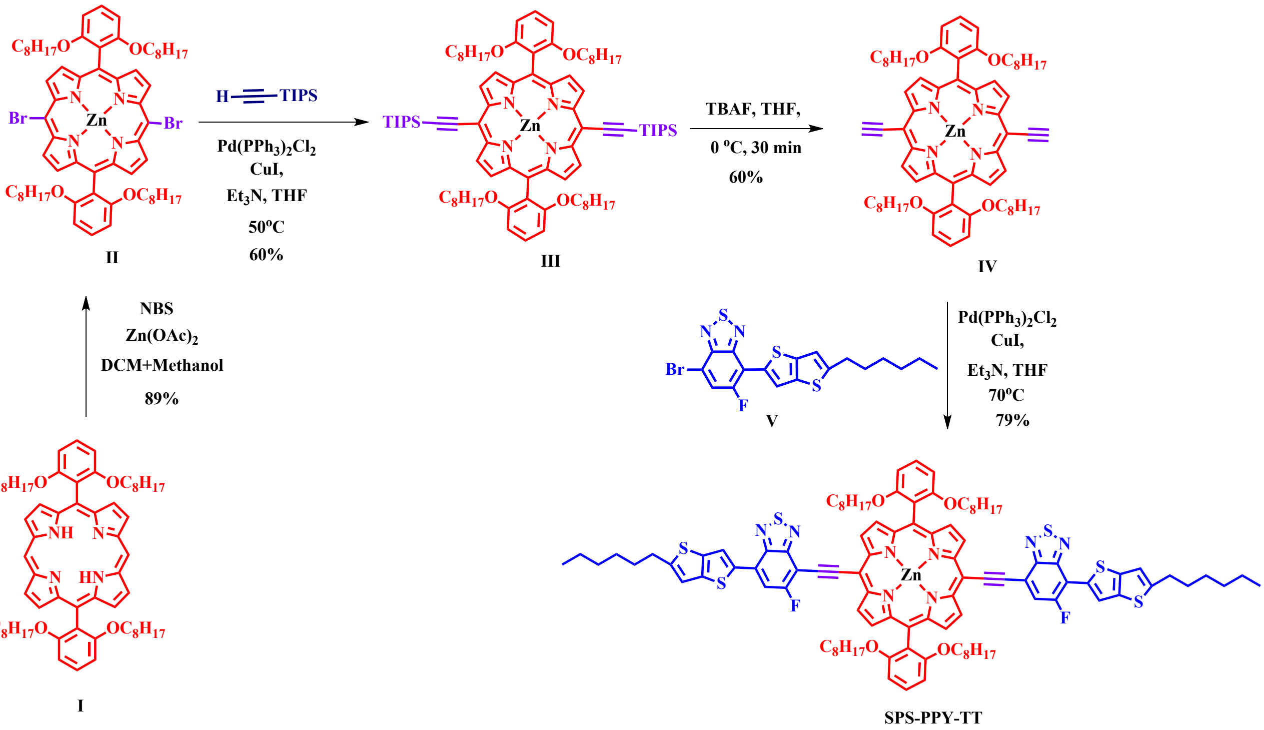
Total					25.25

SPS-PPY-TT: Yield, 79%, 0.133 g, 25.25 $

The cost of 1gm is 189.84 $

This is about **1/3rd** of the costs of purified Spiro-OMeTAD (565 $/g, high purity, commercially available)

4. Synthesis



Scheme 1. Synthesis route of **SPS-PPY-TT**hole transporting materials.

CompoundsIand V were synthesized according to the previously reported literature with moderate to good yields.[1-3]

Synthesis of compound II:

Compound I[1] (2.0 g, 2.05 mmol) was dissolved in anhydrous dichloromethane (DCM) (500 mL) in a round-bottom flask (1000 mL). While stirring, a solution of N-bromosuccinimide (*NBS*) (0.91 g, 5.12 mmol) in DCM (150 mL) was added dropwise under an inert-gas atmosphere. The reaction was monitored by TLC. After completion, a solution of acetone (50%) was added quickly, and the stirring was continued for 30 minutes. Then, the solution was passed through a flash column. To this $Zn(OAc)_2$, $2H_2O$ (2.49 g, 11.31 mmol) was added. The solution was stirred at room temperature for 24 h and then water was added. The resultant mixture was washed with water, brine water, and collected the organic phase. The organic solvent was removed by rotary vacuum and the residue was purified by column chromatography using hexane:DCM (1:1) as eluents. Finally, recrystallization with MeOH: DCM to get compound II (89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.63 (d, J = 4.6 Hz, 4H), 8.88 (d, J = 4.7 Hz, 4H), 7.70 (dd, J = 10.5, 6.4 Hz, 2H), 7.01 – 6.93 (m, 4H), 3.83 (t, J = 6.4 Hz, 8H), 0.97– 0.88 (m, 11H), 0.86 – 0.64 (m, 10H), 0.63 – 0.54 (m, 9H), 0.49 (dd, J = 10.1, 4.8 Hz, 19H), 0.37 (ddd, J = 22.4, 10.5, 4.8 Hz, 11H). **MALDI-TOF**: m/z: Calcd for $C_{64}H_{82}Br_2N_4O_4Zn$: 1196.55 $[M+H]^+$, Found: 1196.59 $[M+H]^+$.

