Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information for:

Expanding the light absorption of poly(3-hexylthiophene) by end-functionalization with π-extended porphyrins

Michèle Chevrier,[a,b] Sébastien Richeter,[a] Olivier Coulembier,[b] Mathieu Surin,[c] Ahmad Mehdi,[a] Roberto Lazzaroni,[c] Rachel C. Evans,[d,e] Philippe Dubois[b] and Sébastien Clément[a]

a Institut Charles Gerhardt, Université de Montpellier, Place Eugène Bataillon, 34095 Montpellier Cedex 05, France

b Service des Matériaux Polymères et Composites (SMPC), Centre d'Innovation et de Recherche en Matériaux et Polymères (CIRMAP), Université de Mons, 20 Place du Parc, 7000 Mons, Belgium.

c Laboratory for Chemistry of Novel Materials, CIRMAP, University of Mons UMONS, Place du Parc 20, 7000 Mons, Belgium.

d. School of Chemistry, Trinity College Dublin, the University of Dublin, Dublin 2, Ireland.

e. Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, the University of Dublin, Dublin 2, Ireland.

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1. Synthetic details

1.1 Materials and methods

All reagents were purchased from Fisher, Sigma, Alfa Aesar and Fluorochem, and used without further purification. THF was dried over CaH_2 and then Na-benzophenone distillations. **NH-NiTPP**, 2-bromo-3-hexyl-5-iodothiophene and P3HT (7600 g mol^{-1}; Đ=1.23) were synthesized according to the previous reported procedures.[1-3]

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded either on a Bruker Avance-300 spectrometer for each monomer synthetic intermediates and on a Bruker Avance-600 spectrometer for the diblock copolymers with tetramethylsilane as internal standard. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) and coupling constants (J) are expressed in Hertz.

Molecular weights of the copolymers were determined by using a size exclusion chromatography (SEC) on a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = 1 mL min^{-1}), a Marathon autosampler (loop volume = 200 mL, solution conc. = 1 mg mL^{-1}), a PL-DRI refractive index detector and three columns: a PL gel 10 mm guard column and two PL gel Mixed-B 10 mm columns (linear columns for separation of MWPS ranging from 500 to 10^6 Daltons). The eluent used was THF at a flow rate of 1 mL min^{-1} at 35 °C. Polystyrene standards were used to calibrate the SEC.

UV-visible spectra were obtained on a Shimadzu UV2401 PC UV/Vis scanning spectrometer. End-functionalized P3HT **2**, P3HT and porphyrin **1** thin films were prepared by drop-casting from xylene solutions (1 mg mL^{-1}) on pre-cleaned quartz substrates. Hydrodynamic diameters of the nanoparticles were determined by dynamic light scattering using a Cordouan Particle Size Analyzer VASCO. The temperature of the dispersion was set at 25°C. For $CHCl_3$–MeOH Mixture (1:1), the refractive index was calculated using the following equation:[4]

$$\frac{{n_{12}}^2-1}{{n_{12}}^2+2}=f_1\frac{{n_1}^2-1}{{n_1}^2+2}+f_2\frac{{n_2}^2-1}{{n_2}^2+2}$$

in which n_1, n_2 and n_{12} are the refractive indices of solvent 1, solvent 2 and the mixture respectively and f_1 and f_2 are their volume fractions.

Viscosities of $CHCl_3$/MeOH mixtures were calculated according to the Arrhenius equation:[5]

$$\log\eta_{12}=\mathrm{x}_1\log\eta_1+x_2\log\eta_2$$

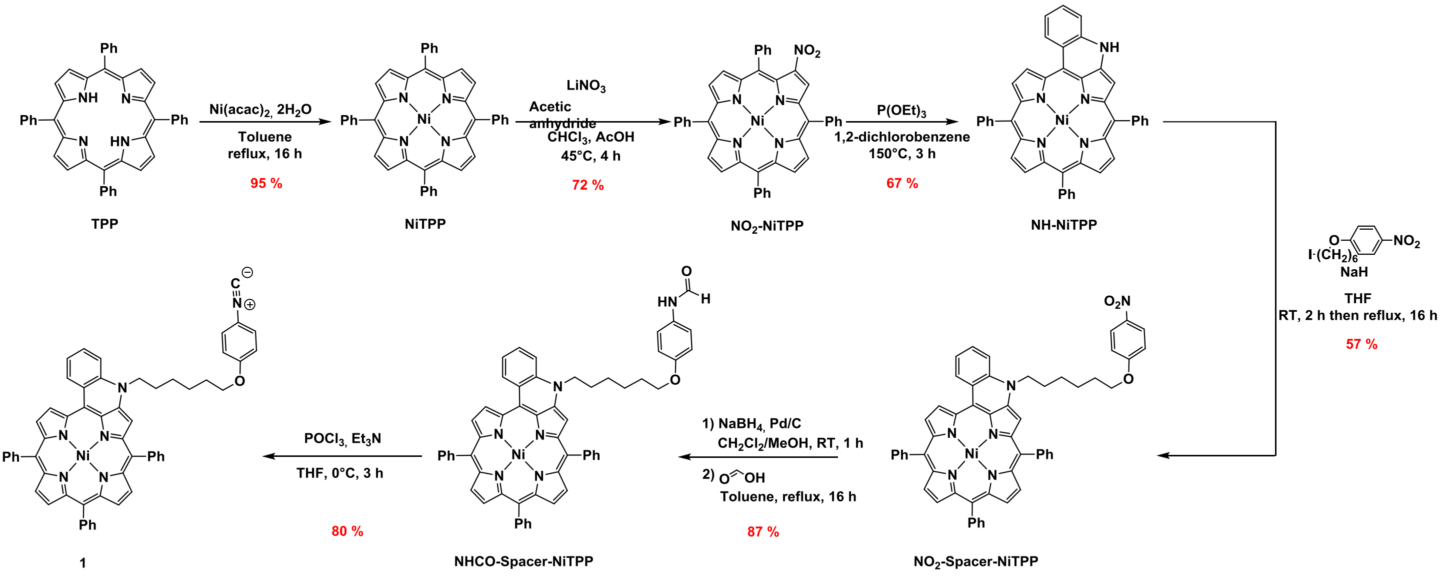
in which η_1, η_2 and η_{12} are the viscosities of solvent 1, solvent 2 and the mixture respectively and x_1 and x_2 their mole fractions.

Autocorrelation curves were recorded during 60 seconds. The Pade–Laplace algorithm implemented on the software provided by Cordouan was used to derive the hydrodynamic diameter. 60 measurements were performed.

Thermogravimetric analysis (TGA) was conducted on a TA Instrument Q500. Samples were first held at a constant temperature, and then, heated to 800 °C at a rate of 20 °C min^{-1} under an inert atmosphere (nitrogen). Differential Scanning Calorimetry (DSC) characterization was performed using a DSC Instrument Q200 under an atmosphere of nitrogen at a heating/cooling rate of 10 °C min^{-1}. All DSC analyses were performed using an aluminum pan with a sample of approximately 5-10 mg. Powder XRD analyses were carried out on a Philips X'pert Pro MPD diffractometer using Cu Kα1 radiation (λ = 1.5406 Å) in Bragg-Brentano scanning mode with a 2θ angle ranging from 4 to 40° (or 4 to 53°), and a time per step of 50 or 300 s, depending on the sample. The AFM measurements were performed on an

Icon Bruker microscope in tapping mode. Samples for atomic force microscopy (AFM) measurements were prepared by drop casting xylene solutions (0.1 mg mL^{-1}) of the polymer onto mica substrates, and then placed under saturation with xylene vapor for 16 h.

1.2 Synthesis of isocyanide porphyrin monomer (1)



Scheme S1 Synthesis of isocyanide porphyrin monomer **1**.

1-((6-iodohexyl)oxy)-4-nitrobenzene. 1,6-diiodohexane (27.9 g, 82.5 mmol), 4-nitrophenol (2.30 g, 16.5 mmol), potassium carbonate (4.6 g, 33 mmol) and 18-crown-6 (436 mg, 1.65 mmol) were dissolved in acetone (100 mL). The reaction mixture was stirred under reflux for 2 days. After cooling, the resulting solution was concentrated by evaporation and water (450 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The combined extracts were washed with a solution of hydrochloric acid 1N (40 mL) and several times with water until pH=7. The organic layer was dried over $MgSO_4$, filtered, evaporated under reduced pressure and purified by column chromatography on silica gel eluting with a gradient of pentane – dichloromethane (100:0 to 50:50) to give the *title compound* as a colorless solid (5.5 g, 95 %). **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.20 (d, 2H, $^3J_{H\text{-}H}$ = 9.2 Hz, NO_2-ArH), 6.94 (d, 2H, $^3J_{H\text{-}H}$ = 9.2 Hz, O-ArH), 4.05 (t, 2H, $^3J_{H\text{-}H}$ = 6.4 Hz, OCH_2), 3.21 (t, 2H, $^3J_{H\text{-}H}$ = 6.9 Hz, ICH_2), 1.99 – 1.70 (m, 4H, CH_2), 1.64 – 1.39 (m, 4H, CH_2) ppm. **^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)**: δ 164.2 (NO_2-C_q), 141.5 (O-C_q), 126.0 (CH), 114.5 (CH), 68.7 (OCH_2), 33.4 (CH_2), 30.2 (CH_2), 28.9 (CH_2), 25.0 (CH_2), 7.0 (ICH_2) ppm. **HRMS (ESI)**: *m/z* = $[M+H]^+$ Calcd for $C_{12}H_{17}INO_3$: 350.0253. Found: 350.0247.

NO_2-Spacer-NiTPP. A solution of **NH-NiTPP** (100 mg, 0.146 mmol) and sodium hydride 60 % (30 mg, 0.73 mmol) in THF (10 mL) was stirred for 15 minutes at room temperature under argon. 1-(6-iodohexyl)-4-nitrobenzene (56 mg, 0.16 mmol) was then added to the resulting solution and the mixture was stirred under reflux overnight. The *N*-alkylation was followed by TLC. When finished, the solvent was evaporated under reduced pressure and the residue was diluted with dichloromethane. The organic layer was washed several times with water to pH=7, dried over $MgSO_4$, filtered, evaporated and purified by column chromatography on silica gel eluting with cyclohexane – ethyl acetate (90:10) to give the *title compound* as a purple solid (75 mg, 57 %). **^{1}H NMR (300 MHz, CD_2Cl_2):** δ 9.38 (d, 1H, $^3J_{H-H}$ = 4.8 Hz, pyrrole), 8.96 (dd, 1H, $^3J_{H-H}$ = 8.1 and 1.6 Hz, ArH), 8.80 (d, 1H, $^3J_{H-H}$ = 4.7 Hz, pyrrole), 8.65-8.49 (m, 4H, pyrrole and ArH-NO_2), 8.13-7.93 (m, 10H, pyrrole and ArH), 7.86-7.59 (m, 11H, ArH), 6.94 (d, 2H, $^3J_{H-H}$ = 9.3 Hz, Ar-OCH_2), 4.94 (t, 2H, $^3J_{H-H}$ = 7.5 Hz, OCH_2), 3.99 (t, 2H, $^3J_{H-H}$ = 6.8 Hz, NCH_2), 2.31 (m, 2H, CH_2), 1.91-1.58 (m, 6H, CH_2) ppm. **^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2)**: δ 164.7 (C_q-NO_2), 143.9 (C_q), 143.8 (C_q), 142.6 (C_q), 141.8 (C_q), 141.4 (C_q), 140.5 (C_q), 138.6 (C_q), 137.5 (C_q), 136.1 (C_q), 135.9 (CH), 134.3 (C_q), 134.3 (CH), 134.1 (CH), 134.0 (CH), 133.7 (C_q), 133.1 (CH), 132.7 (CH), 132.6 (CH), 132.4 (CH), 130.7 (CH), 130.7 (CH), 128.3 (C_q), 128.0 (CH), 128.0 (CH), 127.5 (CH), 127.5 (CH), 126.3 (CH), 122.6 (CH), 121.3 (CH), 116.0 (C_q), 114.9 (CH), 113.9 (CH), 113.3 (CH), 69.3 (OCH_2), 49.2 (NCH_2), 29.4 (CH_2), 27.7 (CH_2), 27.5 (CH_2), 26.5 (CH_2) ppm. **HRMS (ESI)** : *m/z* = $[M+H]^+$ Calcd for $C_{56}H_{43}N_6NiO_3$: 905.2750. Found: 905.2751. **UV-visible ($CHCl_3$):** λ nm (ε $M^{-1}.cm^{-1}$) = 423 (74000), 448 (65500), 556 (6300), 602 (10400), 636 (18200).

