

Polyethylenes Bearing a Terminal Porphyrin Group

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SUPPORTING INFORMATION

MATERIALS

Toluene was distilled over sodium/benzophenone. Butyloctylmagnesium (20% solution in heptane, Crompton), dimethylformamide (DMF, Sigma-Aldrich, 99.8%), d⁸-toluene (euriso-top, H₂O<0.02%, 99.5% D), copper(I) bromide (Aldrich, 98%), N,N,N',N',N''-pentamethylenediethylenetriamine (Aldrich, 99%) were used as received.

ANALYTICAL TECHNIQUES

High-resolution liquid NMR spectroscopy was carried out with a Bruker DRX 400 spectrometer operating at 400 MHz for ¹H and MHz for ¹³C. Spectra were obtained with a 5-mm QNP or a PSEX 10-mm probe at 363K. Polymer samples were examined as 10-15 % (w/v) solutions. A mixture of tetrachloroethylene (TCE) and perdeuterobenzene (C₆D₆) (2/1 v/v) was used as solvent. Chemical shift values (δ) are given in ppm in reference to internal tetramethylsilane (TMS). A coaxial tube containing D₂O was also used for some specific samples with TMS as reference and experiment were in this case performed at 353K.

High temperature SEC analyses were performed using a Waters Alliance GPCV 2000 chromatograph equipped with three columns (2 Styragel HT6E and 1 Styragel HT2). Samples (1 mg.mL⁻¹) were eluted with trichlorobenzene with a flow rate of 1 mL.min⁻¹ at 150°C. Online detection was performed by refractometry and viscosimetric measurements using Waters equipments.

MALDI-TOF mass spectrometry analyses were recorded in the linear and the reflectron mode using an Applied Biosystems Voyager DE-STR equipment using a nitrogen laser (wavelength 337 nm) and an accelerating voltage of 20 kV. The positive ions were detected in all cases. The spectra were the sum of 200 shots, and an external mass calibration was used (mixture of peptides standards, Sequazyme kit). The samples were deposited on a stainless steel target and dried. Samples were prepared by dissolving the polymer in freshly distilled tetrahydrofuran (THF) at a concentration of 10 g.L⁻¹. The matrix was used without further purification and dissolved in distilled THF (10 g.L⁻¹). The samples were prepared by mixing a solution of polymer in THF (10 mg.mL⁻¹), a solution of matrix in THF (20 mg.mL⁻¹), with a volumetric ratio in the ratio 1/10 (V_{sample}/V_{matrix}). 1 mL of the resulting mixture was placed onto the sample plate and the solvent was evaporated at room temperature.

FT-IR analyses were carried out in a Nicolet 460 FT-IR spectrometer at room temperature over 32 scans (sensitivity range 500-3800 cm⁻¹).

UV-Vis spectroscopy (reflectance mode) was carried out using a Perkin Elmer PE950 (sensitivity range 185-3200 nm).

Scanning electron microscopy (SEM) images were obtained using a Hitachi S4800 Field Effect SEM operating at an accelerating voltage of 5kV. Samples for SEM were dropped onto a passified silicon substrate dried in vacuo then coated with platinum (~ 4 nm) using a Hitachi 1030 Ion Sputterer.

Atomic force microscopy (AFM) images were obtained using a Seiko Instruments SPA400-SPI4000 equipped with a calibrated 20- μ m xy-scan range and a 10 μ m z-scan range PZT-scanner. All AFM images were taken in dynamic force mode at optimal force. Samples for AFM were dropped onto a passified silicon substrate and dried in vacuo prior to measurement. Rectangular shaped silicon cantilevers (Tip radius: ~10 nm; SI-DF20; Seiko Instruments Inc.), with spring constant of 11 N/m and resonance frequency of 122 kHz, were used for imaging in air.

Powder X-ray diffraction data was collected from freshly crystallised (toluene) samples using a Rigaku RINT 1000 diffractometer and Cu K(α) radiation ($\lambda = 1.54056 \text{ \AA}$). Samples were spread on a specially prepared glass plate.

METHODS

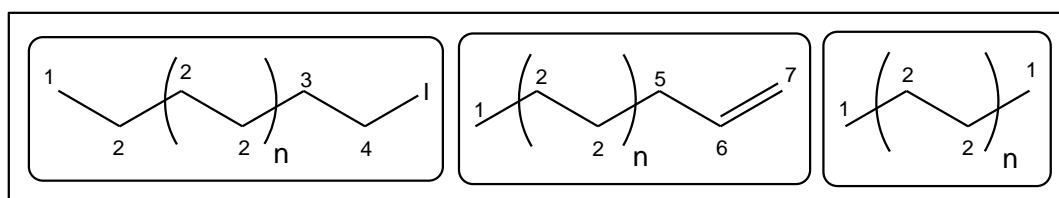
Synthesis of $(C_5Me_5)_2NdCl_2Li(OEt_2)_2$. The neodymocene based catalyst was synthesized following conditions depicted in the literature.¹

Polymerization procedure. Ethylene polymerization was carried out in toluene in a 500 mL reactor connecting to an ethylene reservoir equipped with a pressure sensor. The reactor was charged with a mixture of the chloroneodymocene complex $(C_5Me_5)_2NdCl_2Li(OEt_2)_2$ ($8.3 \cdot 10^{-5}$ mol.L⁻¹), and butyloctylmagnesium (BOMg) in a 400 mL toluene solution. The molar ratio Mg/Nd was adjusted with respect to the targeted molar mass (Mg/Nd = 200). The solution was rapidly set to the polymerization temperature (80°C) and then to an ethylene pressure of 3 bar. The consumption rate of ethylene was measured from the observed drop of pressure in the reservoir. The molar ratio ethylene to BOMg was controlled according to this measure in order to reach the targeted molar mass.

A non functional polyethylene (PE) was prepared according to this procedure for reference sake ($M_n = 1670$ g/mol, PDI = 1.1)

Synthesis of iodine end-functionalized polyethylene (PE-I)

Once ethylene polymerization is assumed to have reached completion, the reactor is degassed with argon before 50 mL of freshly distilled THF is introduced. After cooling to room temperature by external water circulation, the suspension obtained is then flushed into a 1-litre three-necked flask under argon atmosphere. Iodine solution (4 eq. I₂/Mg, in 50 mL THF) is added drop wise for 20 min at 0°C under vigorous magnetic stirring, and the reactor is allowed to come back to room temperature for two hours. Then the mixture is poured into a large amount of methanol and collected by filtration. After washing 3 times with 200 mL methanol, the precipitate is dried under reduced pressure for 10 hours. A fine white powder was then recovered (Functionality = 96.8%) according to ¹H NMR analysis.

