

Organic photovoltaic performance and structural relationship of non-fullerene small molecule acceptors based on tetraarylphenazine core and perylene diimide

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Supporting Information

Nuclear magnetic resonance and mass spectroscopy

¹H and ¹³C NMR spectra were recorded on a Bruker AVII 400 MHz NMR spectrometer or Bruker AVIII 400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm, δ). ¹H NMR and ¹³C NMR spectra were referenced to tetramethylsilane (0 ppm) or solvent residual peak (CDCl₃: ¹H NMR: 7.26 ppm, ¹³C NMR: 77.23 ppm, C₂D₂Cl₄: ¹H NMR: 6.00 ppm, C₆D₆: ¹H NMR: 7.16 ppm, DMSO-*d*₆: ¹H NMR: 2.50 ppm, ¹³C NMR: 39.31 ppm). ¹⁹F NMR spectra were referenced to 0.03%

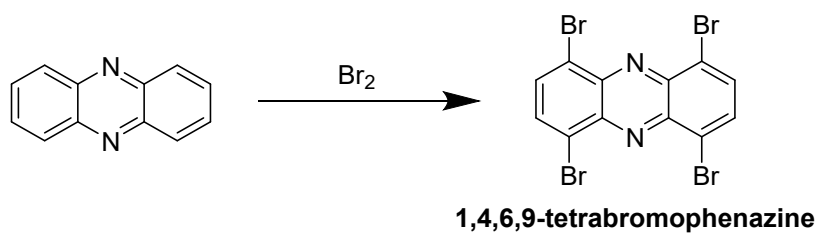
hexafluorobenzene in CDCl₃ (-161.68 ppm). Mass spectroscopy were collected on a MALDI Micro MX mass spectrometer.

Materials and synthesis

All chemicals, unless otherwise specified, were purchased from commercial resources and used as received. Toluene, mesitylene, *n*-heptane, tetrahydrofuran (THF), and 1,4-dioxane were distilled from sodium and benzophenone under nitrogen before using.

PDI-Br¹ (5-bromo-2,9-di(tridecan-7-yl)anthra[2,1,9-def:6,5,10-d'e'f]diisoquinoline-1,3,8,10(2H,9H)-tetraone), tert-butyl dimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)silane² and **P3TEA** (GPC: Mn: 48.4 kDa; Mw: 100.2 kDa; PDI = 2.07)³ were synthesized according to literature.

Synthesis of 1,4,6,9-tetrabromophenazine



To a 100 mL round-bottom flask containing 3000 mg (16.6 mmol, 1.0 eq) of phenazine, 30 mL (585 mmol, 35 eq) of elemental bromine was added in 1 mL portion in 10 min. The solution was stirred at room temperature until no HBr fume evolved. Majority of excess bromine was removed with stream of air. The solution was diluted in methanol, filtered and washed with methanol. The residue was recrystallized with mesitylene, yielding a yellow to greenish yellow needle crystal (7100 mg, 86% yield). ^1H NMR (400 MHz, C_6D_6): 7.26 (s, 4H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$): 140.89, 135.36, 123.17.

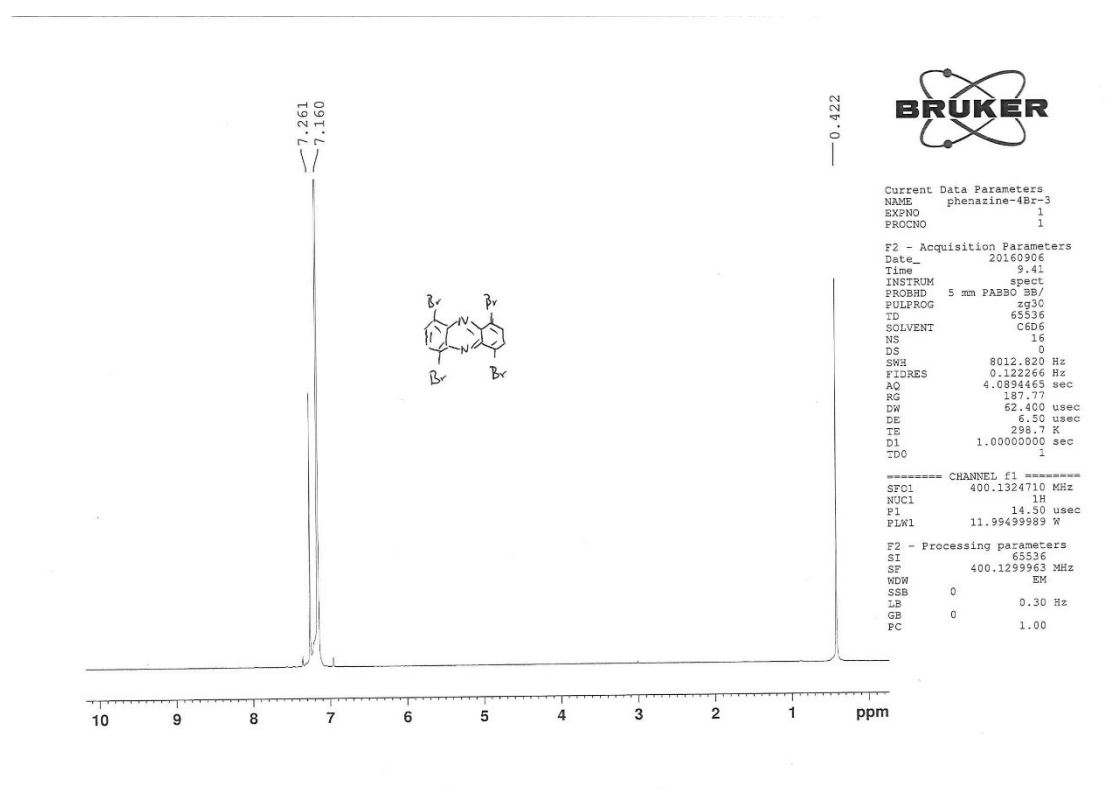


Figure S1 ^1H NMR spectra of 1,4,6,9-tetrabromophenazine.

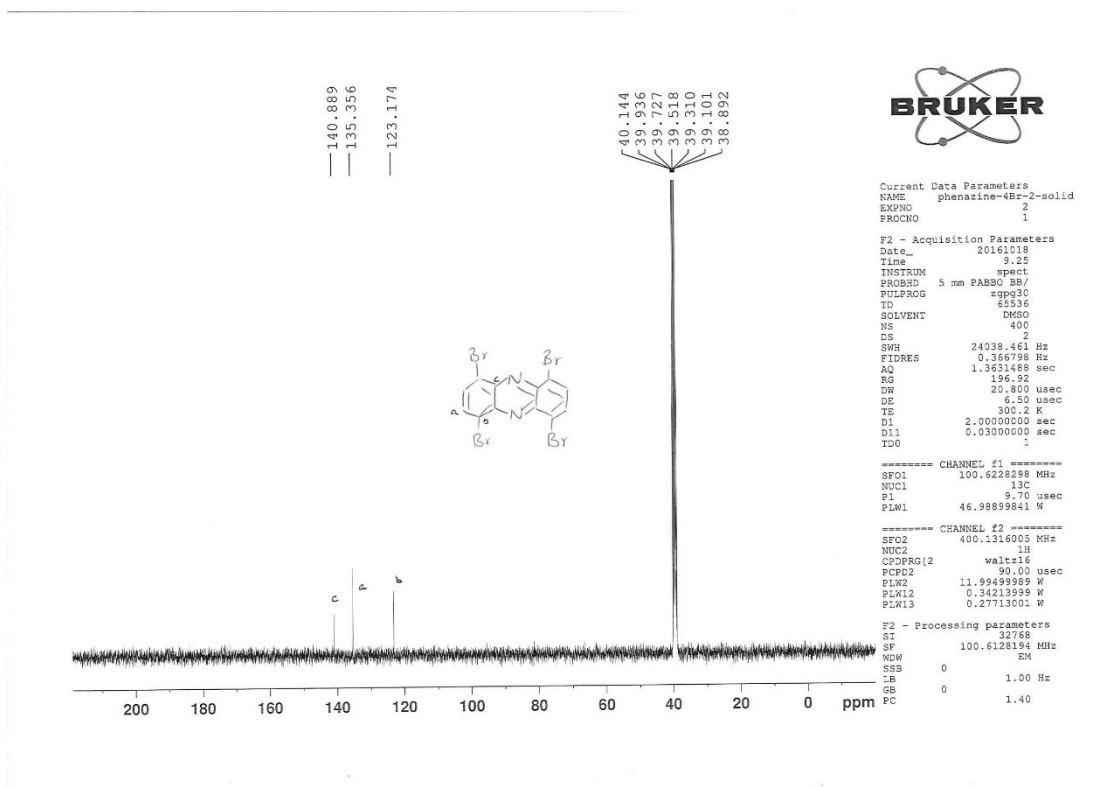
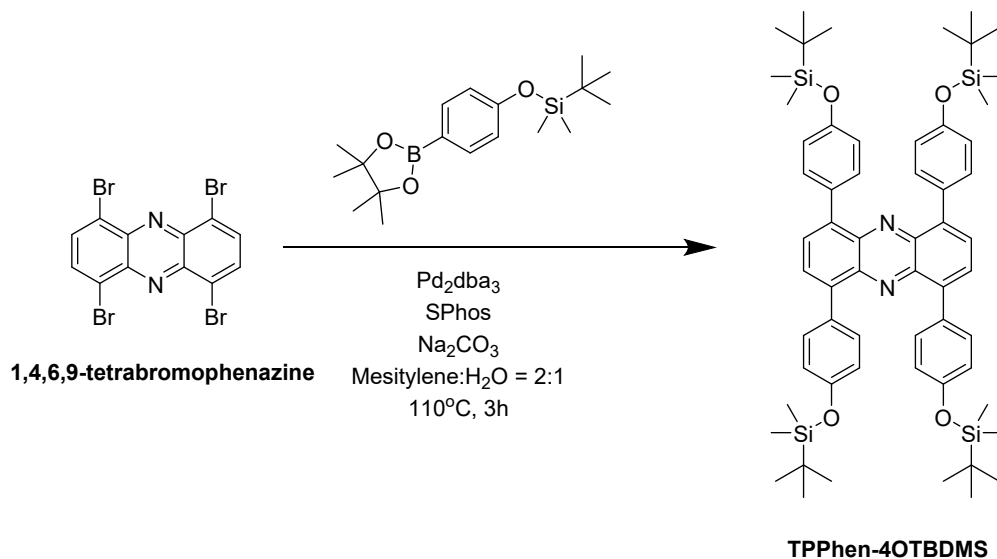


Figure S2 ¹³C NMR spectra of 1,4,6,9-tetrabromophenazine.

