Supporting Information

Spin Fluorescence Silencing Enables an Efficient Thermally Driven Self-Reporting Release System

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Content

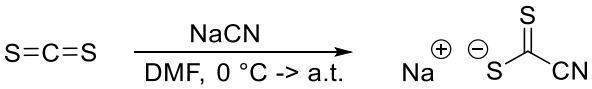
A. Experimental Procedures:

A.1 Chemicals

Azobisisobutyronitrile (AIBN, Sigma-Aldrich) was recrystallized from ethanol prior to use. 2-hydroxyethyl methacrylate (HEMA, Sigma-Aldrich, stabilized with <50 ppm monomethyl ether hydroquinone, >99 %) was passed through a short column of basic alumina and stored at 0 °C prior to use.

Acetic acid (Roth, >99.8 %), acetonitrile (VWR, 99.5 %), anisole (Acros, 99 %), bromoacetyl bromide (Alfa Aesar, 98 %), 11-bromoundecane-1-ol (Alfa Aesar, 97 %), carbon disulphide (Sigma-Aldrich , >99.9 %), cyclohexane (VWR, >99 %), 4-*N*,*N*-dimethyl aminopyridine (DMAP, Sigma-Aldrich, >99 %), dichloromethane (VWR, 99.8 %, stabilized with ethanol), dimethyl formamide (VWR, 100 %), diethyl ether (Fisher Scientific, >99 %), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC*HCl, Roth, > 99 %), ethyl acetate (VWR, >99.5 %), ethyl sorbate (Alfa Aesar, 98 %), hydrochloric acid (Roth, 37 %), isopropanol (Roth, >99.8 %), *meta*-chloroperbenzoic acid (Acros, 70-75 %) pyrene acetic acid (Sigma-Aldrich, 97 %), sodium bicarbonate (Roth, >99 %), sodium chloride (Roth, >99,8 %), sodium cyanide (Sigma-Aldrich, 97 %), sodium cyclopentadiene (ABCR, 2-3 M in THF), sodium disulphate (Roth, >99 %), tetrahydrofuran (VWR, 99.7 %), 2,2-6,6-tetramethyl piperidine methacrylate (ABCR, 98 %), toluene (Acros, >99.8 %), triethylamine (Acros, 99.7 %) were all used as received.

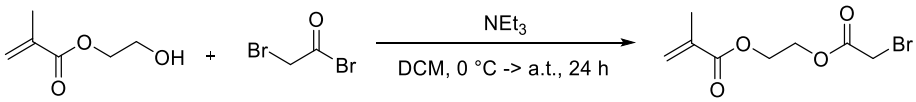
A.2 Synthesis of sodium carbonocyanidodithioate (NaCDTE)



The target compound was synthesised according to literature.[1] 5.46 g Sodium cyanide (111 mmol, 1.10 eq.) were suspended in 20 mL DMF in a 250 mL two-necked round bottom flask and cooled to 0 °C. A solution of 7.75 g carbon disulphide (102 mmol, 1.00 eq.) in DMF (13 mL) was added dropwise. The reaction mixture was allowed to warm to ambient temperature and the brown solution was stirred until complete solidification. After the addition of isopropyl alcohol (150 mL), the precipitate was dissolved again by heating to 90 °C. The warm suspension was filtered to remove unreacted sodium cyanide and the filtrate was cooled with liquid nitrogen. The precipitated solid was filtered and thoroughly washed

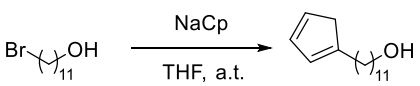
with diethyl ether. The crude product was recrystallized from an isopropanol/diethyl ether mixture (1:1) to yield the final product as a brown solid (7.38 g, 59.0 mmol, 58 %). The final product was used without further characterization.

A.3 Synthesis of 2-(2-Bromoacetoxy) ethyl methacrylate



The target compound was synthesized according to literature.[1] In a round bottom flask, 4.7 mL hydroxyethyl methacrylate (38.4 mmol, 1.00 eq.) and 8 mL triethylamine (57.6 mmol, 1.50 eq.) were dissolved in 50 mL dry DCM under argon atmosphere. The reaction mixture was cooled to 0 °C and bromoacetyl bromide 4 mL (46.2 mmol, 1.20 eq.) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. The reaction was quenched by pouring into water (100 mL). The phases were separated and the aqueous phase was extracted with DCM (2×80 mL). The combined organic layers were washed with water (2×100 mL), 1 M hydrochloric acid solution (3×50 ml) and saturated sodium bicarbonate solution (3×50 mL) and dried over Na_2SO_4. The removal of the solvent under reduced pressure afforded a brown liquid as the crude product, which required further purification by column chromatography with cyclohexane/ethyl acetate (5:1) as the eluent. The product was obtained as a yellow liquid (5.4 g, 21.5 mmol, 56 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.07 (dq, J = 1.9, 1.0 Hz, 1H, C=C***H***), 5.54 (p, J = 1.6 Hz, 1H, C=C***H***), 4.39-4.28 (m, 4H, OC***H₂***C***H₂***O), 3.79 (s, 2H, C***H₂***Br), 1.88 (dd, J = 1.6, 1.0 Hz, 3H, C***H₃***). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 167.07, 167.01, 135.78, 126.26, 63.77, 61.97, 25.46, 18.24.