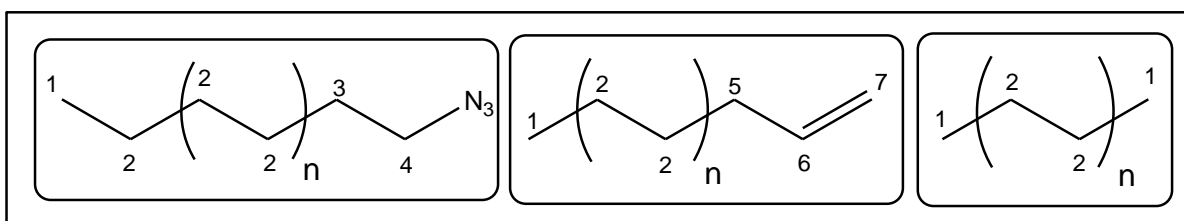


¹ T. Don Tilley, T. ; Andersen, R.A. *Inorg. Chem.* **1981**, *20*, 3267-3270

^1H NMR 400 MHz (TCE/ C_6D_6 , 363K, ppm) δ 0.95 (H1, t, $J = 7$ Hz); 1.30 (H2, br); 1.72 (H3, qt, $J = 7$ Hz); 2.02 (H5, m); 3.00 (H4, t, $J = 7$ Hz), 4.90 (H7, m); 4.96 (H7, m); 5.77 (H6, m).

Synthesis of azide end-functionalized polyethylene (PE-N₃), **1**

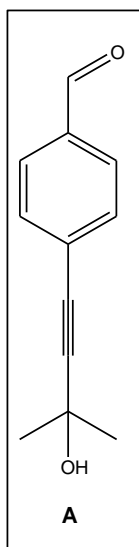
PE-I, NaN₃ (1.2 eq/PE-I) and 50 mL DMF are mixed together in a 100 mL three-necked flask, and the suspension obtained is then heated up 150 °C in DMF. The mixture is observed to remain biphasic, with a molten polyethylene phase floating in the DMF. After 4 h, the suspension is cooled to room temperature. Polyethylene granules formed are crushed before washing with methanol and drying as previously described. Functionality = 90% as determined by ¹H NMR.



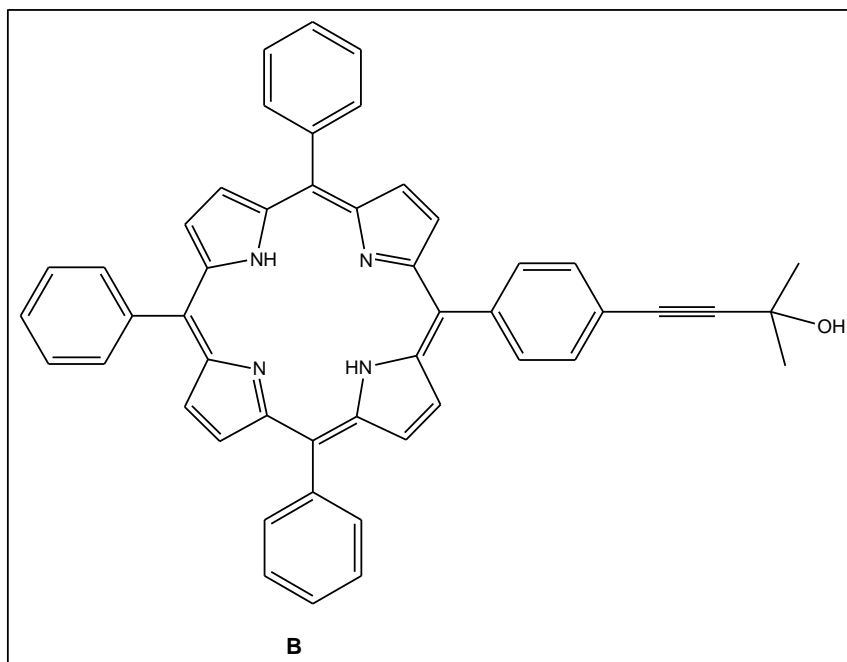
¹H NMR 400 MHz (TCE/C₆D₆, 363K, ppm) δ 0.95 (H1, t, *J* = 7 Hz); 1.30 (H2, br); 1.47 (H3, *J* = 7 Hz); 2.02 (H5, m); 3.04 (H4, t, *J* = 7 Hz); 4.90 (H7, m); 4.96 (H7, m); 5.77 (H6, m).

Synthesis of **2**

4-bromobenzaldehyde (7.4 g, 0.04 mol), 3-methyl-1-butyn-3-ol (5.8 mL, 0.06 mol), CuI (0.46 g, 2.4 mmol) and Pd(PPh₃)₄ (1.4 g, 1.2 mmol) were taken in dry toluene (75 mL) under N₂ atmosphere. After 3 freeze-pump-thaw cycles, diisopropylamine (5.7 mL) was added on the frozen mixture which was again submitted to 3 freeze-pump-thaw cycles. After stirring at RT under N₂ atmosphere for 24 h, dichloromethane was added and the organic phase washed with water (x3), dried with Na₂SO₄ and concentrated. Upon silica gel column chromatography (CH₂Cl₂/hexane, 10/1), the desired compound was isolated as a viscous yellow pale oil which solidified on standing upon to give a white solid (**A**). Yield: 7.29 g (97 %).

