Supporting Information

Folding Polymer Chains with Visible light

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1. Material and Methods

1.1 Materials

Acetic anhydride (97+%, Acros Organics), aminopyrene (97%, Sigma Aldrich), azobis(isobutyronitrile) (98%, TCI) (purification *via* recrystallization before use), 11-bromo-1-undecanol (99%, Sigma Aldrich), cesium carbonate (99.9% Roth),diethyl fumarate (98% Alfa Aesar) N,N-dimethylaminopyridine (99%, Sigma Aldrich), *N,N'*-diisopropylcarbodiimide (99%, Fluorochem),), EDC*HCl (Roth, >99%), ethanolamine (99%, Acros organics), formyl benzoic acid (97%, Sigma Aldrich), hydrochloric acid 37% (Roth), magnesium sulfate (> 99% extra dry, Roth), maleic anhydride (99% Acros),monoethyl fumarate (95%, Sigma Aldrich), poly(ethylene glycol) bis(carboxymethyl) ether (M_n=250, Sigma Aldrich), pyridine (99%, Acros Organics), sodium nitrite (97%, Acros organics), sodium hydrogen carbonate (> 99.5%, Roth), sodium tetrafluorborate (97%, Sigma), succinic anhydride (> 95%, TCI), p-toluenesulfonyl hydrazide (97%, Acros. All solvents such as dry DMF, dry DCM, dry 1,4-dioxane, ethyl acetate, cyclohexane, diethyl ether, acetonitrile (MeCN) were used in p.a. degree.

1.2 Characterization methods

Nuclear Magnetic Resonance (NMR): Nuclear magnetic resonance (NMR) measurements were performed on a Bruker Avance III Microbay 400 at an operating frequency of 400 MHz (^{1}H) and 100 MHz (^{13}C), respectively. All spectra were recorded at ambient temperature. The residual proton signals of the deuterated solvents were used as an internal standard. The solutions were prepared at a concentration of 10 mg in 0.50 mL in the respective deuterated solvent. The NMR solvents used were purchased from Sigma Aldrich (deutero-chloroform).

Size Exclusion Chromatography (SEC): Polymer Laboratories (Varian) PL-SEC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 mm bead-size guard column (50 × 7.5 mm), one PLgel 5 mm Mixed E column (300×7.5 mm), two PLgel 5 mm Mixed C columns (300 × 7.5 mm), and a differential refractive index detector using THF (with 0.01% BHT as additive) as eluent at 35 °C with a flow rate of 1 mL min^{-1}. The present SEC system was calibrated using narrow linear polystyrene standards ranging from 476 to 2.5·10 g mol^{-1} and linear poly(methyl methacrylate) standards ranging from 700 to 2·106 g mol^{-1} (Polymer Standard Service, PSS). The resulting molar mass distributions were determined using Mark-Houwink parameters for polystyrene (K= 14.1·10^{-5} dL g^{-1}, α = 0.7) or poly(methyl methacrylate) (K= 12.8·10^{-5} dL g^{-1}, α = 0.69)[1], respectively. Experimental molar mass (M_n) and dispersity ($Đ$) values were analyzed using the Varian software.

UV/Vis Spectroscopy: UV-Vis spectra were recorded on a Varian Cary 300 spectrometer. Spectra were recorded in DCM at 20 °C with a concentration of 0.2 mg mL^{-1}. Spectra were collected between 200 and 800 nm. Samples were baseline corrected with respect to the pure solvent. A cuvette with an optical path length of 2 mm was used for the UV/Vis measurements.

Fluorescence Spectroscopy: Fluorescence spectra were measured on a Varian Cary Fluorescence Spectrometer with a step width of 1 nm and an integration time of 0.2 s. All spectra were recorded in DCM (c = 0.2 mg mL^{-1}) at 20 °C. The fluorescence emission spectra were recorded in quartz cuvettes loaded with a sample volume of 700 µL and an optical path length of 10 mm.

Diffusion Ordered NMR (DOSY-NMR): DOSY experiments based on ^1H NMR were performed in $CDCl_3$ at 298.00 K on a Bruker Avance III Microbay 400 at an operating frequency of 400 MHz (^1H) using a stimulated echo sequence incorporating bipolar gradient pulses and a longitudinal eddy current delay (BPP-LED) with the standard Bruker pulse program, ledbpgp2s. The gradient strength was linearly incremented in 96 steps from 5 % up to 95 % of the maximum gradient strength. Diffusion times and gradient pulse durations were optimized for each experiment in order to achieve a 95% decrease in the signal intensities at the largest gradient amplitude. After Fourier transformation and phase correction, the diffusion dimension of the 2D DOSY spectra was processed by means of the Bruker Topspin software package (version 3.2) and analyzed with the Bruker Dynamic Center. Spectra for the polymers and their corresponding single-chain nanoparticles were measured and mean values were taken from the found diffusion coefficients of characteristic NMR-peaks.

$$r = \frac{k_{\mathrm{B}}\,\mathrm{T}}{6\pi\,\eta\,D}$$

k_B= Boltzmann constant

T= Temperature

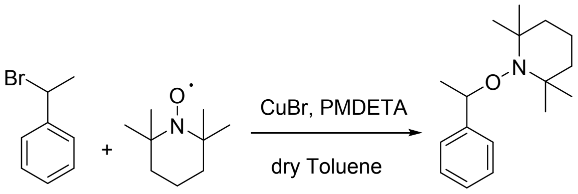
η= Viscosity of solvent

r= Radius

2. Experimental Section

2.1 Synthesis of the small molecules

2.1.1 Synthesis of the NMP initiator



Scheme S1: The NMP-initiator was synthesized according to literature[2]

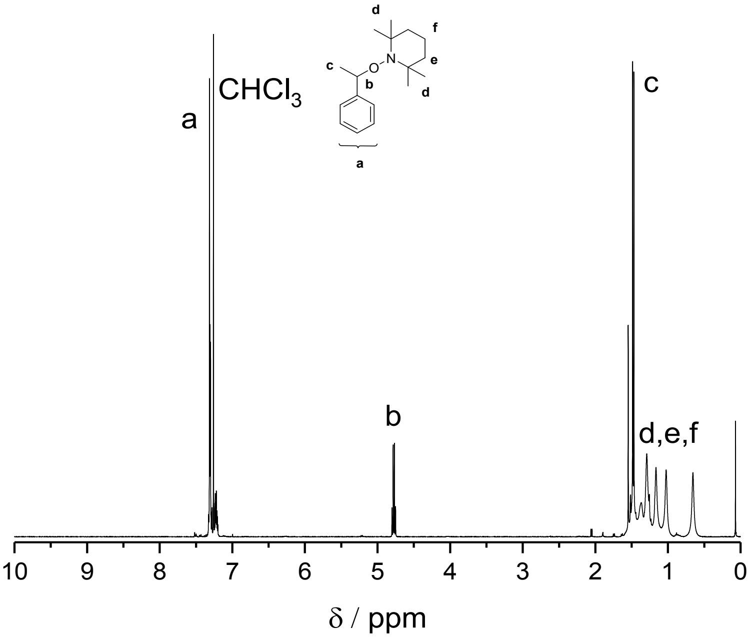
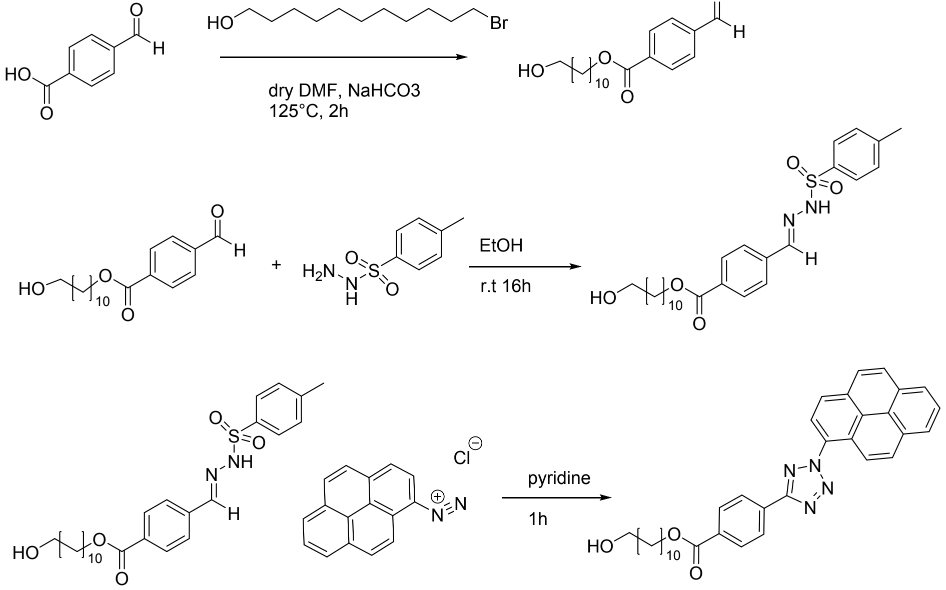


Figure S1: ^{1}H-NMR spectrum of the synthesized NMP-initiator recorded in $CDCl_3$ at 400 MHz

2.1.2 Synthesis of 11-hydroxyundecyl 4-(2-(pyren-1-yl)-2H-tetrazol-5-yl)benzoate (PAT)[3]



Scheme S2: Synthesis of 11-hydroxyundecyl 4-(2-(pyren-1-yl)-2H-tetrazol-5-yl)benzoate (PAT)