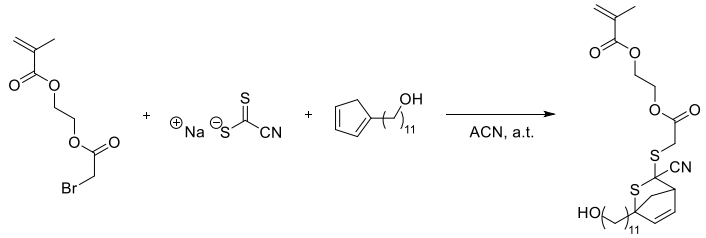
A.4 Synthesis of 11-(cyclopenta-1,3-dien-1-yl) undecan-1-ol



The target compound was synthesized according to the modified literature procedure.[2] In a round bottom flask, 3.00 g 1-Bromoundecanol (12 mmol, 1.00 eq.) were dissolved in 60 mL dry THF under inert atmosphere. The solution was cooled to 0 °C and subsequently 10 mL of a 2-3 M sodium cyclopentadiene solution in THF (2.1 g, 24 mmol, 1.20 eq.) were added in a

dropwise manner. The reaction was stirred overnight at ambient temperature. The obtained solids were filtered of and the filtrate was evaporated. The residue was re-dissolved in DCM, and was washed with water (2×50 mL) and saturated $NaHCO_3$ solution (2×50 mL). The organic layer was dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified via column chromatography (silica, CH/EE, 2:1). The product was obtained as a viscous, yellow oil (1.7 g, 7.19 mmol, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.40–6.31 (m, 1H, Cp-***H***), 6.20-6.15 (m, 1H, Cp-***H***), 6.09-6.05 (m, 1H, Cp-***H***), 5.94-5.90 (m, 1H, Cp-***H***), 3.57 (t, J = 6.6 Hz, 2H, C***H₂***-OH), 2.84 (dq, J = 29.3, 1.5 Hz, 2H, Cp-***2H***), 2.36-2.24 (m, 4H, Cp-C***H₂***-C***H₂***), 1.55-1.39 (m, 2H, C***H₂***-CH_2-OH), 1.33-1.14 (m, 14H, -$(CH_2)_7$-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 150.06, 147.20, 134.62, 133.33, 132.23, 130.11, 125.87, 125.43, 62.79, 43.03, 40.97, 32.59, 30.53, 29.67, 29.57, 29.45, 29.39, 29.31, 29.27, 29.24, 28.68, 27.32, 25.55.

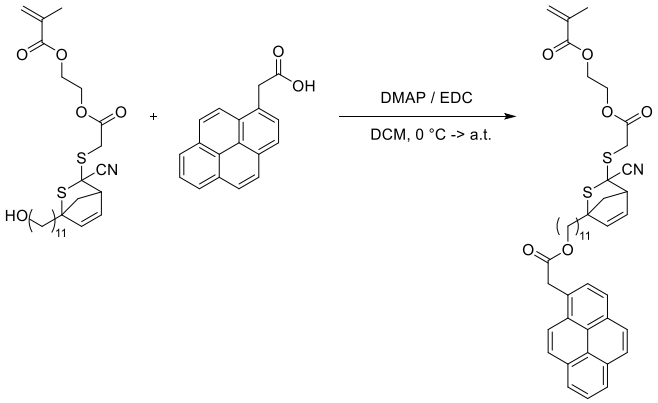
A.5 Synthesis of MMAHDAOH



The synthesis was performed according to literature.[1] In a round bottom flask, 1.50 g bromoacetoxy ethyl methacrylate (6 mmol, 1.00 eq.) and 1.70 g 11-cyclopentadienyl undecanol (7.2 mmol, 1.20 eq.) were dissolved in 75 mL dry acetonitrile under inert atmosphere. 750 mg sodium carbonocyanidodithioate (6 mmol, 1.00 eq.) were dissolved in 5 mL dry acetonitrile and were added in a dropwise manner to the solution. Subsequently the reaction was stirred overnight at ambient temperature. The solids were filtered of and the filtrate was evaporated. The residue was redissolved in DCM, and was washed with saturated $NaHCO_3$ solution and water (3×50 mL). The organic layer was dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified by column chromatography (silica, CH/EE, 2:1). The pure product was obtained as a viscous, yellow oil (1.07 g, 2.1 mmol, 35 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.57 (d, J = 5.5 Hz, 0.5H, HC=C***H*** (HDA)), 6.40 (d, J = 5.4 Hz, 0.5H, ***H***C=CH (HDA)), 6.15-6.10 (m, 1,5H, HC=C***H*** (HDA) + C=C***H₂***), 6.04 (dd, J = 5.4, 3.2 Hz, 0.5H, ***H***C=CH (HDA)), 5.59 (t, J = 1.6 Hz, 1H, C=C***H₂***), 4.48-4.34 (m, 4H, O-C***H₂***-C***H₂***-O), 3.71 (s, 2H, C***H₂***-S), 3.62 (td, J = 6.6, 1.1 Hz, 2H, C***H₂***-OH), 3.77-3.52

(m, 4H, C=CH-C***H₂*** (HDA) + C-C***H₂***-CH_2 (HDA)), 2.22 (q, J = 14.8, 7.5, 1.7 Hz, 2H, C***H₂***), 1.94 (t, J = 1.3 Hz, 3H, C***H₃***), 1.85-1.72 (m, 2H, C***H₂***), 1.6-1.38 (m, 2H, C***H₂***), 1.30-1.21 (m, 14H, C**H₂**). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 168.90, 166.89, 157.03, 153.82, 144.53, 141.55, 135.63, 130.88, 126.10, 123.77, 122.77, 63.31, 62.87, 61.93, 36.04, 32.61, 29.71, 29.52, 29.47, 29.41, 29.32, 29.20, 29.17, 29.09, 28.53, 27.07, 26.73, 25.56, 18.11. HR ESI-MS: $[M+Na]^+$, $[C_{26}H_{39}NNaO_5S_2]^+$, calculated: 532.2168 *m/z*, found: 532.2168 *m/z.*