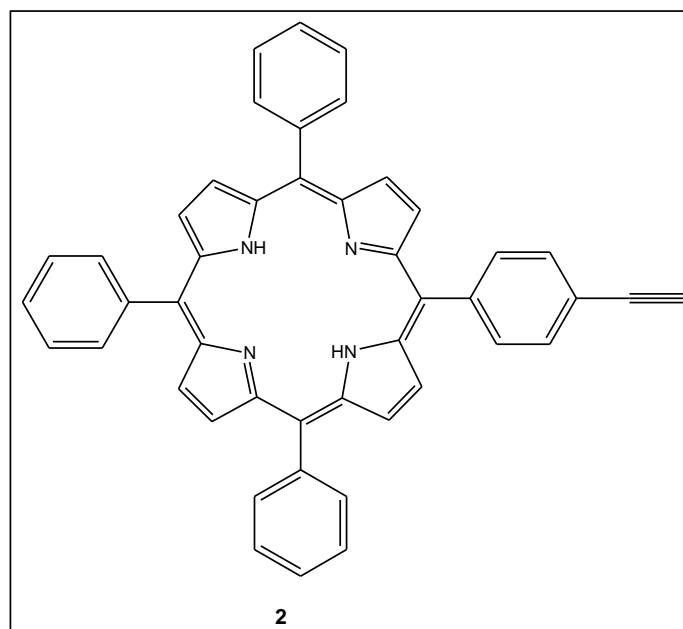


^1H NMR (CDCl_3) d: 1.64 (s, 6H, CH_3), 2.14 (s, 1H, OH), 7.56 (d, $J = 8$ Hz, 2H, Ar), 7.82 (d, $J = 8$ Hz, 2H, Ar), 10.00 (s, 1H, C To a mixture of **A** (6.26 g, 0.033 mol) and benzaldehyde (6.8 mL, 0.066 mol) in refluxing propionic acid (500 mL) was added pyrrole (6.9 mL, 0.1 mol). After refluxing in air for 3 h, the mixture was cooled down and propionic acid removed by vacuum distillation. Upon silica gel chromatography (CH_2Cl_2 /hexane, 10/1), the target compound was isolated as a shiny purple solid (**B**). Yield: 1.53 g (8.8 %).



^1H NMR (CDCl_3) d: -2.71 (s, 2H, NH), 1.81 (s, 6H, CH_3), 7.78 (m, 8H, Ar), 7.86 (m, 3H, Ar), 8.25 (m, 8H, Ar), 8.9 (m, 8H, b-H).

A mixture of **B** (1.3 g, 1.87 mmol) and KOH (280 mg, 5 mmol) in 2-isopropanol (100 mL) was refluxed under N₂ for 16 h. The mixture was then cooled down and concentrated. Upon silica gel column chromatography (CH₂Cl₂/hexane, 1/1), the target compound **2** was isolated as a purple solid. Yield: 1.1 g (90 %).



¹H NMR (CDCl₃) δ: -2.71 (s, 2H, NH), 3.71 (s, 1H, acetylene), 7.80 (m, 8H, Ar), 7.91 (m, 3H, Ar), 8.24 (m, 8H, Ar), 8.89 (m, 8H, b-H).

¹³C NMR (CDCl₃) δ: 78.51, 83.90, 100.73, 119.17, 120.55, 120.66, 121.83, 126.93, 127.98, 130.19, 130.73, 134.70, 134.78, 142.26, 142.31, 143.09.

Synthesis of PE-Por

0.085g of PE-N₃ (2010 g.mol⁻¹, PDI = 1.2, Functionality = 90%) were dissolved in 2.5mL of toluene at 110°C. Simultaneously two flasks containing 183mg of CuBr, 215.9mg of PMDETA and 54.1mg of **2**, were prepared and heated up to 110°C, too. In flask1: CuBr and PMDETA in 1mL of toluene, in flask2: **2** in 1mL of toluene. When heated up to reaction temperature, the content of flask2 has been injected into flask1. This mixture was kept stirring for 1 minute at 10°C and then added drop wise to the PE-N₃ solution. The reaction mixture was kept stirring 40min at 110°C and then allowed to slowly cool back to RT. The purple crystalline product has been precipitated with methanol (900mL), filtered and dried overnight at 40°C under reduced pressure. 0.110g of PE-Por were obtained.

Corresponding FTIR, ^1H and ^{13}C NMR, MALDI-ToF mass spectrometry analyses are given below.

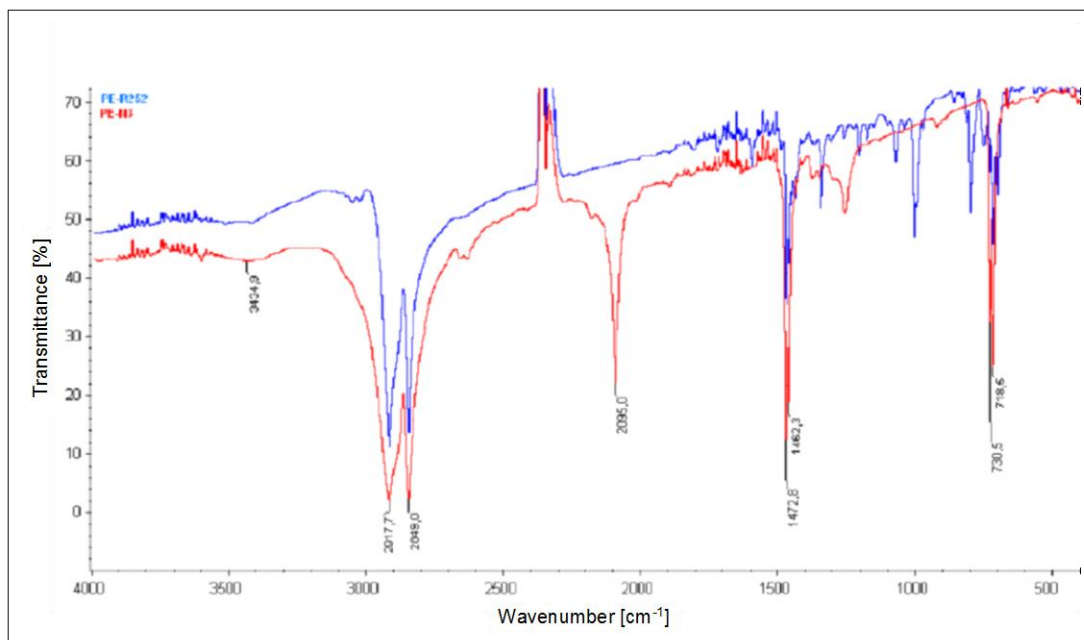


Figure S1: IR spectrum of PE-N₃ 1 (red) and PE-Por (blue).

