

Supplementary Information

Tuning Fullerene Miscibility with Porphyrin-Terminated P3HTs in Bulk Heterojunction Blends

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Materials and Methods

All chemicals were purchased from Sigma-Aldrich or Fisher Scientific unless stated otherwise. Solvents were purified on a MDX-5 solvent purification system. All materials were synthesized using standard Schlenk line techniques under an argon atmosphere and porphyrins were purified via column chromatography using 60 Å silica gel (230-400 mesh size). Polymer molecular weights were measured via size-exclusion chromatography using a Tosoh EcoSEC with HPLC grade tetrahydrofuran (THF) as the eluent. Solutions with a nominal concentration of 1 mg/mL of polymer in THF were used. Fidelity of P3HT end-groups was confirmed using a Voyager Matrix-Assisted Laser Desorption Ionization Time of Flight Mass Spectrometer

(MALDI-TOF) using the dried droplet method in which solutions of P3HT and trans-2[3-(4-tert-butylphenyl)-2-methyl-2-propenyldiene]malonitrile in THF were spotted on the MALDI target. ^1H NMR spectra of synthesized molecules and polymers were acquired using a Varian VNMRS 500 MHz NMR at room temperature in CDCl_3 . Chemical shifts are reported in ppm and referenced to the residual solvent peak. Optical absorbance spectra were obtained via UV-Vis spectroscopy with a Thermo Scientific Evolution 600 spectrophotometer by scanning from 325-800 nm. Solutions of porphyrins in chloroform (CHCl_3) with concentrations of 1-10 μM and solutions of end functional polymers (allyl-P3HT and PP-P3HT) in CHCl_3 with concentrations of 0.0025 mg/mL were used for UV-vis measurements. Thermal transitions were measured by differential scanning calorimetry (DSC) using a TA instruments Q-2000 DSC using a protocol consisting of a heat-cool-heat cycle from 0 $^\circ\text{C}$ to 270 $^\circ\text{C}$ with a heating rate of 10 $^\circ\text{C}/\text{min}$ and a cooling rate of 10 $^\circ\text{C}/\text{min}$.

X-Ray Diffraction Measurements

Silicon substrates used for X-ray diffraction measurements were cleaned prior to film preparation by immersing the silicon substrates in piranha acid solution for 30 min. *Caution! Piranha acid is a strong oxidizer and strong acid; therefore it should be handled with extreme care as it reacts violently with organics.* After 30 min., the substrates were removed from the piranha solution with tweezers, rinsed thoroughly with DI water, and dried under a stream of N_2 . Films were cast from chlorobenzene solution via spin coating at 1,000 rpm for 30 sec followed by spinning at 1,500 rpm for 2 min. After casting, films were annealed under vacuum at 165 $^\circ\text{C}$ for 15 min and then allowed to cool to room temperature. X-ray diffraction measurements were

collected using an X'Pert Model 2000 X-ray diffractometer located in the Center for Nanophase Material Science at Oak Ridge National Laboratory.

Photovoltaic Device Fabrication

Photovoltaic devices of size 0.16 mm^2 were fabricated and tested as previously described.⁴ Briefly, indium tin-oxide (ITO) coated glass substrates were cleaned by sequential rinsing with 1% Aquet detergent solution and water, acetone, and isopropanol, and dried using a stream of N_2 gas. The substrates then were placed in an ozone cleaner for 30 min. After cleaning, anode buffer layers consisting of a 1:6 blend of polyethylenedioxythiophene:polystyrenesulphonate (PEDOT/PSS) at 1.3 wt.% in H_2O were spin-coated onto the ITO coated glass at 1,000 rpm for 1 min. These substrates were then thermally annealed at $110 \text{ }^\circ\text{C}$ for 15 min to remove any residual water from the polymer film. The samples were transferred to a nitrogen-filled glove box where active layer mixtures of P3HT, PP-P3HT, and PCBM were deposited by spin coating from a chlorobenzene solution at 1,000 rpm for 3 min. The P3HT:PCBM ratio was held constant at 1:1 for all BHJ thin films, and in cases where the PP-P3HT additive was used, the mass loading level was based on the mass of the total P3HT content. P3HT used for devices was 96% H-T regioregular, with a weight-average molecular weight of 77.5 kg/mol and dispersity of 1.9 (Merck). Device fabrication was completed by applying aluminum cathode layers of nominally $1 \text{ }\mu\text{m}$ thickness atop each active layer film via metal vapor deposition. While remaining in the N_2 -filled glove box, each device was annealed at $165 \text{ }^\circ\text{C}$ for 15 min and tested under AM 1.5 G 100 mW/cm^2 illumination. Current-voltage characteristics were measured and recorded using a Keithley 2636A source meter.