A.6 Synthesis of MMAHDAPy



In a round bottom flask, 662 mg pyrene acetic acid (2.5 mmol, 1.20 eq.), 128 mg DMAP (1.05 mmol, 0.50 eq.) and 1.2 g EDC*HCl (6.3 mmol, 3.00 eq.) were dissolved in 100 mL dry DCM under inert atmosphere and cooled to 0 °C. 1.07 g MMAHDAOH (2.1 mmol, 1.00 eq.) dissolved in 5 mL dry DCM was added in a dropwise manner. The mixture was allowed to warm to ambient temperature and was stirred overnight. The solution was washed with saturated $NaHCO_3$ solution (3×50 mL), 1 M HCl (3×50 mL) and water/brine (3×50 mL). The organic layer was dried over $NaSO_4$ and the solvent was removed. The crude product was purified by flash chromatography. The pure product was obtained as a highly viscous, yellow oil (250 mg, 0.33 mmol, 16 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.30-7.93 (m, 9H, Py-***H***), 6.57 (d, J = 5.5 Hz, 0.5H, HC=C***H*** (HDA)), 6.41 (d, J = 5.4 Hz, 0.5H, ***H***C=CH (HDA)), 6.16-6.11 (m, 1,5H, HC=C***H*** (HDA) + C=C***H₂***), 6.05 (dd, J = 5.4, 3.2 Hz, 0.5H, ***H***C=CH (HDA)), 5.60 (t, J = 1.6 Hz, 1H, C=C***H₂***), 4.46-4.36 (m, 4H, O-C***H₂***-C***H₂***-O), 4,34 (s, 2H, Py-C***H₂***), 4.09 (t, J = 6.6 Hz, 2H, C***H₂***), 3.71 (s, 2H, C***H₂***-S), 3.66 (td, J = 6.6, 1.1 Hz, 2H, C***H₂***-OH), 3.82-3.53 (m, 4H, C=CH-C***H₂*** (HDA) + C-C***H₂***-CH_2 (HDA)), 2.21 (q, J = 14.8, 7.5, 1.7 Hz, 2H, C***H₂***), 1.95 (t, J = 1.3 Hz, 3H, C***H₃***), 1.85-1.72 (m, 2H, C***H₂***), 1.6-1.38 (m, 2H, C***H₂***), 1.30-1.21 (m, 14H, C**H₂**). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 168.90, 166.89, 157.03, 153.82, 144.53, 141.55, 135.63, 130.88, 130.61, 129.25, 128.18, 127.66,

127.22, 127.06, 126.10, 125.77, 125.05, 124.89, 124.66, 123.77, 122.77, 63.31, 62.87, 61.93, 36.04, 32.61, 29.71, 29.52, 29.47, 29.41, 29.32, 29.20, 29.17, 29.09, 28.53, 27.07, 26.73, 25.56, 18.11. HR ESI-MS: $[M+Na]^+$, $[C_{44}H_{49}NNaO_6S_2]^+$, calculated: 774.2899 *m/z*, found: 774.2874 *m/z*.

A.7 Procedure for the Free Radical Polymerization to Afford P1

The procedure was adapted from literature.[3] In a round bottom flask, the monomers **TMPM** and **MMAHDAPy** (in total 1.00 eq.) were dissolved in acetic acid in the desired ratio (5 mL solvent per 100 mg total amount of monomer). AIBN was added (0.05 eq.), and the solution was purged with argon for 30 min. The polymerizations were conducted at 60 °C for 19 h. The reaction was quenched by exposing to air and cooling to ambient temperature. The polymer **P1** was obtained by precipitation in ice cold ethyl ether several times and drying under high vacuum (yield: 50 mg, 50 %)

A.8 Procedure for the Oxidation of P1 to P2

The procedure was adapted from literature.[3] 25 mg polymer (0.0025 mmol, 1.00 eq.) were dissolved in 4 mL dry DCM and cooled to 0 °C. 31 mg mCPBA (0.18 mmol, 75.00 eq.) were dissolved in 1 mL dry DCM and added in a dropwise manner. The reaction mixture was stirred for additional 3 h, subsequently the volume was reduced to 2 mL under inert gas flow. The polymer **P2** was recovered as a red powder by repetitive precipitation in ice cold diethyl ether.

A.9 Procedure for the Cycloreversion to Afford P3

The reaction was performed according to a modified literature procedure.[1] 15 mg polymer (450 nmol, 1.00 eq.) and 10 µL ethyl sorbate (9.5 mg, 0.068 mmol, 5.00 eq.) were dissolved in 4 mL anisole in an aluminum foil wrapped flask. The solution was purged with inert gas for 30 min. The reaction was conducted at 90 °C for 50 h. Samples were withdrawn after 2, 4, 6 and 50 h of reaction time, and further analyzed by fluorescence spectroscopy. The polymer **P3** was recovered by precipitation in ice cold diethyl ether.

B. Measurements and Analysis

B.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR analysis was conducted on a Bruker Ascend instrument (400MHz). All chemical shifts are reported in ppm (δ) and calibrated on characteristic solvent signals (i.e. deuterated

chloroform ($CDCl_3$) and methanol ($MeOH\text{-}d_4$)) as internal standards. All NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q =quartet), coupling constant(s) in Hertz (Hz) and integration. Multiplets (m) were reported over the range (ppm) where they appeared at the indicated field strength.

B.2 Size Exclusion Chromatography (SEC)

The apparent number average molar mass (M_n) and the molar mass distribution [$Đ$ (polydispersity index) = M_w/M_n] values of the polymers were determined using SEC measurements on a Polymer Laboratories PL-GPC 50 Plus Integrated System. The instrument is comprised of an autosampler, a PLgel 5 μm bead-size guard column (50 × 7.5 mm), which is followed by three PLgel 5 μm Mixed-C columns and one PLgel 3 μm Mixed-E column (300 × 7.5 mm), and a differential refractive index detector. The measurements were conducted with a flow rate of 1 mL/min at 50 °C using DMAc (+0.3 % LiBr) as the eluent. The calibration was carried out by employing different linear poly(styrene) standards ranging from 476 to 2.5×10^6 g mol^{-1}. The polymer samples were dissolved at a concentration of 2 mg mL^{-1} in aforementioned eluent and filtered over a 0.2 μL filter prior to the measurement.

B.3 Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR)

All IR measurements were performed on a Bruker Alpha ATR-IR Spectrometer with a range of 500 to 4000 cm^{-1} at ambient temperature.