6.0 g of formylbenzoic acid (39.9 mmol, 1.00 eq.), 6.71 g of sodium hydrogen carbonate (79.9 mmol, 2.00 eq.) and 13.0 g of 11-bromoundecan-1-ol (51.9 mmol, 1.30 eq.) were dissolved in 50 mL of DMF and heated to 125 °C for 2 h. Subsequently, 300 mL of ethyl acetate were added and the crude reaction mixture was washed with brine 3 times (50 mL). The organic layer was dried over magnesium sulfate and the solvent was evaporated under reduced pressure and dried under high vacuum. The obtained yellow oil was used without further purification. The compound was dissolved in 100 mL of ethanol and 6.96 g of *p*-toluenesulfonylhydrazide (37.4 mmol, 1.1 eq.) was added to the solution and stirred overnight. Subsequently, ethanol was evaporated under reduced pressure and the obtained yellow solid was dried under high vacuum. 0.7 g of the previous synthesized compound was dissolved in 8 mL of pyridine. The first solution contained 0.258 g of aminopyrene (1.18 mmol, 1.00 eq.) in 30 mL of THF and was cooled to -21°C under argon atmosphere. In a second round bottom flask 1.04 g of sodium tetrafluoroborate (9.50 mmol, 8.00 eq.) was dissolved in 15 mL of 50 wt % fluoroboric acid and water (7:3) under argon atmosphere. This solution was slowly added to the aminopyrene solution and stirred for 20 min at -21°C. Subsequently, 94.0 mg of sodium nitrite (1.36 mmol, 1.15 eq.) was dissolved in a third round bottom flask in 2 mL of water under argon atmosphere. The sodium nitrite solution was slowly combined and stirred for 10 min at -21°C. The orange diazonium salt formed was collected and added to the pyridine solution. The combined reaction mixture was stirred for 1h and subsequently precipitated into 80 mL of a 1 M HCl solution. The raw product was recrystallized 3 times from ethanol to yield a brown solid. 220 mg (Yield: 33 %).

^{1}H NMR (400 MHz, $CDCl_3$) [ppm]: 8.81 – 7.78 (m, 13H), 4.38 (t, 2H), 3.64 (t, 2H), 1.87 – 1.73 (m, 2H), 1.69 –1.22 (m, 16H). MS calc. $[M+Na]^+$ 583.26853, MS found 583.26929, MS calc $[2M+Na]^+$ 1143.54725, MS found 1143.55005

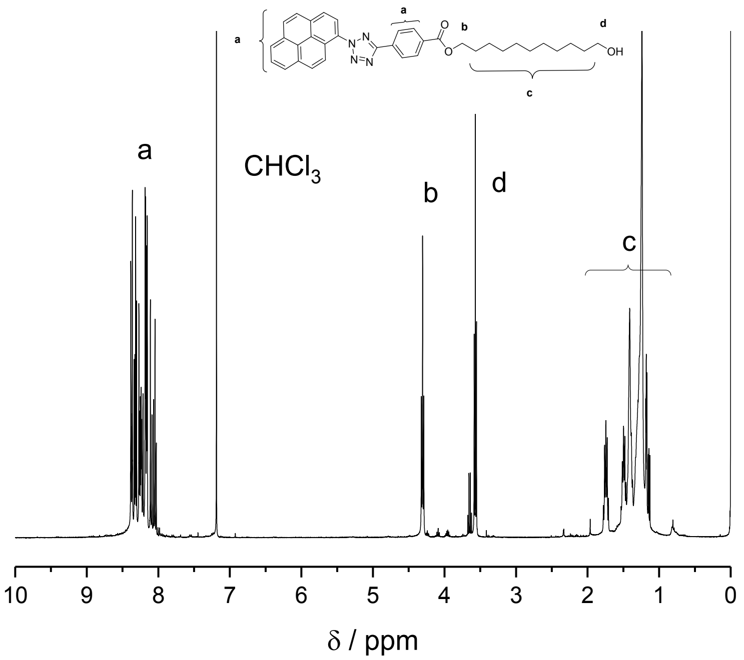


Figure S2: ^{1}H-NMR spectrum of the photoreactive linker pyrene-aryl-tetrazole (PAT) recorded in $CDCl_3$ at 400 MHz

2.1.3 *Synthesis of 4-oxo-4-((11-((4-(2-(pyren-1-yl)-2H-tetrazol-5-yl)benzoyl)oxy) undecyl)oxy)butanoic acid*[4]

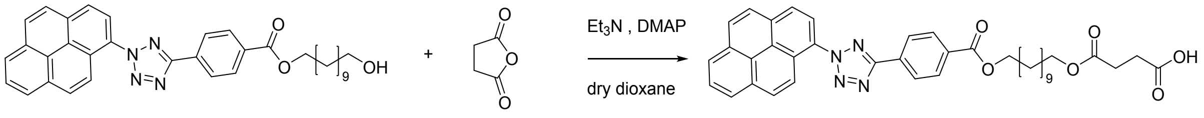


Figure S3: Synthesis of the of the PAT derivative containing a carboxylic group (PAT-acid)

632.2 mg of PAT-OH (1.13 mmol, 1.0 eq.) were dissolved in 10 mL of dry 1,4 dioxane under argon atmosphere. Subsequently, 677 mg of succinic anhydride (6.78 mmol, 6.0 eq.), 303 mg of DMAP (2.48 mmol, 2.20 eq.) and 1.58 mL of triethylamine (11.3 mmol, 10 eq.) were added to the solution. The reaction mixture was stirred for 4 d at 50 °C. After evaporation of the solvent the crude product was recrystallized and washed with brine. The organic solvent was removed and recrystallized from ethanol 2x 80 mL yielding a brown solid 451 mg (Yield: 61%).

^{1}H NMR (400 MHz, CDCl$_3$) δ [ppm] = 8.50 – 8.16 (m, 13H), 4.38 (t, 2H), 4.09 (t, 2H), 2.65 (m, *J* = 12.7, 6.0 Hz, 4H), 1.82 (s, 2H), 1.65 – 1.43 (m, 4H), 1.32 (dd, *J* = 30.1, 11.8 Hz, 12H).

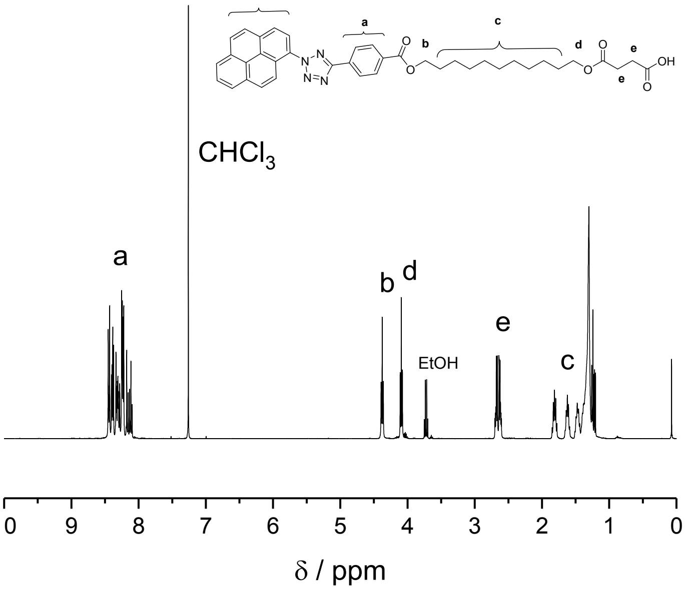
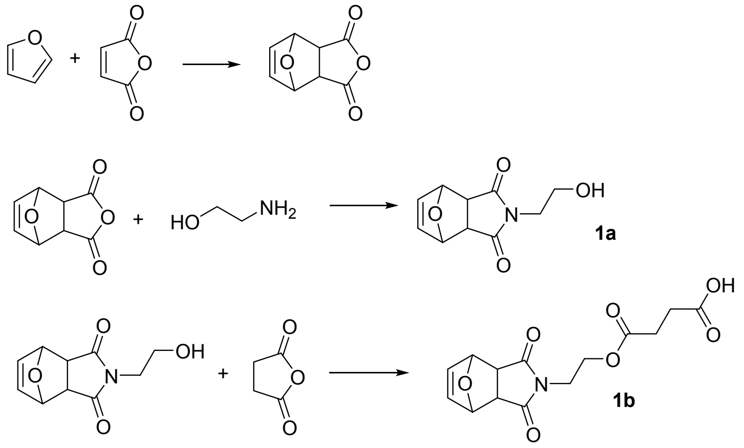


Figure S4: ^{1}H-NMR spectrum of the PAT acid derivative recorded in CDCl$_3$ at 400 MHz

2.1.4 Synthesis of 2-(2-hydroxyethyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxy isoindole-1,3(2H)-dione (1a) and 4-(2-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-epoxyisoindol-2-yl)ethoxy)-4-oxobutanoic acid (1b)