Synthesis of 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin (HOTTP)

5-(4-Hydroxyphenyl)-10,15,20-tritoylporphyrin (HOTTP) was synthesized following literature procedures.¹ In short, *p*-tolualdehyde (3 equiv.) and 4-hydroxybenzaldehyde (1 equiv.) were added to a 3-neck round bottom flask containing a Teflon stir bar and equipped with a reflux condenser. The mixture of aldehydes was dissolved in propionic acid and then heated to reflux. Freshly distilled pyrrole (4 equiv.) subsequently was added dropwise and the solution was stirred for 30 min. After 30 min, the reaction mixture was cooled to room temperature, filtered, and then washed with methanol. The crude purple solid was then purified via column chromatography using dichloromethane (DCM) as the mobile phase. The second fraction was collected as HOTTP and it was purified via recrystallization from a DCM/MeOH mixture. Results from ¹H NMR analysis and mass spectral analysis were consistent with previous reports.¹

P3HT Hydrosilylation

Monochlorosilane-terminated P3HT chains were synthesized according to the procedure outlined in our previous work.² In brief, freshly distilled 2,5-dibromo-3-hexylthiophene (Puyang Huicheng Chemical Co., Ltd) was activated using isopropylmagnesium chloride (*i*-PrMgCl) while GC-MS was used to ensure complete consumption of the Grignard reagent, which is critical for control of end groups.³⁻⁵ Next, allyl-terminated P3HTs were obtained by Kumada Catalyst Transfer Polycondensation (KCTP) polymerization using Ni(dppp)Cl₂ as the catalyst followed by quenching with allylmagnesium bromide. Allyl-terminated P3HTs were purified via successive Soxhlet washes with methanol and acetone, followed by extraction with chloroform. The chloroform fraction was concentrated via rotary evaporation and freeze-dried from benzene. NMR analysis confirmed the formation of allyl-terminated P3HTs and are consistent with our previous

reports, as well as characterization reported by McCullough and coworkers.^{6,7} (See Figure S1.) The allyl-P3HTs synthesized herein contained 90% mono-allyl, 3% di-allyl, and 7% Br/Br terminated P3HTs, as determined by MALDI-TOF MS. The P3HT was estimated to be 91% regioregular with a number-average molecular weight, $M_n=3,000$ g/mol, as assessed by ¹H NMR.

The allyl-terminated P3HT chains were hydrosilylated with dimethylmonochlorosilane (Sigma, 98%) by refluxing a 0.1 M benzene solution in the presence of Karsteadt's catalyst (Sigma, Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex) at 80 °C for 18 h. After refluxing for 18 h, the benzene was removed via sublimation and the dried polymer was stored under an inert atmosphere.