B.4 Dynamic Light Scattering (DLS)

The apparent hydrodynamic diameters ($D_{h,app}$) were determined at 25 °C by means of a dynamic light scattering (DLS) analysis using a Zetasizer Nano ZS light scattering apparatus (Malvern Instruments, UK) equipped with He-Ne laser (at a wavelength of 633 nm, 4 mW). The Nano ZS instrument incorporates a non-invasive backscattering (NIBS) optic with a detection angle of 173°. The polymer samples were dissolved at a concentration of 2 mg/mL in DMAc (+0.3 % LiBr) and filtered into quartz cuvettes over a 0.2 μL filter prior to the measurement. The prepared samples were stabilized for 30 min prior to DLS analysis at ambient temperature. All values of the apparent hydrodynamic diameter for each polymer mixture were averaged over three measurements (60 runs/measurement), and were automatically provided by the instrument using a cumulative analysis.

B.5 High-Resolution Electrospray Ionization Mass Spectrometry (ESI-MS)

ESI-MS spectra were recorded on a Q Exactive (Orbitrap) mass spectrometer (ThermoFisher Scientific, San Jose, CA, USA) equipped with a HESI II probe. The instrument was calibrated in the *m/z* range of 74-1822 by using a S2 premixed standard containing caffeine, Met-Arg-Phe-Ala acetate (MRFA) and a mixture of fluorinated phosphazenes (Ultramark 1621). A constant spray voltage of 4.6 kV and a dimensionless sweep gas flow rate of 5 were applied. The capillary temperature and the S-lens RF level were set to 320 °C and 62.0, respectively. The samples were dissolved in a mixture of THF and MeOH (3:1) containing 100 µmol sodium trifluoracetate (NaTFA). Finally, the samples were infused with a flow rate of 5 μL min^{-1}.

B.6 Flash Chromatography

Flash chromatography was performed on an Isolera Biotage One (OS 578). The fractions were collected via an ultraviolet detector (254 nm). A SNAP Ultra (10 g) cartridge was employed for the purification in direct mode and a SNAP C18 (12 g) cartridge for the reverse mode (both column volume of 15 mL). The analyte was dried on an adapted short pre-column before purification.

B.7 Fluorescence Spectroscopy

Fluorescence emission spectra were recorded on a Varian Cary Eclipse fluorescence spectrometer, using quartz cuvettes loaded with 400 µL of sample. An excitation wavelength of 344 nm (slit 2.5 nm) was used and the emission was recorded from 350 to 800 nm (slit 10 nm).

B.8 Ultraviolet/Visible light (UV/Vis) Spectroscopy

The UV / Vis spectra were recorded on a Cary 100 UV-Visible Spectrophotometer (Agilent Technologies, USA) equipped with a tungsten halogen light source (190 to 900 nm, accuracy +/- 2 nm) and a R928 PMT detector. The analysis was performed at ambient temperature.

B.9 Electron Paramagnetic Resonance (EPR) Spectroscopy

Electron paramagnetic resonance (EPR) spectroscopy was performed on a Magnettech MiniScope MS400 spectrometer. All samples were recorded in chloroform.

B.10 Refractometer

The Refractive Index was measured on an Exacta Optech Mod. RMI at 20 °C and 25 °C.

C. Additional Data and Figures

C.1 NMR data

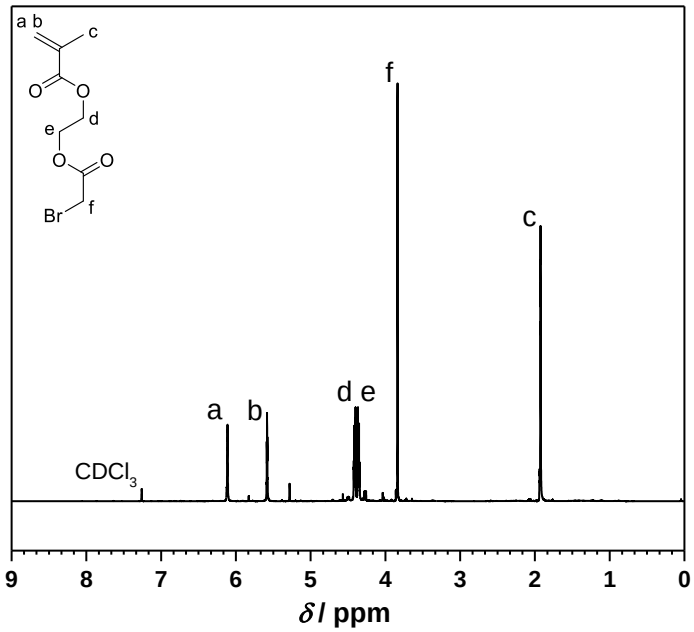


Figure S 1: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of bromoacetoxy ethyl methacrylate at ambient temperature.

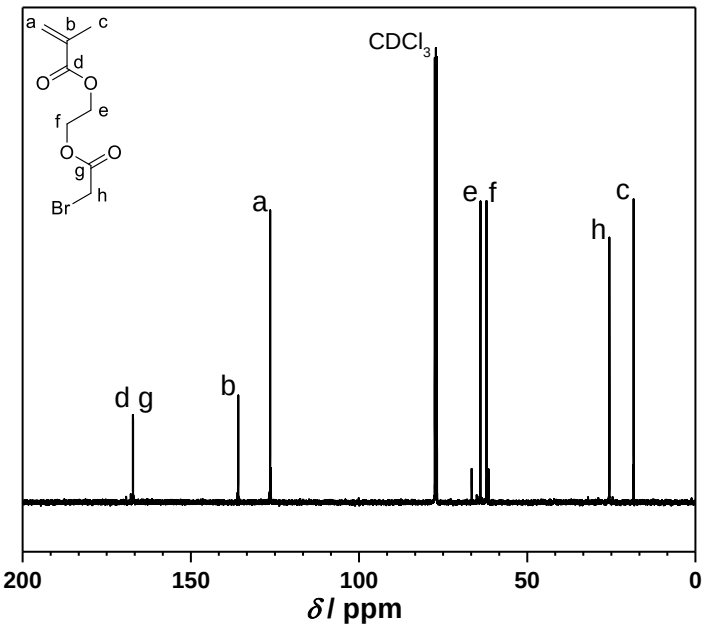


Figure S 2: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of bromoacetoxy ethyl methacrylate at ambient temperature.