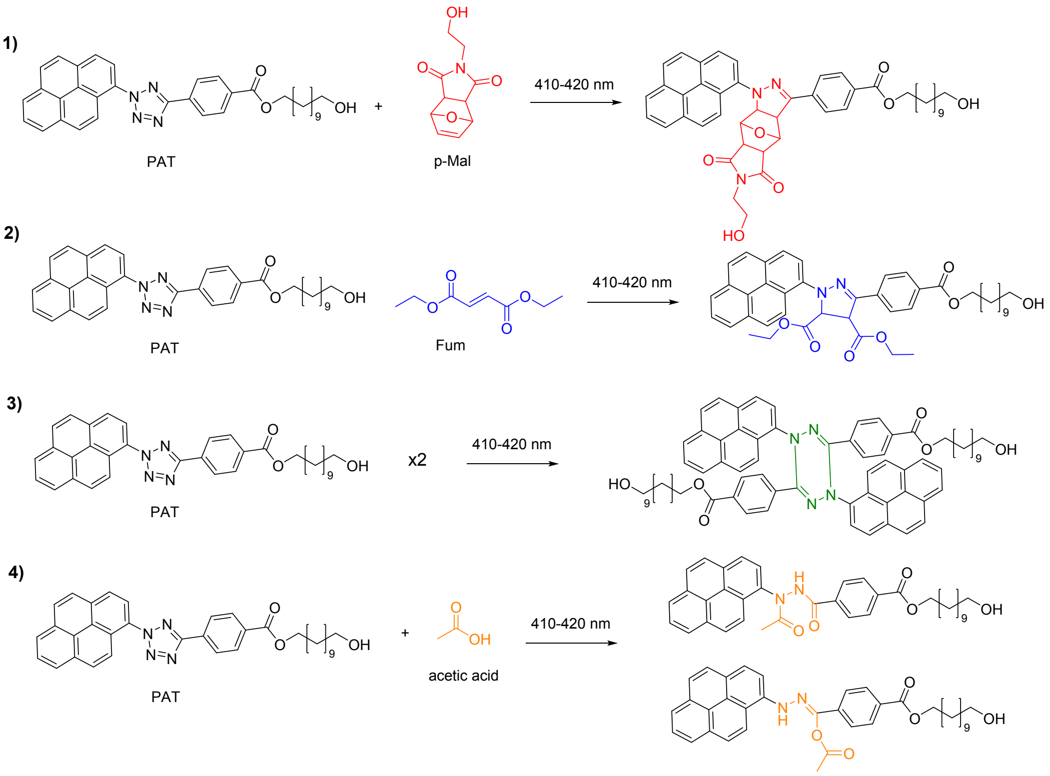
Scheme S3: The synthesis of the p-Mal derivatives were performed according to a procedure reported in the literature[2]

2.2 Irradiation tests

The irradiation tests were performed in a 50 mL round bottom flask equipped with a stir bar. 10.0 mg of PAT-OH (0.017 mmol, 1.0 eq.) were dissolved in 30 mL of DCM and the corresponding molecules were added for the different tests: 1) 4.8 mg of furan-protected maleimide (p-Mal) (0.023 mmol, 1.3 eq.), 2) 4.0 mg of diethylfumarate (0.023 mmol, 1.3 eq) or 4) 1.3 µL of acetic acid (0.023 mmol, 1.3 eq.). The conditions of the reactions are collated in Table S1.

Table S1: Reaction conditions for the small molecule studies

Reaction	***PAT-OH***	***p-Mal***	***Diethyl fumarate***	***Acetic acid***
1)	1.0 eq.	1.3 eq -	-	-
2)	1.0 eq.		1.3 eq	-
3)	1.0 eq.	-		-
4)	1.0 eq	-	-	1.3 eq



Scheme S4: Overview of the small molecule study showing **1**) NITEC reaction with p-Mal, **2**) NITEC reaction with diethyl fumarate **3**) dimerization of the tetrazole **4**) NICAL reaction with acetic acid.

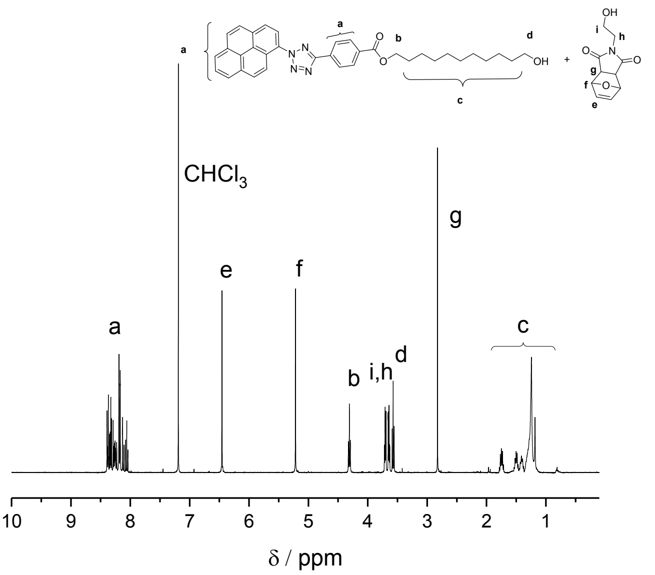


Figure S5: Exemplary ^{1}H-NMR spectrum of the starting materials of reaction 1 (PAT and p-Mal) before irradiation recorded in CDCl$_3$ at 400 MHz.

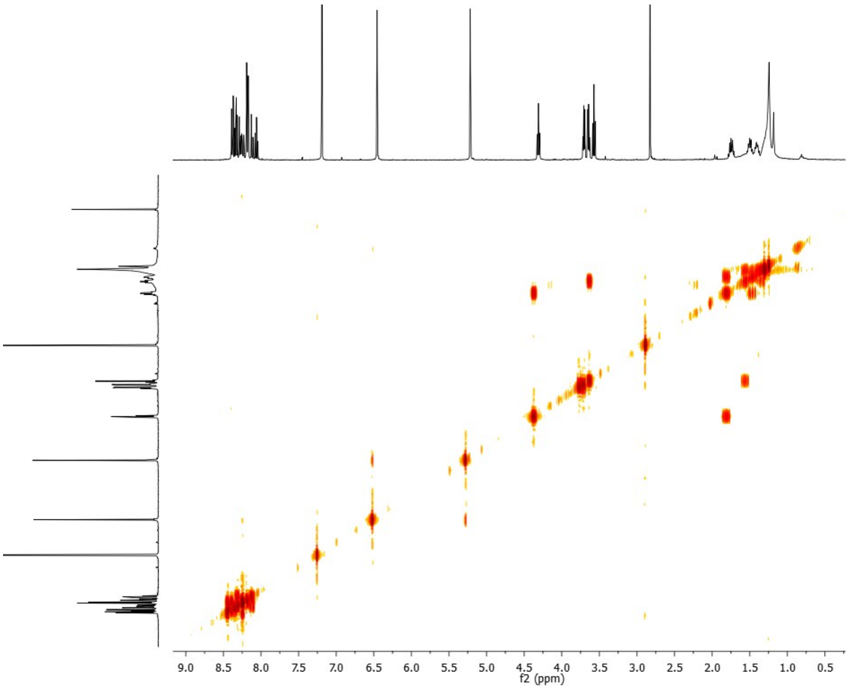
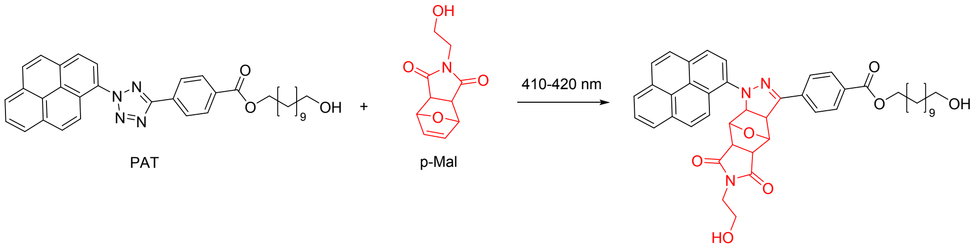


Figure S6: COSY NMR of the starting material for reaction **1** (PAT and p-Mal).

1) NITEC Reaction between PAT and p-Mal



Scheme S5: Reaction **1**, PAT and p-Mal resulting in the pyrazoline adduct.

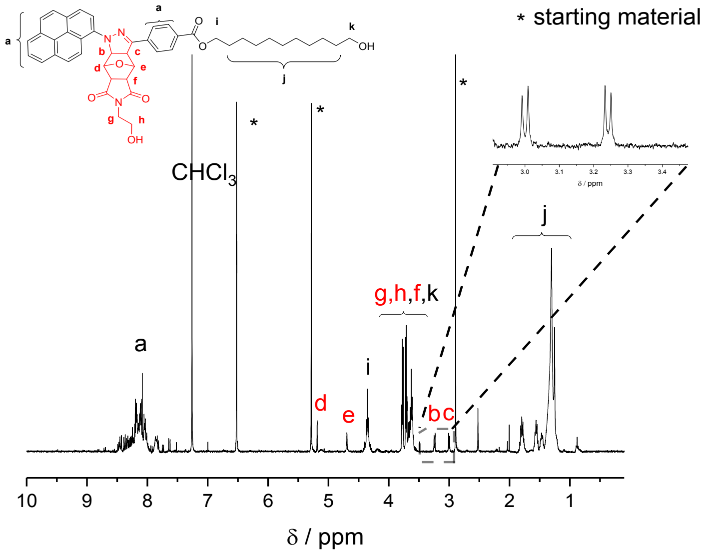


Figure S7: ^{1}H-NMR spectrum of reaction **1** (NITEC adduct between PAT and p-Mal) recorded in $CDCl_3$ at 400 MHz. The zoom shows the corresponding signals of the pyrazoline product with the furan protected maleimide.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 8.81 – 7.78 (m, 13H), 5.20 (s, 1H), 4.63 (s, 1H) 4.35 (t, 2H), 3.78 – 3.72 (m, 4H), 3.67-3.64 (m, 2H), 3.63-3.61 (t, 2H), 3.24 (d, *J* = 6.9 Hz, 1H), 3.00 (d, *J* = 7.0 Hz, 1H). 1.87 – 1.22 (m, 18H). ESI-MS [m/z]: MS calc. $[M+Na]^{+}$ 764.33117, MS found 764.33250