Synthesis of compound III:

compound II (2.0 g, 2.05 mmol), (triisopropylsilyl)acetylene (0.75 mL, 3.34 mmol), triethylamine (12 mL), triphenyl phosphine (15 mg), and dry 1,4-dioxane (50 mL) was takend in a dry round-bottom flask (100 mL) under nitrogen atmosphere. The mixture was degassed with nitrogen gas (N_2) for up to 30 minutes, then the copper iodide (25 mg) and $Pd(PPh_3)_2Cl_2$ (10%) catalyst was added. Then the reaction mixture refluxed overnight at 100 ^{o}C. The completion of the reaction monitored by TLS. The solvent was removed by rotary evaporation and work-up with water and brine solution, extracted with DCM, and dried over anhydrous sodium sulphate. Further, the organic solvent was completely removed by rotary evaporation, the resultant mixture was purified by using column chromatography technique with DCM and hexane (4:1) as eluent, to afford the compound-III yield (60%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.66 (d, J = 4.5 Hz, 4H), 8.86 (d, J = 4.5 Hz, 4H), 7.66 (t, J = 8.5 Hz, 2H), 6.97 (d, J = 8.5 Hz, 4H), 3.81 (s, 8H), 1.50 (s, 14H), 1.42 (s, 35H), 1.09 (s, 27H), 0.46 (s, 26H). **MALDI-TOF**: m/z: Calcd for $C_{86}H_{124}N_4O_4Si_2Zn$: 1399.01 $[M+H]^+$, Found: 1399.00 $[M+H]^+$.

Synthesis of compound IV:

Compound III (200 mg, 0.14 mmol) dissolved in tetrahydrofuran (20 mL) in a round-bottom flask. To this added tetra-n-butylammonium fluoride (0.6 mL,1 M in THF) at 0 ^{o}C and continued stirring for 30 minutes under an inert atmosphere. The reaction was monitored by TLC, the mixture was quenched with H_2O and then extracted with DCM. The crude mixture was washed with water, brine solution, and extracted with DCM. The resultant organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Finally, the deprotected compound was obtained in moderate to good yield (60%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.62 (t, J = 10.5 Hz, 4H), 8.87 (t, J = 18.7 Hz, 4H), 7.69 (t, J = 8.5 Hz, 2H), 7.01 (t, J = 7.4 Hz, 4H), 3.84 (t, J = 6.5 Hz, 8H), 3.70 (s, 2H), 1.21 (s, 14H), 1.05 (s, 8H), 0.97 – 0.91 (m, 8H), 0.85 (dt, J = 14.6, 7.3 Hz, 8H), 0.68 – 0.62 (m, 8H), 0.51 (d, J = 4.8 Hz, 6H), 0.40 (dt, J = 14.8, 7.5 Hz, 8H). **MALDI-TOF**: m/z: Calcd for $C_{68}H_{84}N_4O_4Zn$: 1086.80 $[M+H]^+$, Found: 1086.92 $[M+H]^+$.

Synthesis of SPS-PPY-TT:

Compound-IV (100 mg, 0.09 mmol), compound V (88 mg, 0.193 mmol), triethyl amine (Et_3N) (10 mL), triphenyl phosphine (PPh_3) (15 mg), and dry THF (30 mL) were taken in a dry round-bottom flask (50 mL) under a nitrogen atmosphere. The reaction mixture was degassed with nitrogen gas for up to 30 minutes, after which the copper iodide (20 mg) and $Pd(PPh_3)_4$ (10%) catalyst were added. Then reflux the reaction mixture upto 24 h at 70^{o}C. The reaction solvent was removed by rotary evaporation, work-up with water and NaCl solution, and extracted with DCM, dried over anhydrous Na_2SO_4. Finally, the organic solvent was removed by rotary evaporation, the crude material was purified by using column chromatography by using DCM and hexane (4:1) as eluent, to afford the **SPS-PPY-TT**yield (79%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.95 – 9.40 (m, 4H), 9.15 – 8.63 (m, 5H), 7.85 – 7.67 (m, 4H), 7.59 – 7.28 (m, 2H), 7.06 (d, J = 8.5 Hz, 5H), 3.93 (s, 8H), 1.42 (dt, J = 13.4, 4.5 Hz, 10H), 1.27 (d, J = 15.4 Hz, 4H), 1.06 (d, J = 9.5 Hz, 10H), 0.85 (d, J = 21.7 Hz, 8H), 0.73 (t, J = 7.2 Hz, 4H), 0.67 – 0.45 (m, 44H), 0.41 (t, J = 7.3 Hz, 6H). **MALDI-TOF**: m/z: Calcd for $C_{104}H_{114}F_2N_8O_4$ S_6Zn: 1835.84 $[M+H]^+$, Found: 1835.85 $[M+H]^+$. CHNSO: $C_{104}H_{114}F_2N_8O_4$ S_6Zn calcd, C 68.04, H 6.26, N 6.10, S 10.48, O 3.49; found C 68.03, H 6.27, N 6.11, S 10.47, O 3.50.