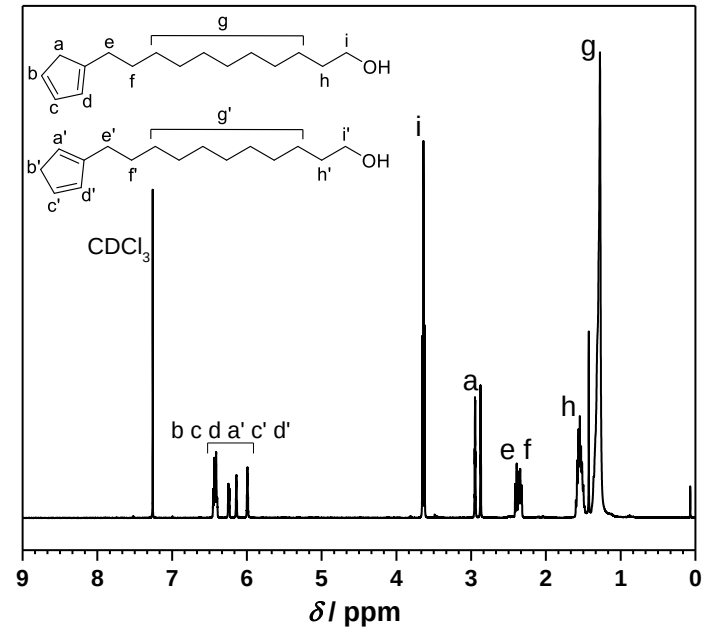


Figure S 3: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 11-(cyclopenta-1,3-dien-1-yl) undecan-1-ol at ambient temperature.

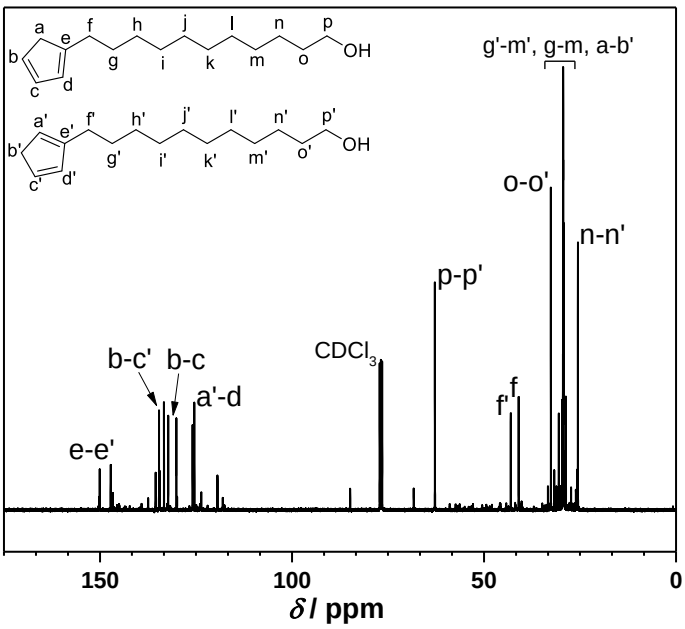


Figure S 4: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 11-(cyclopenta-1,3-dien-1-yl) undecan-1-ol at ambient temperature.

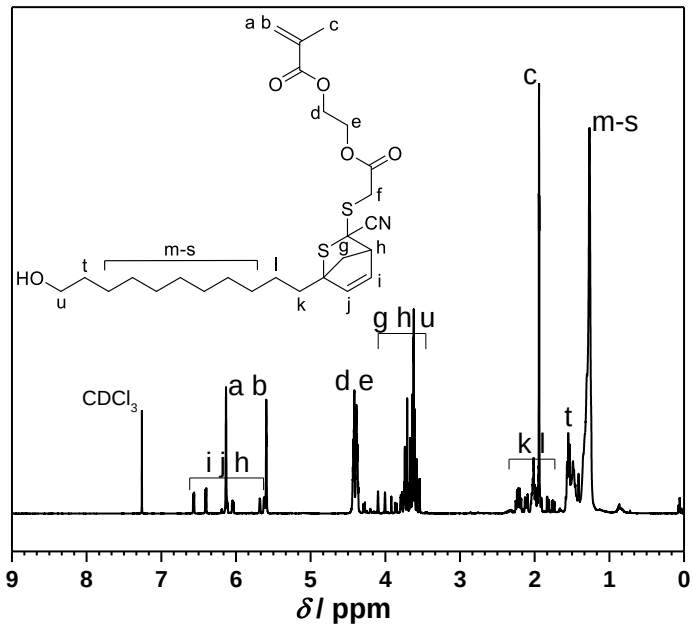


Figure S 5: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the novel **MMAHDAOH** monomer at ambient temperature.