Synthesis of PP-P3HT

First, a benzene solution of HOTTP (7.2×10^{-5} mol, 48.4 mg, 3 equiv. with respect to P3HT) and imidazole (2.16×10^{-4} mol, 14.7 mg, 3 equiv. with respect to porphyrin) was prepared and stirred for 30 min. Then, the solution of imidazole and HOTTP was added via cannula to the flask containing dry monochlorosilane-functionalized P3HTs under an inert atmosphere. After the addition, the reaction mixture was stirred overnight at ambient temperature (while maintaining an inert environment). The reaction was halted by precipitating the mixture into copious amounts of MeOH. The precipitate was collected and filtered into a Soxhlet thimble and then purified with successive washes using MeOH and acetone to remove residual catalyst, imidazole, and untethered porphyrin. Finally, the porphyrin-functionalized P3HT product was extracted using CHCl₃. ¹H NMR (500 MHz, CDCl₃), δ (ppm): 0.92 (br, s), 1.26 (s), 1.31-1.51 (br, m), 1.66-1.77 (br), 2.75-2.87 (br), 6.95-7.02 (br, s), 7.55 (br, d), 7.80 (br, d), 8.10 (br, d), 8.44-8.55 (br, m), 8.85 (br, s). Characterization of PP-P3HT molecular weight by size exclusion chromatography using THF as

the mobile phase yielded $M_n = 5,700$ g/mol, $M_w = 6,500$ g/mol relative to polystyrene standards, and a dispersity ($D = M_w/M_n$) of $D = 1.13$.

NMR Spectroscopy

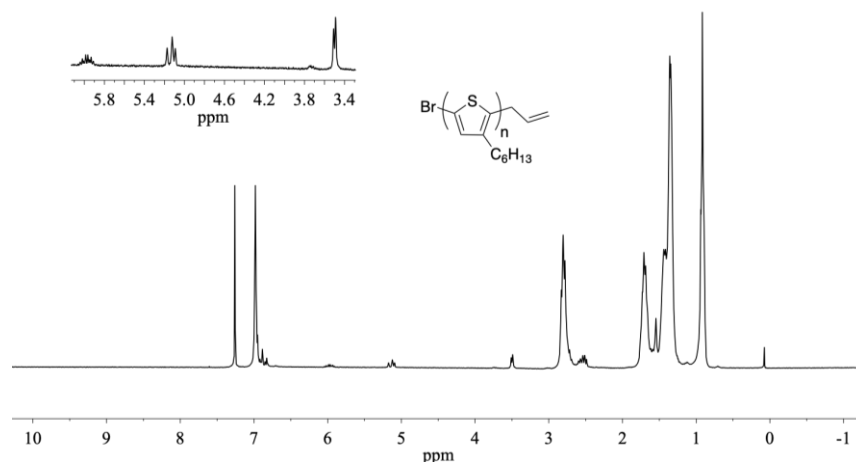


Figure S1. ¹H NMR spectrum (500 MHz, 25 °C, CDCl₃) of the allyl-P3HT. The inset is a magnification of the peaks corresponding to the allyl end-groups; δ , ppm: 0.92 (br, s), 1.26-1.51 (br, m), 1.55, (s), 1.66-1.77 (br), 2.47-2.62 (m), 2.67-2.88 (br, m), 3.50 (d), 5.08-5.19 (m), 5.91-6.05 (m), 6.95-7.02 (br, s).