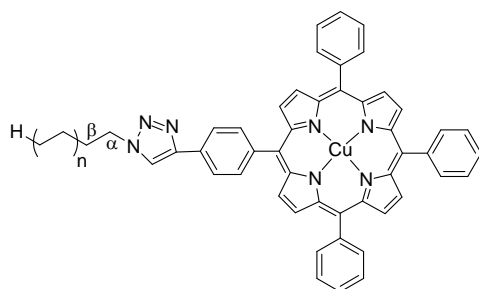
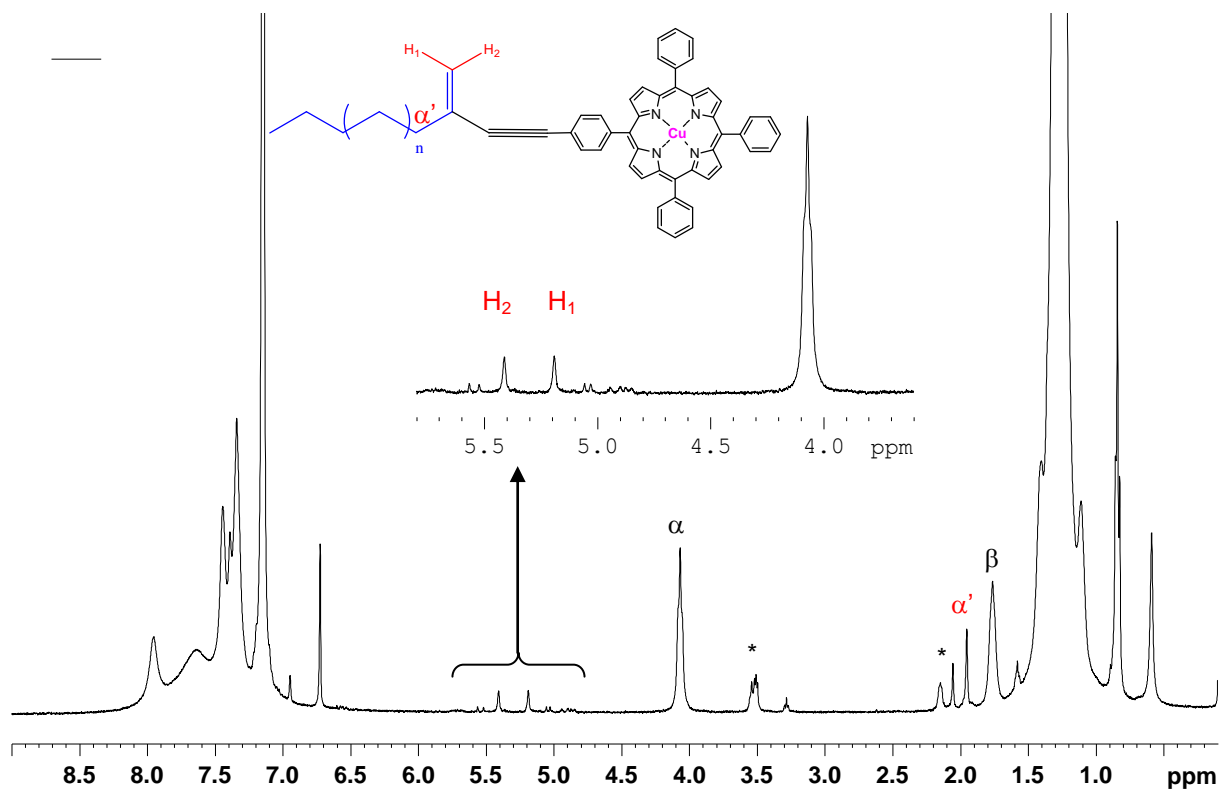
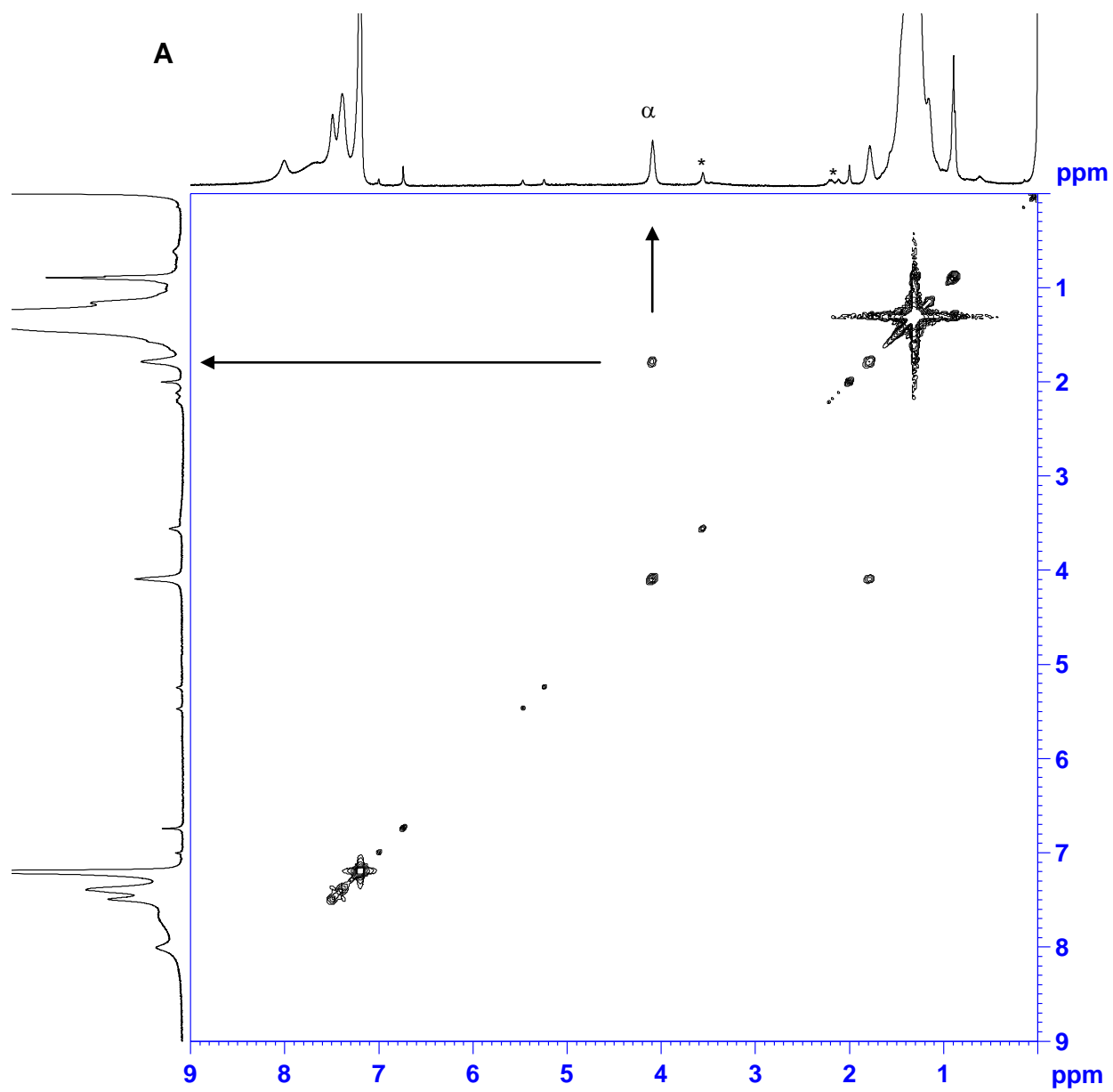


