

Electronic Supplementary Information

Synthesis of macrocyclic poly(ethylene oxide)s containing a protected thiol group: a strategy for decorating gold surfaces with ring polymers

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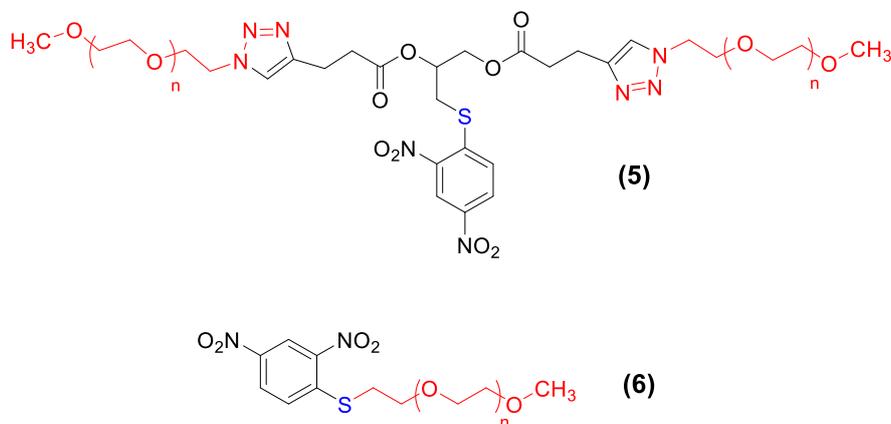
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Synthesis of pSH-2armPEO (Product 5): The reaction route for the synthesis of (5) was chosen similarly to the procedure reported to synthesize pSH-CPEO (4). However, as the target product was not cyclic, dilute concentration was not considered. 1.04 mL of PMDETA (866.5 mg, 5 mmol) was slowly added to a solution of CuBr (0.717 g, 5 mmol) in anhydrous DCM (20 mL) under inert atmosphere and the solution was stirred for 15 min. In a separate flask, a non-stoichiometric solution (1 : 2.4) of (3) (10.86mg, 0.025 mmol) and MeO-PEO-N₃ 1 kg/mol (60 mg, 0.06 mmol) was prepared in 10 mL of anhydrous DCM. The latter solution was added drop by drop to CuBr/ PMDETA, the reaction mixture was stirred at room temperature overnight. The day after the reaction mixture was washed with 2 M solution of ammonium chloride (3 × 60 mL) and the last time with pure water. The solution was dried with MgSO₄, filtered, and concentrated under reduced pressure at 30 °C in a rotary evaporator. The final product (5) was precipitated in hexane. Finally, to remove excess of MeO-PEO-N₃, the product was dissolved in pure water and the obtained solution was dialyzed against milli-Q water for 3 days by using a dialysis membrane with a molecular-weight cutoff of 2000 Da.

Synthesis of pSH-PEO-OMe (Product 6). SH-PEO-OMe 6k (50 mg, 8.3 μmol) and 1-fluoro-2,4-dinitrobenzene (2 mg, 11 μmol) were dissolved in 2 mL of CHCl₃ and the mixture was cooled using ice bath. Triethylamine (5 μL) was slowly added to the reaction mixture under stirring. The ice bath was removed and the reaction was stirred for 17 h at room temperature. The product was purified by precipitation (twice) to cold diethyl ether from chloroform solution and dried in a vacuum oven at 40 °C overnight. Other molecular weight products were obtained in a similar way.



Scheme S1. Chemical structures of pSH-2armPEO (Product 5) and pSH-PEO-OMe (Product 6).

Characterization techniques

Fourier Transform Infrared Spectroscopy. FTIR spectra were measured at room temperature over the range 600–4000 cm⁻¹ in a JASCO 6300 spectrometer using an attenuated-total-reflectance (ATR) stage. Each spectrum was collected with a resolution of 4 cm⁻¹ and an average of 200 repetitive scans. The spectra were neither baseline-corrected nor smoothed.