Synthesis of TPPhen-4OTBDMS



Under nitrogen atmosphere, to a 100 mL Schlenk tube, 1090 mg (2.2 mmol, 1.0 eq) of 1,4,6,9-tetrabromophenazine, 2950 mg (8.8 mmol, 4.0 eq) of tert-butyldimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)silane, 100 mg (0.11 mmol, 0.05 eq) of Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct, 180 mg

(0.44 mmol, 0.2 eq) of SPhos, 1865 mg of sodium carbonate (17.6 mmol, 8.0 eq), and 30 mL of solvent were added. The tube was sealed and heated to 110 °C with stirring for 3 hours. The product was extracted by toluene, washed with deionised water then brine. The organic layer was dried by anhydrous sodium sulphate, and the solvent was removed under vacuum. The orange residue was purified by flash column chromatography (30% dichloromethane in *n*-hexane) yielding an orange solid (1514 mg, 68% yield). ¹H NMR (400 MHz, CDCl₃): 7.89 (s, 4H), 7.75 (d, *J* = 8.4 Hz, 8H), 6.94 (d, *J* = 8.4 Hz, 8H), 1.08 (s, 36H), 0.32 (s, 24H). ¹³C NMR (101 MHz, CDCl₃): 155.37, 140.78, 139.27, 132.16, 131.55, 129.85, 119.55, 25.84, 18.30, -4.17.

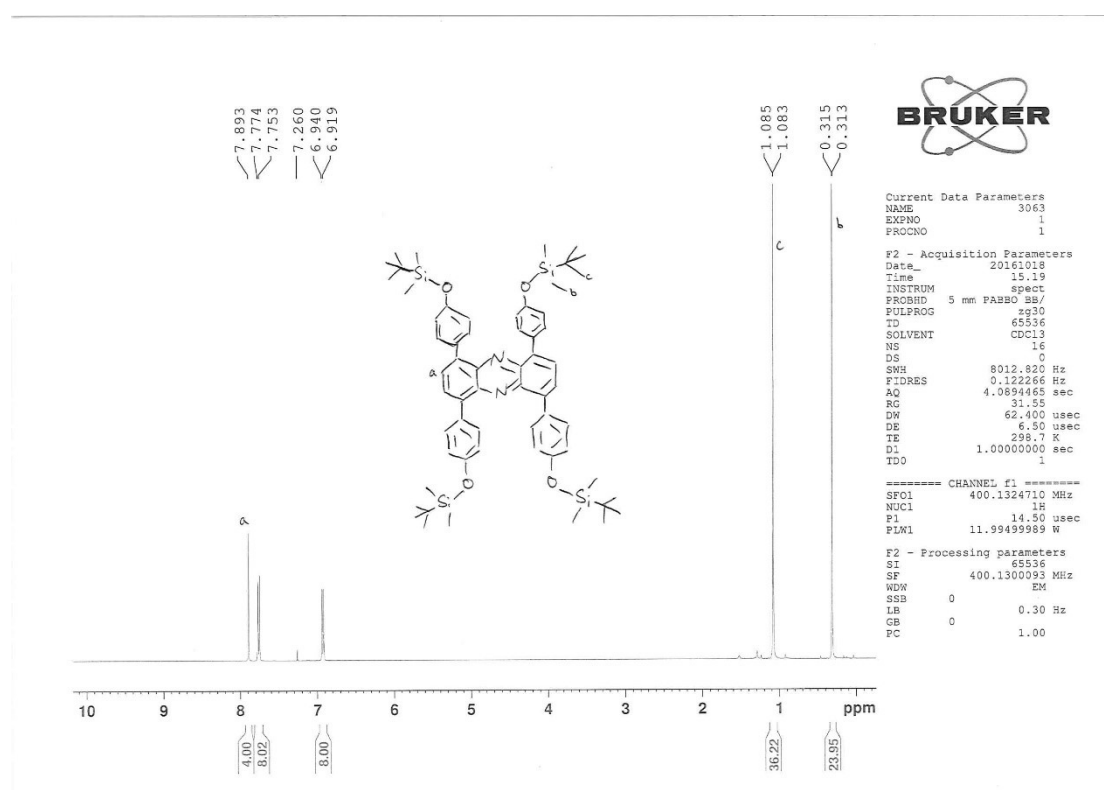


Figure S3 ¹H NMR spectra of TPPhen-4OTBDMS.

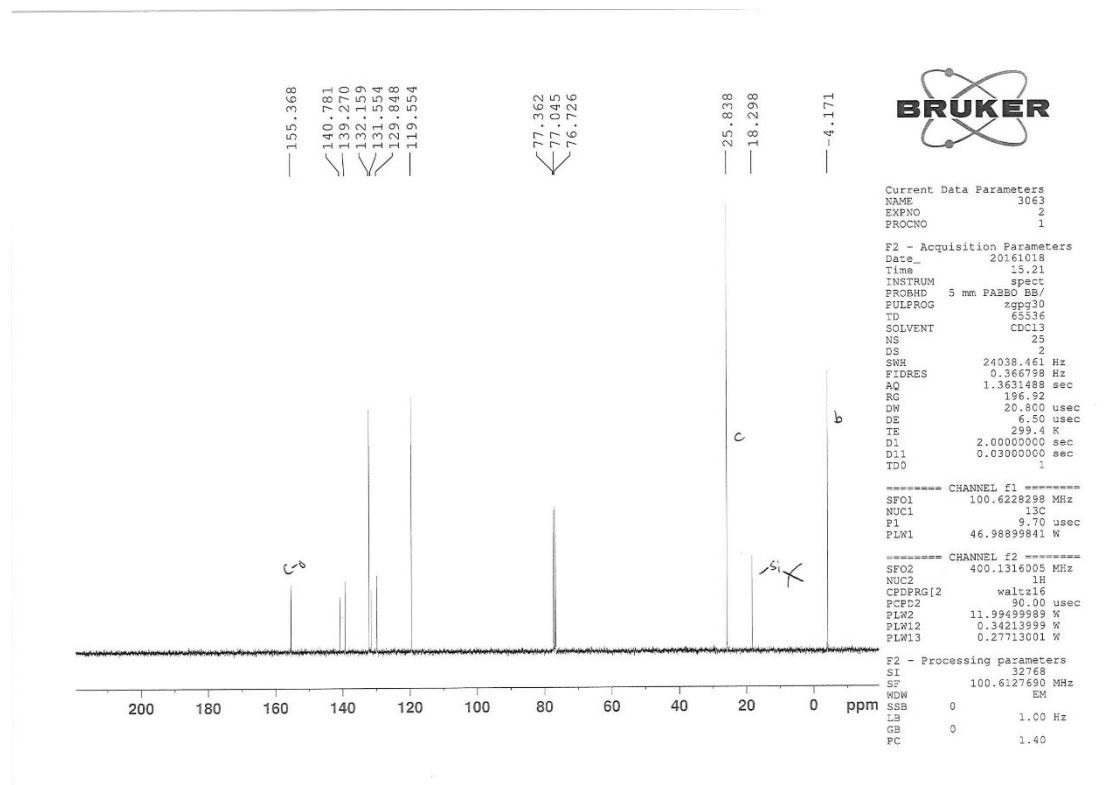
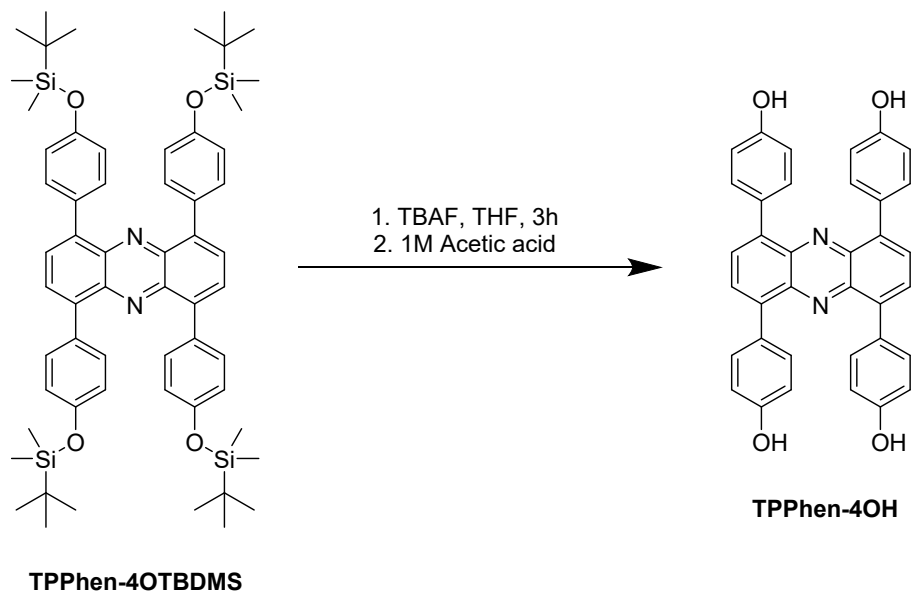


Figure S4 ^{13}C NMR spectra of TPPhen-4OTBDMS.