Figure S2: ¹H NMR analysis (400MHz, C₆D₆/TCE:1/2 v/v, 128 scans) of PE-Por. Assignments of the resonances between 5 and 6 ppm to enynes compounds. *: solvent impurities.



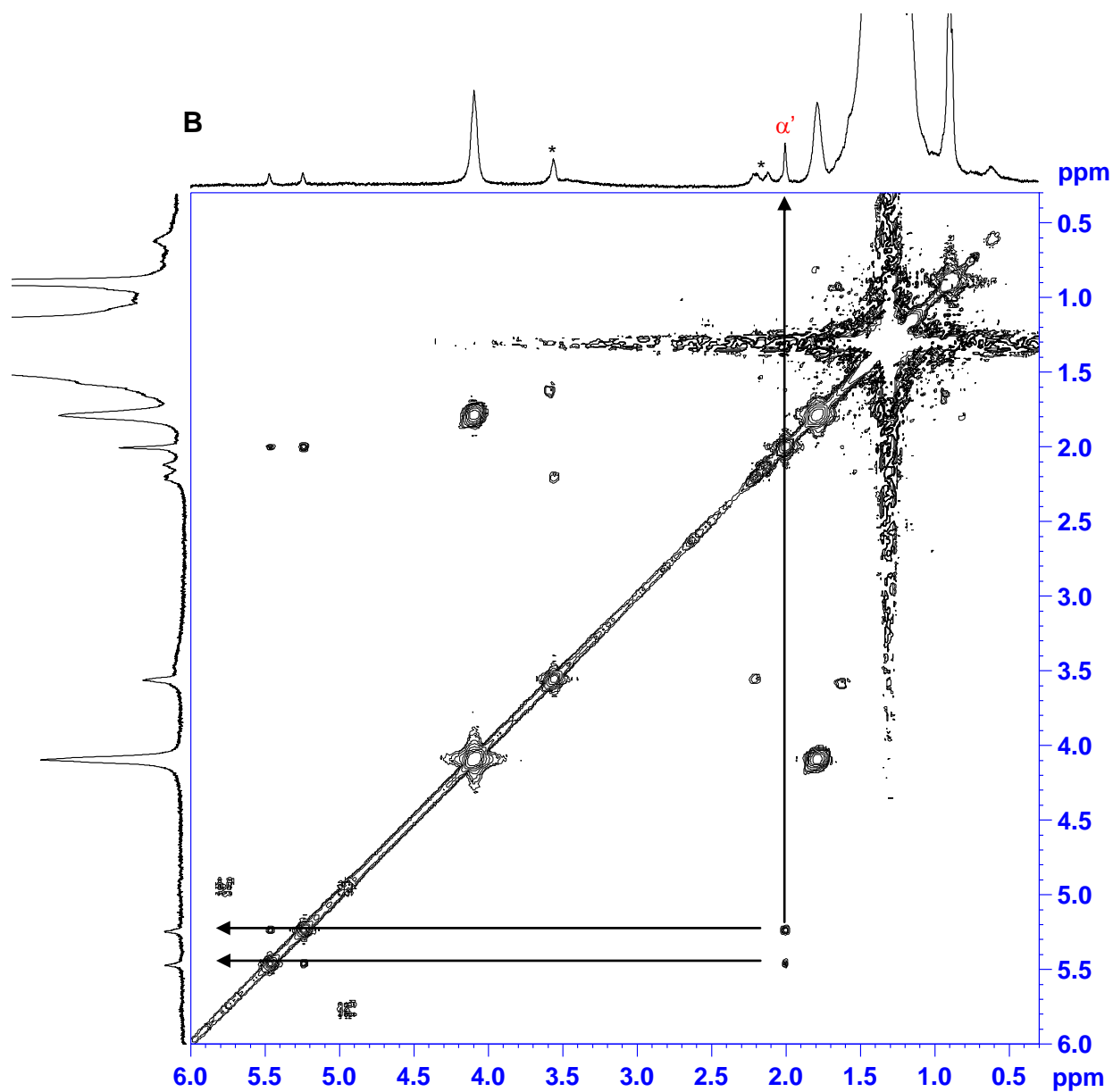
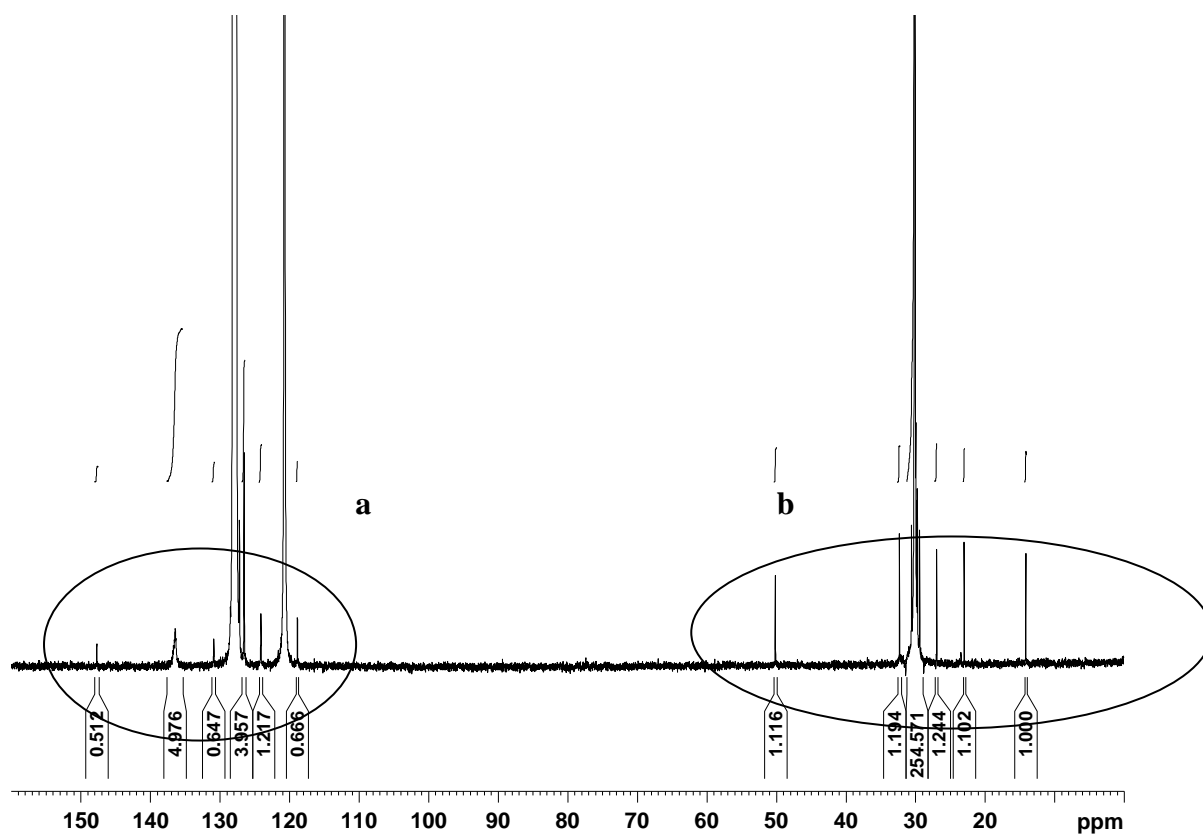
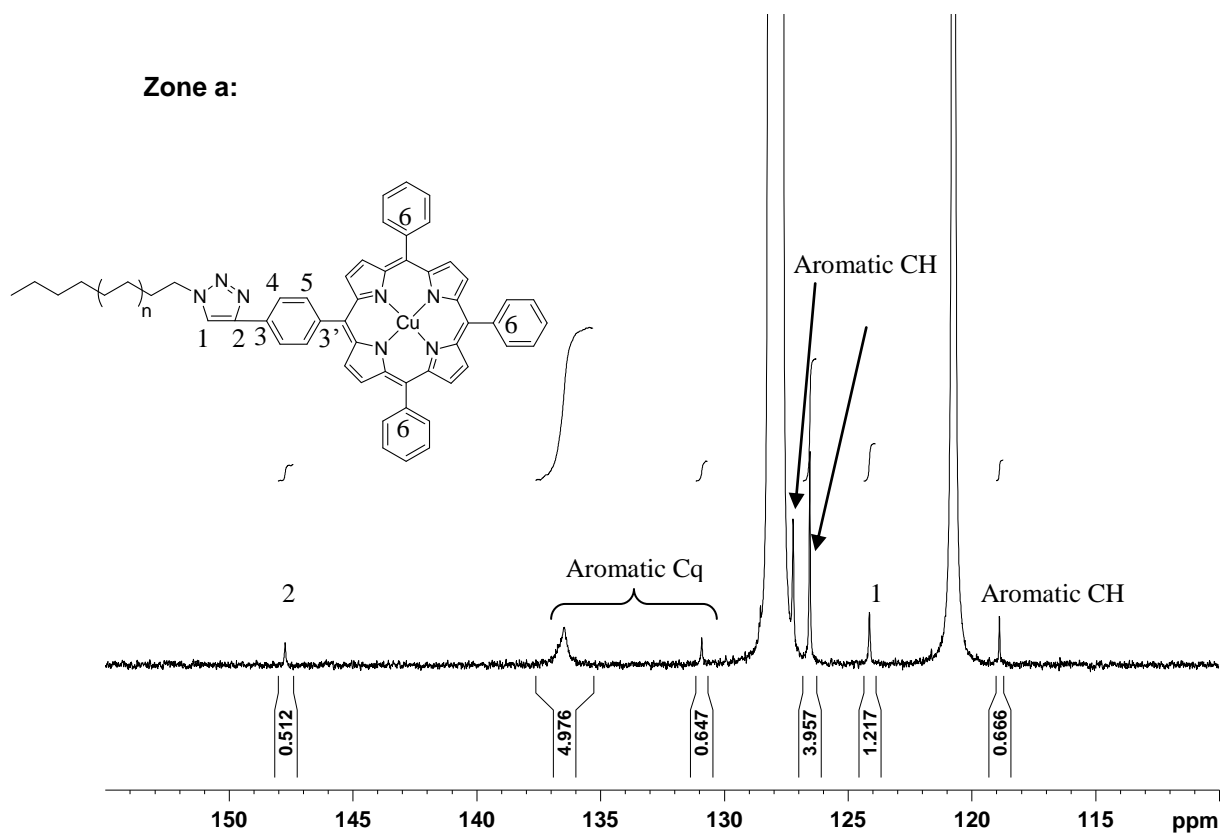