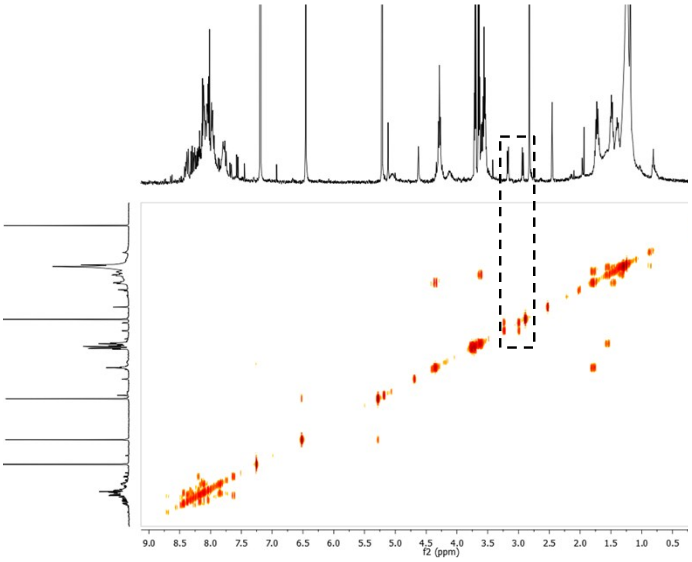
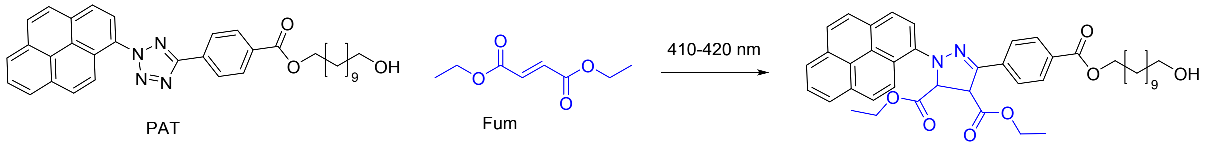


Figure S8: COSY NMR of reaction **1** (NITEC adduct between PAT and p-Mal) reaction after 3h, showing the correlation of the newly generated pyrazoline formation at 3.0 ppm and 3.2 ppm.

2) NITEC reaction between PAT and diethyl fumarate



Scheme S6: Reaction **2)** PAT and diethyl fumarate resulting in the pyrazoline adduct

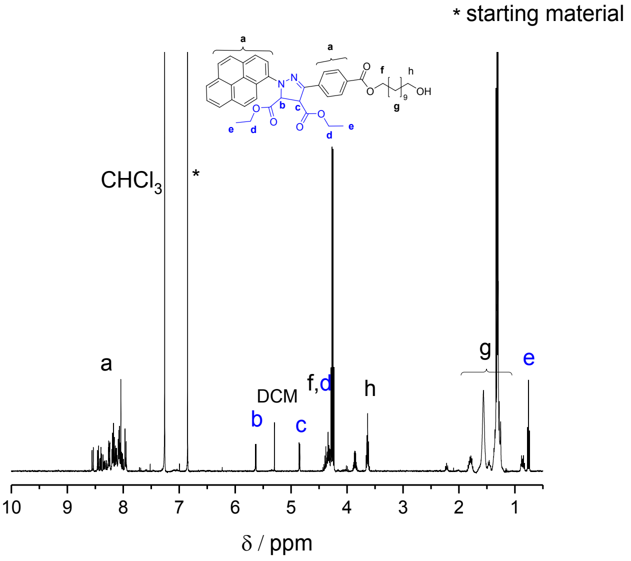


Figure S9: ^{1}H-NMR spectrum of reaction **2** (NITEC adduct with diethyl fumarate) recorded in $CDCl_3$ at 400 MHz. The rearomatized reaction product is not shown

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 – 7.50 (m, 13H), 5.63 (d, *J* = 5.0 Hz, 1H), 4.85 (d, *J* = 4.9 Hz, 1H), 4.57 – 4.01 (m, 6H) 3.63 (m, *J* = 9.0, 4.2 Hz, 2H), 2.07 – 0.92 (m, 18H), 0.76 (t, *J* = 7.1 Hz, 6H). ESI-MS [m/z]: MS calc. $[M+Na]^+$ 727.33537, MS found 727.33617, MS calc rearomatized $[M+Na]^+$ 725.31972, MS found 725.32038

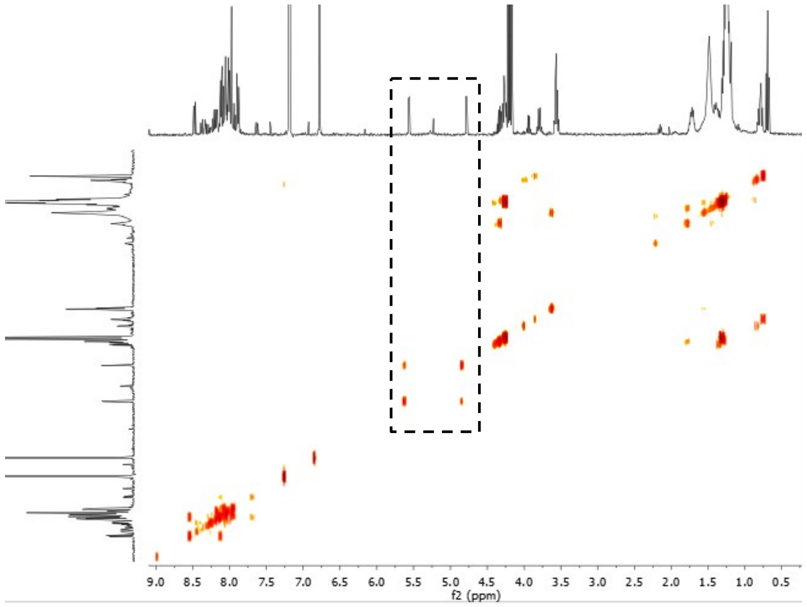
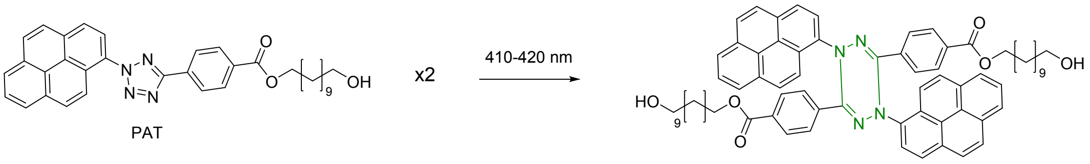


Figure S10: COSY NMR of reaction **2** (NITEC adduct with diethyl fumarate) after 2h, showing the correlation of the newly generated pyrazoline formation at 5.5 ppm and 4.8 ppm

3) PAT dimerization



Scheme S7: Reaction **3** PAT was irradiated only, resulting in a dimerization of the PAT.

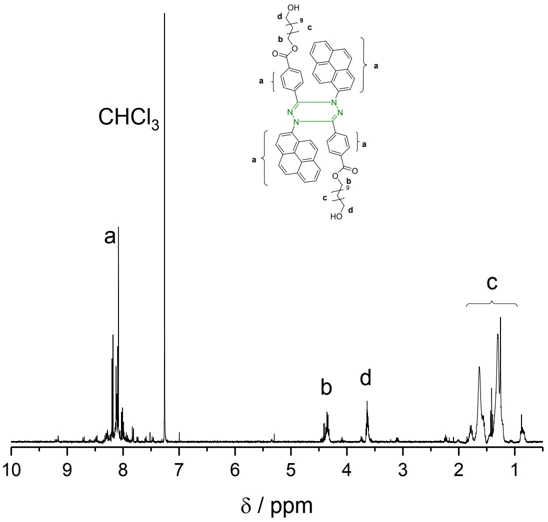


Figure S11: ^{1}H-NMR spectrum of reaction **3** (PAT tetrazole dimer) recorded in $CDCl_3$ at 400 MHz.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 – 7.35 (m, 26H), 4.47 – 4.30 (dt, *J* = 14.8, 6.9 Hz, 4H), 3.63 (m, 4H), 1.80 (dd, *J* = 22.5, 15.1 Hz, 4H), 1.53 – 1.15 (m, 36H). ESI-MS [m/z]: MS calc. $[M+Na]^+$ 1087.53441, MS found 1087.53613, MS calc. $[M+H]^+$ 1065.55246 MS found 1065.55146.

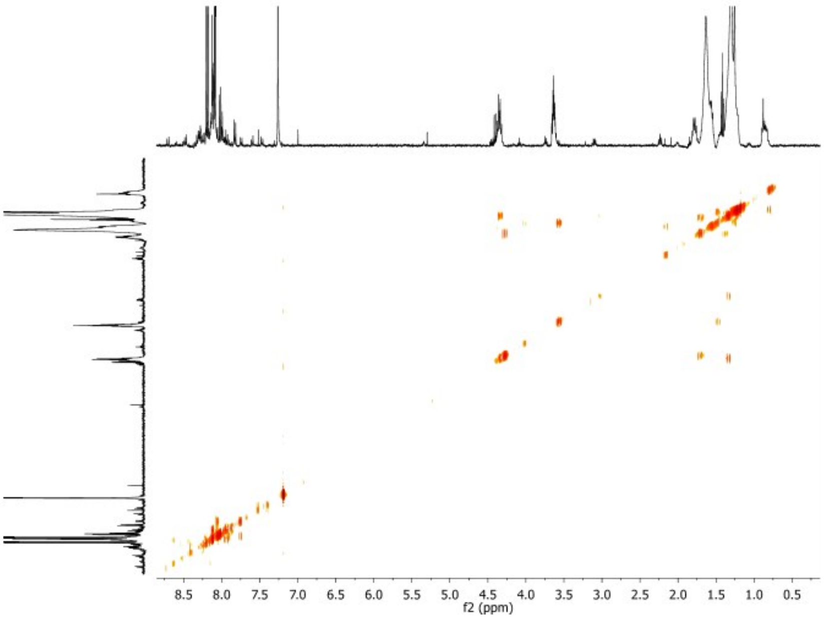
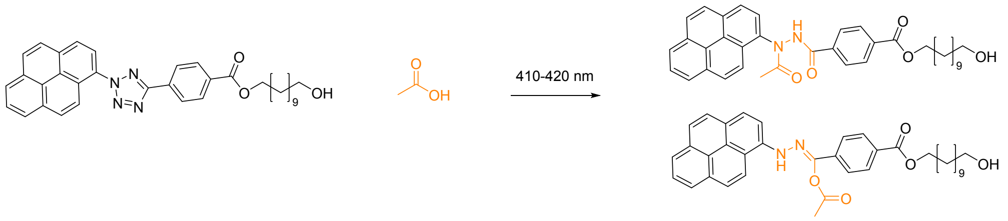


Figure S12: COSY NMR of the PAT dimerization reaction recorded in $CDCl_3$ at 400 MHz.