Synthesis of TPPhen-4OH



To a 250 mL round-bottom flask, 1500 mg (1.5 mmol, 1.0 eq) of TPPhen-4OTBDMS and 30 mL of THF were added. With stirring, 18 mL of 1M tetramethylammonium fluoride (18 mmol, 12 eq) in THF was added. After 3 hours, 40 mL of 1M acetic acid was added and stirred for 1 hour. The majority of the solvent was removed under

vacuum. The orange precipitate was filtered, washed with methanol and dried under vacuum (750 mg, 88% yield). $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): 9.59 (s, 4H), 7.91 (s, 4H), 7.67 (d, $J = 8.4$ Hz, 8H), 6.87 (d, $J = 8.4$ Hz, 8H).

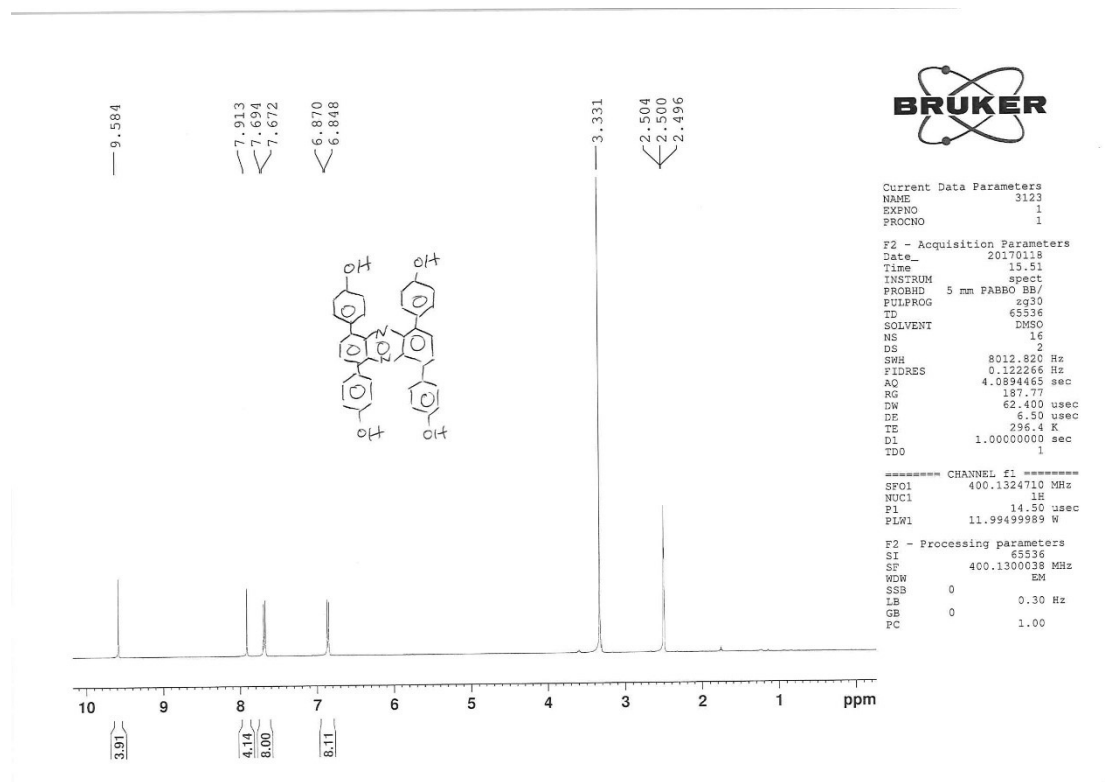
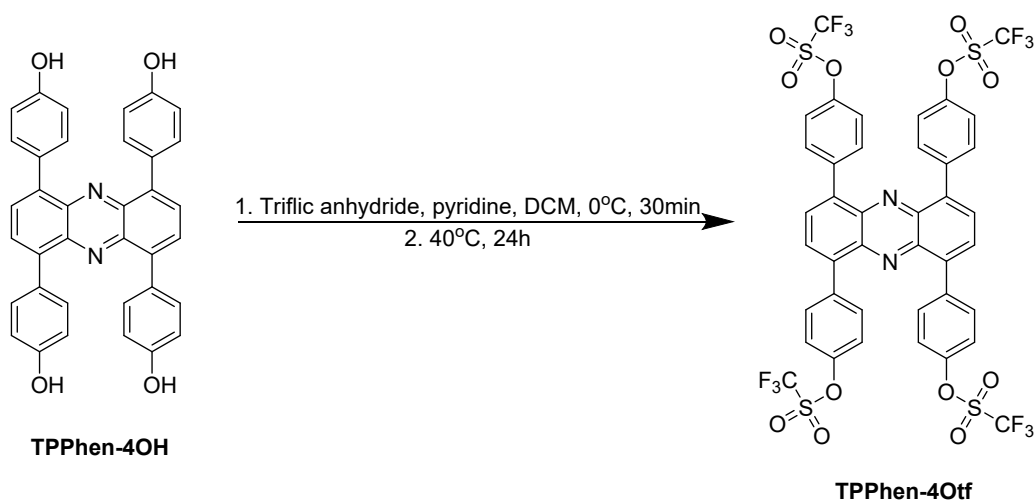


Figure S5 $^1\text{H NMR}$ spectra of TPPhen-4OH.

Synthesis of TPPhen-4Otf



Under nitrogen atmosphere, a 250 mL Schlenk tube was charged with 540 mg (0.99 mmol, 1.0 eq) of TPPhen-4OH, 50 mL of dichloromethane and 2.5 mL of pyridine (29.3

mmol, 30 eq). The solution was cooled to 0 °C. With stirring, 5 mL of 1.95 M triflic anhydride (9.9 mmol, 10 eq) in dichloromethane was added dropwise to the solution. The solution was stirred for 30 min then heated to 40 °C for 24 hours. The yellow suspension was filtered out, washed with methanol and dried under vacuum (455 mg, 43% yield). ¹H NMR (400 MHz, CDCl₃): 8.00 (s, 4H), 7.79 (d, *J* = 8.8 Hz, 8H), 7.34 (d, *J* = 8.8 Hz, 8H). ¹⁹F NMR (376 MHz, CDCl₃): -73.09 (s, 1F).

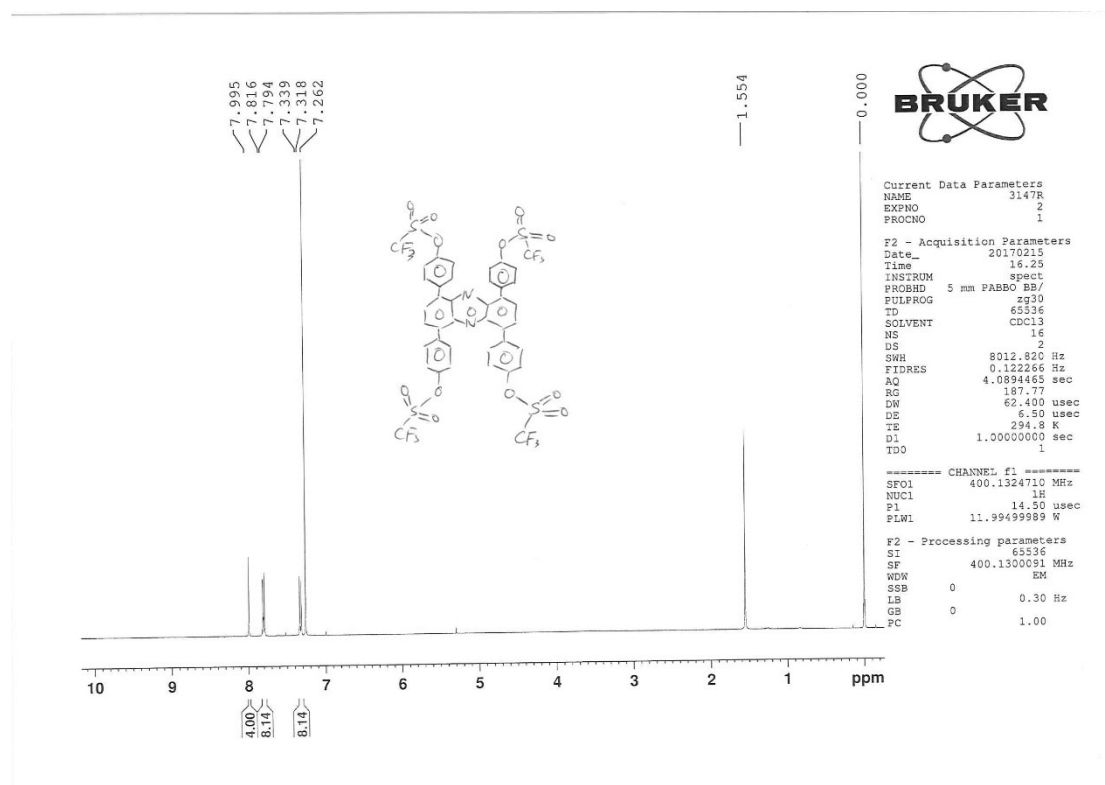


Figure S6 ¹H NMR spectra of TPPhen-4Otf.