Figure S3: 250 MHz ^1H correlation spectroscopy (COSY) of PE-Por in $\text{C}_6\text{D}_6/\text{TCE}=1:2$ at 90°C , 16 scans. A. Correlation between proton α and the protons of the main chain. B. Correlation between the proton in α position to the enyne and the protons of the main chain. *: solvent impurities.



Zone a:



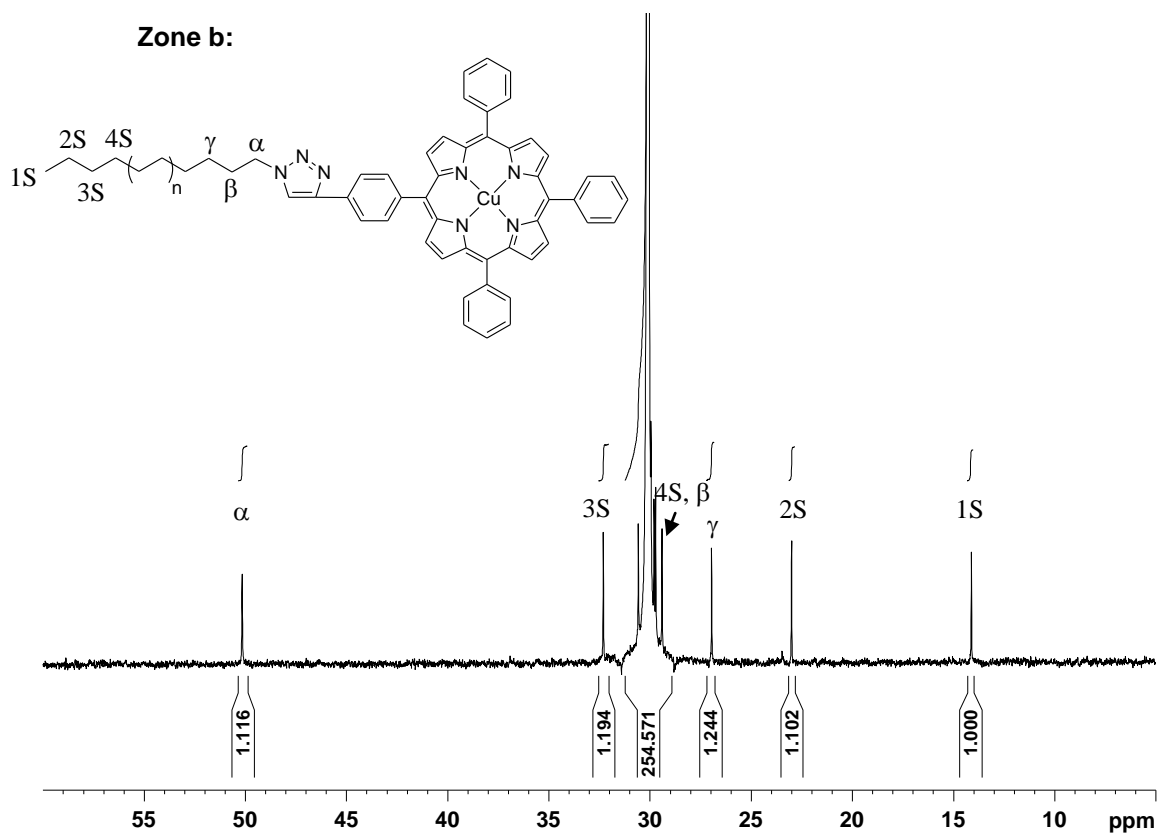


Figure S4: ^{13}C spectrum of PE-Por (100MHz, 6144 scans

in $\text{C}_6\text{D}_6/\text{TCE}=1:2$ (v/v) at 90°C) and corresponding enlargments on zones a and b. Triazolic carbons chemical shifts were based on our previous cycloaddition reactions involving PE- N_3 . In addition, remaining assignments are based on additional DEPT analyses (Figure S5).

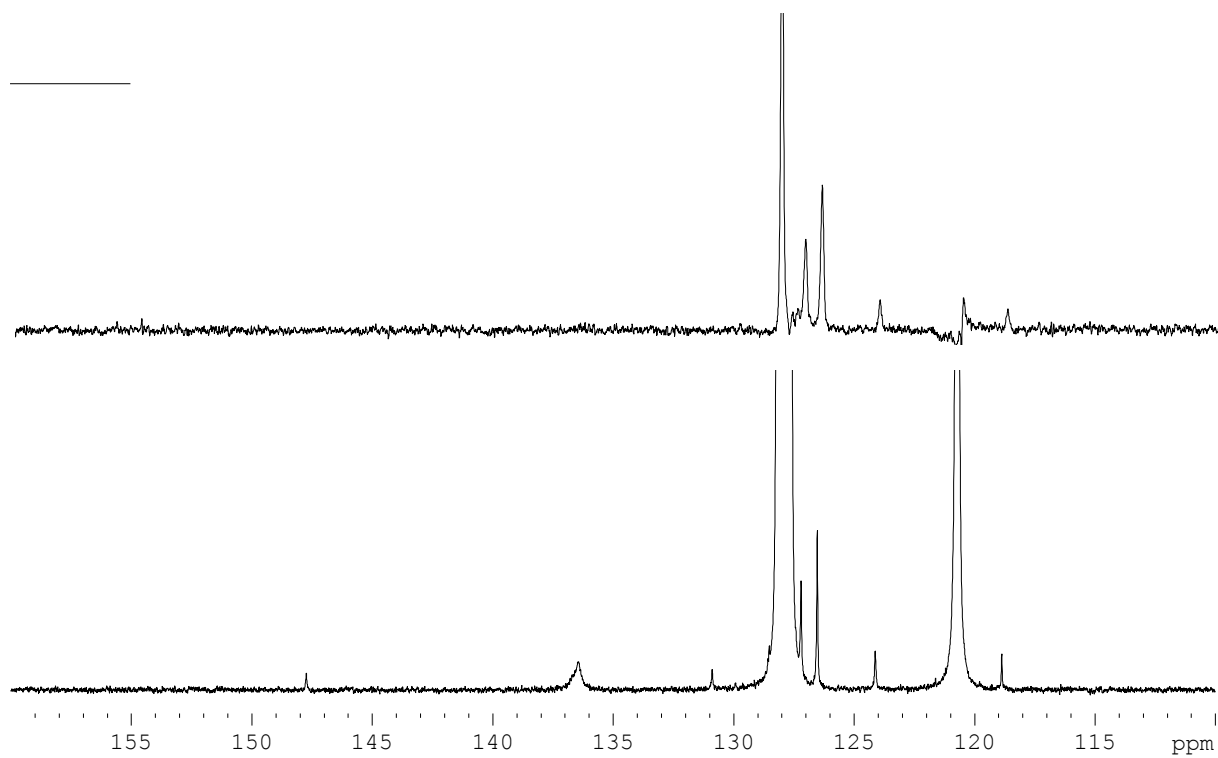


Figure S5: DEPT 135 analyses of of **PE-Por** between 110 and 160 ppm.