NHCO-Spacer-NiTPP. To a degassed solution of **5** (66 mg, 0.073 mmol) in CH_2Cl_2 (66 mL) and methanol (7.3 mL) was added 10 % Pd/C (3 mg, 0.03 mmol) and then, sodium borohydride (66 mg, 1.7 mmol). The mixture was stirred for 1 hour at room temperature under argon. The reaction was followed by TLC. When finished, the solvent was evaporated under reduced pressure and the residue was diluted with dichloromethane. The organic layer was filtered to eliminate salts and evaporated. To a degassed solution of the residue in toluene (5 mL) was added formic acid (5 mL). The mixture was stirred under reflux overnight. The reaction was followed by TLC. When finished, the solvent was evaporated under reduced pressure and the residue was diluted with dichloromethane. The organic layer was washed with aqueous saturated $NaHCO_3$ and water to pH=7, dried over $MgSO_4$, filtered, evaporated and purified by column chromatography on silica gel eluting with dichloromethane to give the *title compound* as a purple solid (56 mg, 87 % in 2 steps). **^{1}H NMR(300 MHz, CD_2Cl_2):** δ 9.34 (dd, 1H, $^3J_{H-H}$ = 4.8 Hz and 1.2 Hz, pyrrole), 8.91 (dd, 1H, $^3J_{H-H}$ = 8.0 and 1.7 Hz, ArH), 8.78 (dd, 1H, $^3J_{H-H}$ = 4.8 Hz and 1.3 Hz, pyrrole), 8.64-8.54 (m, 4H, pyrrole), 8.37 (d, 0.3H, $^3J_{H-H}$ = 11.5 Hz, amide), 8.16 (d, 0.7H, $^3J_{H-H}$ = 1.8 Hz, amide), 8.08-7.92 (m, 7H, ArH), 7.92 (dd, 1H, $^3J_{H-H}$ = 8.6 Hz and 1.3 Hz, ArH), 7.74-7.61 (m, 11H, ArH), 7.26 (d, 1.3 H, $^3J_{H-H}$ = 9 Hz, NHCHO-ArH), 6.93 (broad s, 1H, NH), 6.97 (d, 0.7 H, $^3J_{H-H}$ = 8.9 Hz, NHCHO-ArH), 6.73 (d, 2H, $^3J_{H-H}$ = 9 Hz, ArH-O), 4.75 (t, 2H, $^3J_{H-H}$ = 7.7 Hz, OCH_2), 3.83 (t, 2H, $^3J_{H-H}$ = 6.3 Hz, NCH_2), 2.20 (m, 2H, CH_2), 1.90-1.56 (m, 6H, CH_2) ppm. **^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2)**: δ 162.8 (NHCHO), 159.0 (C_q), 145.1 (C_q), 143.9 (C_q), 143.8 (C_q), 143.4 (C_q), 142.6 (C_q), 141.8 (C_q), 141.4 (C_q), 141.4 (C_q), 140.5 (C_q), 138.7 (C_q), 138.5 (C_q), 136.0 (C_q), 135.8 (CH), 134.3 (CH), 134.1 (CH), 134.0 (CH), 133.0 (CH), 132.8 (CH), 132.6 (CH), 132.4 (CH), 130.7 (CH), 130.6 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.5 (CH), 127.5 (CH), 122.5 (CH), 122.0 (CH), 121.9 (CH), 121.2 (C_q), 116.0 (C_q), 115.8 (CH), 115.2 (C_q), 115.1 (CH), 113.8 (CH), 109.7 (C_q), 98.5 (CH), 68.5 (OCH_2), 49.2 (NCH_2), 29.7 (CH_2), 27.7 (CH_2), 27.5 (CH_2), 26.5 (CH_2) ppm. **HRMS (ESI)**: *m/z* = $[M+H]^+$ Calcd for $C_{57}H_{45}N_6O_2Ni$: 903.2957. Found: 903.2959. **IR ATR:** 3150 (NH), 1690 (C=O) cm^{-1}. **UV-visible ($CHCl_3$):** λ nm (ε $M^{-1}.cm^{-1}$) = 427 (78000), 448 (74000), 558 (8000), 602 (12000), 638 (20000).

Synthesis of 1. NHCO-Spacer-NiTPP (50 mg, 0.055 mmol) was dissolved in THF (5 mL) and cooled to 0°C. Triethylamine (39 µL, 0.28 mmol) and $POCl_3$ (6 µL, 0.06 mmol) were added by micro-seringue to the mixture and stirring was continued at 0°C for 3 hours. A saturated sodium carbonate solution (5 mL) wad added at room temperature and the resulting solution was stirred for 1 hour. Then, the aqueous layer was extracted with dichloromethane. The organic layer was washed several times with water and brine to pH=7, dried over $MgSO_4$, filtered, evaporated and purified by column chromatography on alumina gel eluting with cyclohexane – dichloromethane (50:50) to give the *title compound* as a purple solid (40 mg, 80 %). **^{1}H NMR (300 MHz, $CDCl_3$):** δ 9.35 (d, 1H, $^3J_{H\text{-}H}$ =4.8 Hz, pyrrole), 8.92 (d, 1H, $^3J_{H\text{-}H}$ =7.6 Hz, ArH), 8.81 (d, 1H, $^3J_{H\text{-}H}$ = 4.8 Hz, pyrrole), 8.61 (d, 1H, $^3J_{H\text{-}H}$ = 5.1 Hz, pyrrole), 8.55 (s, 2H, pyrrole), 8.07-7.90 (m, 7H, ArH/pyrrole), 7.82-7.57 (m, 13H, ArH), 7.21 (d, 2H, J=8.9 Hz, O-ArH), 6.76 (d, 2H, $^3J_{H\text{-}H}$ = 8.9 Hz, CN-ArH), 4.67 (t, 2H, $^3J_{H\text{-}H}$ = 7.5 Hz), 3.78 (t, 2H, $^3J_{H\text{-}H}$ = 6.2 Hz), 2.12 (m, 2H, CH_2), 1.73-1.54 (m, 6H, CH_2) ppm. **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** : δ 159.3 (C_q), 144.6 (C_q), 143.4 (C_q), 143.3 (C_q), 143.0 (C_q), 142.2 (C_q), 141.5 (C_q), 141.1 (C_q), 141.0 (C_q), 140.2 (C_q), 138.3 (C_q), 138.1 (C_q), 135.5 (CH), 135.4 (C_q), 133.8 (CH), 133.7 (CH), 133.5 (CH), 132.8 (CH), 132.4 (CH), 132.2 (CH), 130.5 (CH), 130.4 (CH), 129.7 (C_q), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.6 (CH), 127.5 (CH), 127.3 (CH), 127.1 (CH), 127.0 (CH), 122.0 (CH), 120.9 (C_q), 120.8 (C_q), 115.7 (C_q), 115.0 (CH), 114.6 (C_q), 113.0 (CH), 109.2 (C_q), 98.0 (CH), 68.1 (OCH_2), 48.4 (NCH_2), 29.0 (CH_2), 27.2 (CH_2), 27.1 (CH_2), 26.0 (CH_2) ppm. **HRMS (ESI)** : *m/z* = $[M+H]^+$ Calcd for $C_{57}H_{43}N_6NiO$: 885.2841. Found: 885.2852. **IR ATR:** 2118 cm^{-1} ($\nu_{N\equiv C}$). **UV-visible ($CHCl_3$):** λ nm (ε $M^{-1}.cm^{-1}$) = 423 (48000), 448 (44000), 557 (4300), 601 (7300), 637 (13000).

1.3. General procedure for the synthesis of P3HT end-functionalized with π-extended porphyrins (2)

To a dried round-bottomed flask containing 2-bromo-3-hexyl-5-iodothiophene (X mmol), previously dried by three successive azeotropic distillations with toluene, was added dry THF (C = 0.2 M). *i*PrMgCl.LiCl (1.3 M in THF, X mmol) was then added via a syringe and the mixture was stirred at 0°C for 30 minutes. To a second dried round-bottomed flask containing the $Ni(dppp)Cl_2$ catalyst ($(166X+885Y)/M_n$) in THF (C = 0.01 M), was added the first solution of 2-bromo-5-chloromagnesio-3-hexylthiophene. The resulting orange mixture was stirred at room temperature under nitrogen and the polymerization was monitored by GPC. After stirring the reaction mixture for 3 hours, the isocyanide porphyrin **1** (Y mmol) was added in one portion and the resulting green solution was stirred overnight. By pouring aq. HCl (5 M) quickly, the polymerization was quenched and then, the mixture was poured into cold MeOH causing a dark precipitate. The solids were filtered off, washed with methanol and dried under vacuum to afford a black solid.

2a: 70 %. **Ratio (P3HT/Porphyrin):** 90/10. **^{1}H NMR (600 MHz, $CDCl_3$) :** δ 8.52 (broad), 7.92 (broad), 7.56 (broad), 7.00 (s), 2.89 (broad), 1.74 (broad), 1.46-1.29 (broad), 0.94 (broad) ppm. **$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$):** δ 140.0, 133.8, 130.6, 128.7, 127.5, 127.0, 31.8, 30.6, 29.8, 29.8, 29.6, 29.4, 22.8, 14.2 ppm. **SEC (THF, PS standards):** M_n = 12 200 g.mol^{-1}, M_w = 16 900 g.mol^{-1}, PDI = 1.39. **UV-visible ($CHCl_3$):** λ nm = 426, 451, 555, 600, 636.

2b: 62 %. **Ratio (P3HT/Porphyrin):** 86/14. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.52 (broad), 7.94 (broad), 7.58 (broad), 6.99 (s), 4.80 (broad), 3.89 (broad), 2.81 (broad), 2.56 (broad), 1.72 (broad), 1.44-1.27 (broad), 0.92 (broad) ppm. **^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$):** δ 143.6, 141.2, 140.2, 140.1, 138.4, 135.7, 134.0, 133.9, 133.7, 132.4, 130.7, 130.4, 129.0, 127.8, 127.6, 127.1, 121.9, 120.8, 115.7, 114.7, 113.1, 109.1, 98.0, 33.9, 31.9, 30.7, 29.9, 29.7, 29.4, 27.1, 22.8, 14.2 ppm. **GPC (THF, PS standards):** M_n = 9 200 g.mol^{-1}, M_w = 11 800 g.mol^{-1}, PDI = 1.28. **UV-visible ($CHCl_3$):** λ nm = 426, 451, 555, 600, 636.

2c: 60 %. **Ratio (P3HT/Porphyrin):** 68/32. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.47 (broad), 7.85 (broad), 7.47 (broad), 6.99 (broad), 6.80 (broad), 2.83 (broad), 2.61 (broad), 1.61 (borad), 1.35-1.29 (broad), 0.93 (broad) ppm. **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$):** δ 143.4, 142.2, 141.2, 140.3, 138.3, 133.8, 133.5, 132.2, 130.3, 128.4, 127.5, 126.9, 125.7, 125.3, 124.7, 121.7, 120.7, 118.2, 115.7, 109.1, 97.8, 68.4, 48.8, 31.9, 31.8, 30.7, 29.9, 29.8, 29.6, 29.4, 29.0, 26.8, 22.7, 14.2 ppm. **GPC (THF, PS standards):** M_n = 5 000 g.mol^{-1}, M_w = 5 900 g.mol^{-1}, PDI = 1.18. **UV-visible ($CHCl_3$):** λ nm = 426, 451, 555, 600, 636.