NMR spectroscopy. ^1H and ^{13}C NMR data were recorded on a Bruker Avance spectrometer at 400 MHz. CDCl_3 or $(\text{CD}_3)_2\text{CO}$ at 25 °C were used as a solvent.

Raman Scattering. Unpolarised Raman scattering measurements were performed at room temperature in a Jasco RFT-6000 system equipped with a semiconductor excitation YAG laser (wavelength 1,064 nm) over the energy-transfer range 100–3200 cm^{-1} (Stokes scattering).

Size Exclusion Chromatography. The molecular weight distribution data were determined by SEC on an Agilent 1200 series HPLC system connected to miniDAWN MALS, and Optilab rEX dRI detectors from Wyatt. All the detectors were at 25 °C. Guard column (PL1110-1120) with specifications: PLgel MIXED, 7.5 x 50 mm, 10 μm , and the main column (PL1110-6100LS) with specifications: PLgel MIXED-B LS, 7.5 x 300 mm, 10 μm , were used for separation. Both columns were kept in a thermostated column compartment at 30 °C. THF, GPC grade provided by Scharlab, S.L with a flow of 1.0 mL/min was used as an eluent. ASTRA software (Wyatt, version 6.1.2.84) was used for data collection and processing.

Matrix-Assisted Laser Desorption Ionization-Time-of-Flight Mass Spectrometry (MALDI-TOF MS). MALDI-TOF MS measurements were performed on a Bruker Autoflex Speed system (Bruker, Germany) equipped with a Smartbeam-II laser (Nd:YAG, 355nm, 2 kHz). Spectra were acquired in linear mode. Each mass spectrum was measured with an average of 5000 shots. The laser power was adjusted during the experiments. Polymer samples were dissolved in THF at a concentration of ~10 mg/ml. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, Sigma-Aldrich) was used as a matrix. The matrix was dissolved in THF at a concentration of 10 mg/ml. Sodium trifluoroacetate (NaTFA) (Fluka) was used as cation donor (~10 mg/ml dissolved in THF). The polymer samples were mixed with the matrix and salt at a 10:1:1 (matrix/polymer/salt) ratio. Approximately 0.5 μL of the obtained mixture were hand spotted on the ground steel target plate.

Spectra were accumulated and processed using FlexControl (v3.4) and FlexAnalysis softwares (v3.4), respectively. Peaks were detected in centroid mode with a signal-to-noise threshold of 4.00 before being processed with a Savitzky-Golay smoothing algorithm (0.05 m/z width, one cycle) and “TopHat” baseline subtraction. External calibration was performed in quadratic mode with a mixture of different polyethylene glycol standards (PEO, Varian).

Fast scanning calorimetry (FSC). FSC experiments were performed in a Flash DSC 1 of Mettler Toledo based on chip calorimetry technology and equipped with a two-stage intracooler allowing for temperature control between -90 and 450 °C. FSC samples were manually placed onto the active area of a chip sensor, and the actual mass was determined by comparing the step in the heat capacity obtained by this technique with the one obtained by conventional DSC. FSC samples of approximately 90 to 140 ng were analyzed. The furnace was constantly flushed with a 20 mL min^{-1} nitrogen gas flow. Thermal properties were characterized upon heating at 1000 K s^{-1} from -80 °C to 80 °C after quenching all samples from 80 °C at the same rate. A reproducibility test was

performed using a second sample for each cyclic and linear polymer. Identical results were therewith obtained. Thermal lag correction and temperature calibration were estimated as described in a previous work.^{S1}

X-ray photoelectron spectroscopy. XPS experiments were performed in a SPECS Sage HR 100 spectrometer with a non-monochromatic X-ray source (Al K α line of 1486.6 eV energy and 300 W), placed perpendicular to the analyzer axis and calibrated using the 3d_{5/2} line of Ag with a full width at half maximum (FWHM) of 1.1 eV. The selected resolution for the spectra was 15 eV of Pass Energy and 0.15 eV/step (0.1 eV/step was used for sulfur). All measurements were made in an ultra-high vacuum (UHV) chamber at a pressure around 8·10⁻⁸ mbar. An electron flood gun was used to neutralize for charging. In the fittings, asymmetric and Gaussian-Lorentzian functions were used (after linear background correction), where the FWHM of all the peaks were constrained and the peak positions and areas were set free. Spin-orbit intensity ratio of the S 2p_{1/2} and 2p_{3/2} components was set to 0.5, and the spin-orbit splitting was kept at 1.2 eV.