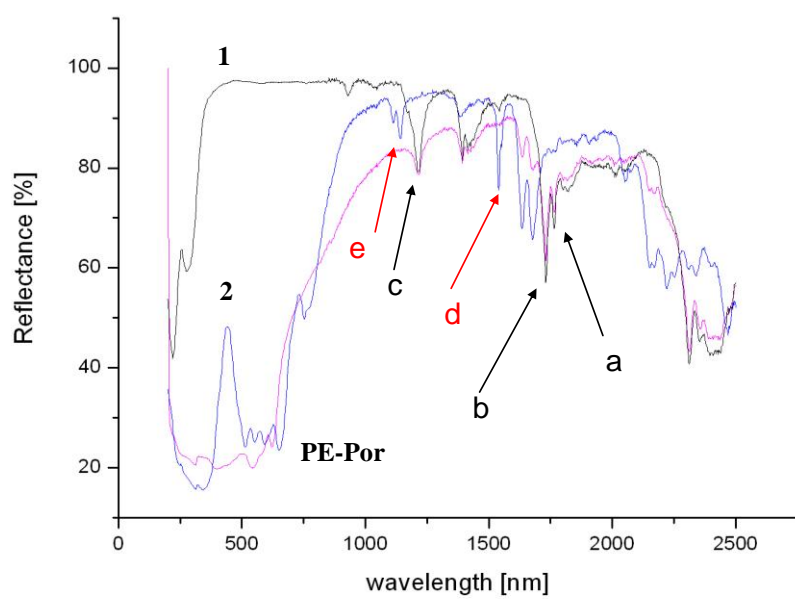


Figure S6: Solid state UV-NIR spectroscopy of **PE-Por**, **2** and **1**

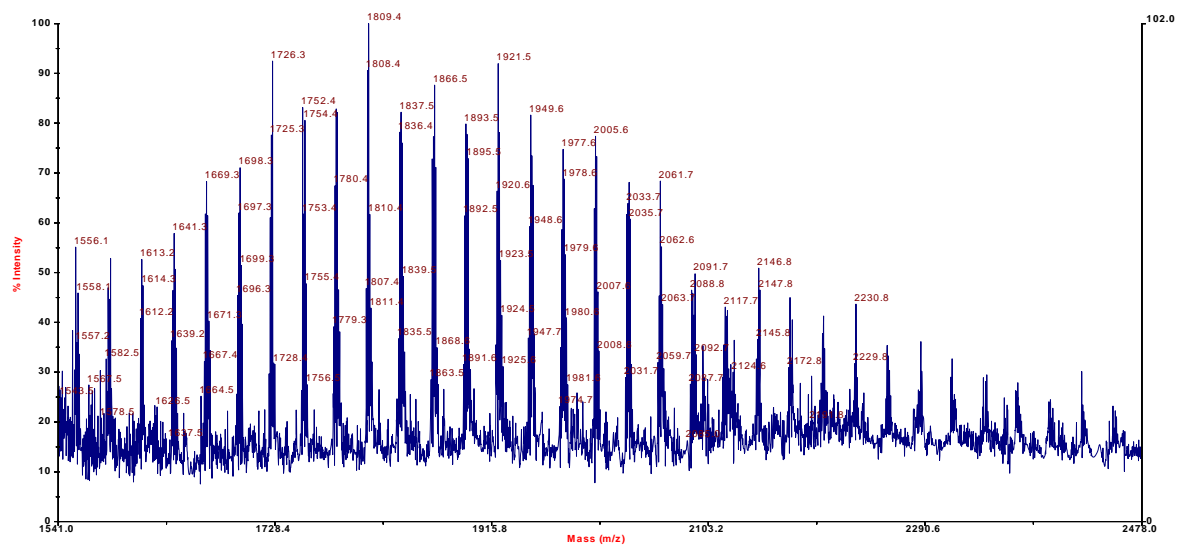


Figure S7: MALDI-ToF mass spectrometry analysis of PE-Por

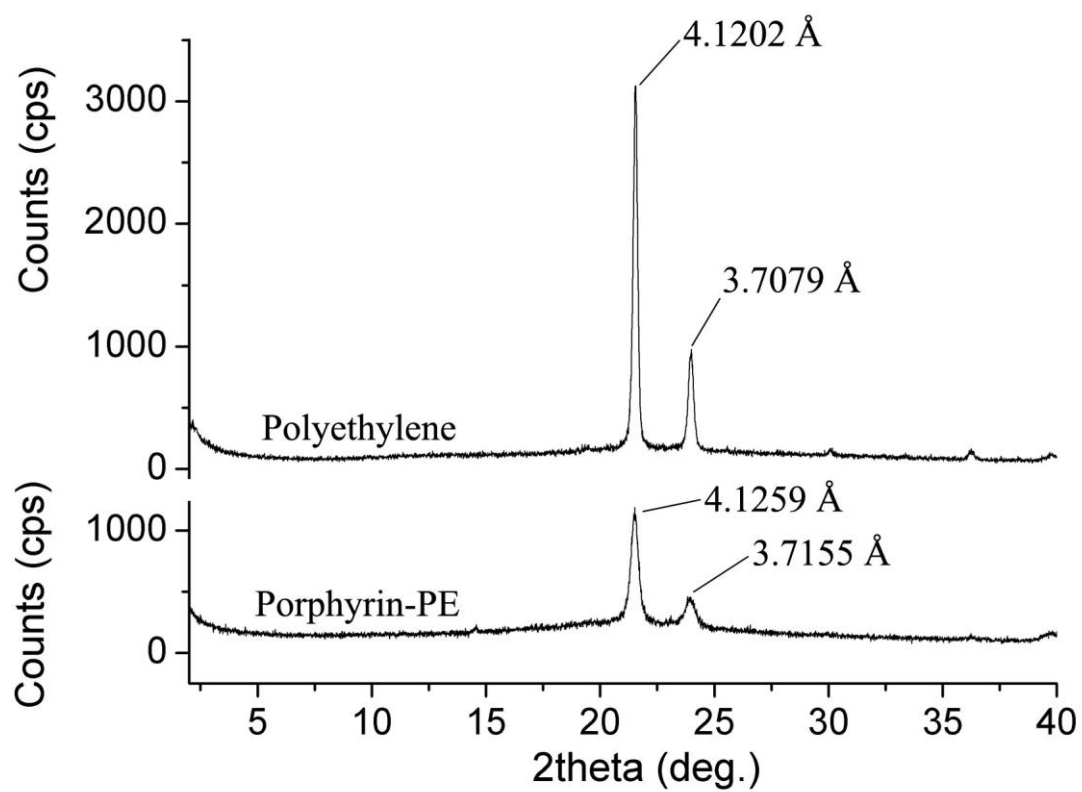


Figure S8: Powder X-ray diffraction data of PE and PE-Por