4) NICAL reaction



Scheme S8: Reaction **4**) PAT and acetic acid resulting in the NICAL adducts.

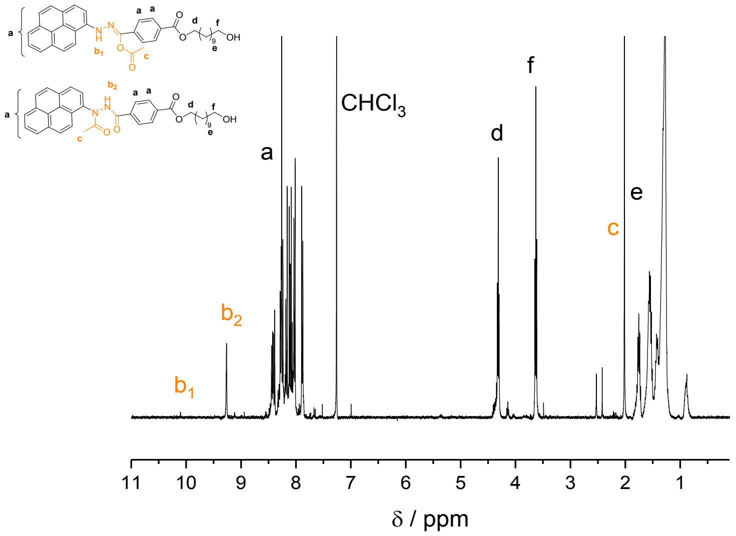


Figure S13: ^{1}H-NMR spectrum of reaction **4** (NICAL adduct) recorded in $CDCl_3$ at 400 MHz.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 10.0 (s,1H), 9.03 (s, 1H), 8.81 – 7.78 (m, 13H), 4.38 (t, 2H), 3.64 (t, 2H), 1.87 – 1.73 (m, 2H), 1.69 –1.22 (m, 18H). ESI-MS [m/z]: MS calc. $[M+Na]^+$ 583.26853, MS found 583.26929, MS calc $[2M+Na]^+$ 1143.54725, MS found 1143.55005

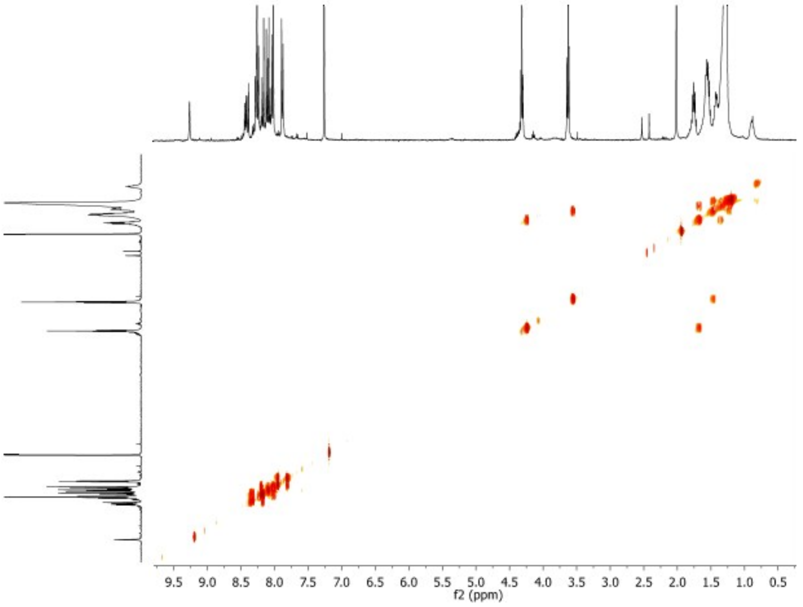


Figure S14: COSY NMR of reaction **4** NICAL reaction recorded in $CDCl_3$ at 400 MHz.

2.2.1 UV/Vis and fluorescence spectroscopy

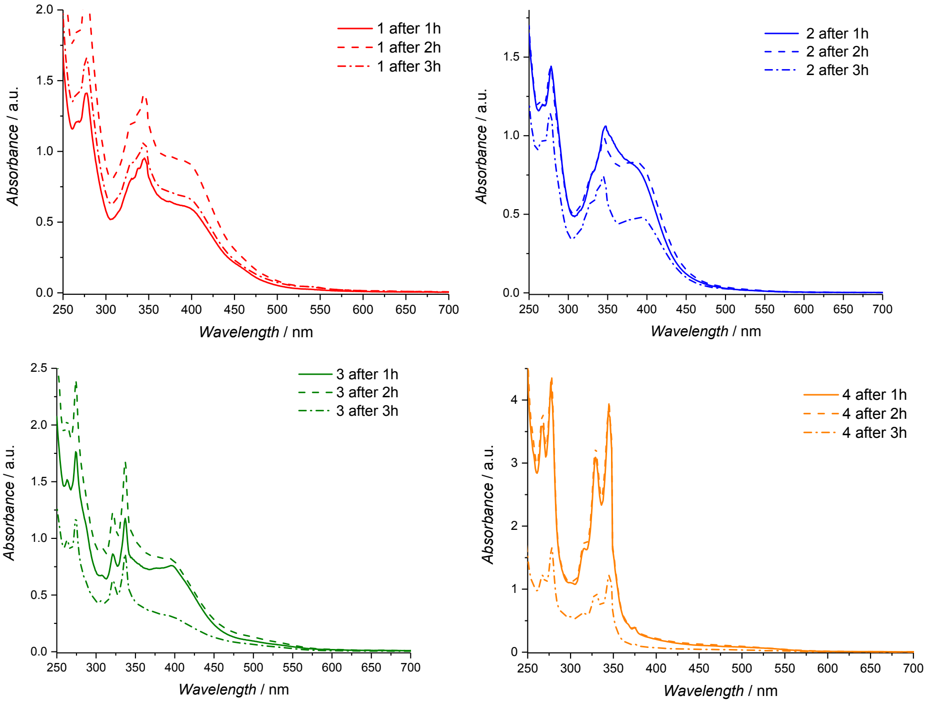


Figure S15: UV/Vis spectra of the small molecule studies **1-4** measured in DCM with a concentration of 0.2 mg mL^{-1}

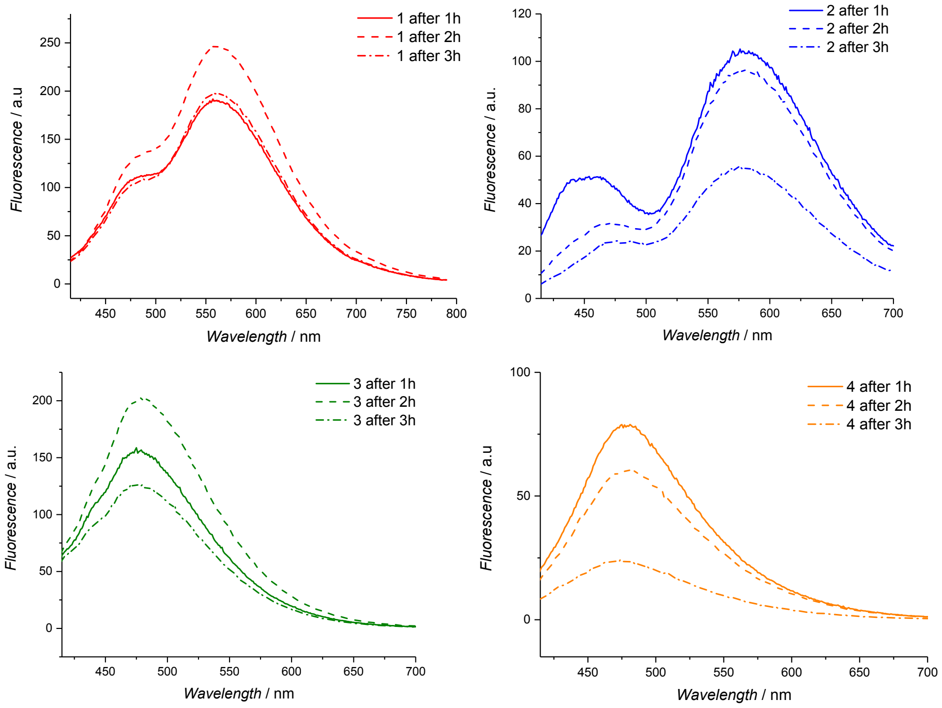


Figure S16: Fluorescence spectra of the small molecule studies **1-4** measured in DCM with a concentration of 0.2 mg mL^{-1}.