Contact angle (CA). The contact angles of water droplets were measured on an OCA 15EC equipment from Dataphysics Instruments GmbH by using static sessile drop method. A syringe dispensed small droplets of 3 μ L at a rate of 0.5 μ L/s for 100 s. The data were evaluated by using the SCA 20 software supplied by Dataphysics Instruments GmbH. Average contact angle values of at least 3 individual measurements and their standard deviation values are provided.

Assignment of ¹³C NMR signals

3-((2,4-dinitrophenyl)thio)propane-1,2-diol (Product 2)

¹³C NMR (101 MHz, Acetone) δ 37.25 (SCH₂CH), 66.09 (CHCH₂OH), 71.10 (CH₂CHOH), 122.02 (NCCH=CN), 127.89 (SC=CHCH), 129.25 (SC=CHCH), 141.10 (SC=CHCH), 145.2 (CHCN).

3-((2,4-dinitrophenyl)thio)propane-1,2-diyl bis(pent-4-ynoate) (Product 3)

¹³C NMR (101 MHz, CDCl₃) δ 14.31 (CH₂C \equiv CH), 32.13 (SCH₂CH), 33.11, 33.18 (CH₂CH₂C \equiv CH), 63.41 (CHCH₂OCO), 69.25 (CH₂CHOCHO), 69.35, 69.50 (C \equiv CH), 81.81, 82.14 (C \equiv CH), 121.84 (NCCH=CN), 127.14 (SC=CHCH), 127.45 (SC=CHCH), 144.35 (SC=CHCH), 144.71 (CNO₂), 171.10, 171.22 (CH₂C=O).

Supplementary figures

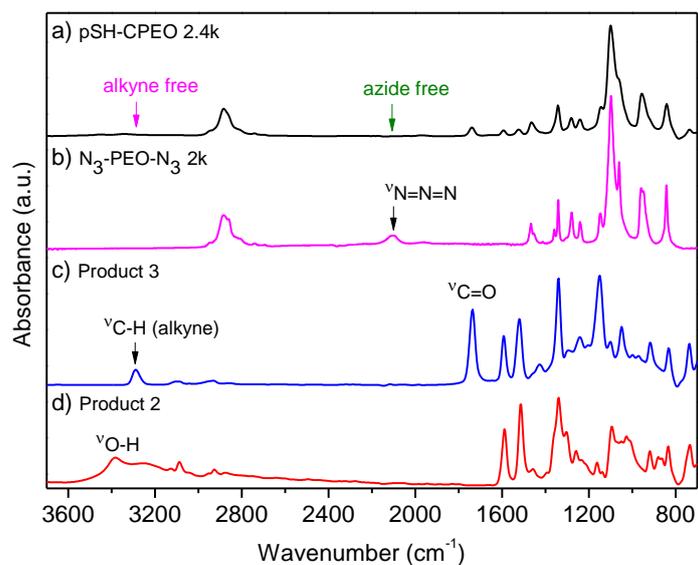


Figure S1. FTIR spectra of the different products involved in the synthesis of SH-CPEO samples.