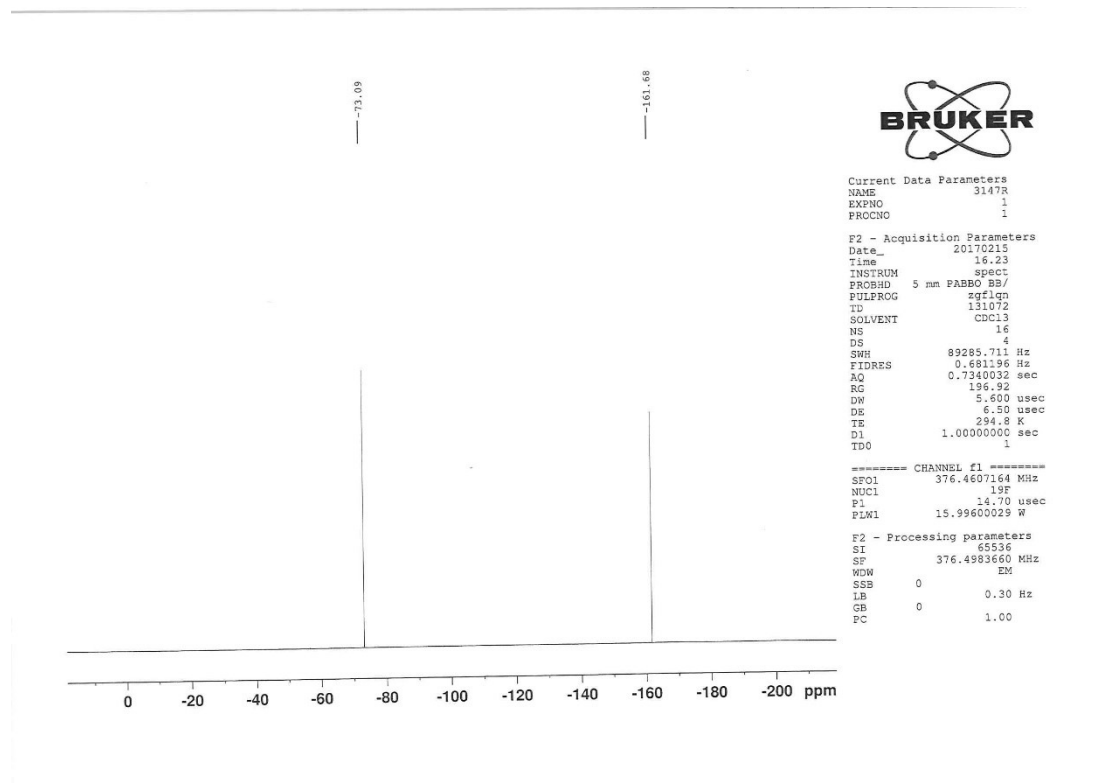
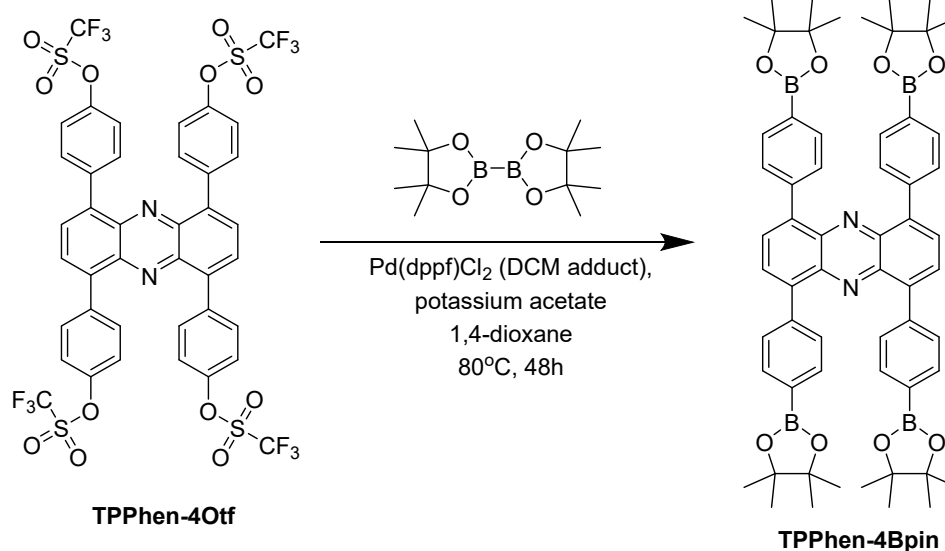


Figure S7 ^{19}F NMR spectra of TPPhen-4Otf.

Synthesis of TPPhen-4Bpin



Under nitrogen atmosphere, to a 100 mL Schlenk tube, 455 mg (0.42mmol, 1.0 eq) of TPPhen-4Otf, 516 mg (2.0 mmol, 4.8 eq) of Bis(pinacolato)diboron, 138 mg (0.17mmol, 0.4 eq) of [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II)-dichloromethane adduct, 500 mg (5 mmol, 12 eq) of potassium acetate, and 30 mL of

1,4-dioxane were added. The solution was heated to 80 °C for 48 hours with stirring. The suspension was filtered out and washed with THF:methanol (1:3) solution, water, methanol and diethyl ether. The yellow residue was dried under vacuum (340 mg, 81% yield). ¹H NMR (400 MHz, CDCl₃:C₆D₆ = 1:5): 8.18 (d, *J* = 8.4 Hz, 8H), 7.85 (d, *J* = 8.4 Hz, 8H), 7.55 (s, 4H), 1.30 (s, 48H).

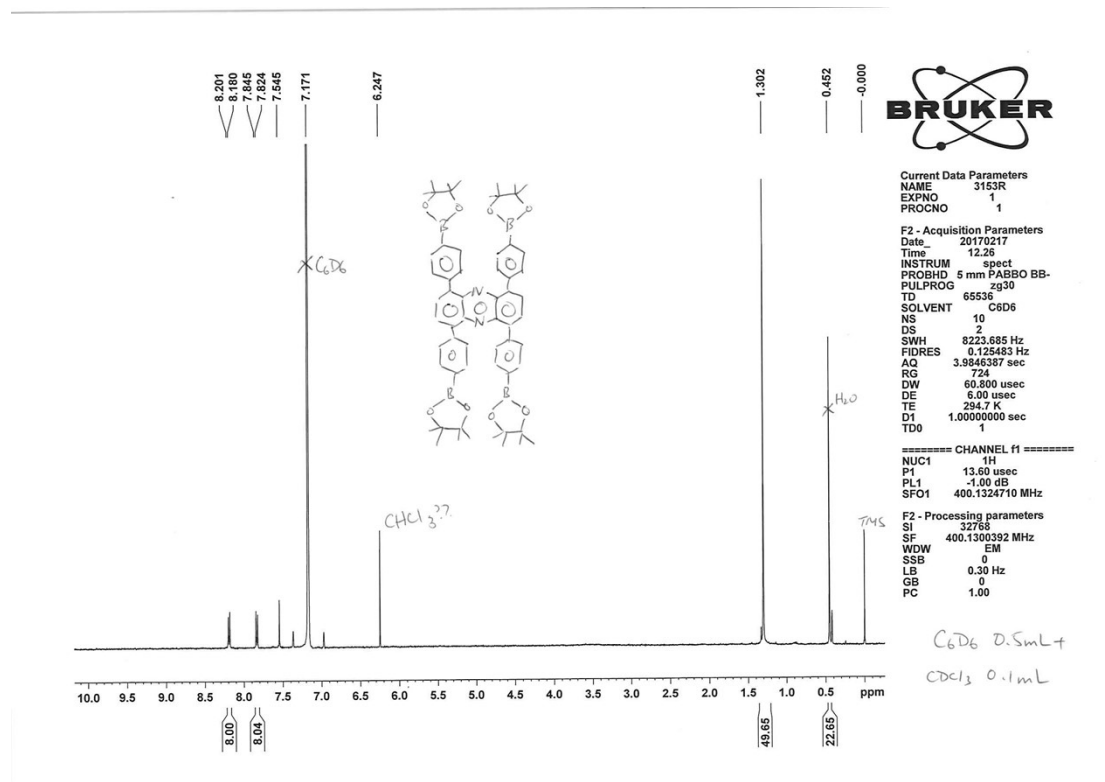
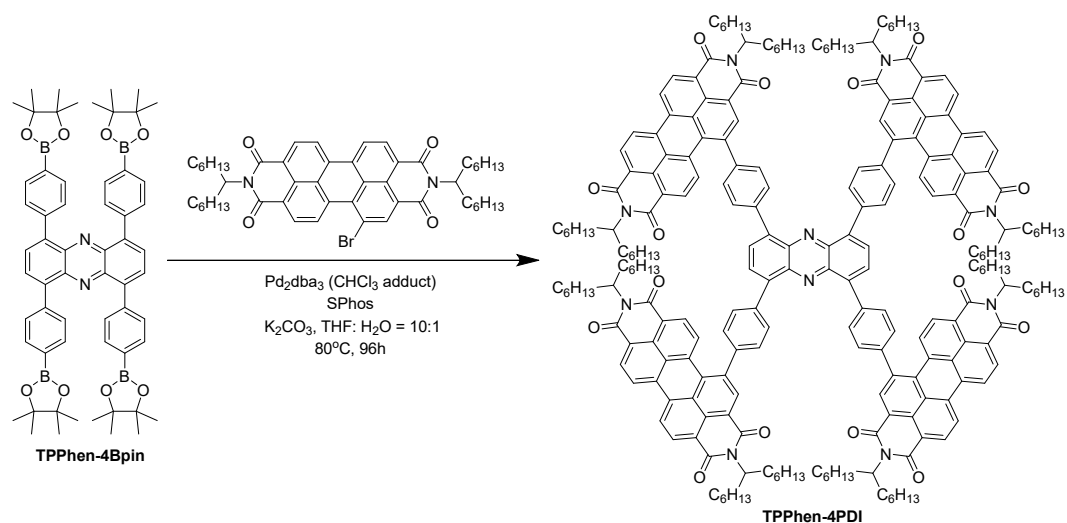


Figure S8 ¹H NMR spectra of TPPhen-4Bpin.

Synthesis of TPPhen-4PDI



Under nitrogen atmosphere, to a 100 mL Schlenk tube, 127 mg (0.13 mmol, 1.0 eq) of TPPhen-4Bpin, 860 mg (1.0 mmol, 7.7 eq) of PDI-Br, 13 mg (0.013 mmol, 0.1 eq) of tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct, 11 mg (0.03mmol, 0.2 eq) of SPhos, 142 mg (1.0 mmol, 7.7 eq) of potassium carbonate and 18 mL of solvent were added. The solution was heated to 80 °C for 96 hours with stirring. The solution was extracted with toluene for three times. The organic phase was washed with water and brine, then dried with anhydrous sodium sulphate. The solvent was removed under reduced pressure. The product was purified by flash column chromatography (30% dichloromethane in *n*-hexane to 50% dichloromethane in *n*-hexane) yielding a red solid (153 mg, 34% yield). ¹H NMR (400 MHz, C₂D₂Cl₄, 334 K): 8.85 (br, 4H), 8.48 (br, 4H), 8.35 (s, 4H), 8.19 (br, 12H), 8.03 (br, 4H), 7.78 (br, 12H), 6.81 (br, 8H), 5.24 (br, 4H), 4.92 (br, 4H), 2.36 (br, 4H), 2.01 (br, 4H), 1.77 (br, 8H), 1.61 (br, 8H), 1.35 (br, 112H), 1.12 (br, 8H), 0.93 (br, 48H).