2. NMR spectra

2.1. Monomer synthesis

1-(6-iodohexyloxy)-4-nitrobenzene

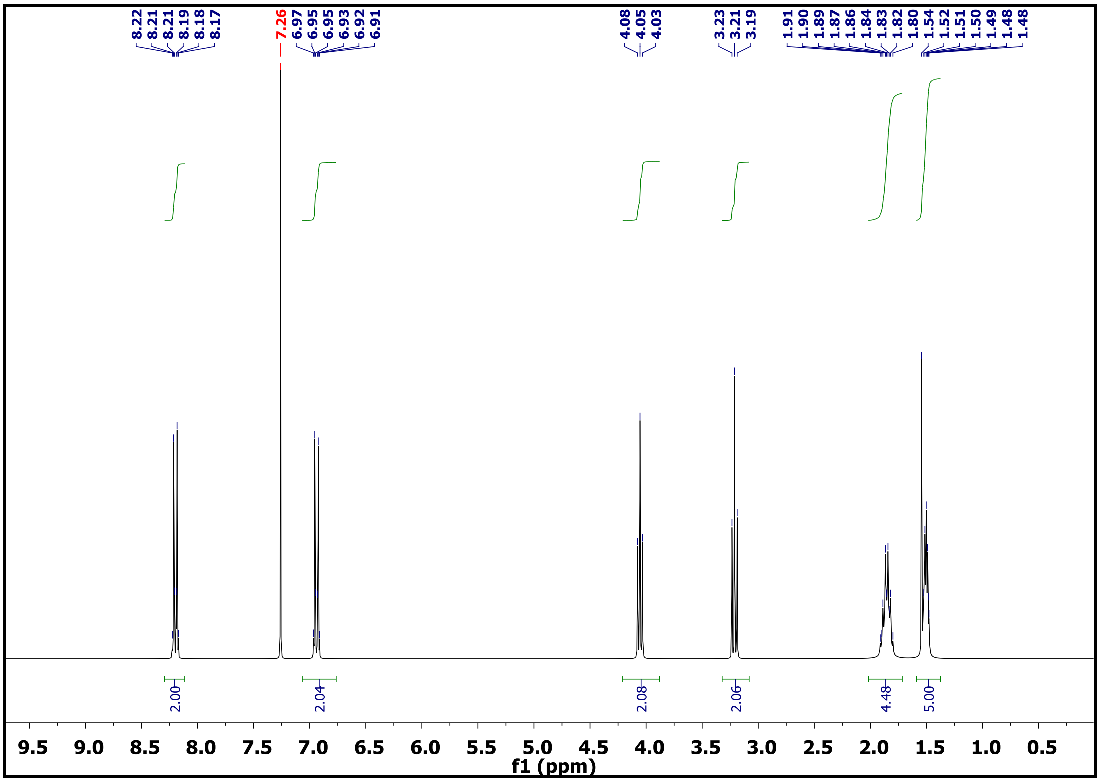


Fig. S2 ^{1}H NMR spectrum of 1-(6-iodohexyloxy)-4-nitrobenzene in $CDCl_3$.

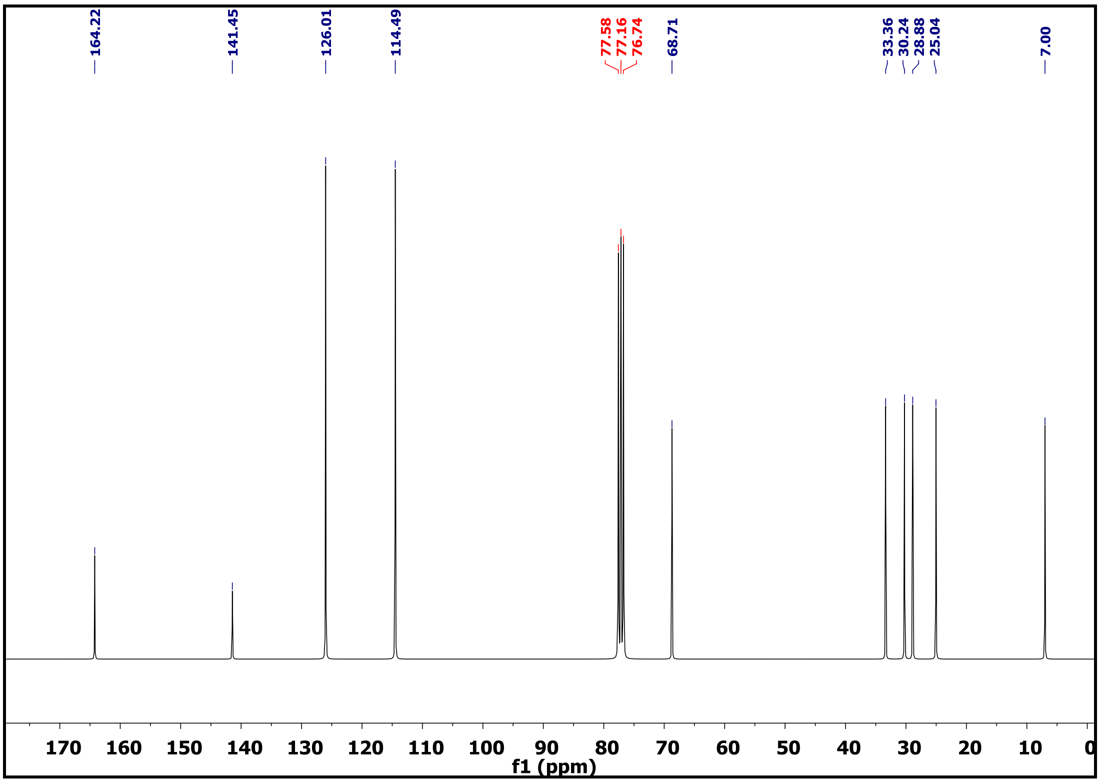


Fig. S3 $^{13}C\{^{1}H\}$ NMR spectrum of 1-(6-iodohexyloxy)-4-nitrobenzene in $CDCl_3$.

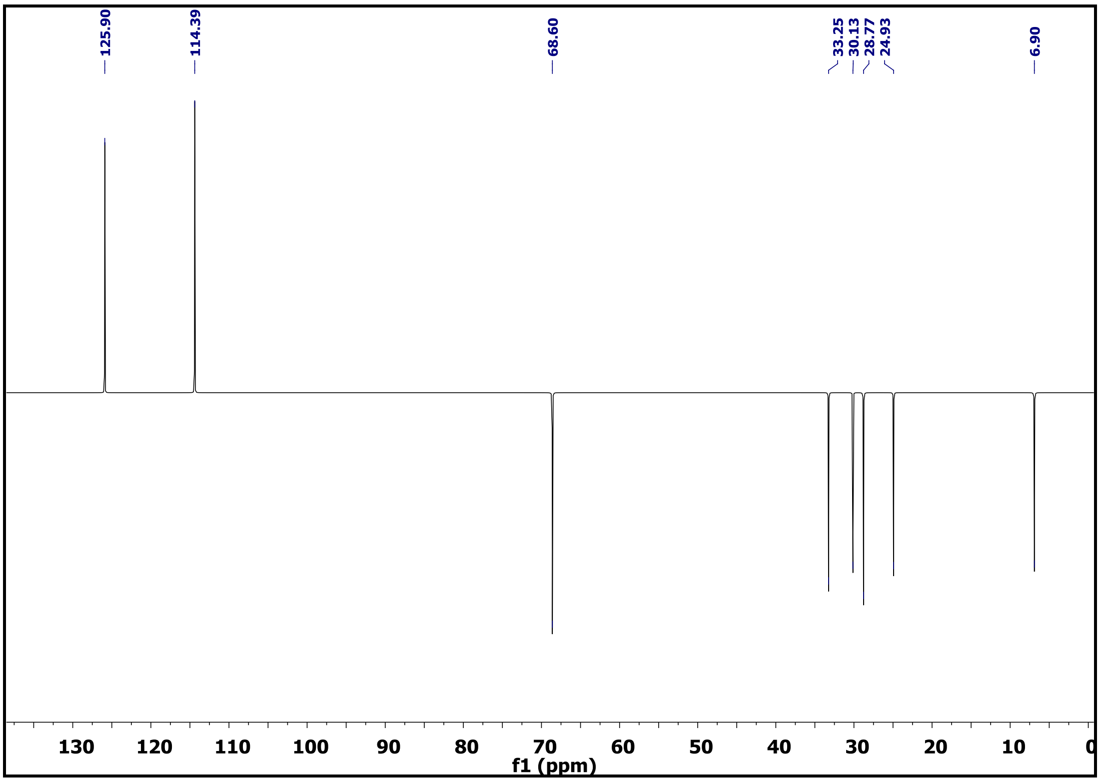


Fig. S4 DEPT 135 NMR spectrum of 1-(6-iodohexyloxy)-4-nitrobenzene in $CDCl_3$.

NO$_2$-Spacer-NiTPP

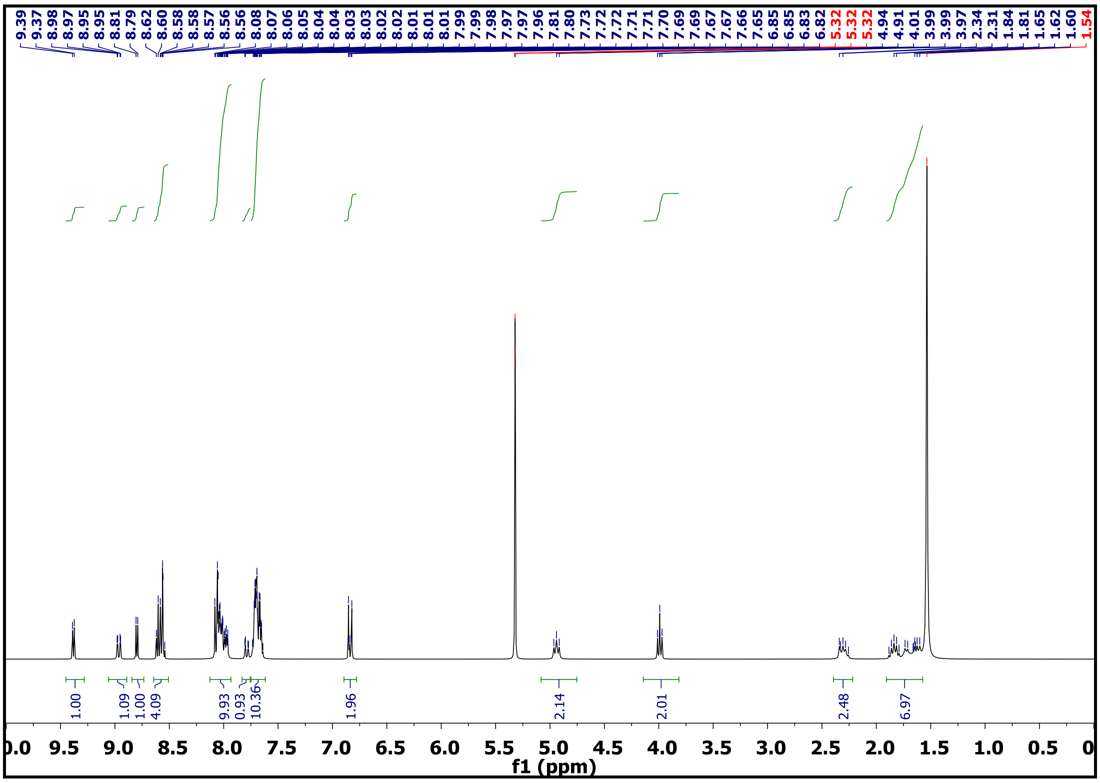


Fig. S5 ^{1}H NMR spectrum of **NO$_2$-Spacer-NiTPP** in CD$_2$Cl$_2$.