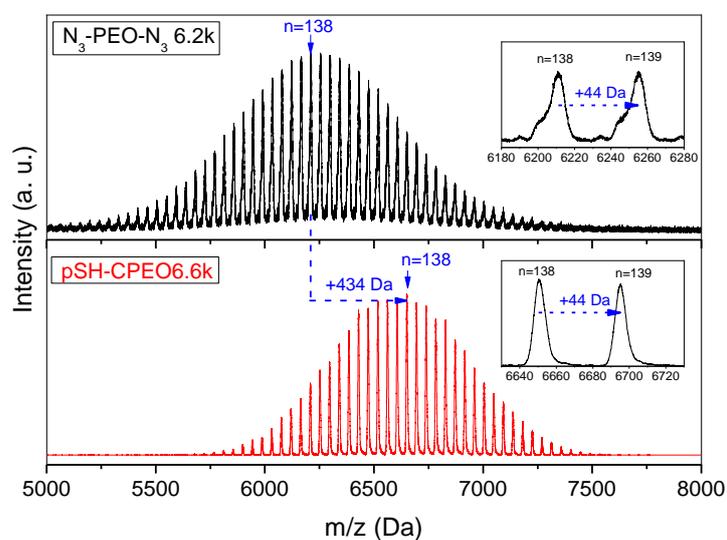


Figure S2. MALDI-TOF MS data of N_3 -PEO- N_3 6.2k and pSH-CPEO6.6k. The mass shift of +434 Da corresponds to the mass of one (3) moiety, and that of +44 Da to the ethylene oxide monomer unit. Cation: Na^+ .

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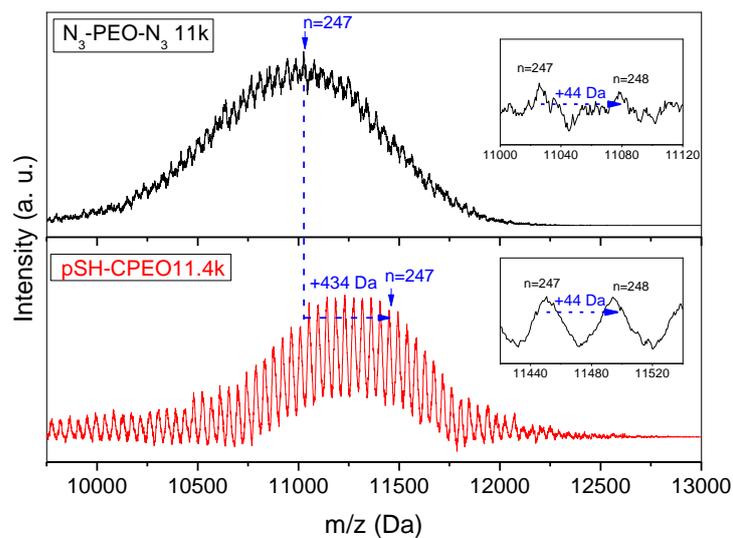


Figure S3. MALDI-TOF MS data of N_3 -PEO- N_3 11k and pSH-CPEO11.4k. The mass shift of +434 Da corresponds to the mass of one (3) moiety, and that of +44 Da to the ethylene oxide monomer unit. Cation: Na^+ .

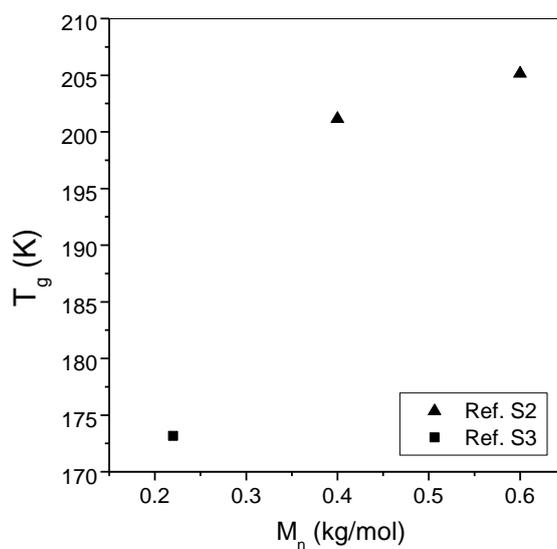


Figure S4. Glass transition temperatures of cyclic PEO of low molecular weight obtained from Ref. S2 and Ref. S3. The data was obtained by fast cooling and heating at $10\text{ }^\circ\text{C}/\text{min}$ in a differential scanning calorimetry equipment.