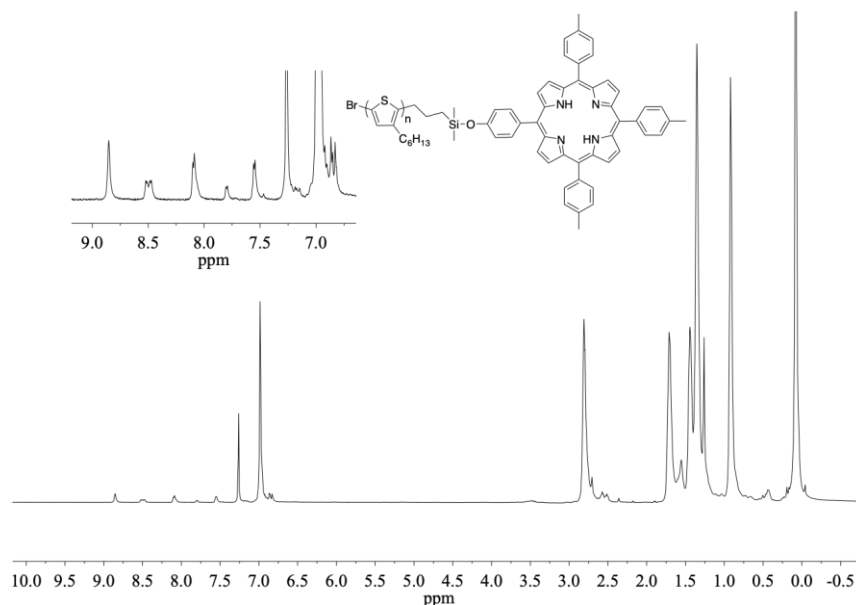


Figure S2. ¹H NMR spectrum (500 MHz, 25 °C, CDCl₃) of PP-P3HT. The inset is a magnification of the aromatic region, where peaks of the porphyrin end-group are observed; δ , ppm: 0.92 (br, s), 1.26 (s), 1.31-1.51 (br, m), 1.66-1.77 (br), 2.75-2.87 (br), 6.95-7.02 (br, s), 7.55 (br, d), 7.80 (br, d), 8.10 (br, d), 8.44-8.55 (br, m), 8.85 (br, s).

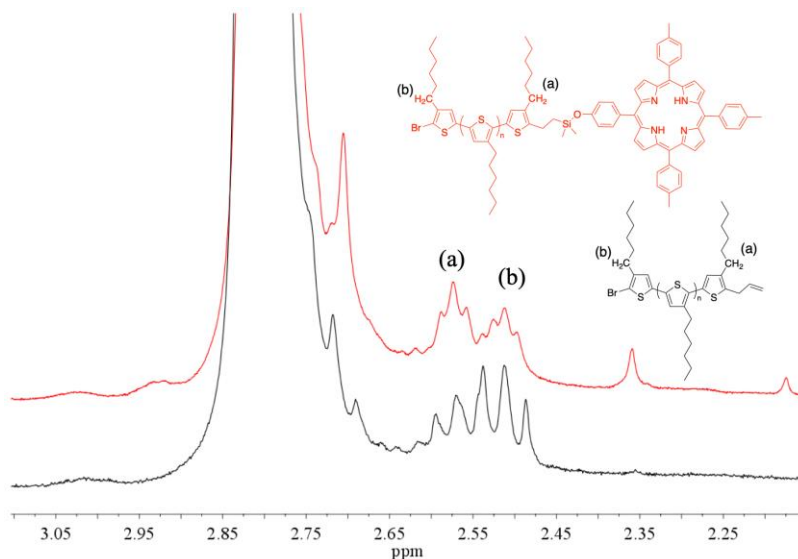


Figure S3. Overlay of aliphatic region of ^1H NMR spectra of allyl-P3HT (black trace, bottom) and PP-P3HT (red trace, top). The multiplet centered at ~ 2.55 ppm present in allyl-P3HT (bottom spectrum) is a well-known feature due to methylene protons in hexyl side chains at chain ends. This feature evolves into two distinct triplets at 2.51 and 2.56 ppm after end-group functionalization to produce PP-P3HT.