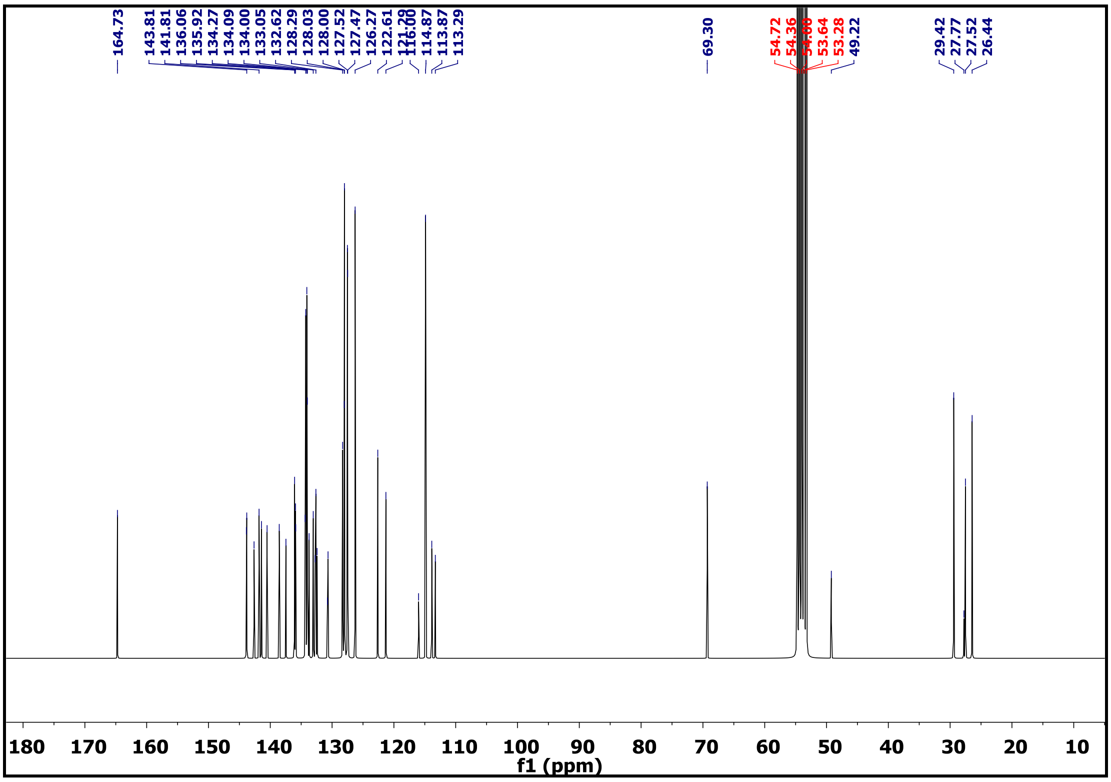


Fig. S6 ^{13}C{^{1}H} NMR spectrum of **NO$_2$-Spacer-NiTPP** in CD$_2$Cl$_2$.

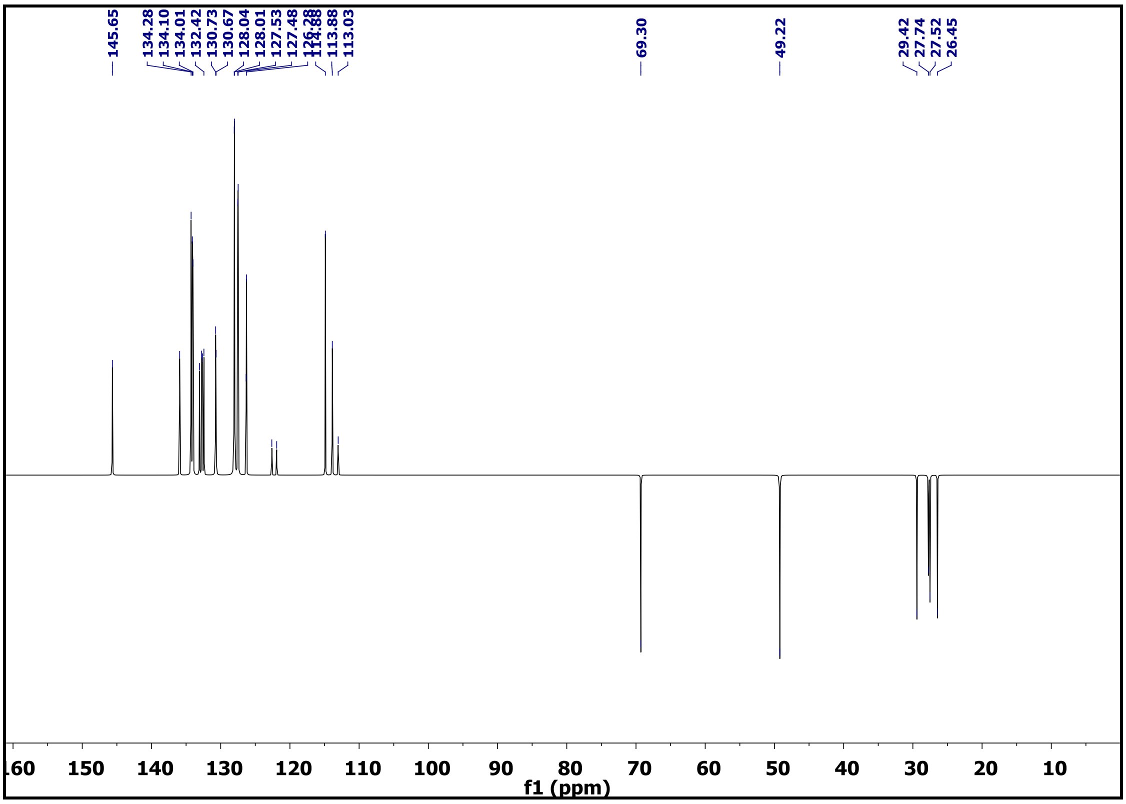


Fig. S7 DEPT NMR spectrum of **NO_2-Spacer-NiTPP** in CD_2Cl_2.

<u>NHCO-NiTPP</u>

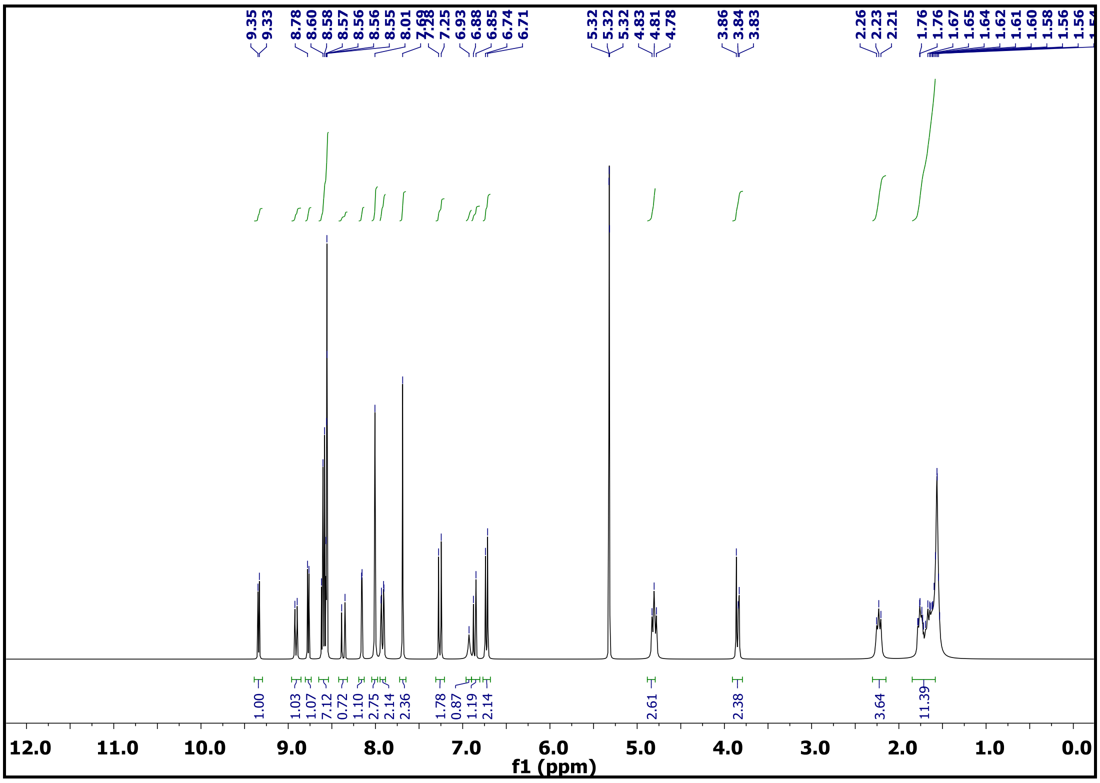


Fig. S8 ^1H NMR spectrum of **NHCO-NiTPP** in CD_2Cl_2.

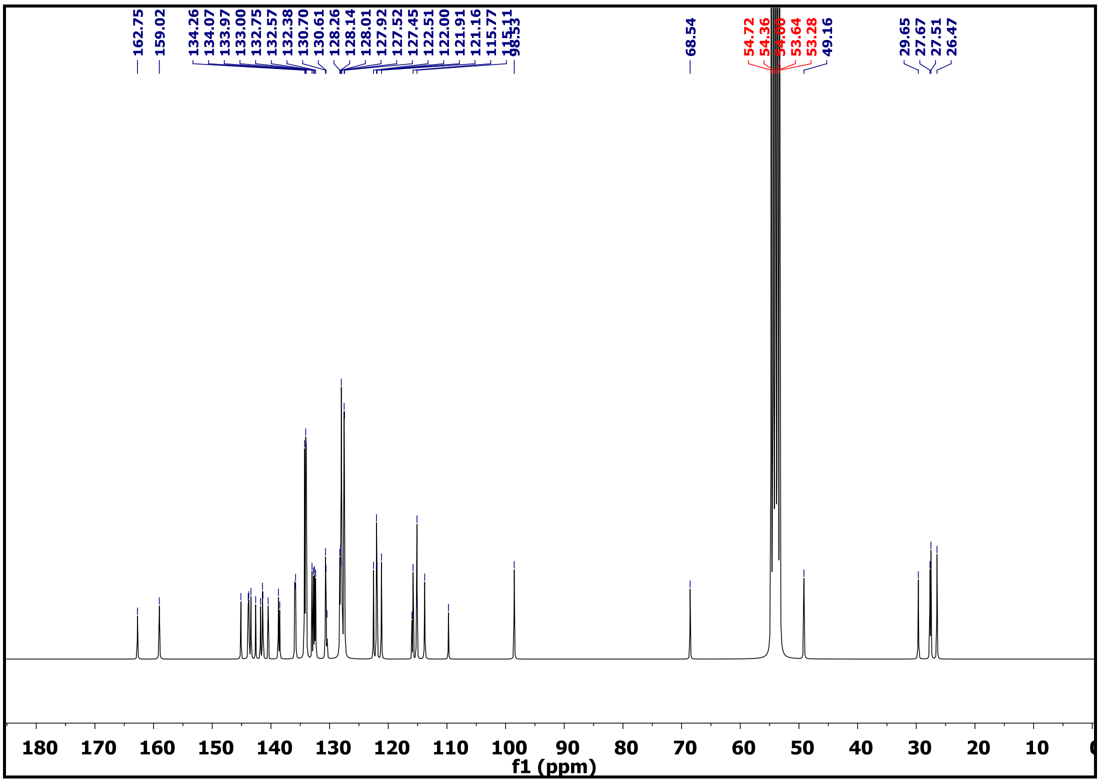


Fig. S9 $^{13}C\{^{1}H\}$ NMR spectrum of **NHCO-NiTPP** in CD_2Cl_2.

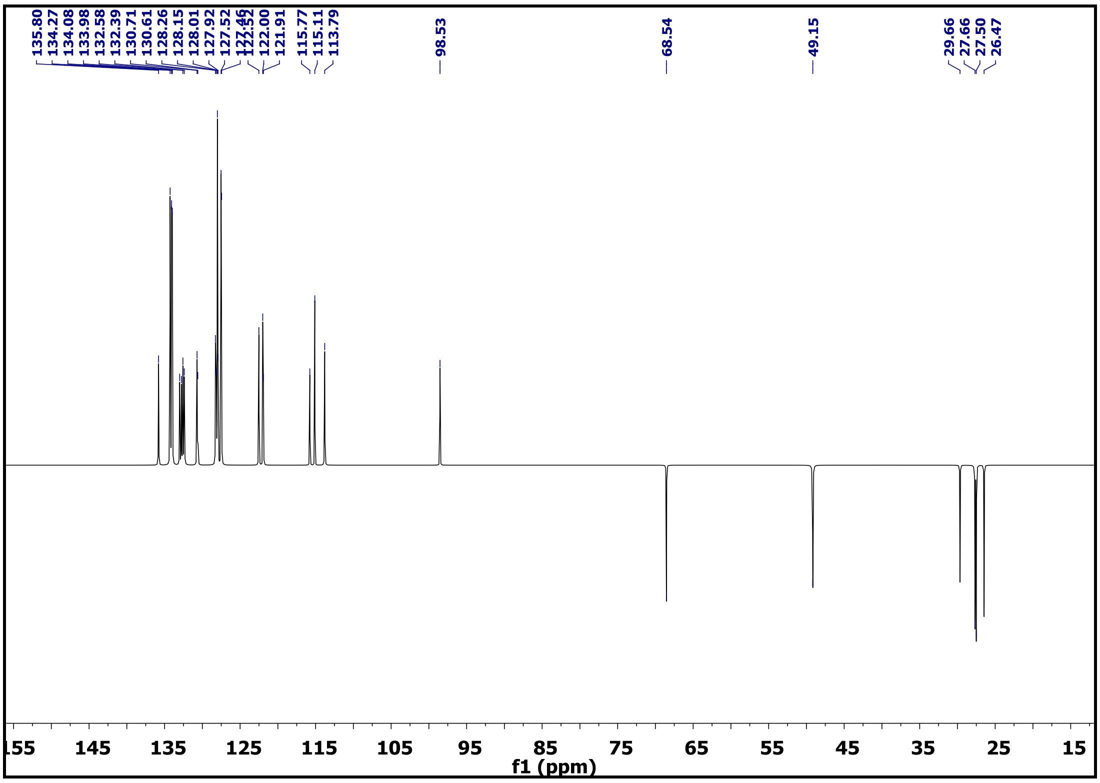


Fig. S10 DEPT 135 NMR spectrum of **NHCO-NiTPP** in CD_2Cl_2.