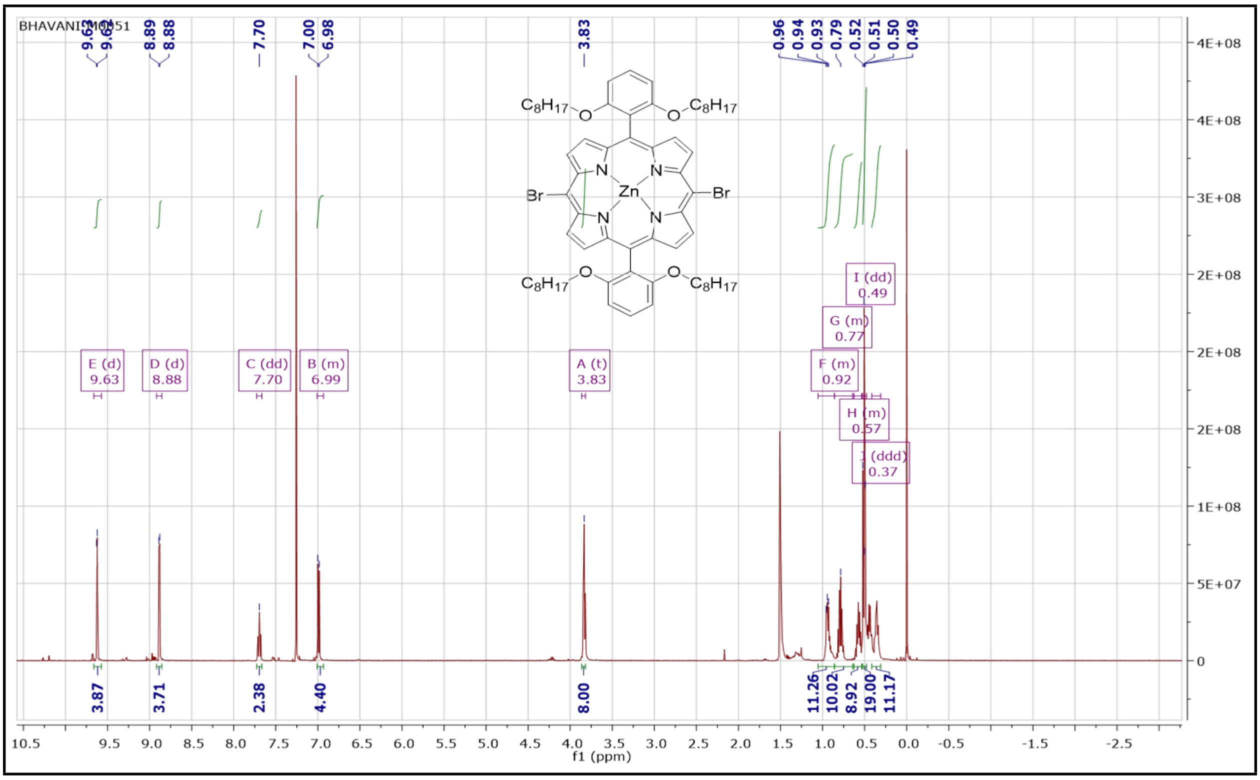


Figure S1: ^{1}H NMR of II in $CDCl_3$.

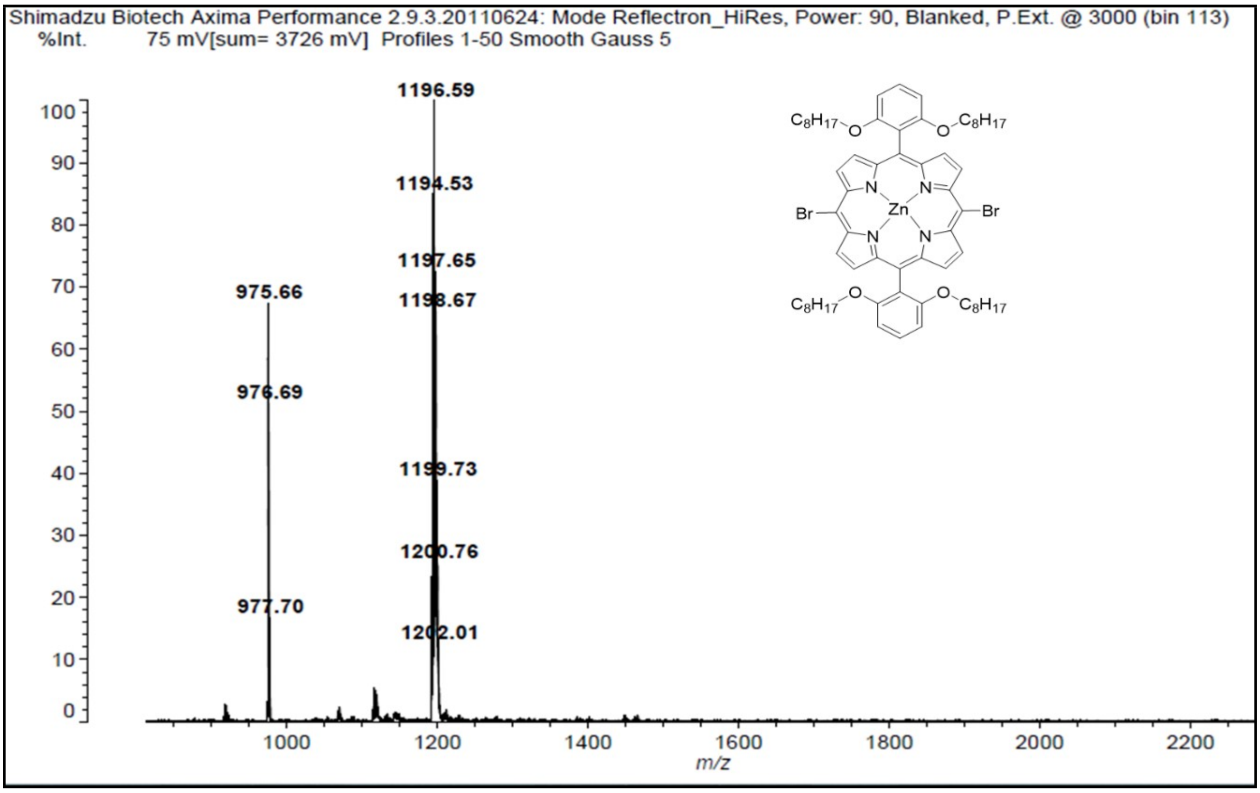


Figure 2: MALDI-MS spectrum of II.