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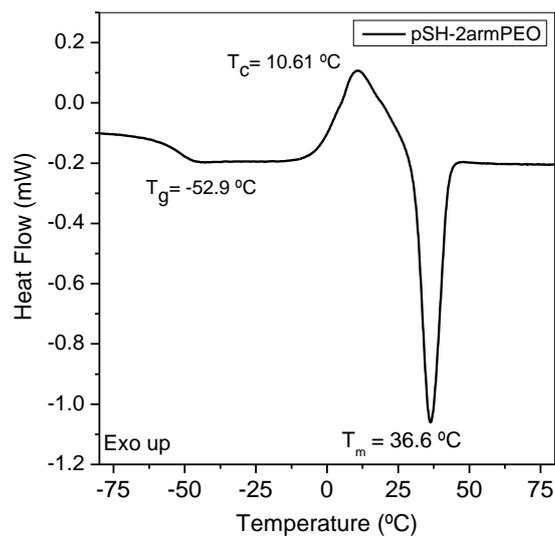


Figure S5. FSC data of pSH-2armPEO of $M_n = 2.4$ kg/mol. Cooling and heating rates: 1000 K s^{-1} .

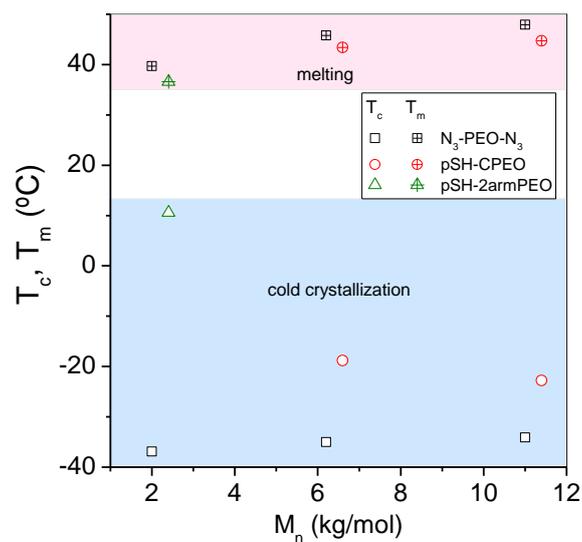


Figure S6. Cold crystallization and melting temperatures for N_3 -PEO- N_3 , pSH-CPEO and pSH-2armPEO samples obtained by FSC. All measurements were performed at cooling and heating rates of 1000 K s^{-1} .

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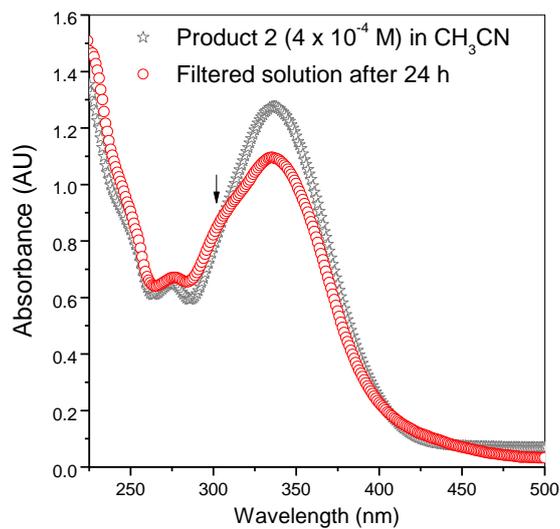


Figure S7. UV-Vis spectra of Product 2 in acetonitrile before and after reaction with gold substrates.