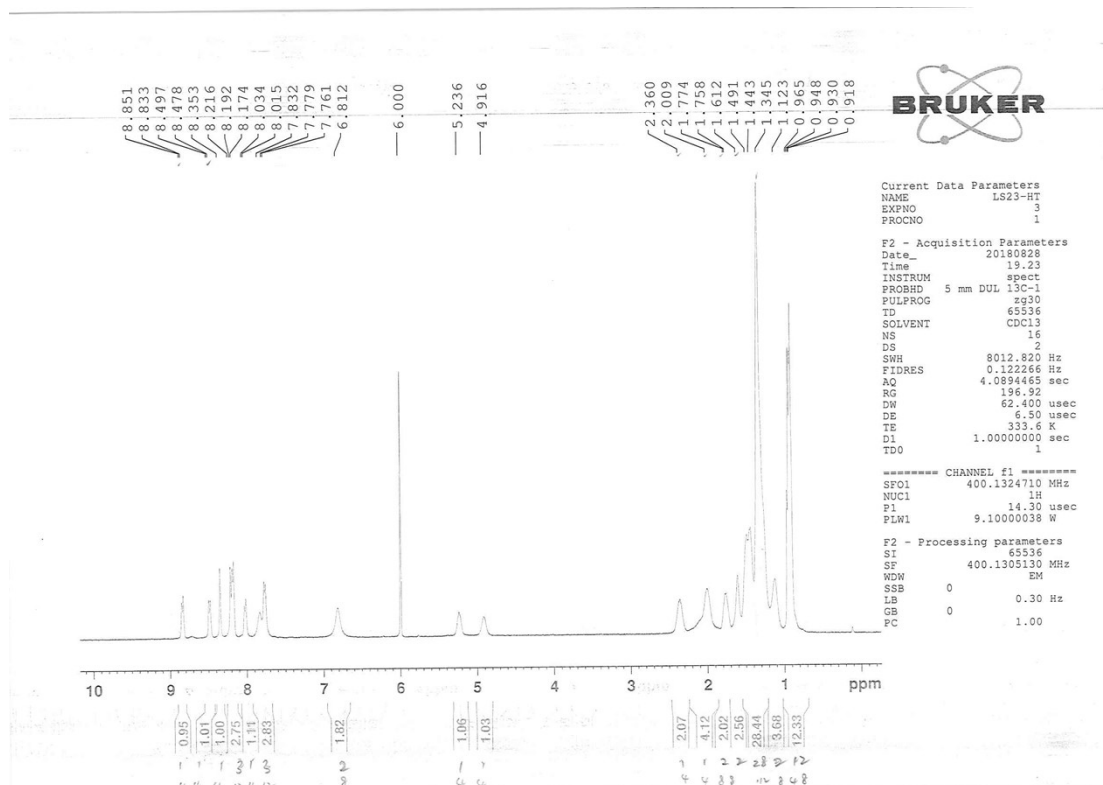
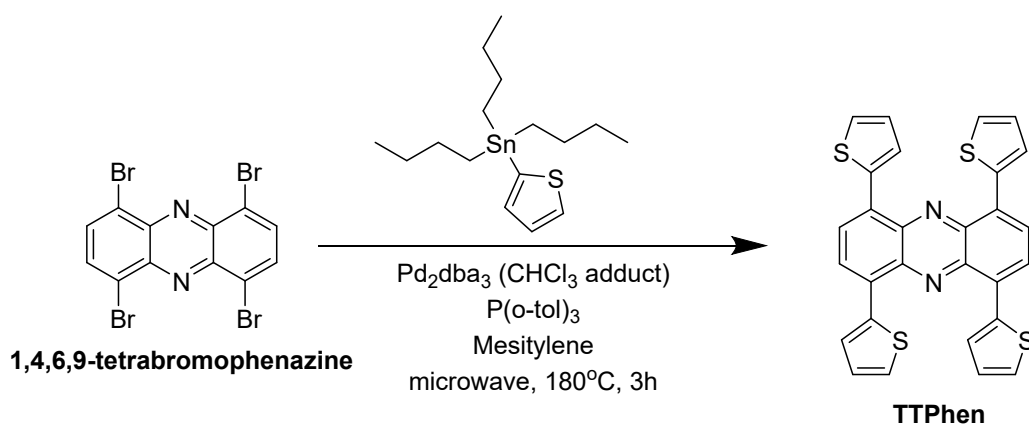


Figure S9 ¹H NMR spectra of TPPhen-4PDI.



Figure S10 Mass spectra of TPPhen-4PDI.

Synthesis of TTPhen



Under nitrogen atmosphere, to a 10 mL microwave reaction tube, 270 mg (0.55 mmol, 1.0 eq) of 1,4,6,9-tetrabromophenazine, 900 mg (2.4 mmol, 4.4 eq) of tributyl(thiophen-2-yl)stannane, 31 mg (0.03 mmol, 0.05 eq) of Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct, 36 mg (0.12 mmol, 0.22 eq) of Tri(*o*-tolyl)phosphine and 4 mL of mesitylene were added. The tube was sealed and heated to 180°C with stirring for 3 hours by microwave radiation. The solution was cooled to -20°C in freezer and filtered. The dark red crystal filtered out was washed with methanol and dried under vacuum (265 mg, 94% yield). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 8.26 (s, 4H), 7.92 (dd, $J = 3.6$ Hz, 1.2 Hz, 4H), 7.71 (dd, $J = 5.2$ Hz, 1.2 Hz, 4H), 7.22 (dd, $J = 3.6$ Hz, 5.2 Hz, 4H).

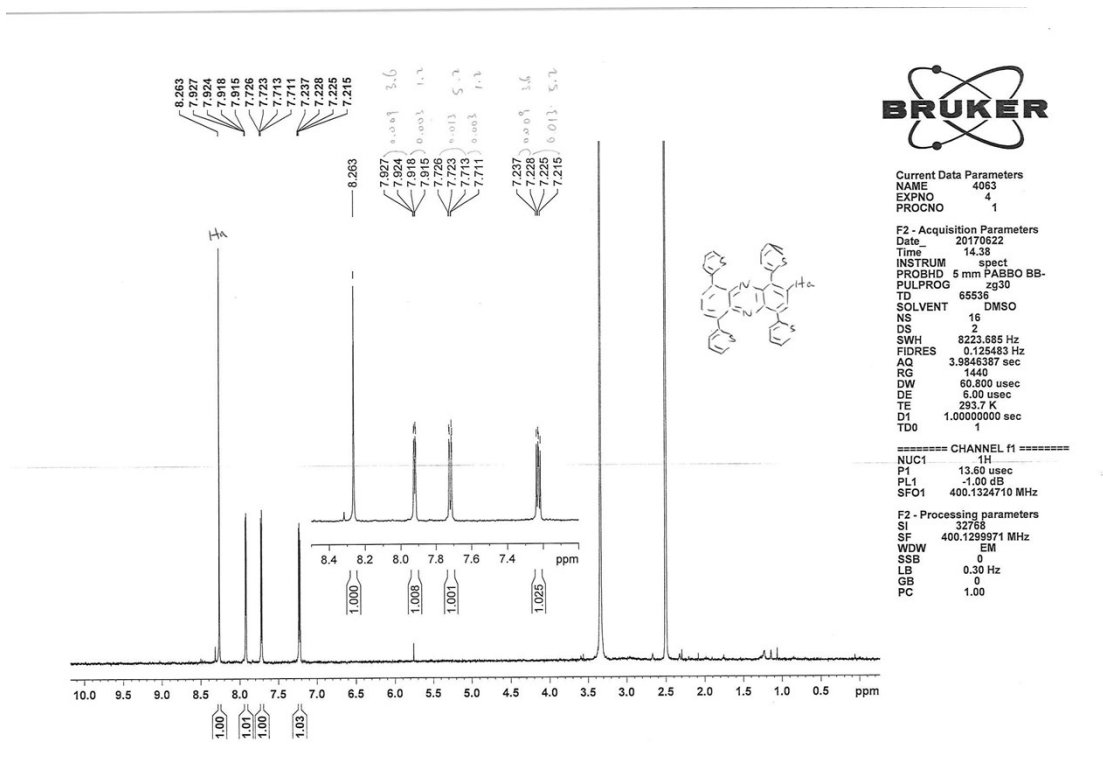
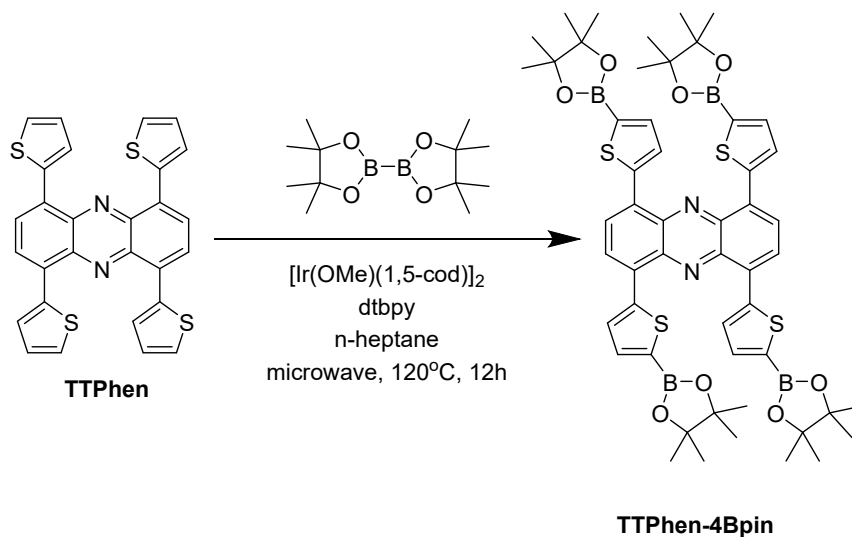


Figure S11 ^1H NMR spectra of TTPhen.