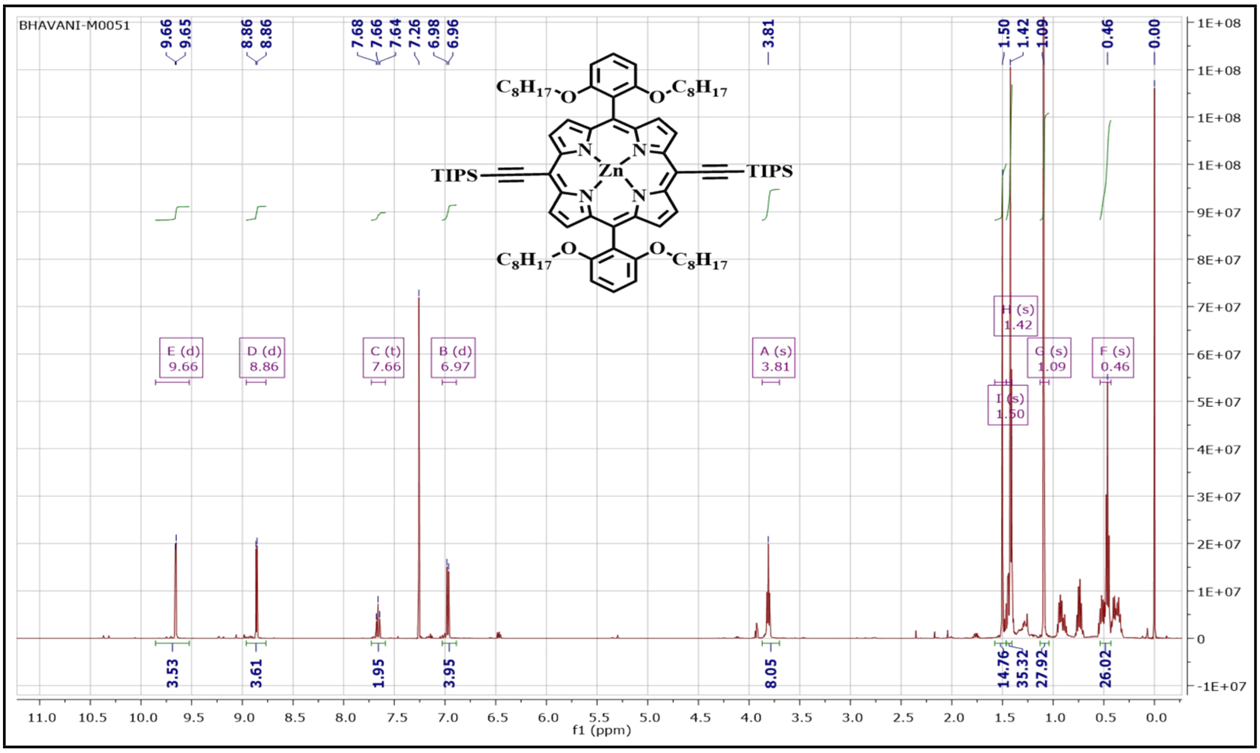


Figure S3: ^{1}H NMR of III in $CDCl_3$.