Isocyanide-based porphyrin monomer (1)

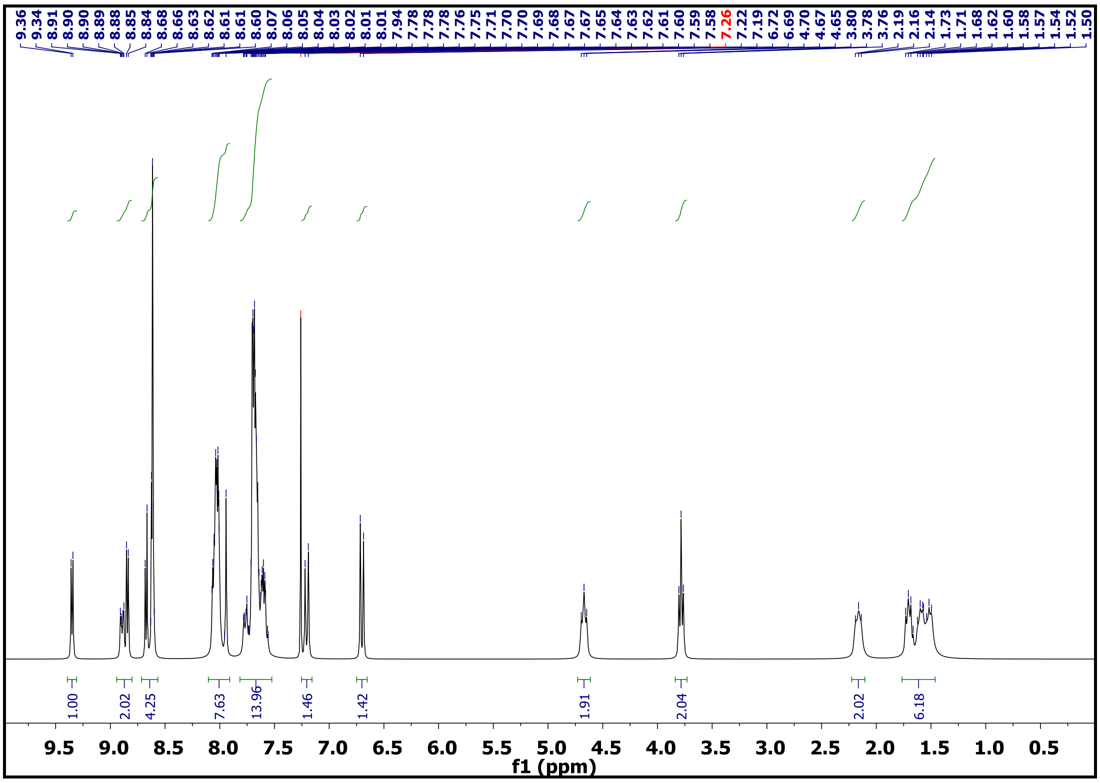


Fig. S11 ^{1}H NMR spectrum of isocyanide-based porphyrin monomer **1** in $CDCl_3$.

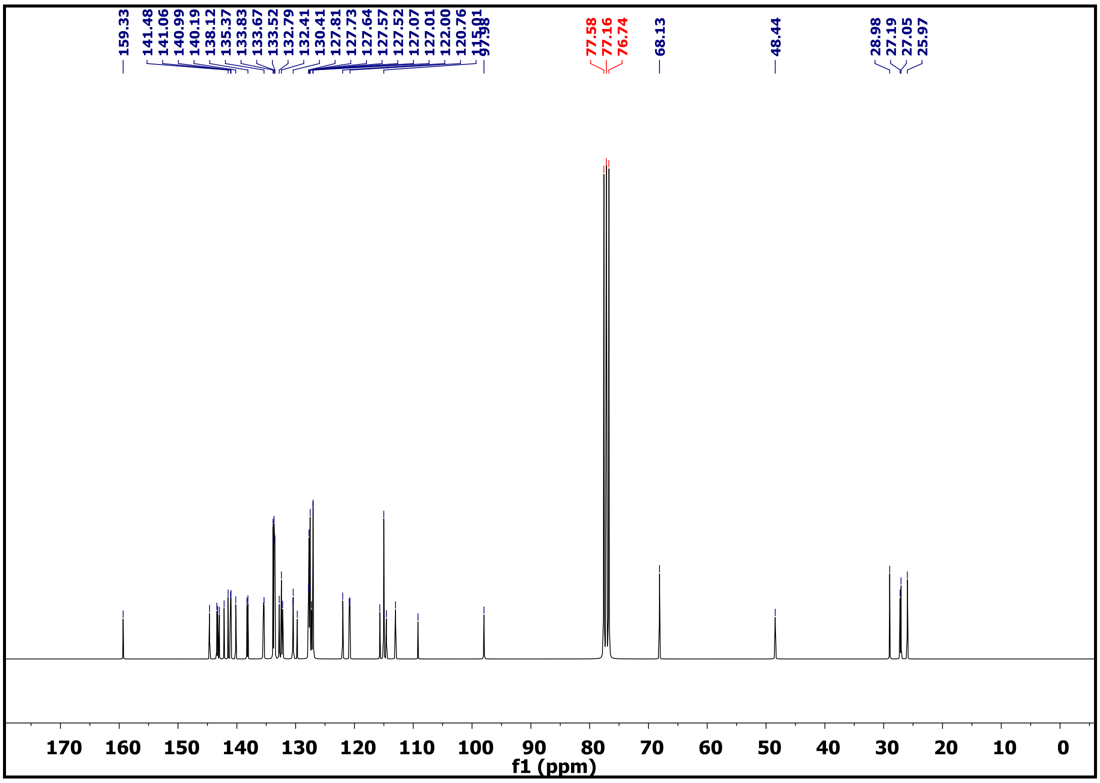


Fig. S12 ^{13}C{^{1}H} NMR spectrum of isocyanide-based porphyrin monomer **1** in $CDCl_3$.

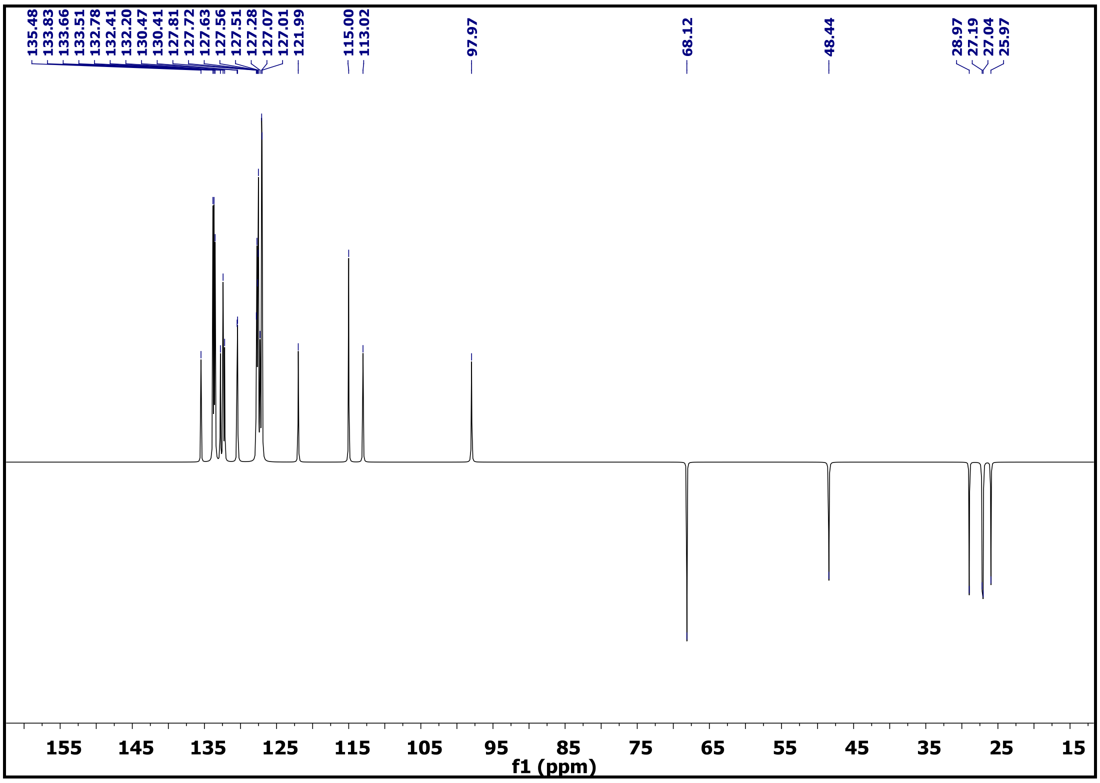


Fig. S13 DEPT 135 NMR spectrum of of isocyanide-based porphyrin monomer **1** in $CDCl_3$.

2.2. P3HT end-functionalized with π-extended porphyrins (2)

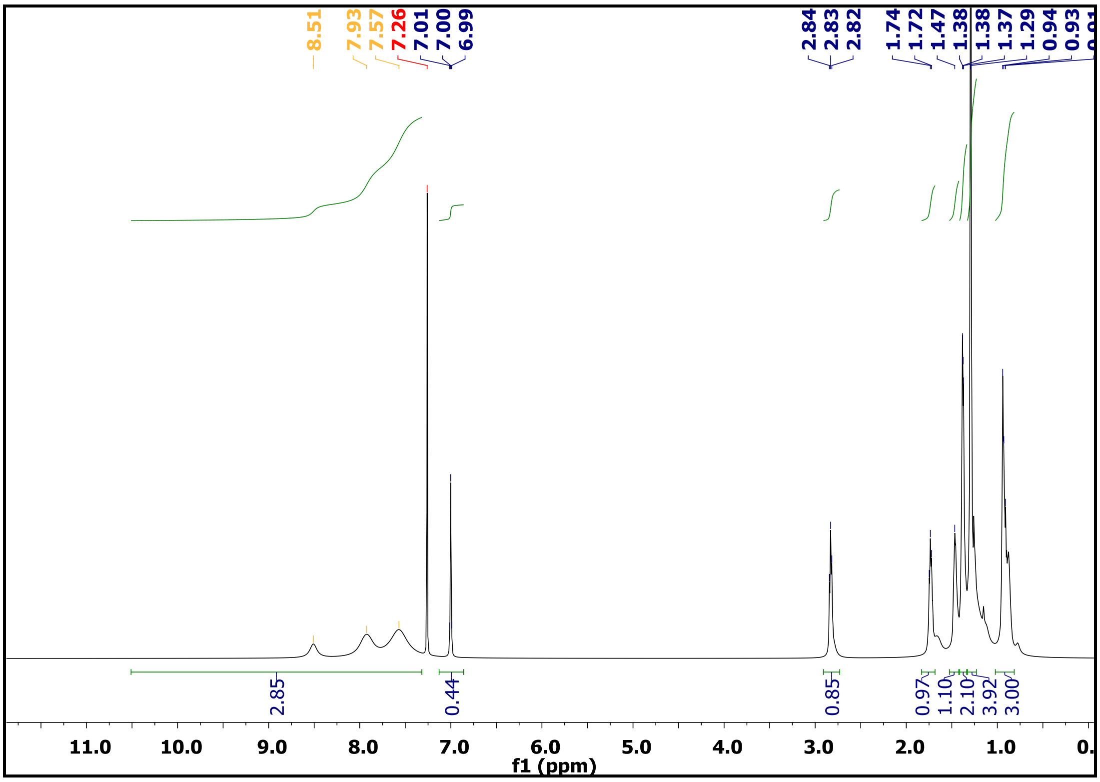


Fig. S14 ^1H NMR spectrum of **2a** in $CDCl_3$.