Synthesis of TTPhen-4Bpin



Under nitrogen atmosphere, to a 10 mL microwave reaction tube, 220 mg (0.44 mmol, 1.0 eq) of TTPhen, 560 mg (2.2 mmol, 5.0 eq) of bis(pinacolato)diboron, 27 mg (0.04 mmol, 0.1 eq) of bis(1,5-cyclooctadiene)di- μ -methoxydiiridium(I), 54 mg (0.2 mmol, 0.5 eq) of 4,4'-di-tert-butyl-2,2'-bipyridine, and 6 mL of *n*-heptane were added. The tube was sealed and heated to 120 °C with stirring for 12 hours by microwave

radiation. The solvent was removed under reduced pressure. The residue was treated with methanol and filtered. The purple precipitate was filtered out, washed with methanol and dried under vacuum. (290 mg, 66% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): 8.14 (s, 4H), 8.09 (d, $J = 3.6$ Hz, 4H), 7.71 (d, $J = 3.6$ Hz, 4H).

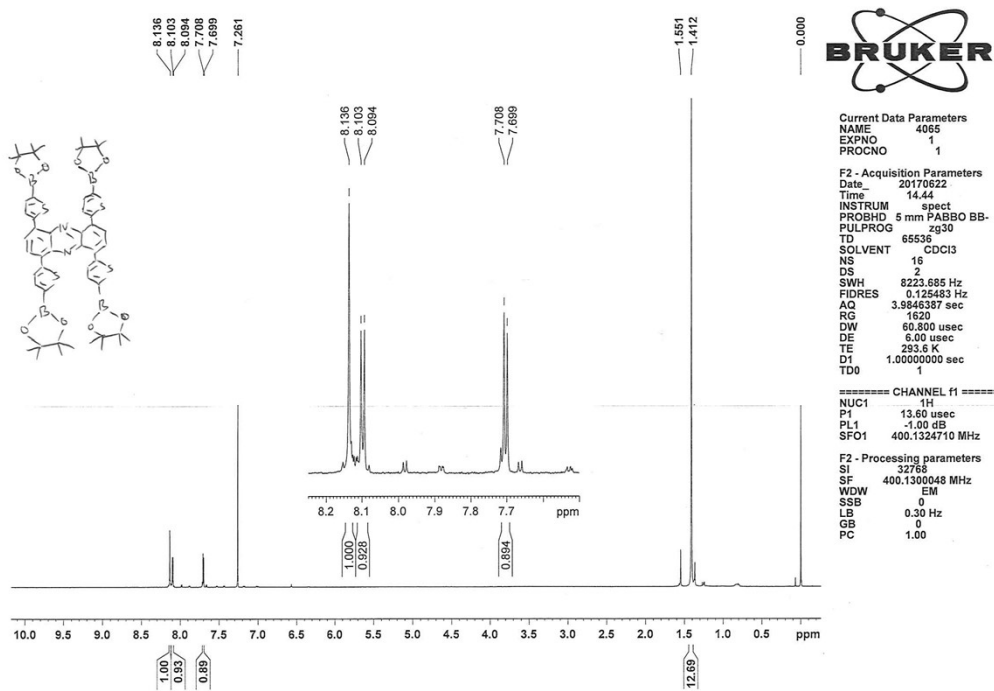
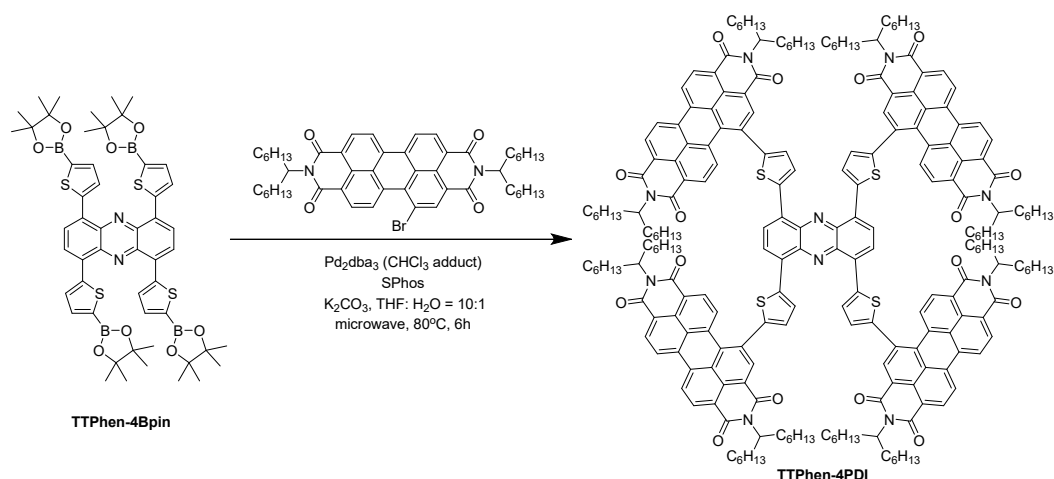


Figure S12 $^1\text{H NMR}$ spectra of TTPhen-4Bpin.

Synthesis of TTPhen-4PDI



Under nitrogen atmosphere, to a 10 mL microwave reaction tube, 117 mg (0.12 mmol, 1.0 eq) of TTPhen-4Bpin, 770 mg (0.93 mmol, 7.8 eq) of PDI-Br, 12 mg (0.012 mmol, 0.1 eq) of tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct, 10 mg (0.024 mmol, 0.2 eq) of SPhos, 192 mg (1.4 mmol, 12 eq) of potassium carbonate and 18 mL of solvent were added. With stirring, the solution was heated to 80 °C for 6 hours under microwave radiation. The solution was extracted with toluene for three times. The organic layer was washed with water and brine, then dried with anhydrous sodium sulphate. The solvent was removed under reduced pressure. The product was purified by flash column chromatography (30% dichloromethane in *n*-hexane to 50% dichloromethane in *n*-hexane) yielding a purple solid (127 mg, 38% yield). ¹H NMR (400 MHz, C₂D₂Cl₄, 334 K): 8.64 (br, 4H), 8.44 (br, 12H), 8.34 (br, 4H), 8.29 (br, 4H), 8.22 (br, 4H), 8.11 (br, 4H), 8.00 (br, 4H), 7.17 (br, 4H), 4.98 (br, 8H), 2.12 (br, 8H), 1.89 (br, 24H), 1.61 (br, 8H), 1.24 (br, 120H), 0.85 (br, 48H).

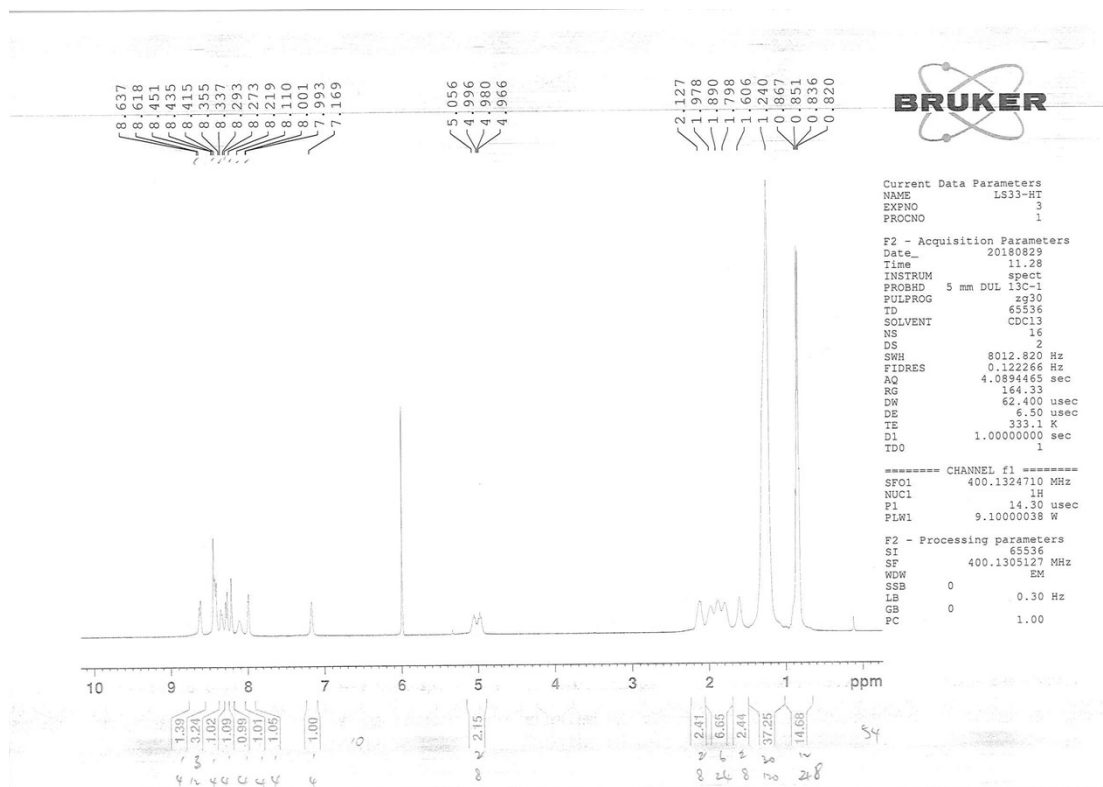


Figure S13 ^1H NMR spectra of TTPhen-4PDI.