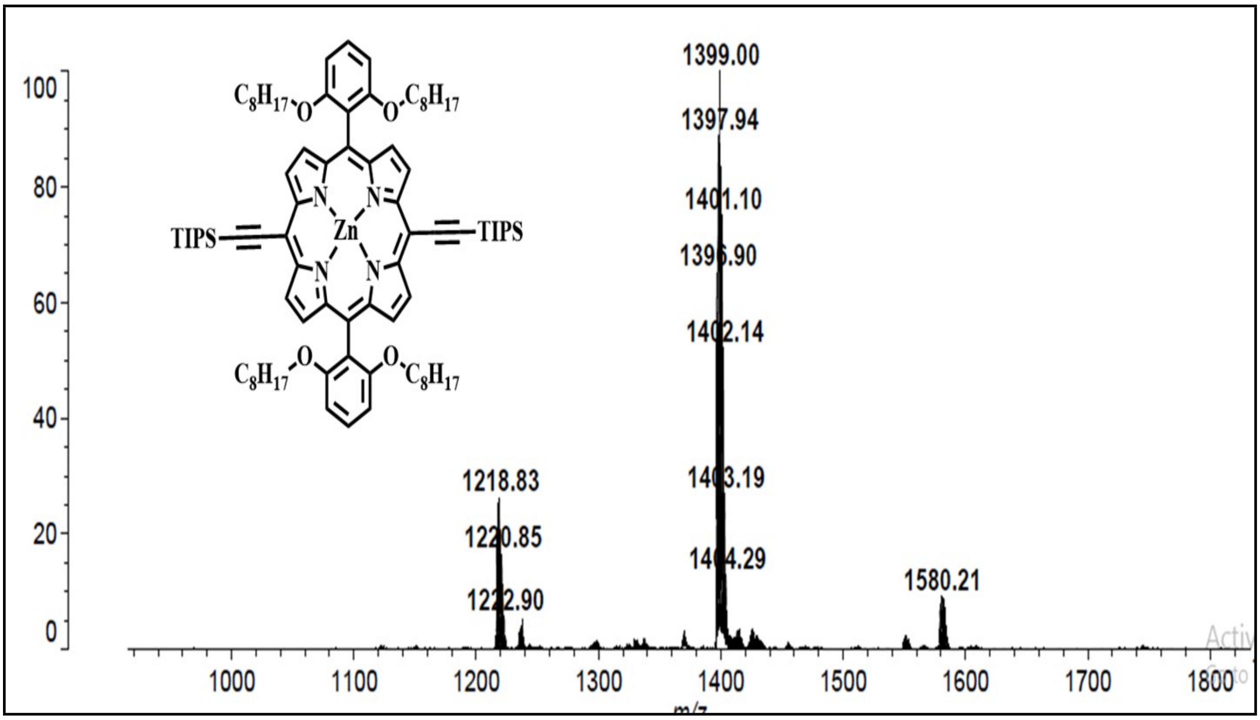


Figure S4: MALDI-TOF of III

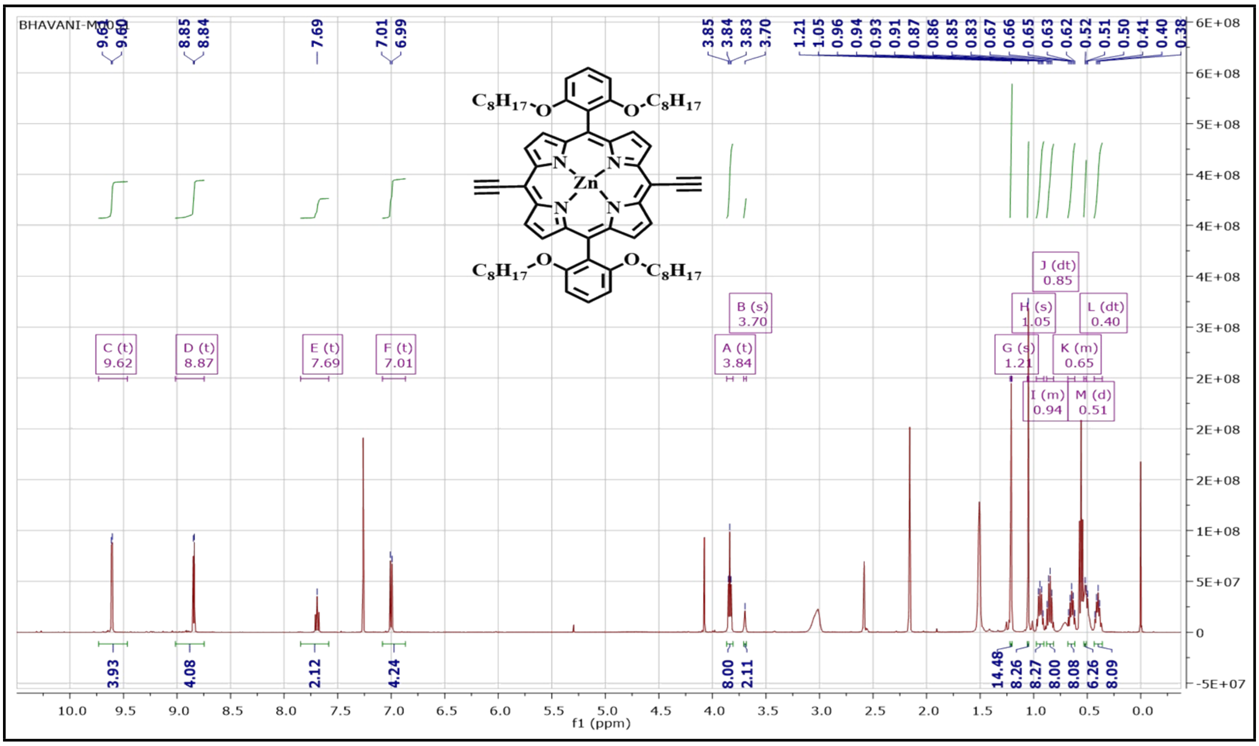


Figure S5: ^{1}H NMR of IV in $CDCl_3$.