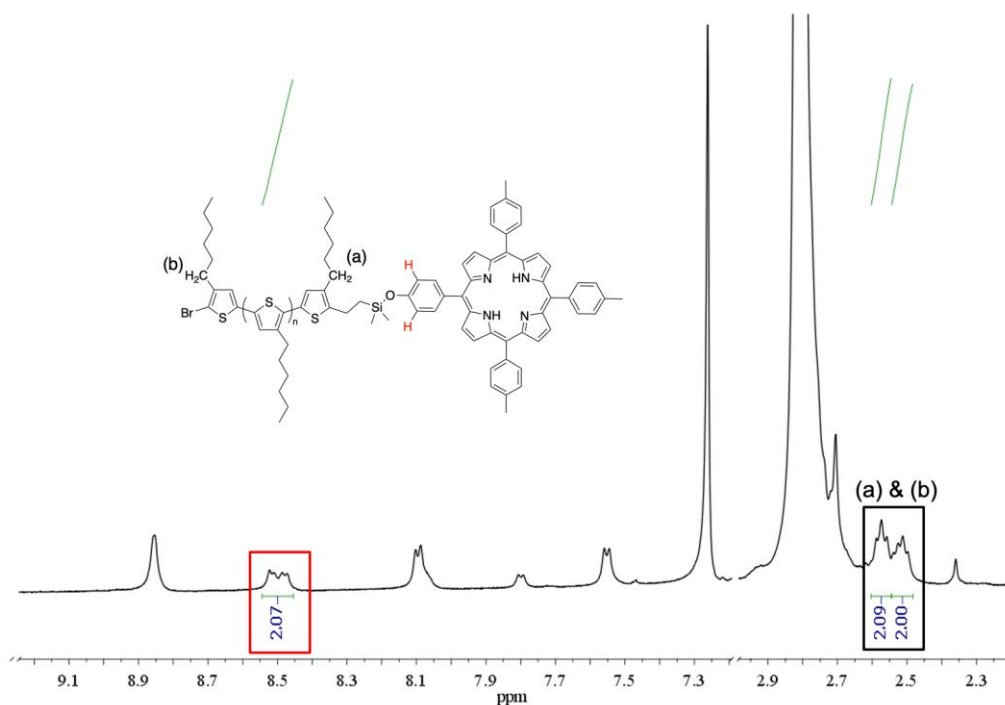


Figure S4. Magnified view of the aromatic and aliphatic regions of the ^1H NMR spectra of PP-P3HT after purification and extraction from chloroform. (Note the break in the x-axis.) The ratio of peak areas attributed to protons of the α -methylene in thienyl repeats at chain ends and to aryl protons adjacent to the silyl ether linkage are used to assess the level of porphyrin functionalization. The 1:1 ratio indicates quantitative conversion in the purified, isolated PP-P3HT.

Size-Exclusion Chromatography

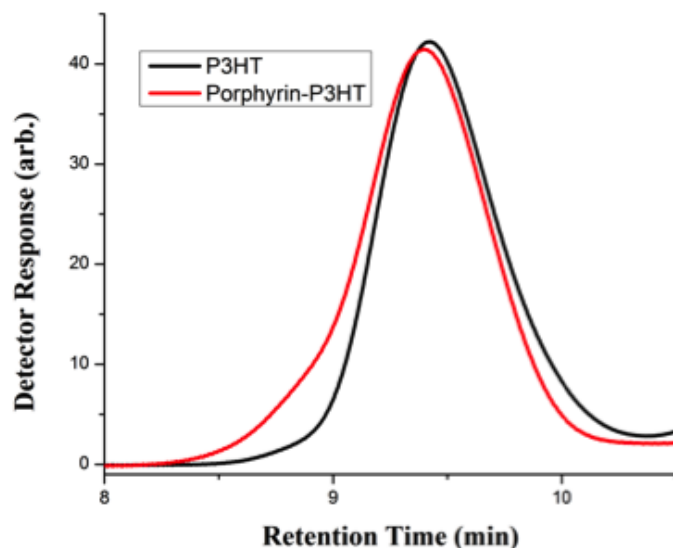


Figure S5. Size-exclusion chromatography (SEC) elugrams for allyl-terminated P3HT (black trace), which broaden and slightly shift to a lower retention time after functionalization with HOTTP (red trace).