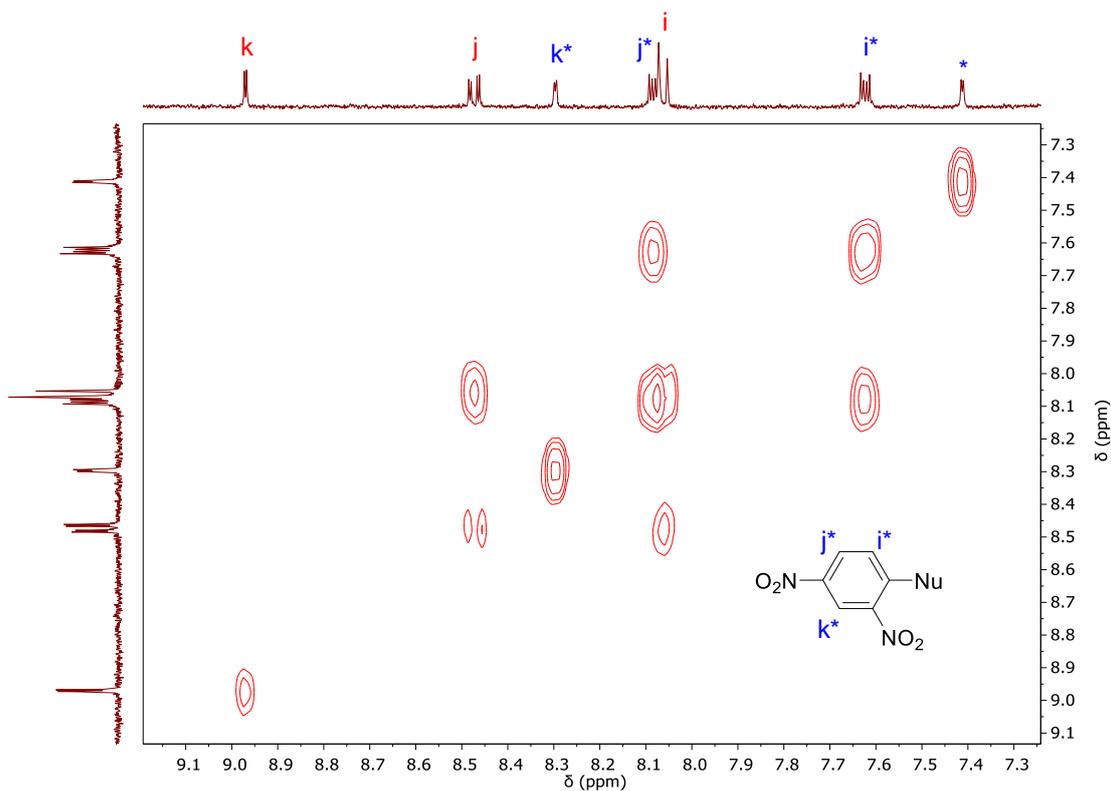


Figure S8. COSY spectrum (acetone- d_6) of product 2 after reaction with gold metal pieces in acetonitrile for 24 h. Suggested structure containing a 2,4-dinitrobenzene moiety.

X-ray photoelectron spectroscopy resultsTable S1. Peak position of the S 2p_{3/2} components.

Sample	Fitted S 2p _{3/2} position	
	S-C (eV) [at%]	S-Au (eV) [at%]
pSH-CPEO6.6k	163.5 [100]	-
pSH-CPEO6.6k / Au	164.2 [40]	162.5 [60]
pSH-PEO-OMe6.2k	163.8	-
pSH-PEO-OMe6.2k / Au	163.8 [30]	161.9 [70]
SH-PEO-OMe6k / Au	163.8 [45]	162.1 [55]

References

- S1. X. Monnier, A. Saiter and E. Dargent, *Thermochim. Acta*, 2017, **658**, 47-54.
S2. S. Singla and H. W. Beckham, *Macromolecules*, 2008, **41**, 9784-9792.
S3. F. Barroso-Bujans and A. Alegria, *Phys. Chem. Chem. Phys.*, 2017, **19**, 18366-18371.