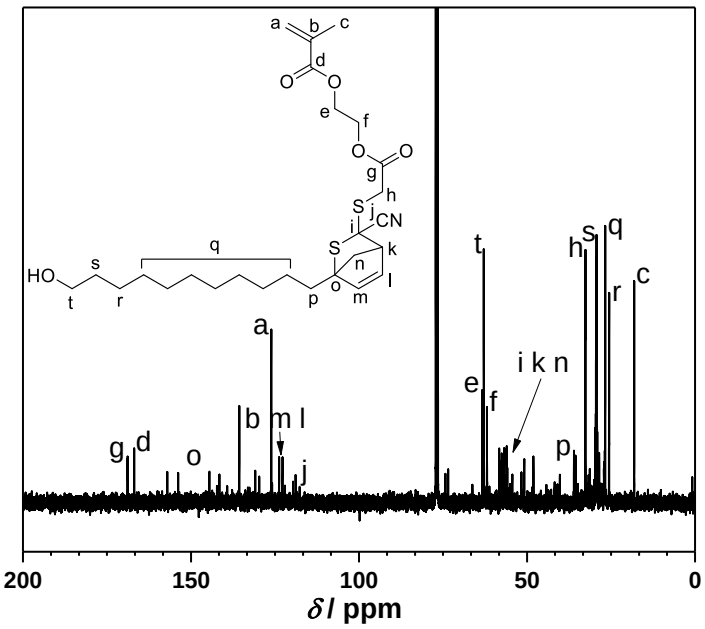


Figure S 6: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the novel **MMAHDAOH** monomer at ambient temperature.

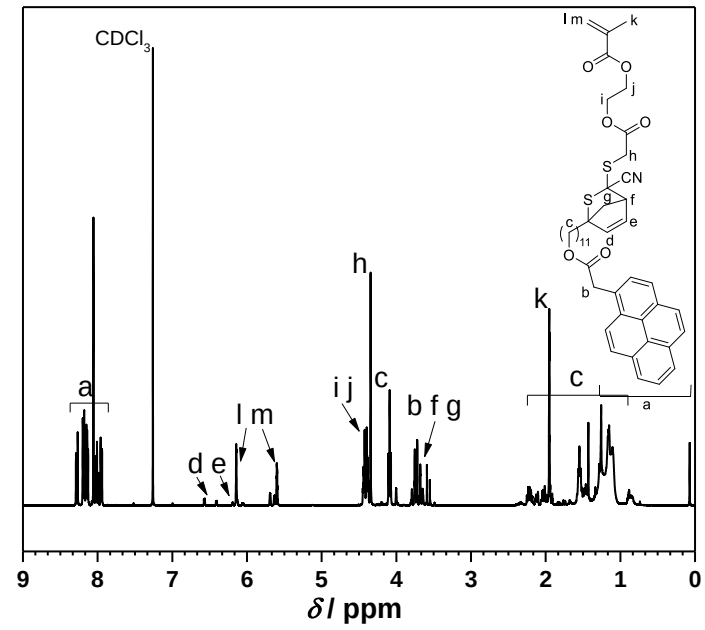


Figure S 7: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the novel **MMAHDAPy** monomer at ambient temperature.

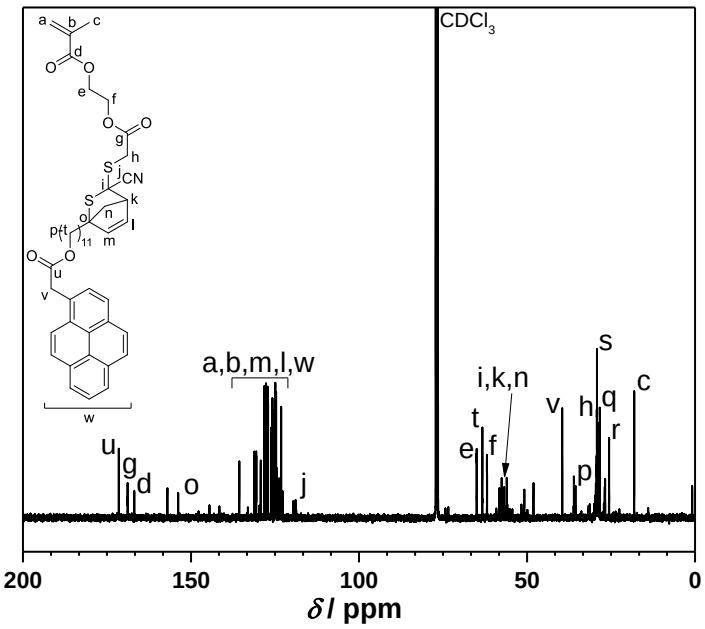


Figure S 8: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the novel **MMAHDAPy** monomer at ambient temperature.

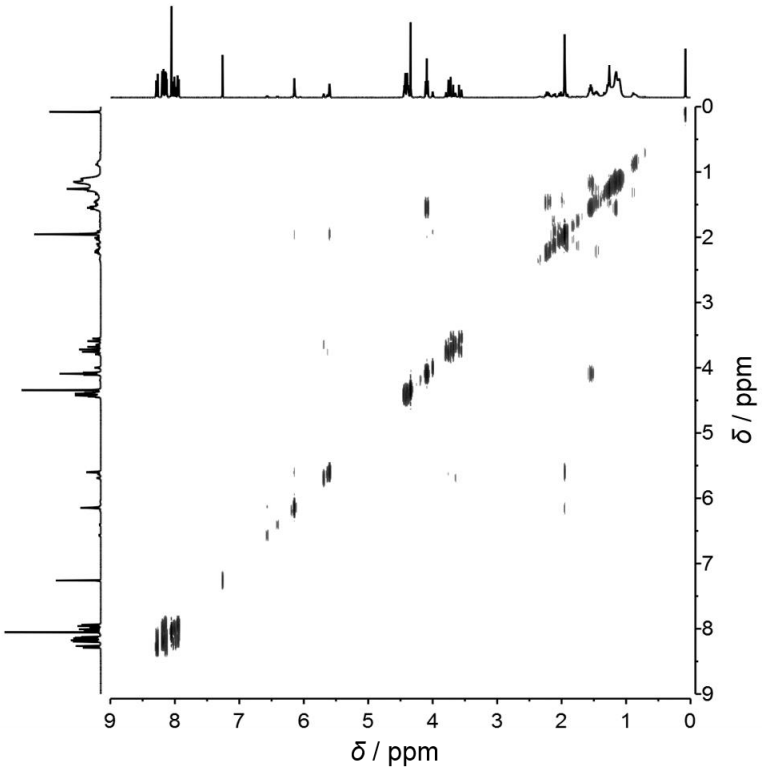


Figure S 9: 2D NMR spectrum (400 MHz, $CDCl_3$) of the **MMAHDAPy** monomer in at ambient temperature.