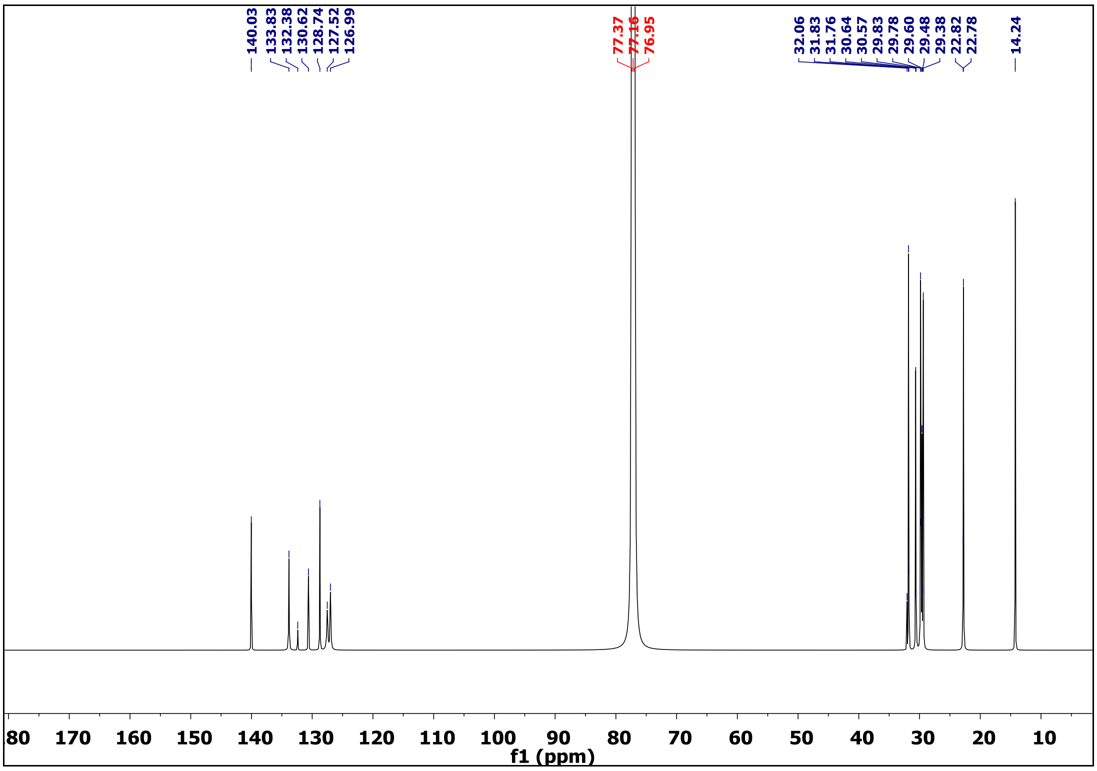


Fig. S15 $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in $CDCl_3$.

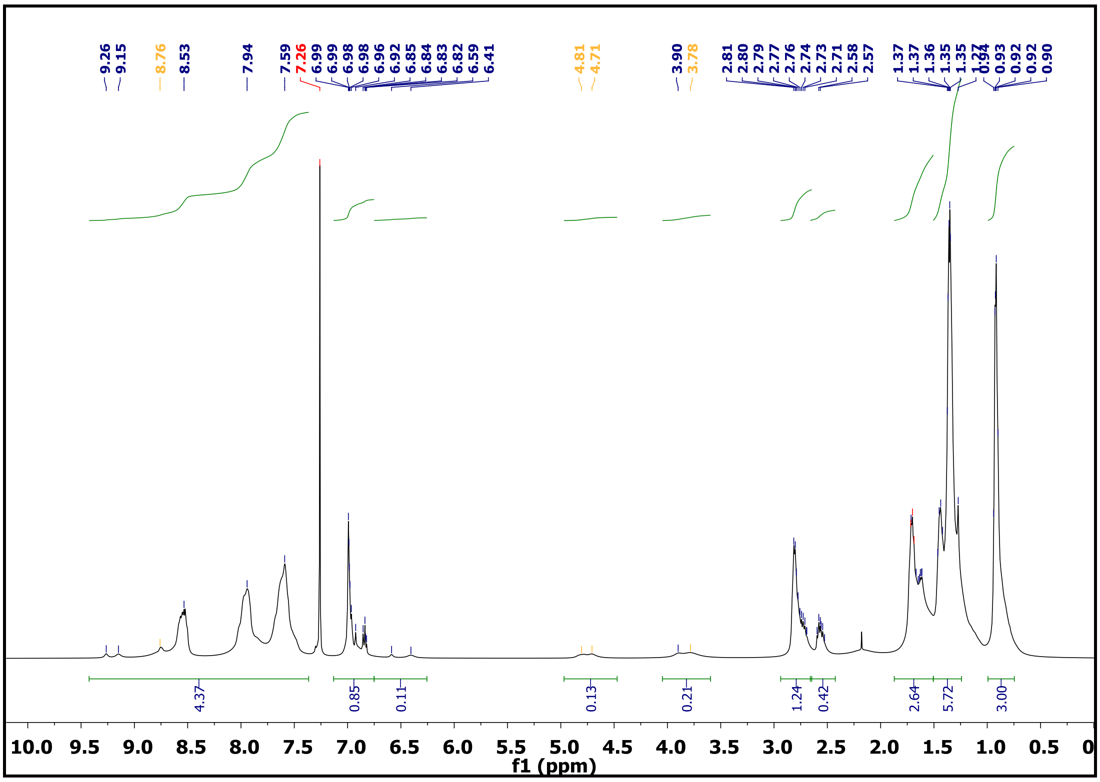


Fig. S16 ^{1}H NMR spectrum of **2b** in $CDCl_3$.

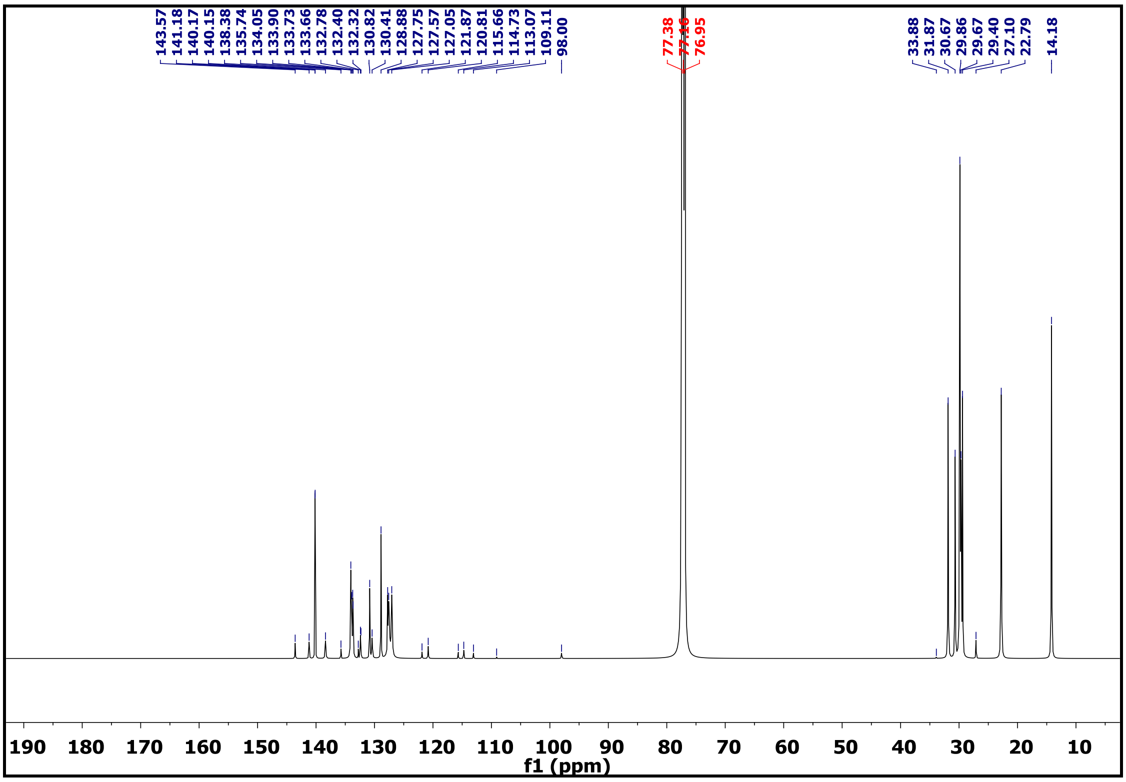


Fig. S17 $^{13}C\{^1H\}$ NMR spectrum of **2b** in $CDCl_3$.

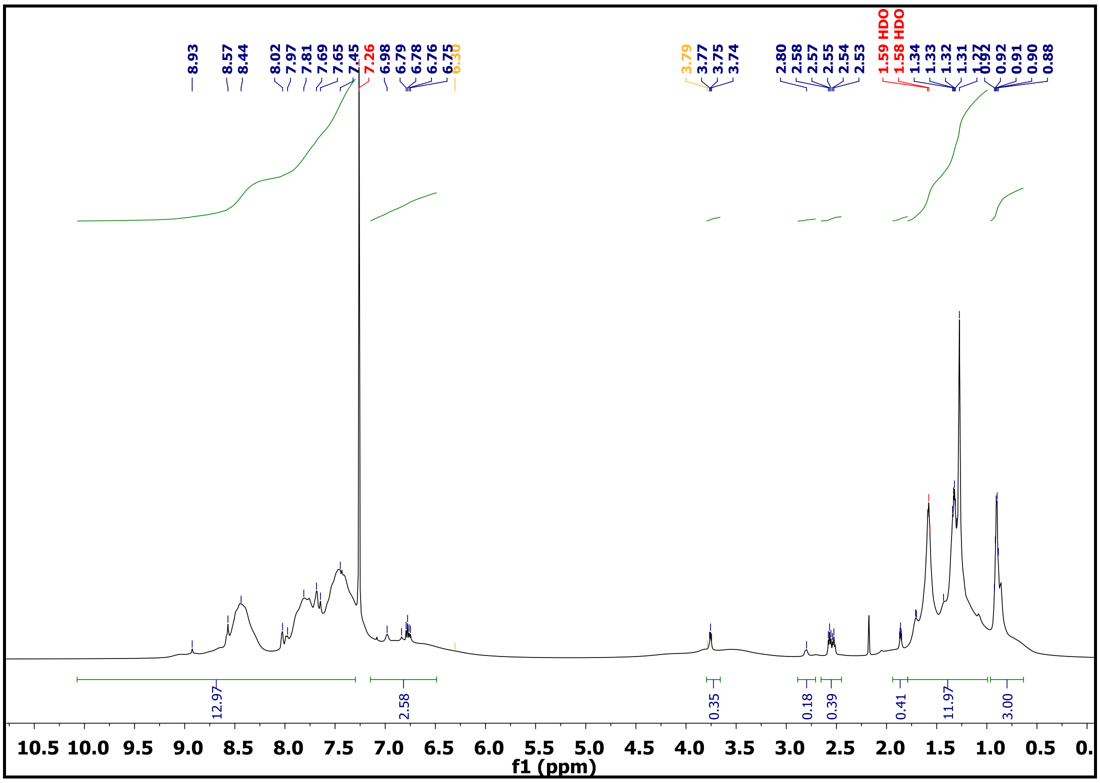


Fig. S18 ^1H NMR spectrum of **2c** in $CDCl_3$.