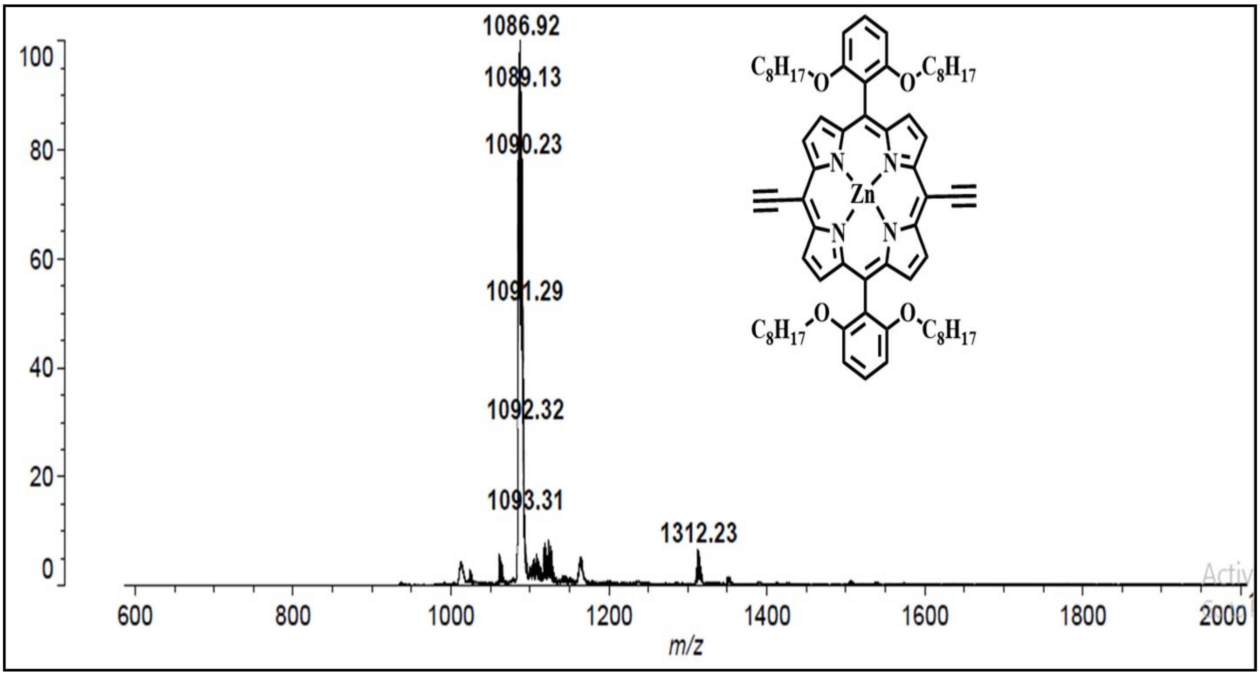


Figure S6: MALDI-TOF of IV.

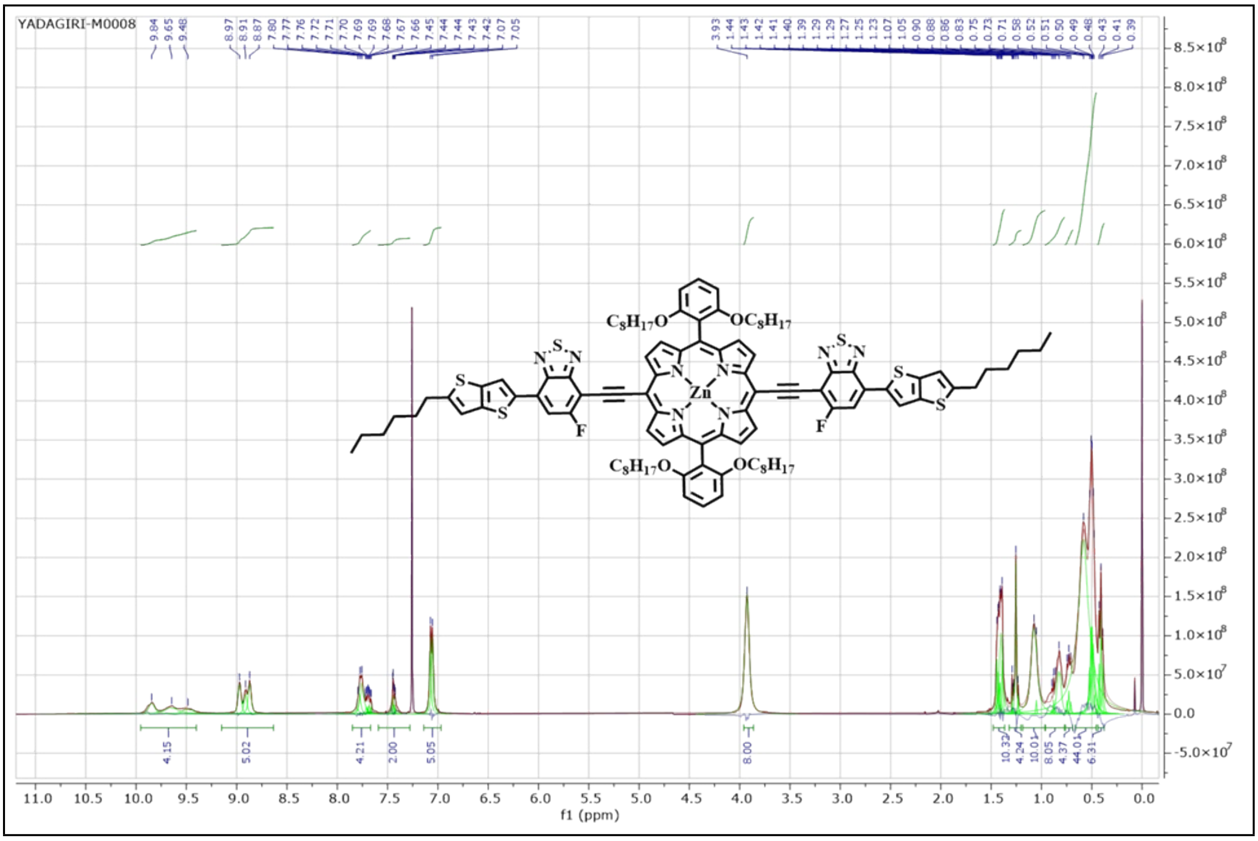


Figure S7: ^{1}H NMR of **SPS-PPY-TT** in $CDCl_3$.