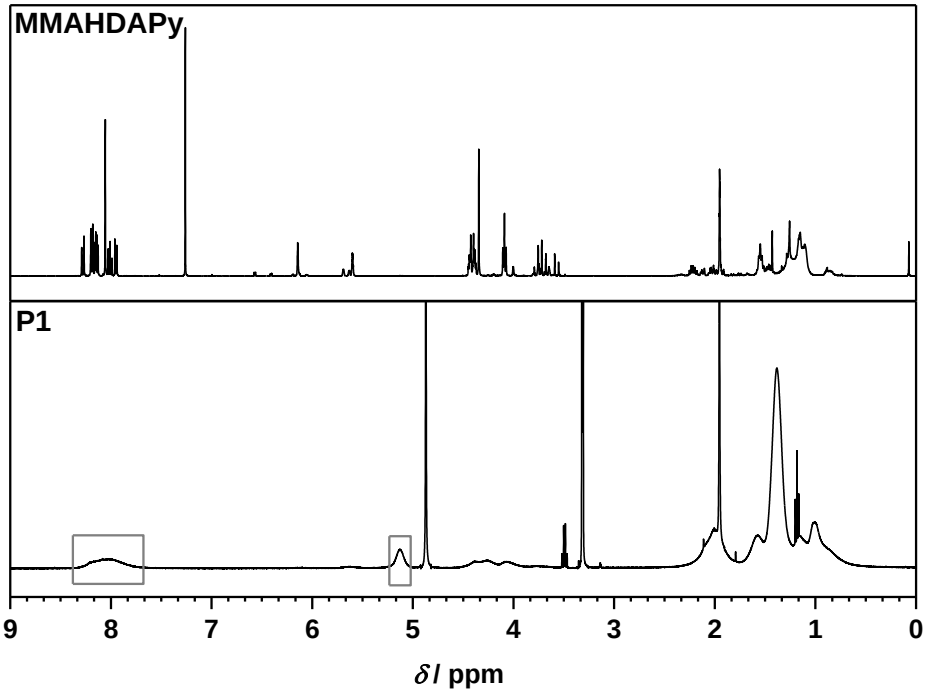


Figure S 10: ^1H NMR spectrum (400 MHz) comparison of the parent polymer **P1** and the monomer **MMAHDAPy**, in $CDCl_3$ and MeOH-d_4.

C.2 High-Resolution ESI-MS data

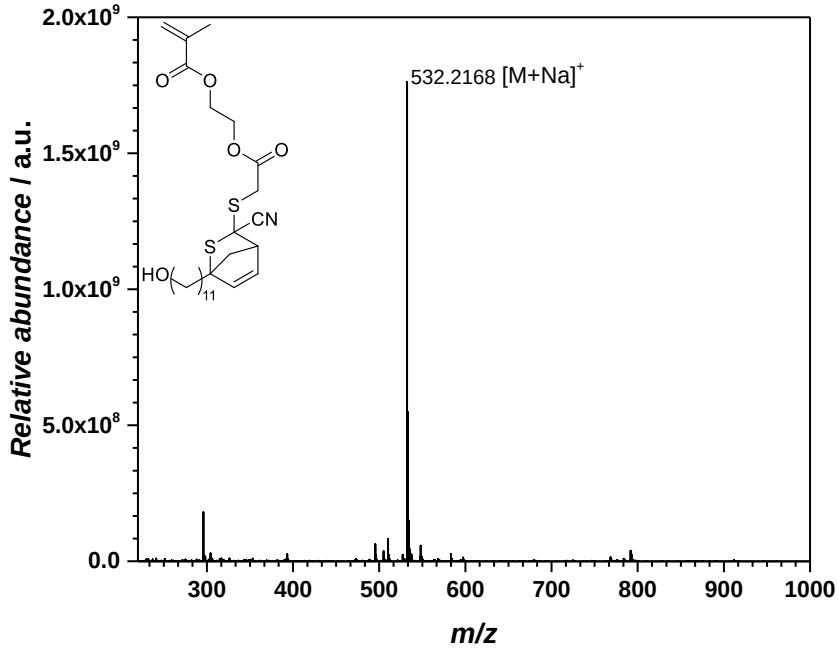


Figure S 11: High resolution mass spectrum of the **MMAHDAOH** monomer.

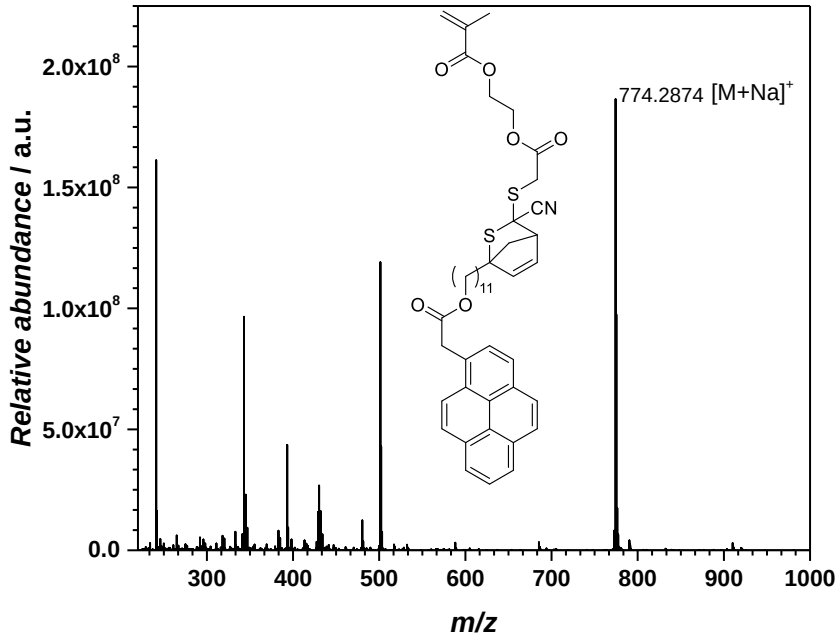


Figure S 12: High-resolution mass spectrum of the **MMAHDAPy** monomer.