2.3 Polymerization of styrene / 4-chloromethylstyrene (PS/CMS)

The copolymerization of styrene/cms was performed in a 50 mL vial. The stabilizers were removed with basic alumina before use. 6.37 g of styrene (61.2 mmol,160 eq.), 1.75 g of 4-chloromethylstyrene (11.5 mmol, 30 eq.) and 100 mg of the NMP initiator (0.38 mmol, 1 eq.) were dissolved in 4 mL toluene. The vial was sealed with a crimping tong and the solution was percolated with nitrogen for 30 min. The reaction was allowed to proceed for 20 h at 125 °C. Subsequently, the reaction was terminated by rapidly reducing the temperature by immersion in liquid nitrogen, opening the flask and letting the solution stir at ambient conditions for several minutes. The crude product was purified *via* precipitation three times each in ice cold methanol yielding a white powder. The powder was dried under high vacuum. The percentage of CMS in the polymer was calculated as reported in literature resulting in 14 % of CMS units.

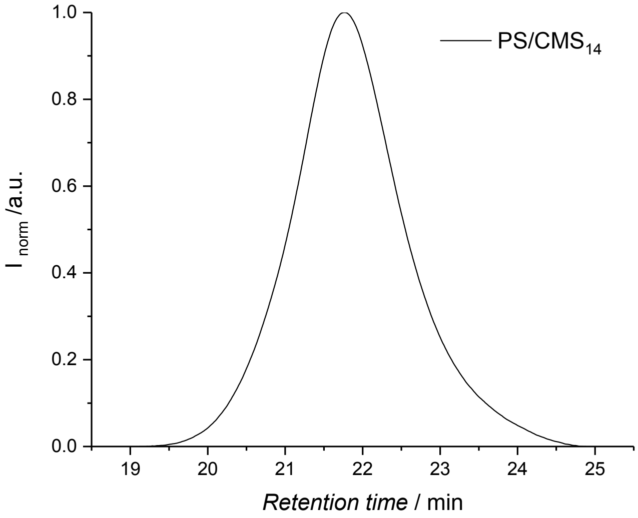


Figure S17: SEC traces of the synthesized polymer PS/CMS_{14} showing a monomodal molecular weight distribution (M_n =12500 g mol^{-1}, $Đ_M$=1.3).

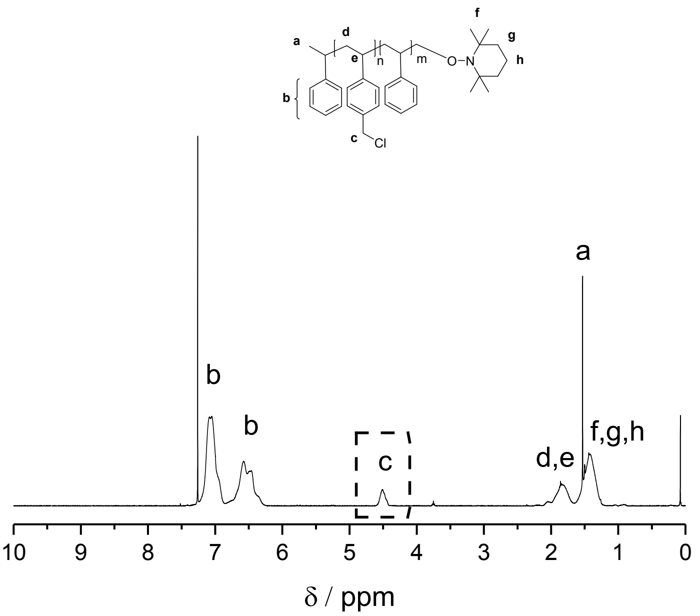


Figure S18: ^{1}H-NMR of spectrum the copolymer PS/CMS$_{14}$ recorded in CDCl$_3$ at 400 MHz showing the peak c at 4.5 ppm, which was used for the calculation of the chloromethylstyrene groups according to literature.[2]

2.4. Post-Functionalization of PS/CMS

200 mg of the copolymer PS/CMS$_{14}$ (0.016 mmol, 1.00 eq) were dissolved in 8 mL dry DMF and functionalized with the corresponding carboxylic acid derivatives as follows: for a) PS/CMS$_{\text{p-maL}}$ **(P1)** 46.1 mg of p-Mal acid (0.151 mmol, 0.6 eq) and 83.4 mg of the PAT acid (0.094 mmol, 0.5 eq.); b) PS/CMS$_{\text{Fum}}$ **(P2)** 21.8 mg of fumaryl monoethylester (0.151 mmol, 0.6 eq.) and 83.4 mg of the PAT acid (0.094 mmol, 0.5 eq.) and c) PS/CMS$_{\text{(PAT)}}$ **(P3)** 150 mg of the PAT acid (0.227 mmol, 0.9 eq.) were used for functionalization.

Table S2: THF SEC data evidencing a shift towards higher molecular weight after functionalization of the linear precursor

Polymer	***M_n* [g mol^{-1}]**	**$Đ_M$**
PS/CMS$_{14}$	12500	1.3
P1	18500	1.4
P2	15200	1.3
P3	18300	1.4

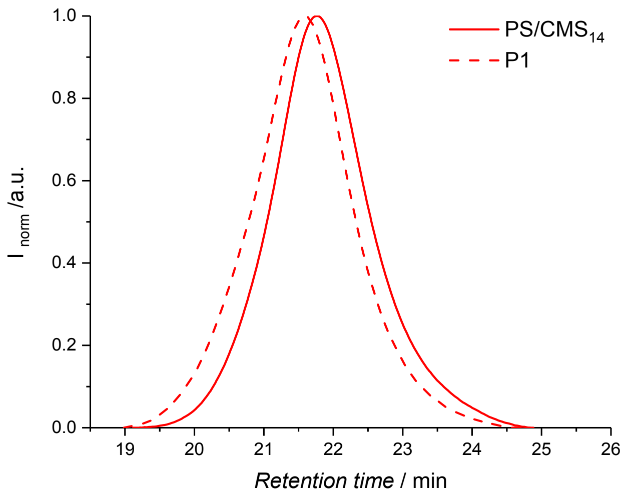


Figure S19: SEC traces of PS/CMS$_{14}$ and **P1** after functionalization with p-Mal and PAT. The shift towards lower retention times proves the increase of the molecular weight due to the successful functionalization.

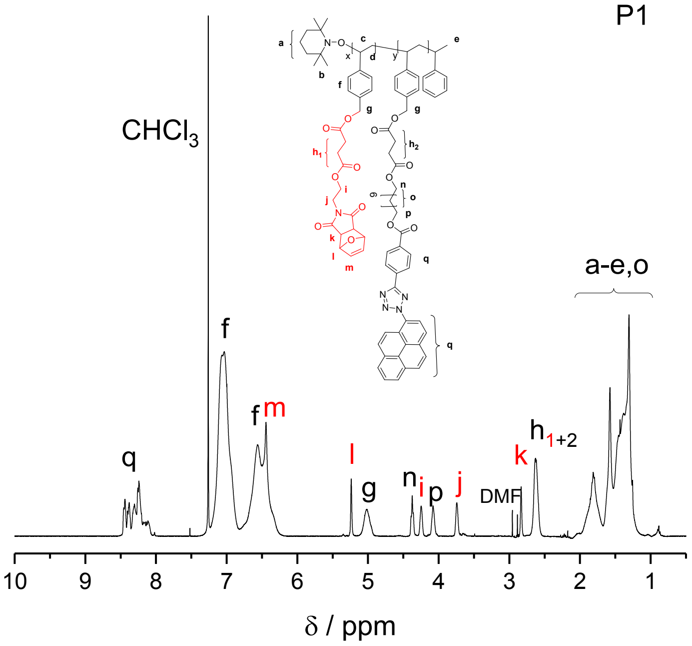


Figure S20: ^{1}H-NMR spectrum of **P1** recorded in CDCl$_3$ at 400 MHz. The resonances corresponding to the protected maleimide functional unit are highlighted in red.

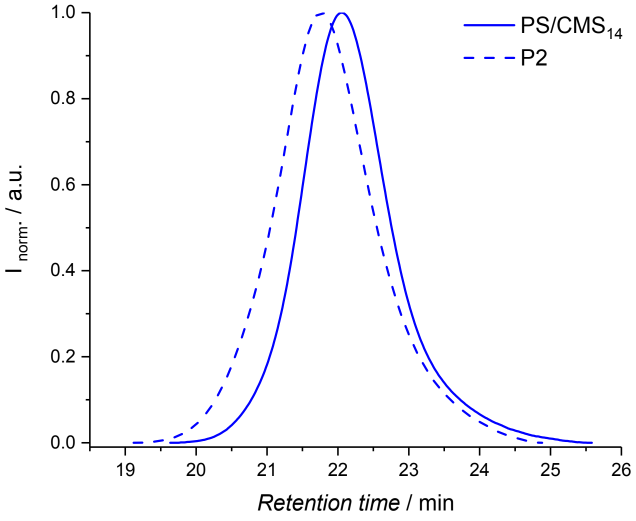


Figure S21: SEC traces of PS/CMS_{14} and **P2** after functionalization with monoethylfumarate and PAT. The shift towards lower retention times proves the increase of the molecular weight due to the successful functionalization.