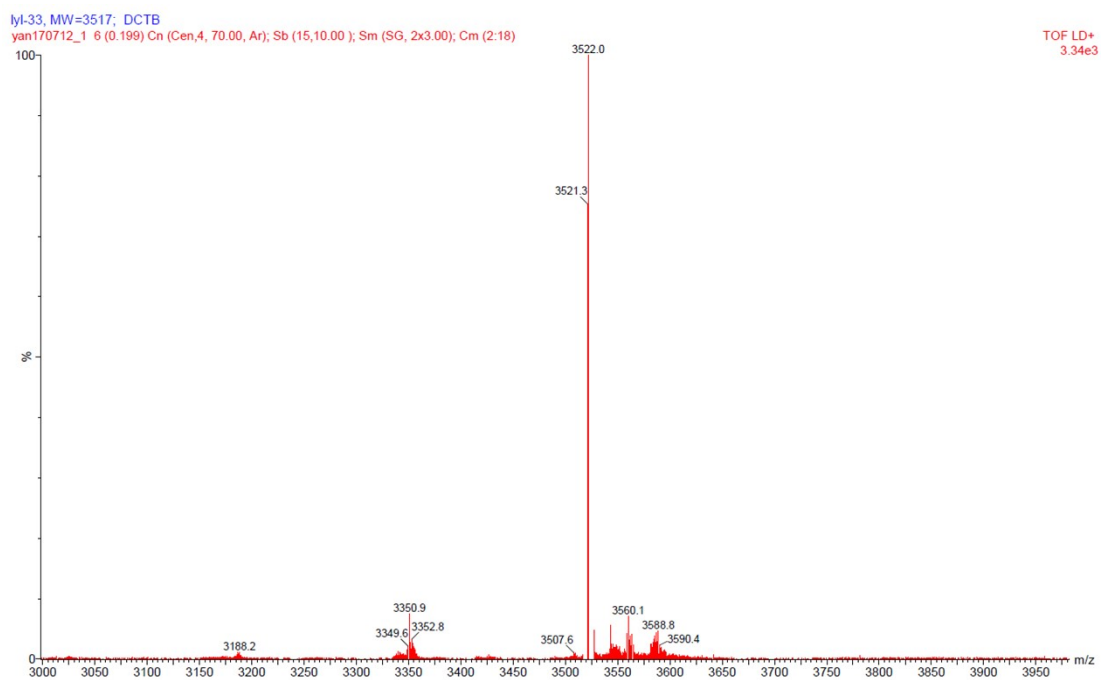


Figure S14 Mass spectra of TTPhen-4PDI.

Solar cell fabrication and characterisation

The device structure of the OPV was ITO/ZnO/Polymer:SMA/MoO₃/Al. Pre-patterned ITO-coated glass with a sheet resistance of ~15 Ω per square was used as the substrate. The substrate was cleaned by sequential sonication in soap deionized water, deionized water, acetone, and isopropanol for 30 min in each step. After UV/ozone treatment for 60 min, a ZnO electron transport layer was prepared by spin-coating at 5000 rpm from a ZnO precursor solution (diethyl zinc). Active layer solutions (D/A ratio 1:1.5, polymer concentration 8.5 mg/mL) were prepared in chlorobenzene (1% 1,8-octanedithiol). To completely dissolve the polymer, the active layer solution should be stirred on hotplate at 90 °C for at least 1 hour. Before spin coating, both the polymer solution and ITO substrate are preheated on a hotplate at about 100 °C. Active layers were spin-coated from the warm polymer solution on the preheated substrate in a N₂ glovebox at 1400 rpm to obtain thicknesses of ~120 nm. The polymer:SMA blend films were then thermally annealed before being transferred to the vacuum chamber of a thermal evaporator inside the same glovebox. At a vacuum level of 3×10⁻⁶ Torr, a thin layer (20 nm) of MoO₃ was deposited as the anode interlayer, followed by deposition of 100 nm of Al as the top electrode. All cells were encapsulated using epoxy inside the glovebox. Device *J-V* characteristics was measured in forward direction under AM1.5G (100 mW cm⁻²) at room temperature using a Newport solar simulator. The dwell times is 2 s and the speed is 0.8 V/s. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement) to bring spectral mismatch to unity. *J-V* characteristics were recorded using a Keithley 236 source meter unit. Typical cells have devices area of 5.9 mm², which is defined by a metal mask with an aperture aligned with the device area. EQE was characterized using a Newport EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.

Optical characterisation

Film UV-Vis absorption spectra were acquired on a Perkin Elmer Lambda 20 UV/VIS Spectrophotometer. All film samples were spin-cast on ITO/ZnO substrates. Solution UV-Vis absorption spectra were collected from the solution of the small molecule acceptor with a concentration of 1.0 × 10⁻⁴ g/mL in chloroform. A cuvette with a stopper (Sigma Z600628) was used to avoid solvent loss during measurement.

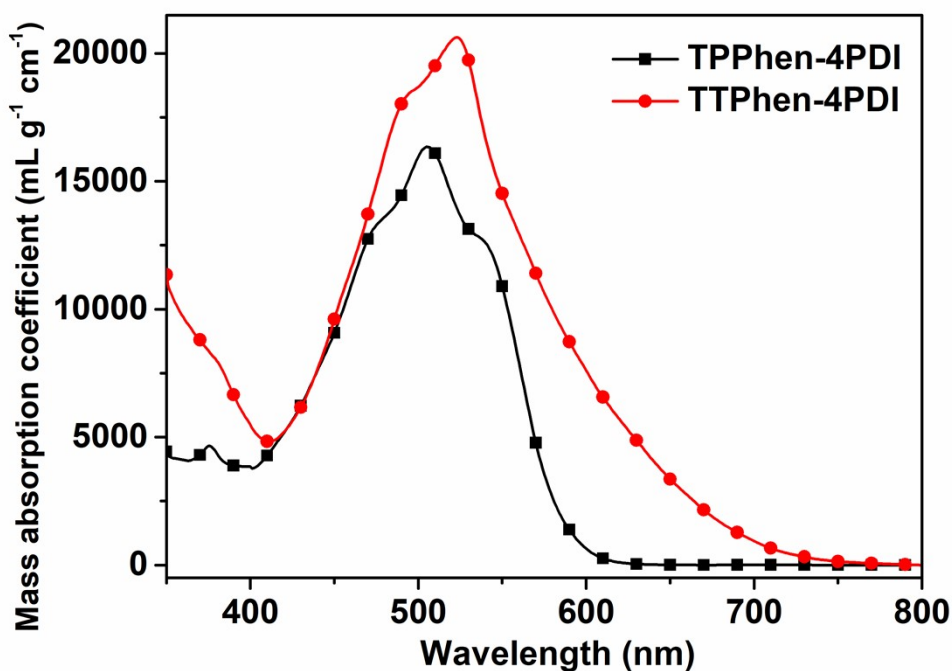


Figure S15 UV-Vis absorption spectra of SMA solution.

Electrochemical characterisation

Cyclic voltammetry was carried out on a CHI610E electrochemical workstation with three electrodes configuration, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. 0.1M tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the supporting electrolyte. Small molecule was drop-cast onto the glassy carbon electrode from dichloromethane solution (5 mg/mL) to form a thin film. Potentials were referenced to the ferrocenium/ferrocene couple by using ferrocene as external standard in 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile solution. The scan rate is 100 mV/s. For small molecules, the LUMO energy levels were determined by $E_{\text{LUMO}} = -[q(E_{\text{ox}} - E_{\text{ferrocene}}) + 4.8]$, while the HOMO energy levels were determined by $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{g}}$, where E_{g} is the optical band gap.

SCLC measurement

The electron and hole mobility of **TPPhen-4PDI** and **TTPhen-4PDI** neat and blend films were measured by using the method of space-charge limited current(SCLC). The electron-only SCLC device structure was ITO/ZnO/active layer/Zr(acac)/Al, and the

hole-only SCLC device structure was ITO/V₂O₅/active layer/V₂O₅/Al. The electron-only and hole-only SCLC devices fabricating condition was the same with those for OPVs. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation: $J = 9\epsilon_0\epsilon_r\mu V^2/8d^3$, where J is the current density, d is the film thickness of the active layer, μ is the charge carrier mobility, ϵ_r is the relative dielectric constant of the transport medium, and ϵ_0 is the permittivity of free space. $V = V_{app} - V_{bi}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage. The carrier mobility can be calculated from the slope of the $J^{1/2} - V$ curves.

GIWAXS characterisation

GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source⁴. Samples were prepared on Si substrates using identical blend solutions and condition as those used in OPV fabrication. The 10 keV X-ray beam was incident at a grazing angle of 0.11° - 0.15°, which maximized the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 2M photon counting detector. In-plane and out-of-plane sector averages were calculated using the Nika software package⁵. The uncertainty for the peak fitting of the GIWAXS data is 0.3 Å. The coherence length was calculated using the Scherrer equation: $CL = 2\pi K/\Delta q$, Where Δq is the full-width at half-maximum of the peak and K is a shape factor (0.94 was used here).

R-SoXS characterisation

R-SoXS transmission measurements were performed at beamline 11.0.1.2 at the Advanced Light Source⁶. Samples for R-SoXS measurement were prepared on a PSS modified Si substrate under the same conditions as those used for device fabrication, and then transferred by floating in water to a 1.5 mm × 1.5 mm, 100 nm thick Si₃N₄ membrane supported by a 5 mm × 5 mm, 200 μm thick Si frame (Norcada Inc.). 2D scattering patterns were collected on an in-vacuumS5 CCD camera (Princeton Instrument PI-MTE). The sample detector distance was calibrated from diffraction peaks of a triblock copolymer poly (isoprene-b-styrene-b-2-vinyl pyridine), which has a known spacing of 391 Å. The beam size at the sample is approximately 100 μm by 200 μm. The composition variation (or relative domain purity) over the length scales

probed can be extracted by integrating scattering profiles to yield the total scattering intensity. The median domain spacing is calculated from $2\pi/q$, where q here corresponds to half the total scattering intensity⁷. The purer the average domains are, the higher the total scattering intensity. Owing to a lack of absolute flux normalization, the absolute composition cannot be obtained only by R-SoXS.