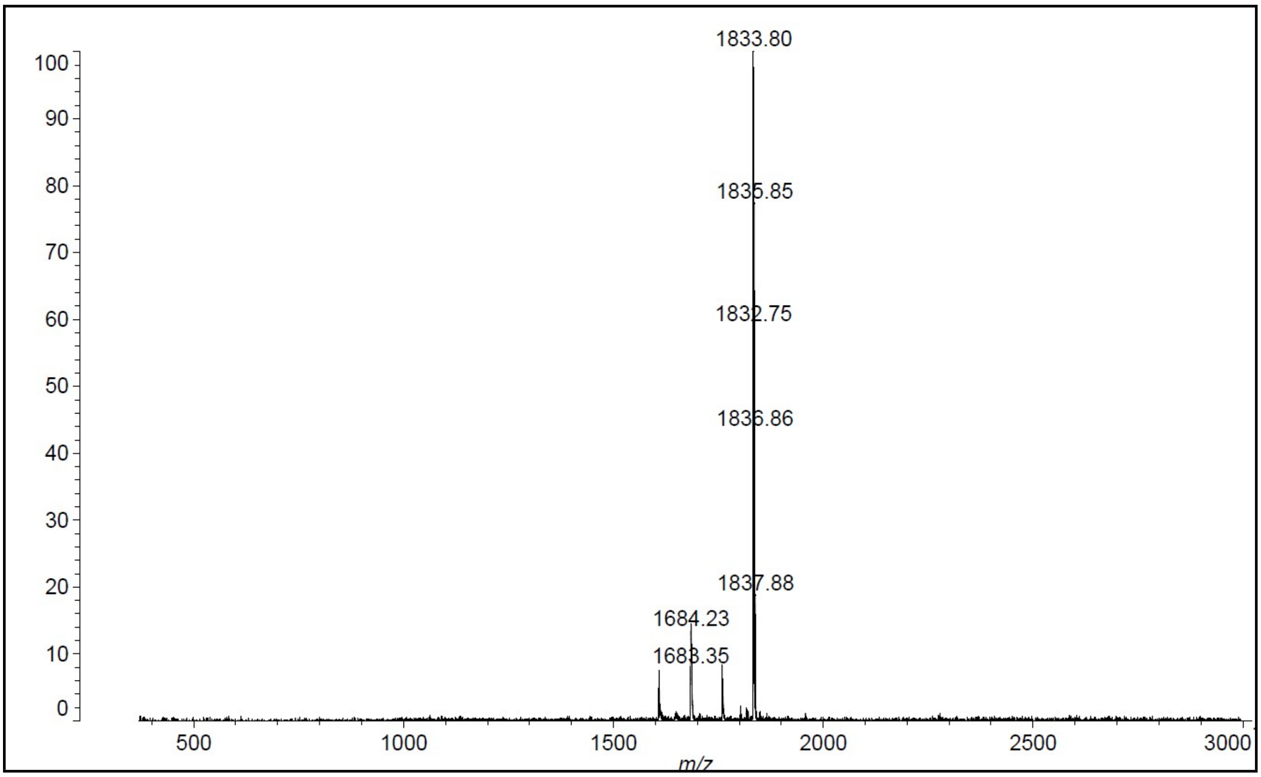


Figure S8: MALDI-TOF of SPS-PPY-TT.

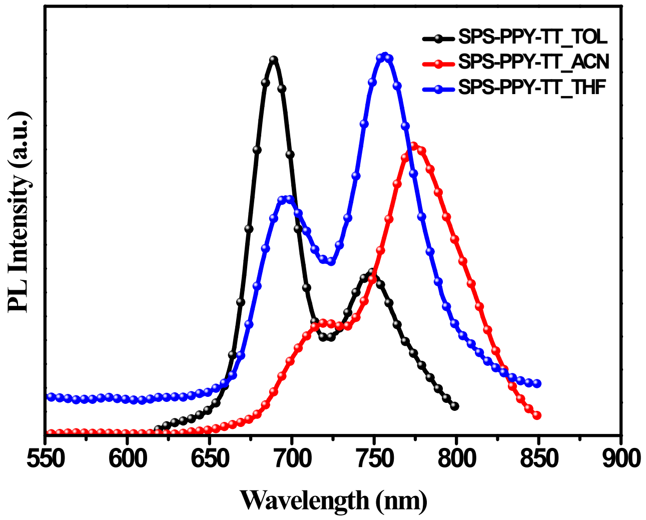


Figure S9. Solvantochromic property of **SPS-PPY-TT** in different solvents (TOL, ACN, and THF).

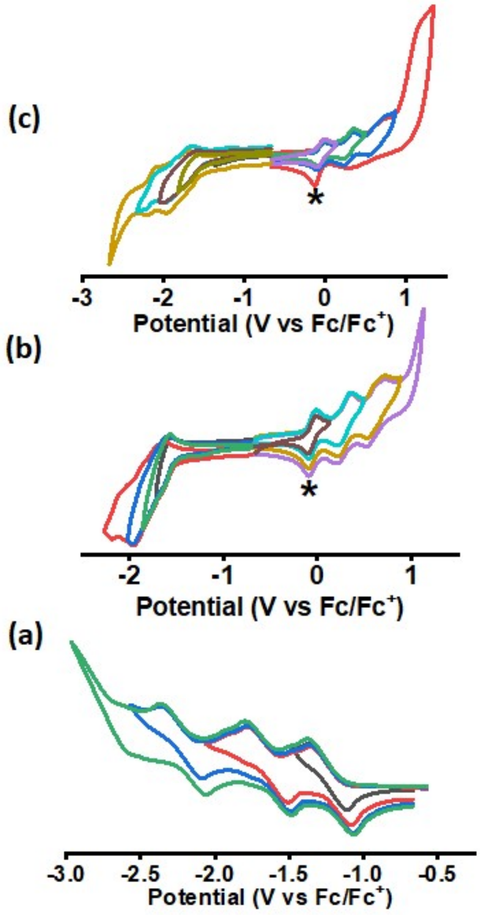
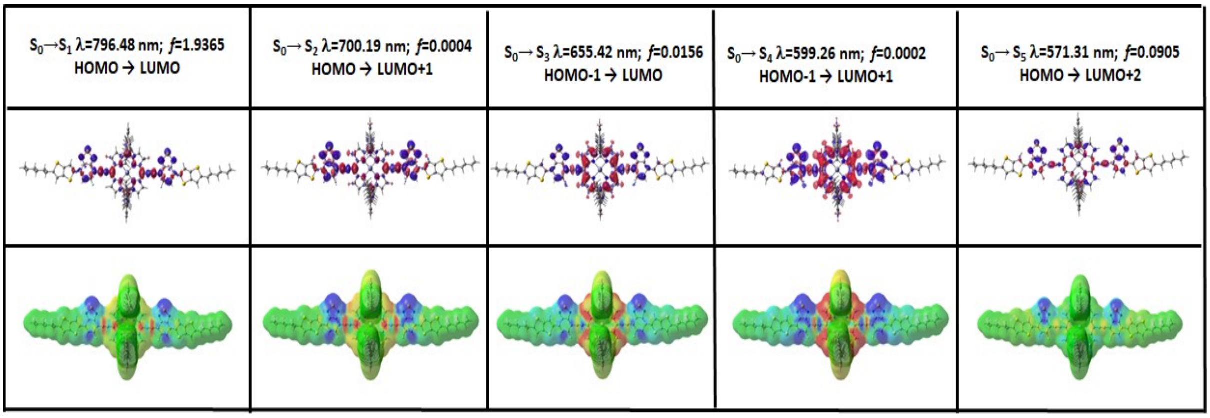