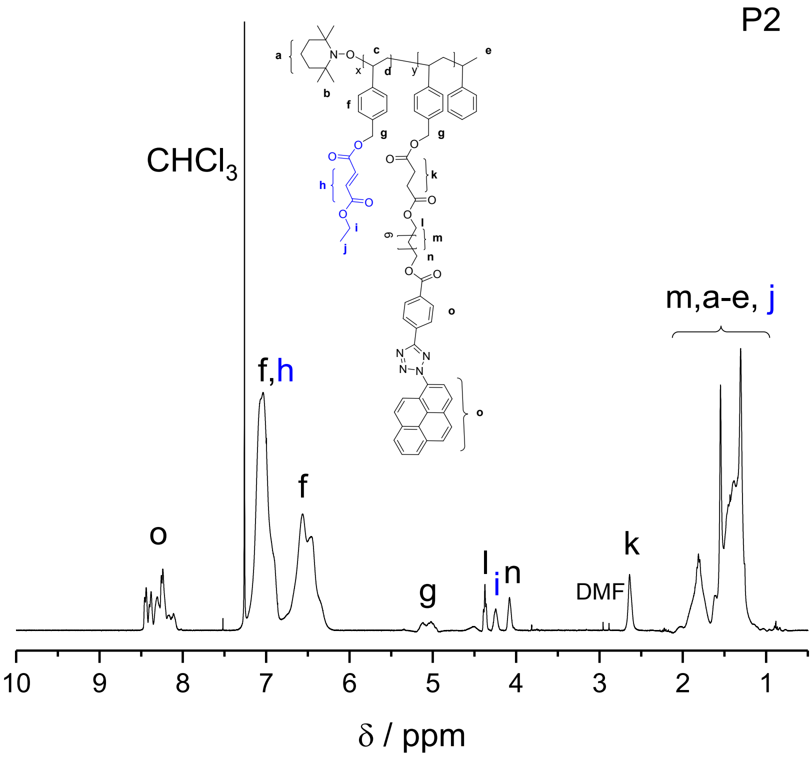


Figure S22: ^{1}H-NMR spectrum of the **P2** precursor recorded in $CDCl_3$ at 400 MHz. The resonances corresponding to the ethyl fumarate functional unit are indicated in blue.

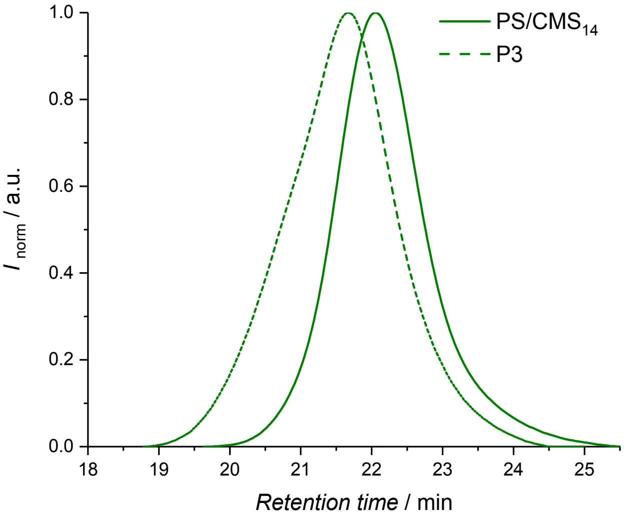


Figure S23: SEC traces of PS/CMS$_{14}$ and **P3** after functionalization with PAT. The shift towards lower retention times evidences the increase of the molecular weight due to the successful functionalization.

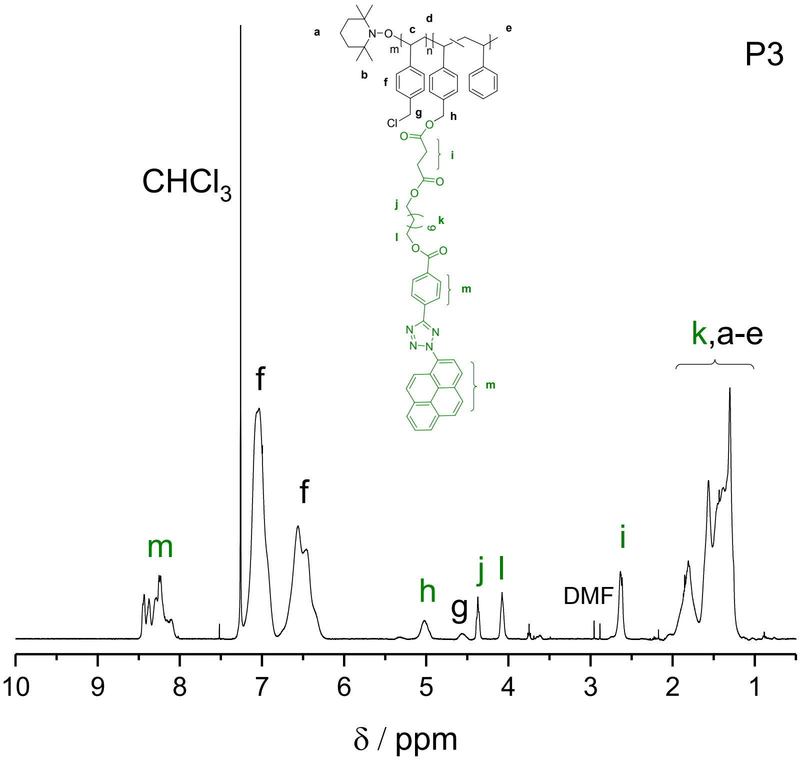


Figure S24: ^{1}H- NMR spectrum of **P3** precursor recorded in CDCl$_3$ at 400 MHz. The resonances corresponding to the PAT functional unit are indicated in green.

2.5 SCNP Analysis

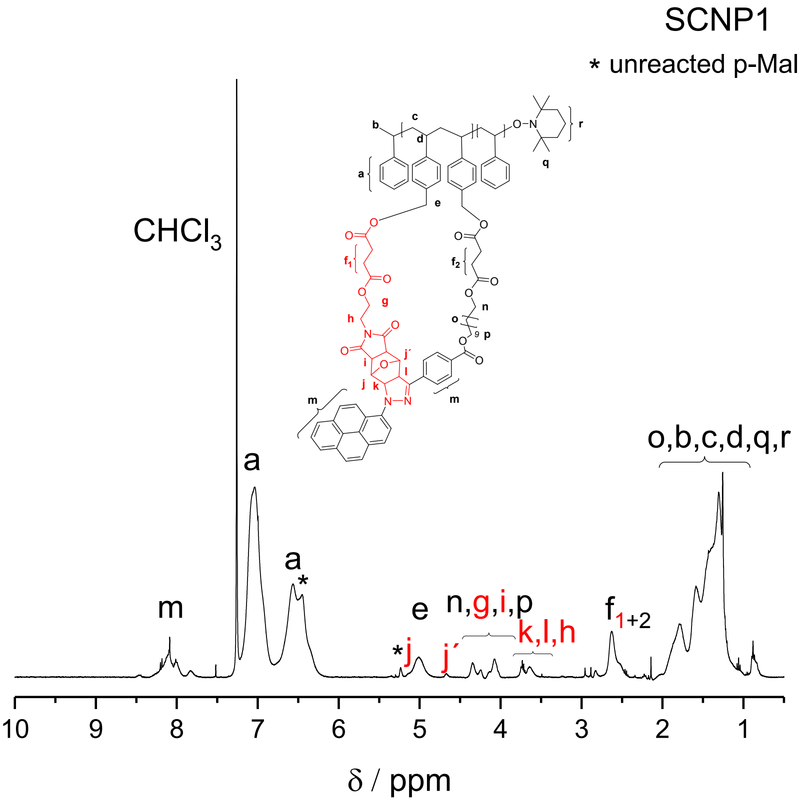


Figure S25: ^{1}H-NMR spectrum of **SCNP1** recorded in CDCl$_3$ at 400 MHz. Resonances corresponding to the generated pyrazoline adduct are highlighted in red.

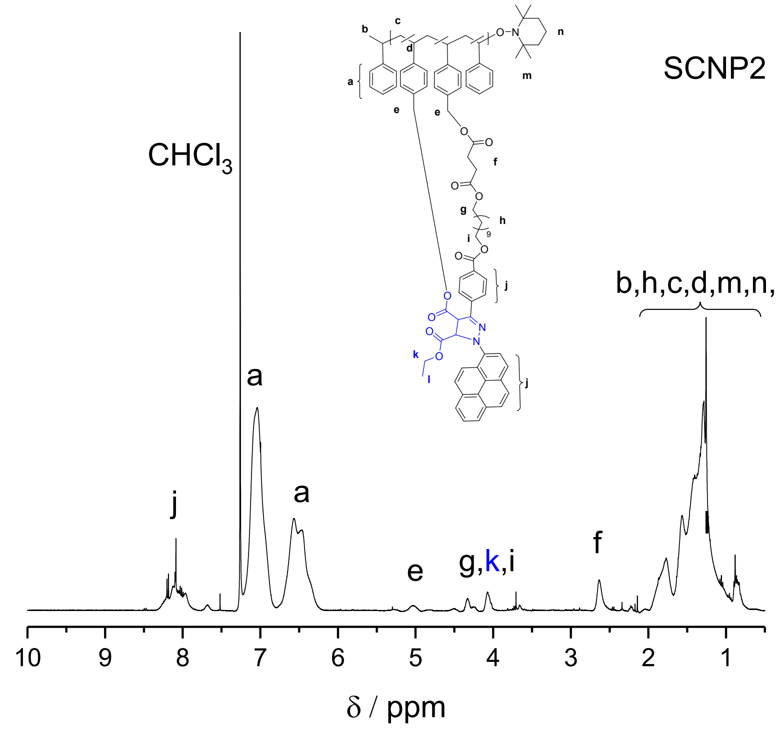


Figure S26: ^{1}H-NMR spectrum of the **SCNP2** recorded in $CDCl_3$ at 400 MHz. Resonances corresponding to the generated pyrazoline adduct are highlighted in blue.