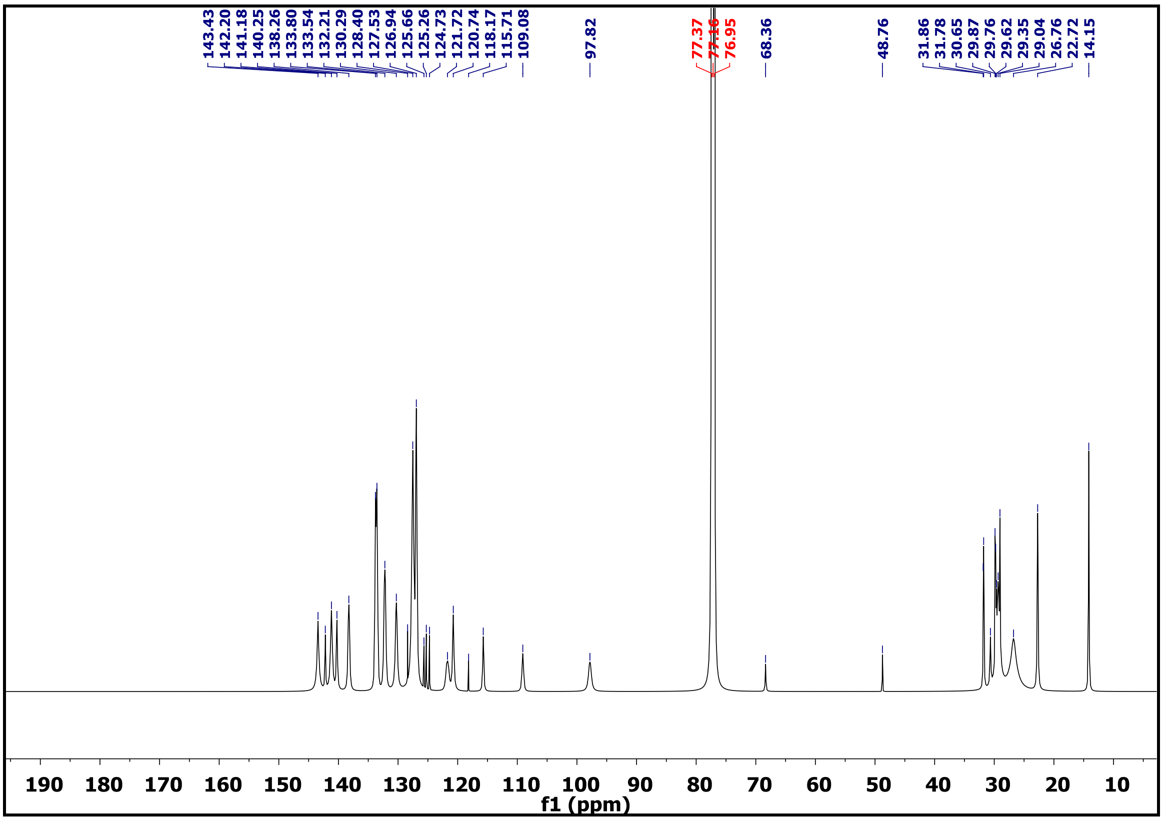


Fig. S19 $^{13}C\{^{1}H\}$ NMR spectrum of **2c** in $CDCl_3$.

3. GPC traces

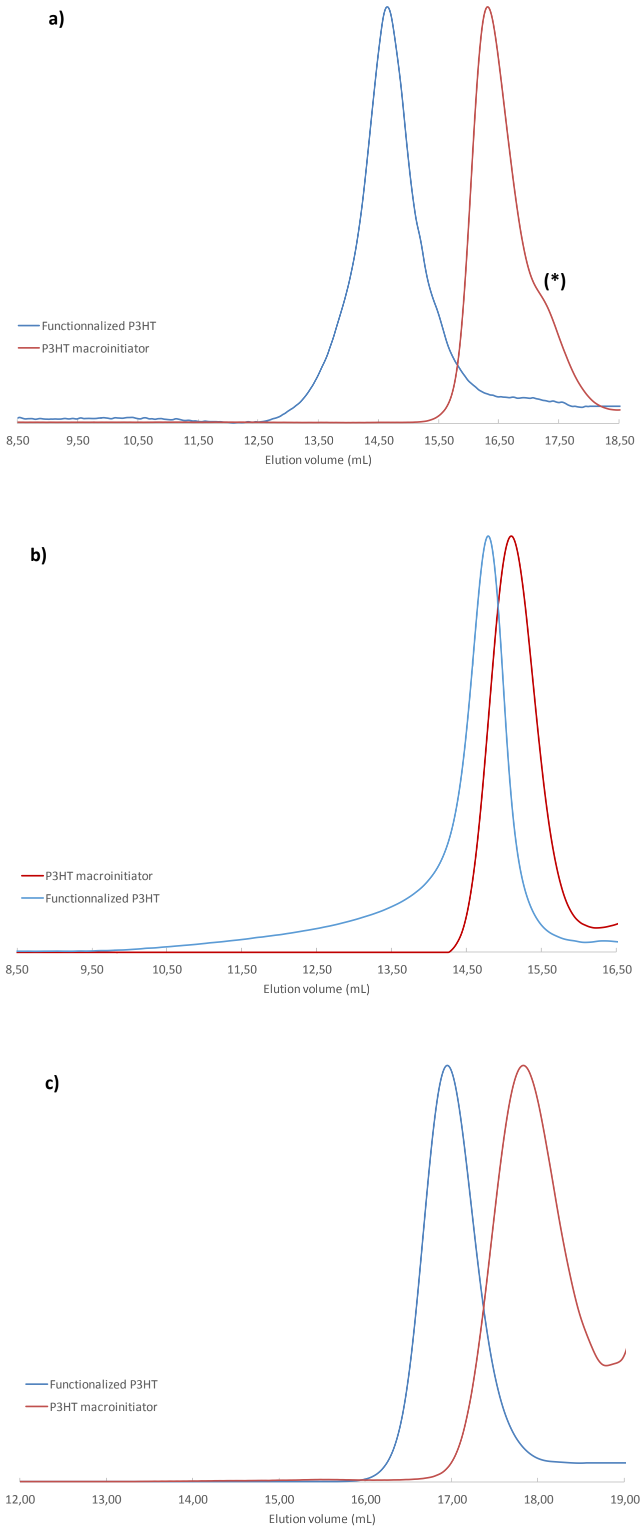


Fig. S20 Representative GPC chromatograms of homopolymer P3HT (black line) and a representative P3HT end-functionalized with π-extended porphyrin (**2**, red line) [a) **2a** ; b) **2b** ; c) **2c**]. (*) oligomer species or impurities coming from the sample preparation.

4. IR analysis

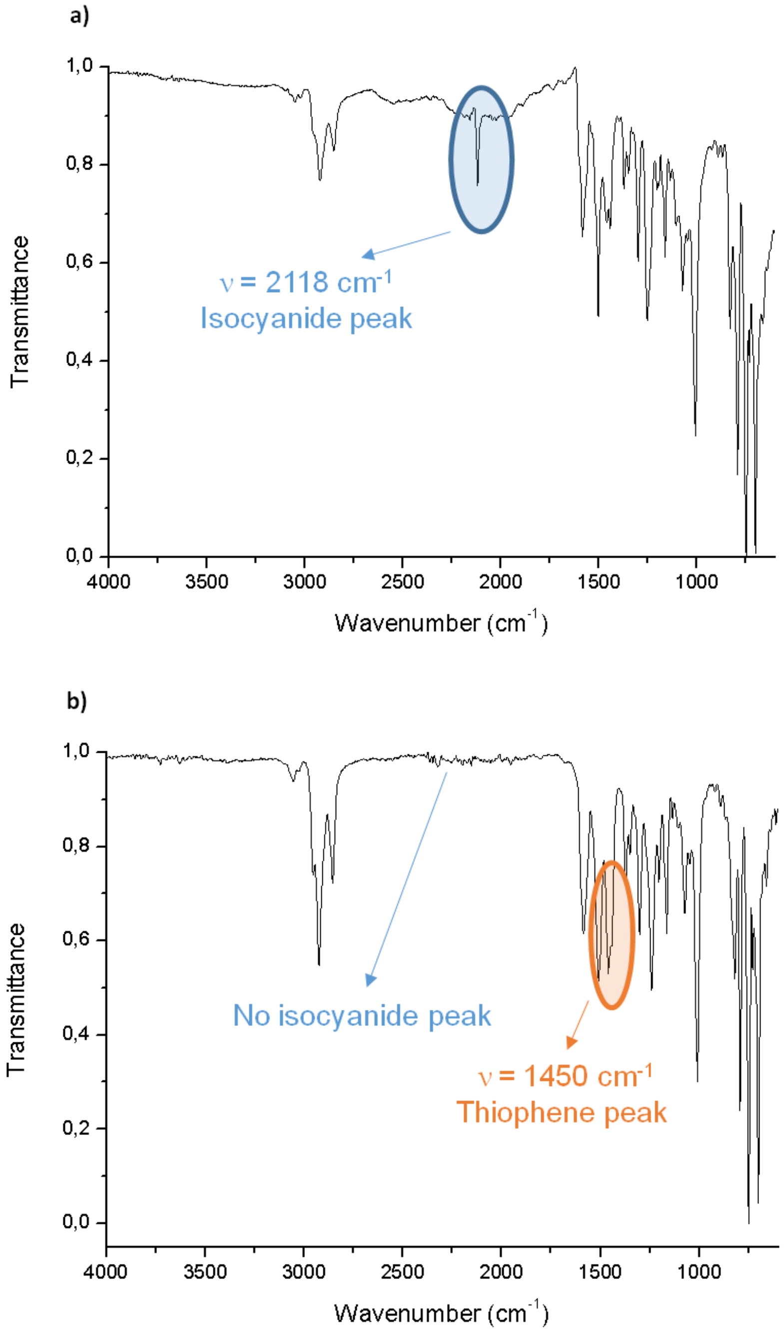


Fig. S21 ATR-IR spectra of isocyanide porphyrin monomer (a) and P3HT end-functionalized with π-extended porphyrins (b) measured at room temperature.

4. Optical properties

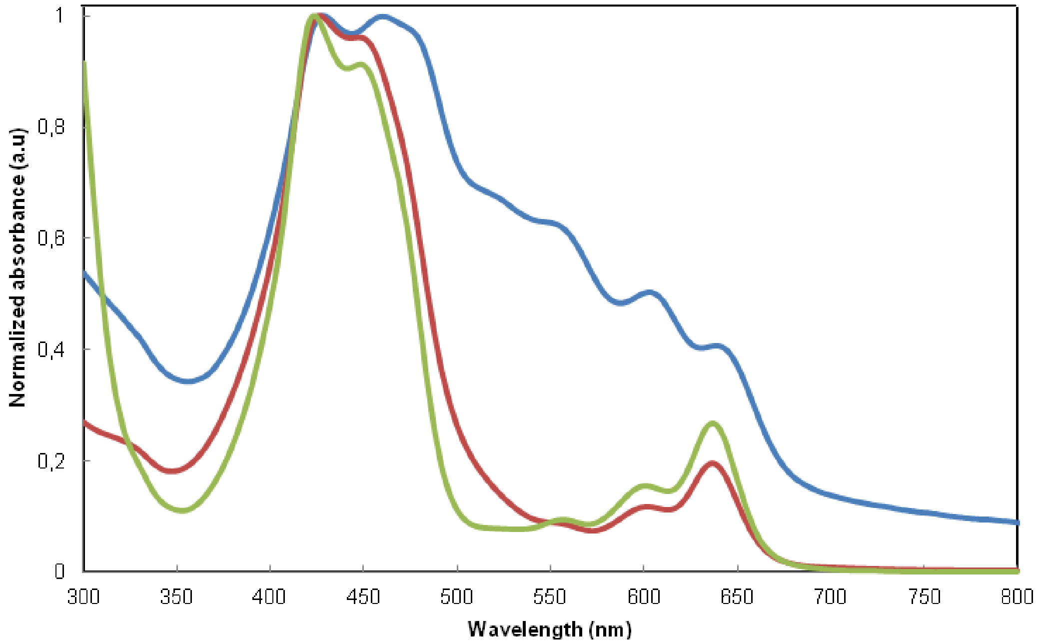


Fig. S22 UV-Visible absorption spectra of isocyanide porphyrin monomer **1** in chloroform (green curve), **2a** in chloroform (red curve) and **2a** in solid state (blue curve).