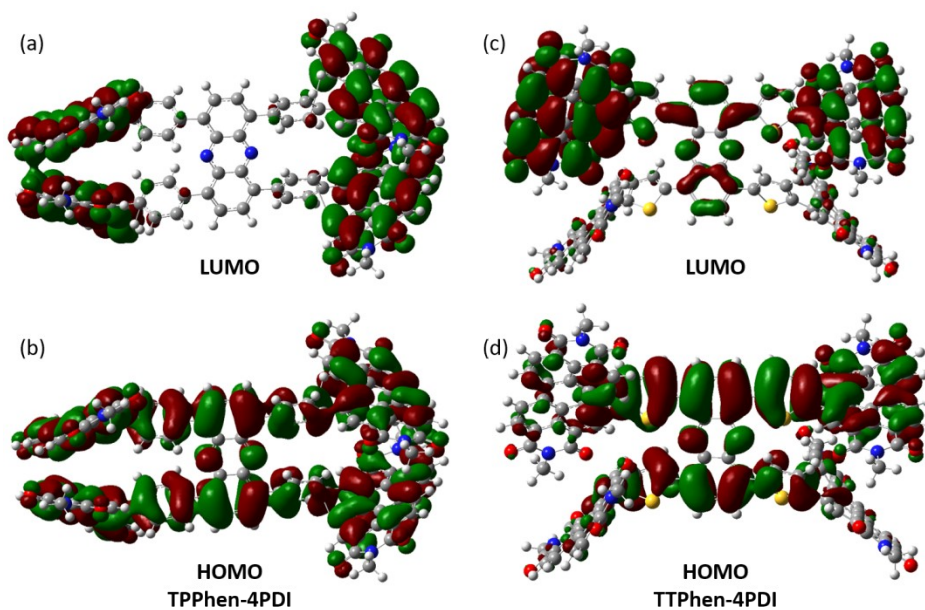


Figure S16. LUMO and HOMO of TPPhen-4PDI (a, b) and TTPhen-4PDI (c, d).

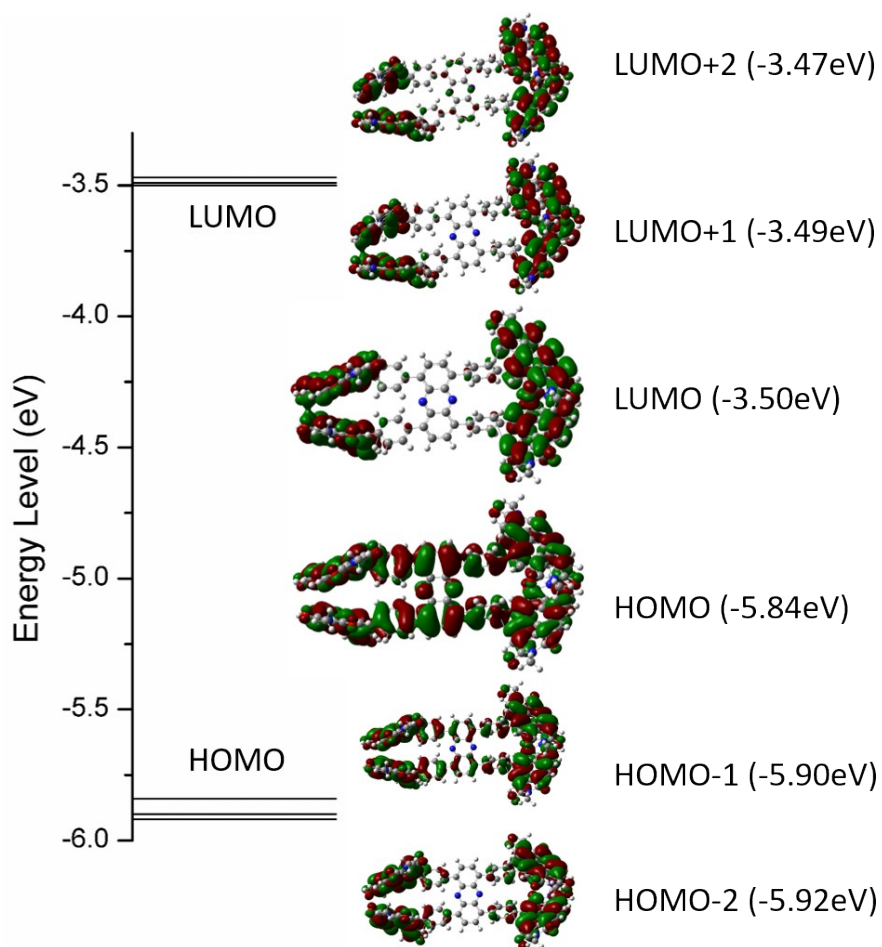


Figure S17. MOs and their energy levels of TPPhen-4PDI.

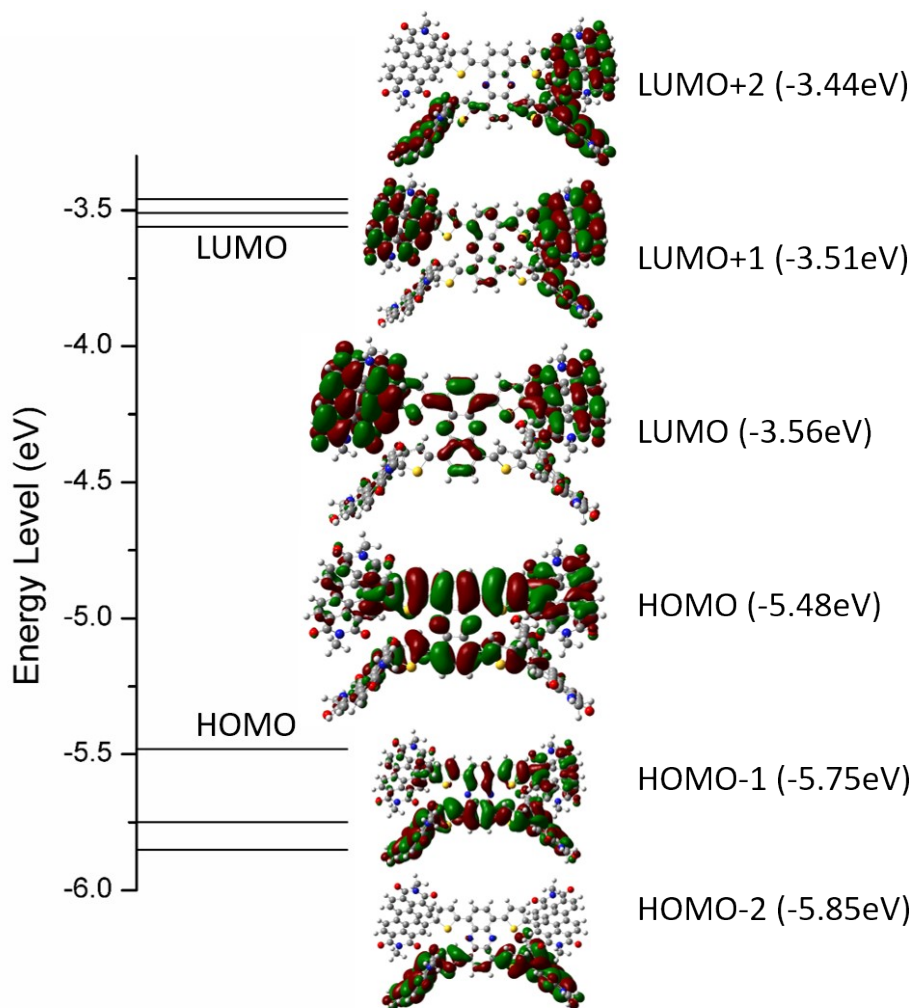


Figure S18. MOs and their energy levels of **TTPhen-4PDI**.

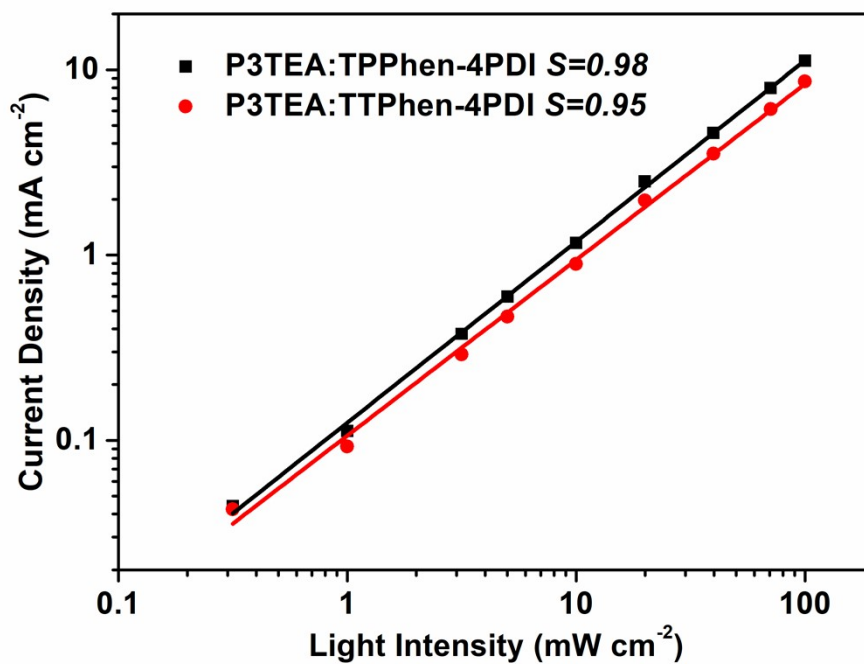


Figure S19. J_{sc} versus light intensity of P3TEA:TPPhen-4PDI and P3TEA:TTPhen-4PDI

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