C.3 EPR Data

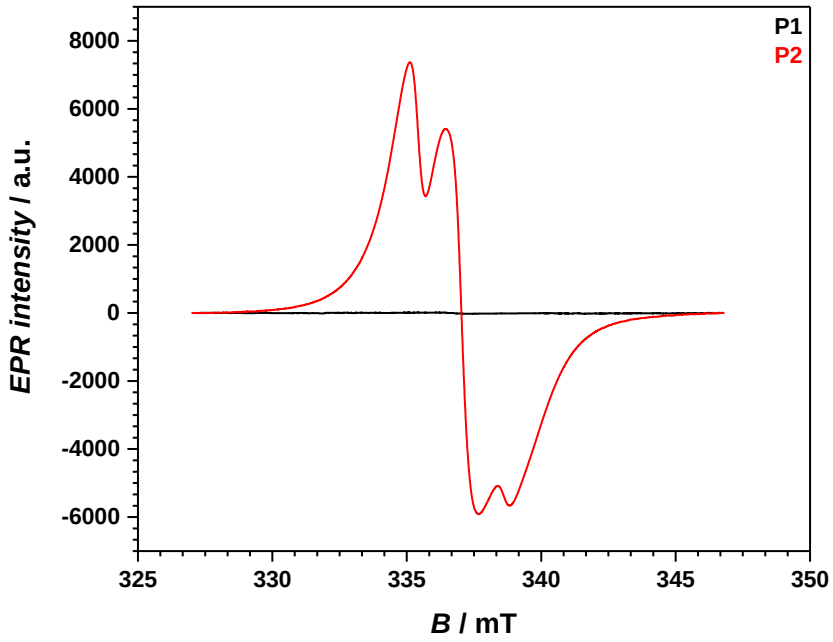


Figure S 13: EPR spectrum of the polymers **P1** and **P2**, mearsured in chloroform at ambient temperature.

C.4 Fluorescence Data

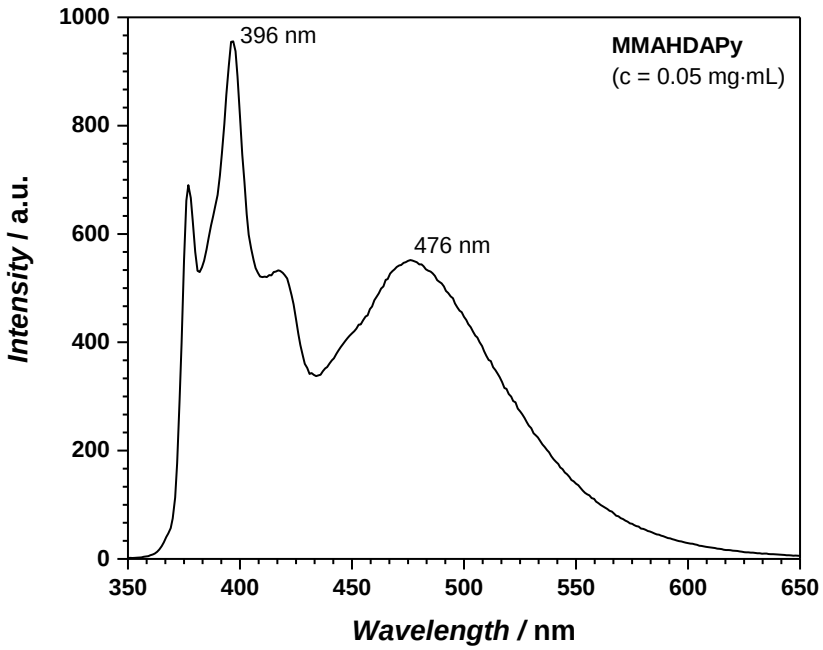


Figure S 14: Fluorescence spectrum of the monomer **MMAHDAPy** in DCM.

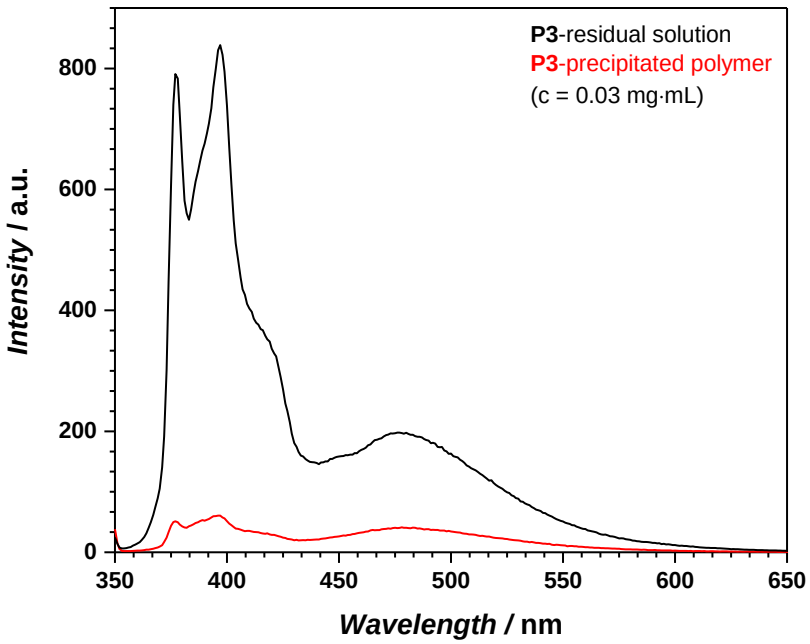


Figure S 15: Fluorescence emission spectra at an excitation wavelength of 344 nm of the precipitated polymer **P3** and the isolated residual solution, respectively, in diethyl ether and anisole.

D. References

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