Figure S10. Cyclic voltammogramsof (a) ImC$_{60}$, (b) SPS-PPY-TT, and (c) SPS-PPY-TT: ImC$_{60.}$



FigureS11. Hole-electron isosurfaces and the charge density difference maps of SPS-PPY-TT. (red: charge donor, blue: charge acceptor; (-2.000x10^{-5} V – 2.000x10^{-5} V).

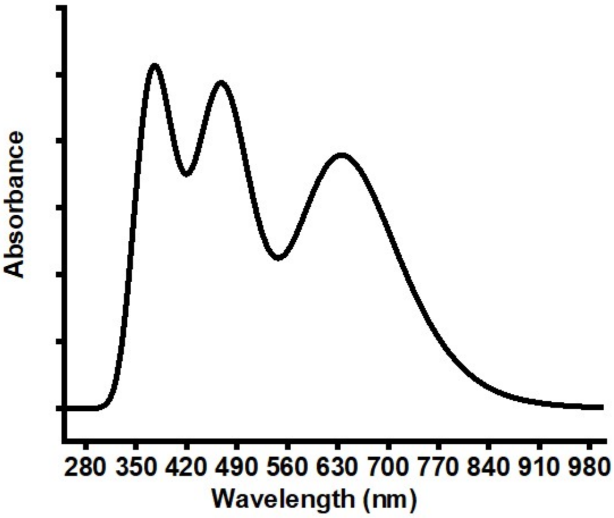


Figure S12. UV-Vis absorption spectra generated from the TD-DFT calculations.

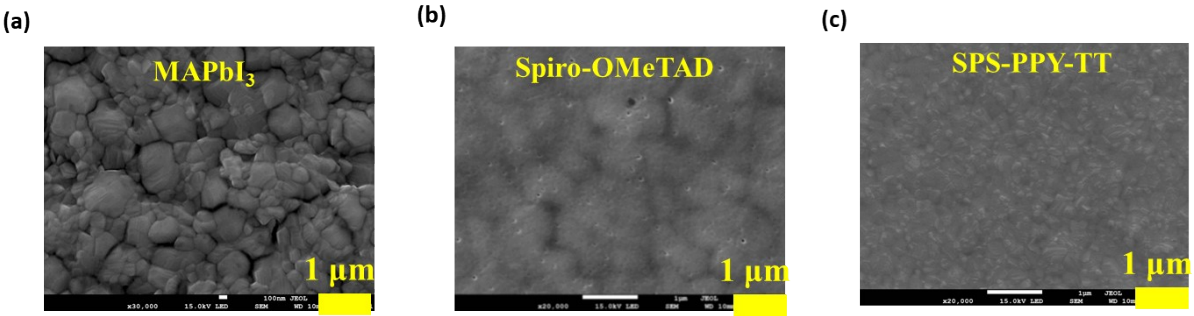


Figure S13. Field emission scanning electron microscopy (FESEM) images of (a) MAPbI3, (b) Spiro-OMeTAD, and (c) **SPS-PPY-TT**.

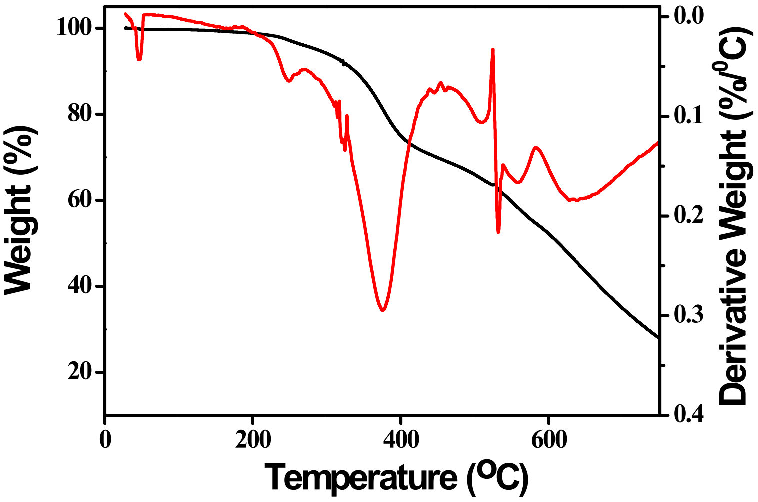


Figure S14. TG/DTG curves of LG5 with a heating rate 10 °C min^{-1} under nitrogen gas.

5. References

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