MALDI-TOF Mass Spectrometry

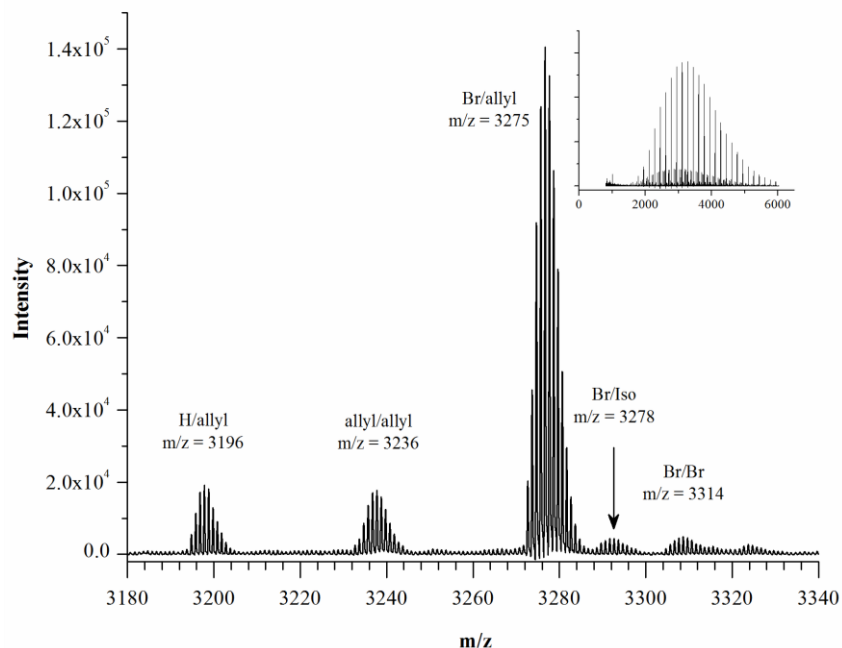


Figure S6. High resolution MALDI spectra associated with the 19-mer region of allyl-terminated P3HT used for coupling reactions to synthesize the porphyrin-functionalized P3HT, PP-P3HT. The end groups are labelled and the distribution of products is consistent with a highly monofunctional allyl-terminated P3HT. The inset graph shows the full spectrum.

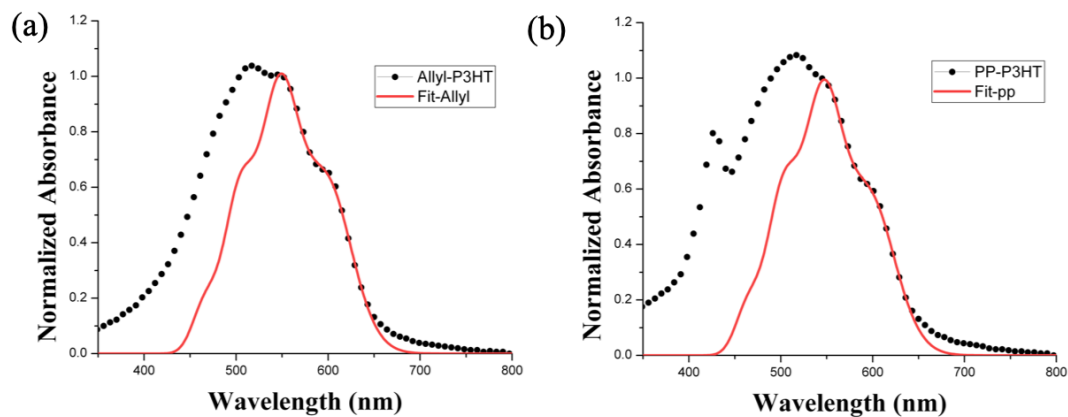


Figure S7. Normalized UV-vis absorbance spectra (black) and corresponding “Spano model”^{8,9} fits (red) of the aggregate region of (a) allyl-P3HT and (b) PP-P3HT. Both fits possess RMS of residuals < 0.05.

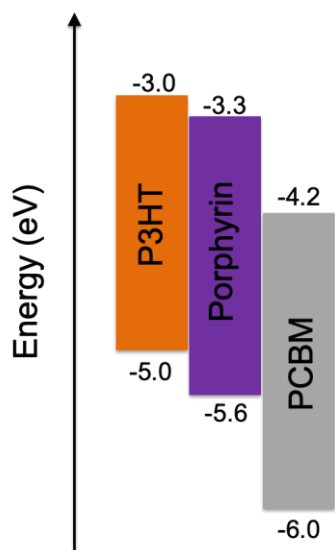


Figure S8. Representative frontier molecular energy levels of P3HT, free-base tetraphenylporphyrin, and PCBM.

References

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