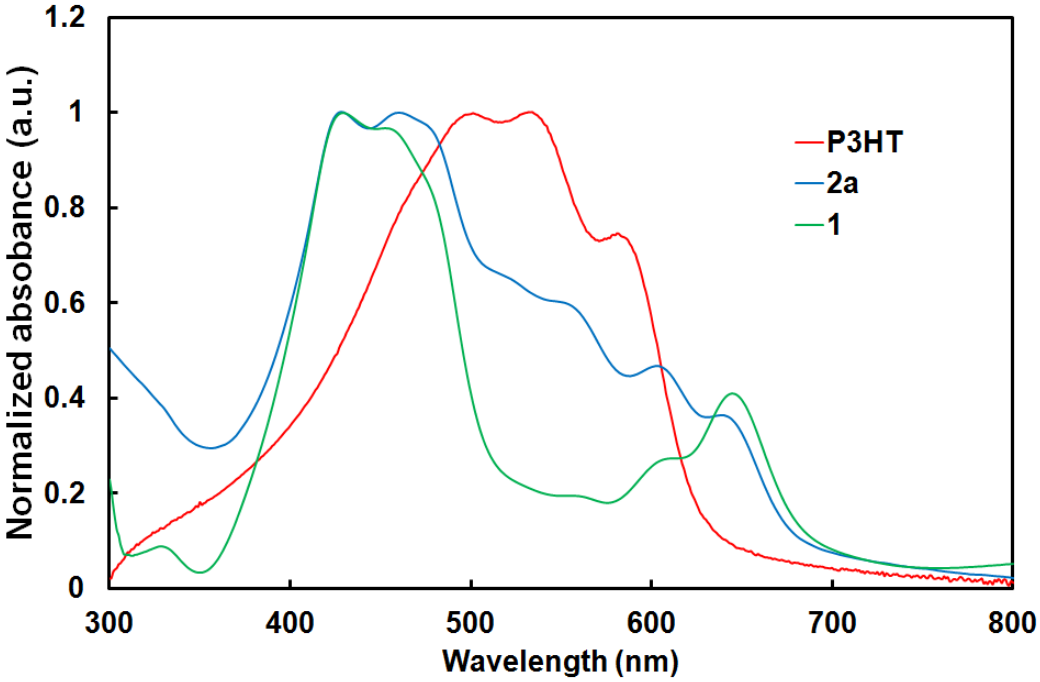


Fig. S23 UV-Visible absorption spectra of isocyanide porphyrin monomer **1** (green curve), **2a** (blue curve) and **P3HT** (red curve) in solid state.

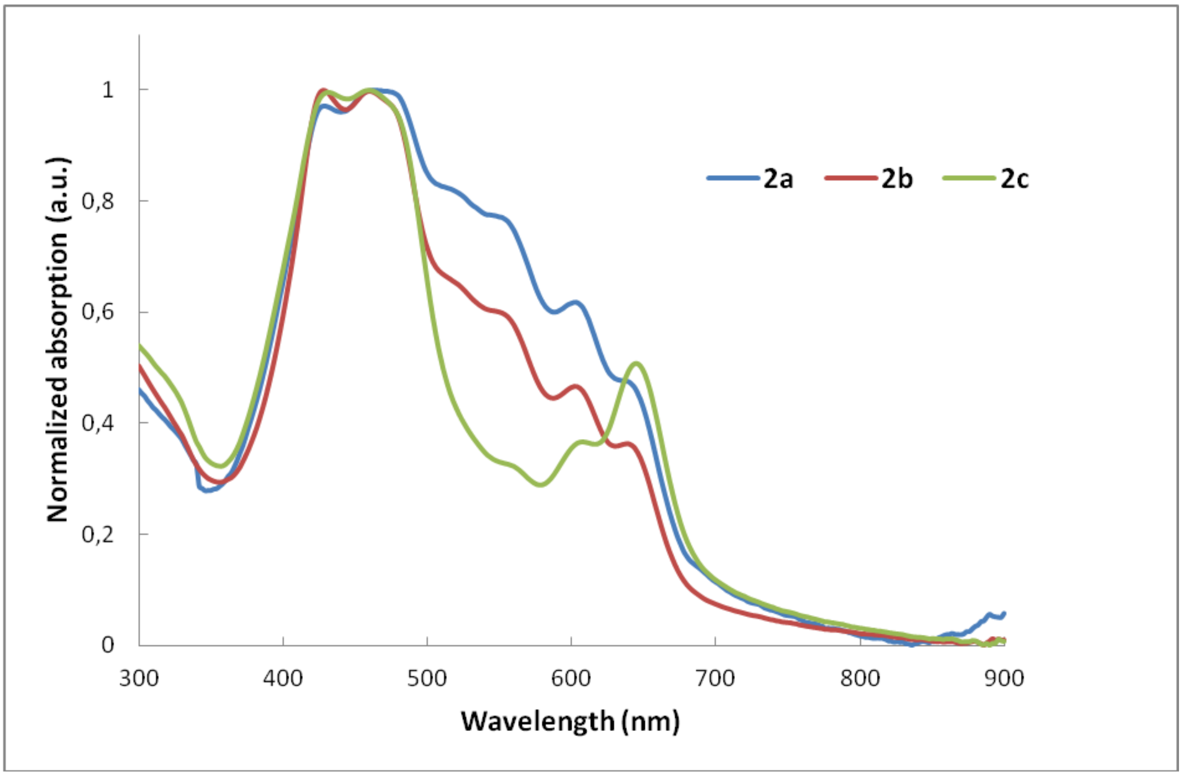


Fig. S24 UV-Visible absorption spectra of P3HT end-functionalized with π-extended porphyrins in the solid state at different molar ratios of the porphyrin block.

5. Aggregation properties

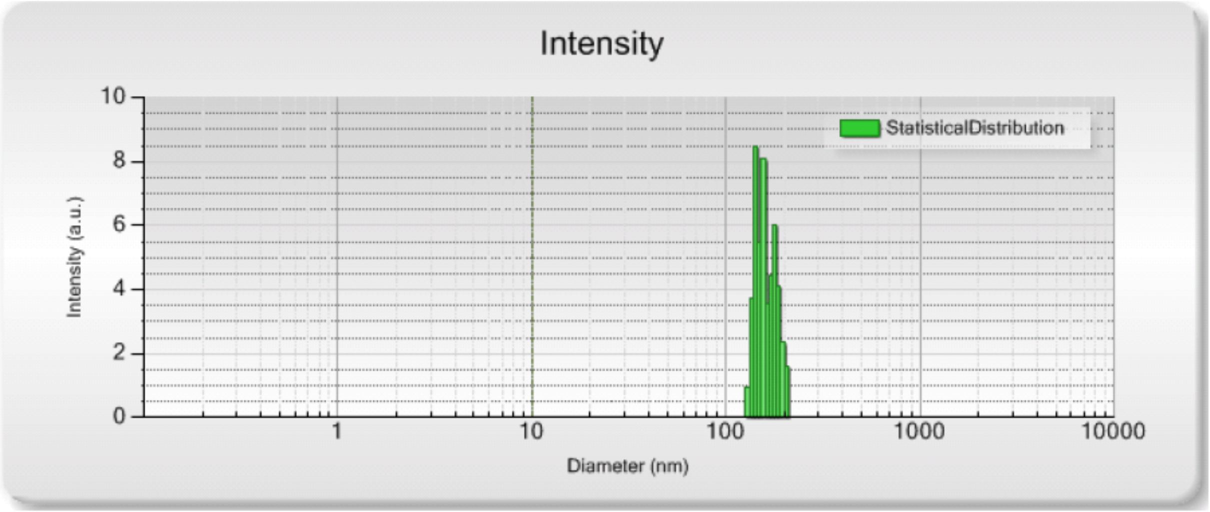


Fig. S25 Intensity weighted size dispersion of the polymer **2a** (C = 0.12 mg.mL^{-1}) in CHCl$_3$:MeOH (1:1 v/v ratio) at 25°C.

6.Thermal properties

6.1. TGA

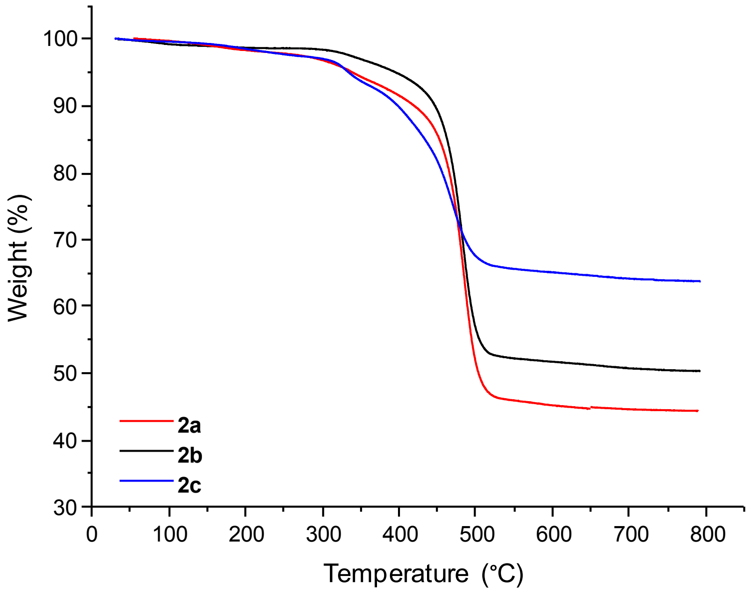


Fig. S26 TGA thermograms of P3HTs end-functionalized with π-extended porphyrins at different molar ratios of the porphyrin block.

6.2. DSC

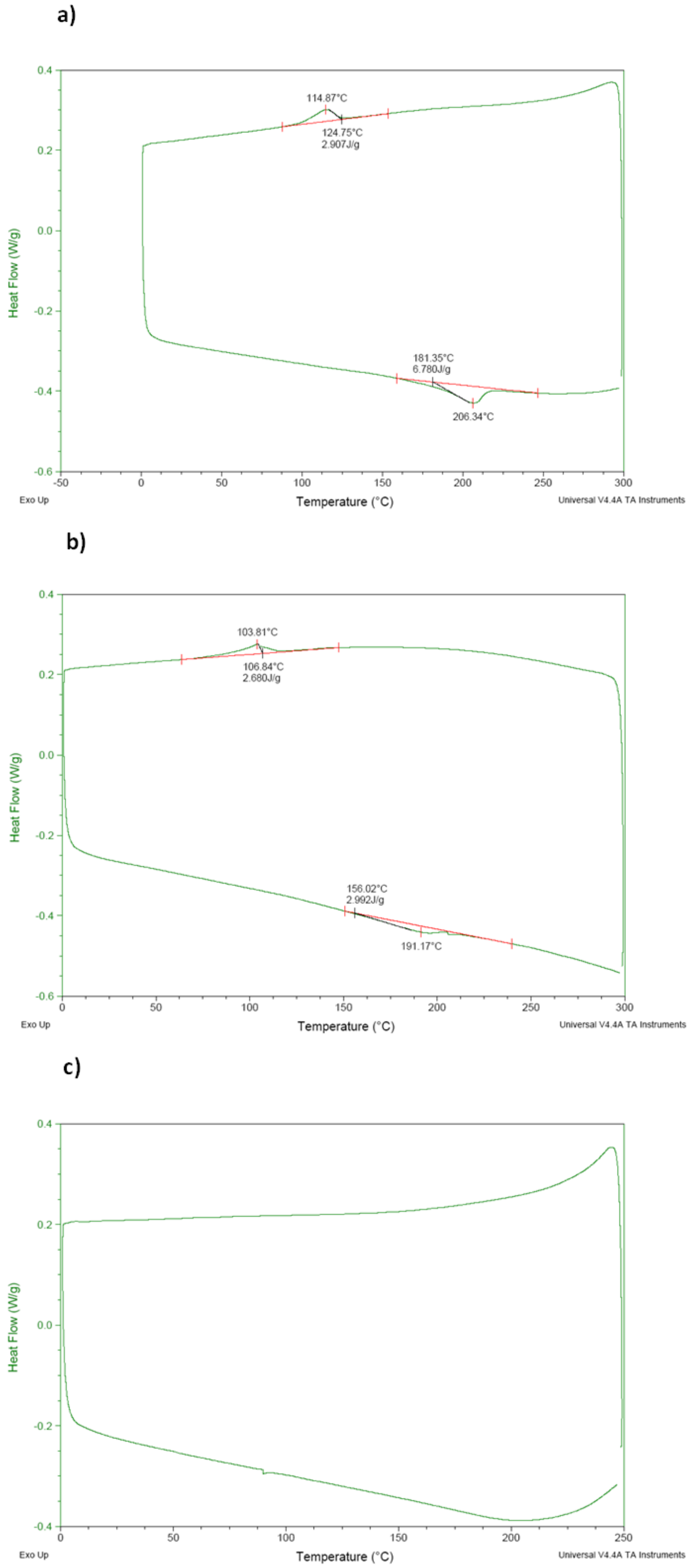


Fig. S27 DSC traces of P3HTs end-functionalized with π-extended porphyrins depending on the molar ratio of porphyrin block [a) **2a**; b) **2b**; c) **2c].**

7. References

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