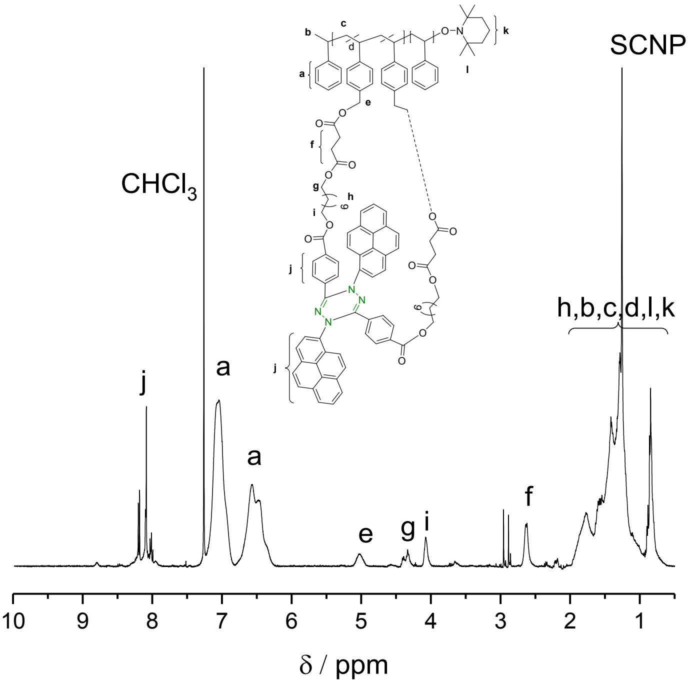


Figure S27: ^{1}H-NMR spectrum of the **SCNP3** recorded in $CDCl_3$ at 400 MHz.

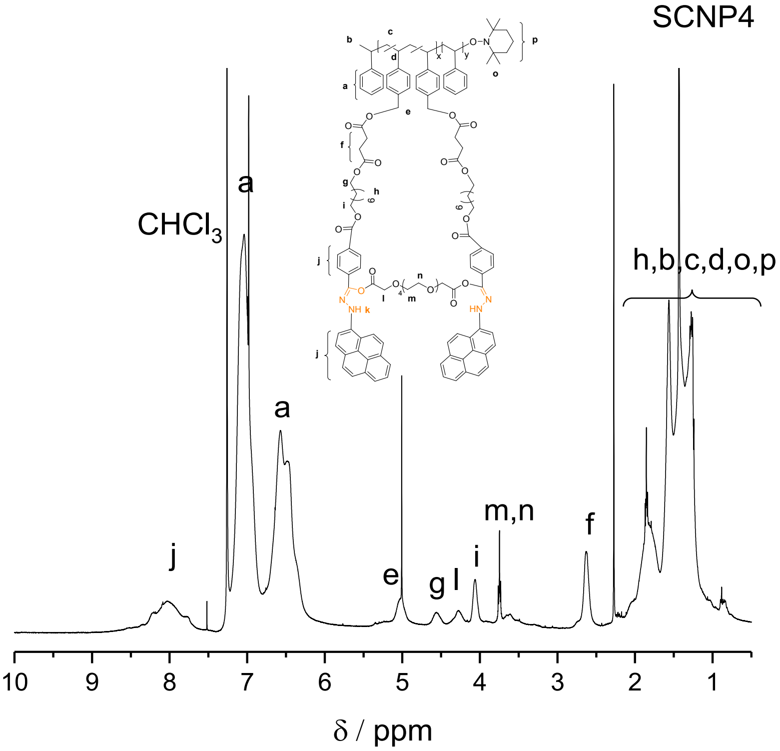


Figure S28: ^{1}H-NMR spectrum of the **SCNP4** recorded in $CDCl_3$ at 400 MHz.

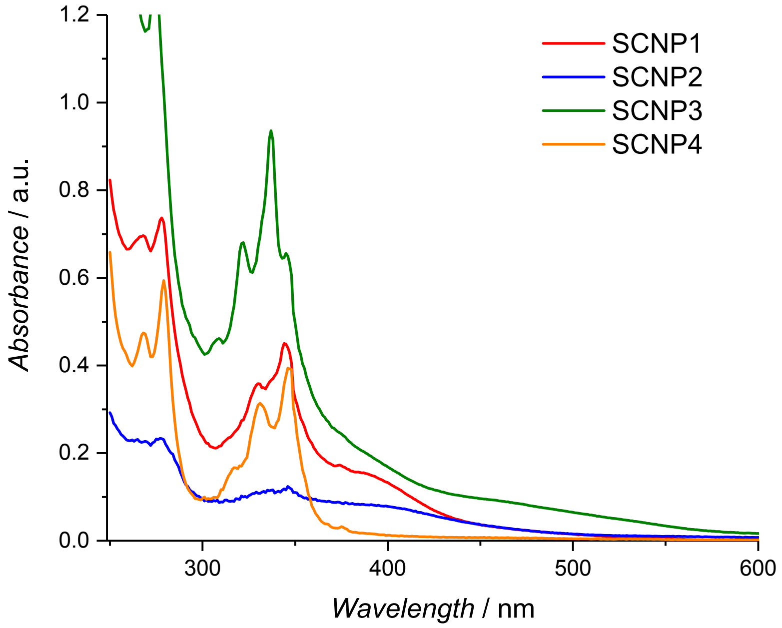


Figure S29: UV/Vis spectra of the synthesized **SCNP1-4**

3. DOSY-NMR experiments

3.1 Exemplary DOSY data fit for PS/CMS (P1-P3) precursors and SCNPs

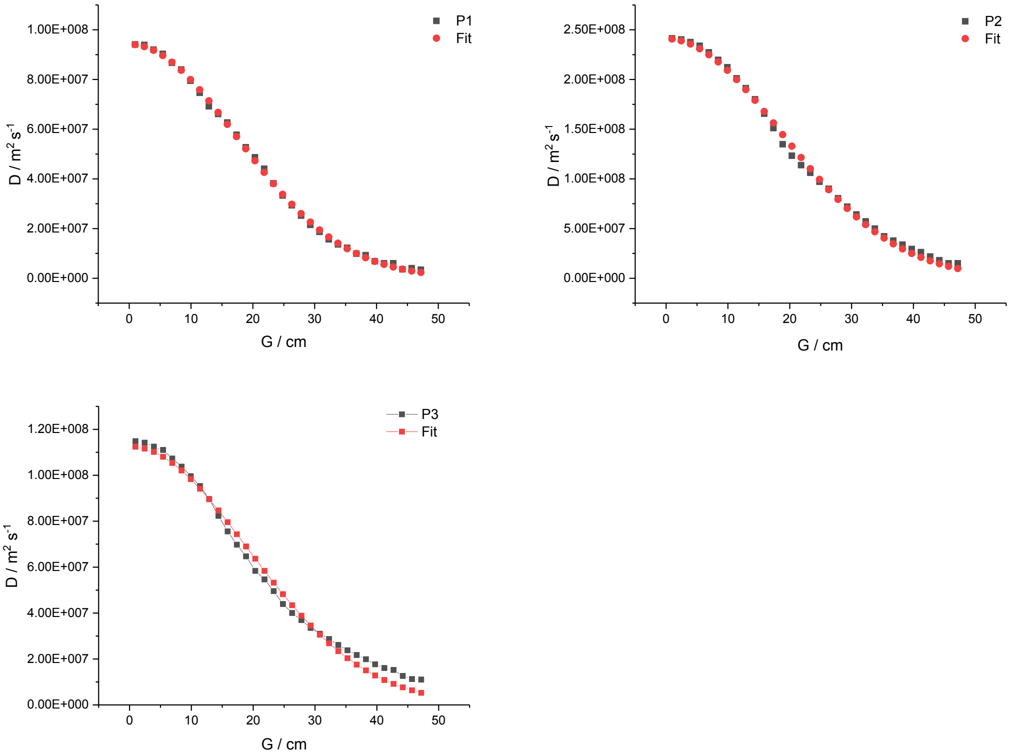


Figure S30: DOSY data fit of the polymer precursors (7.09 ppm, polymer backbone signal)

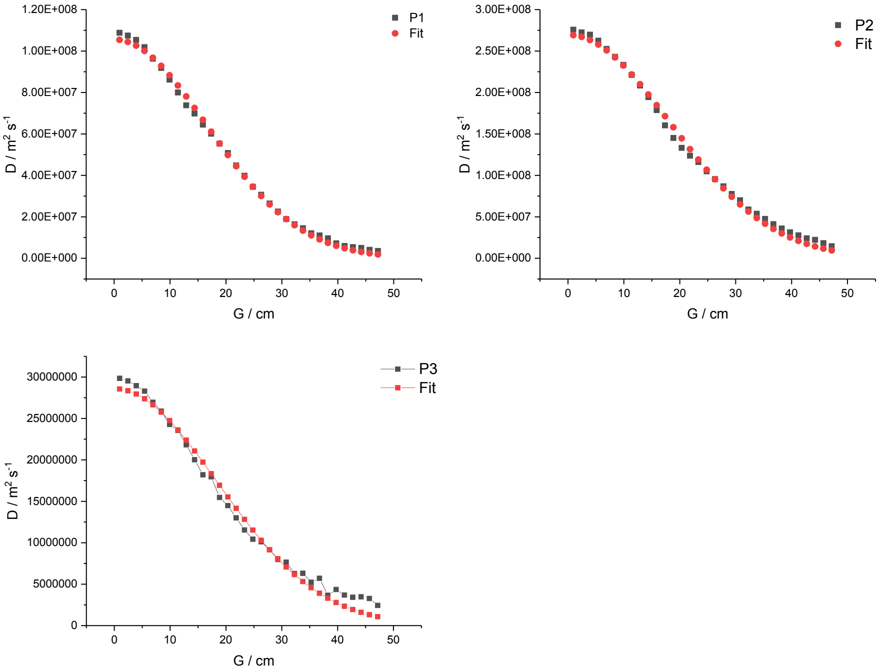


Figure S31: DOSY data fit of the polymer precursors (2.66 ppm, tetrazole signal)

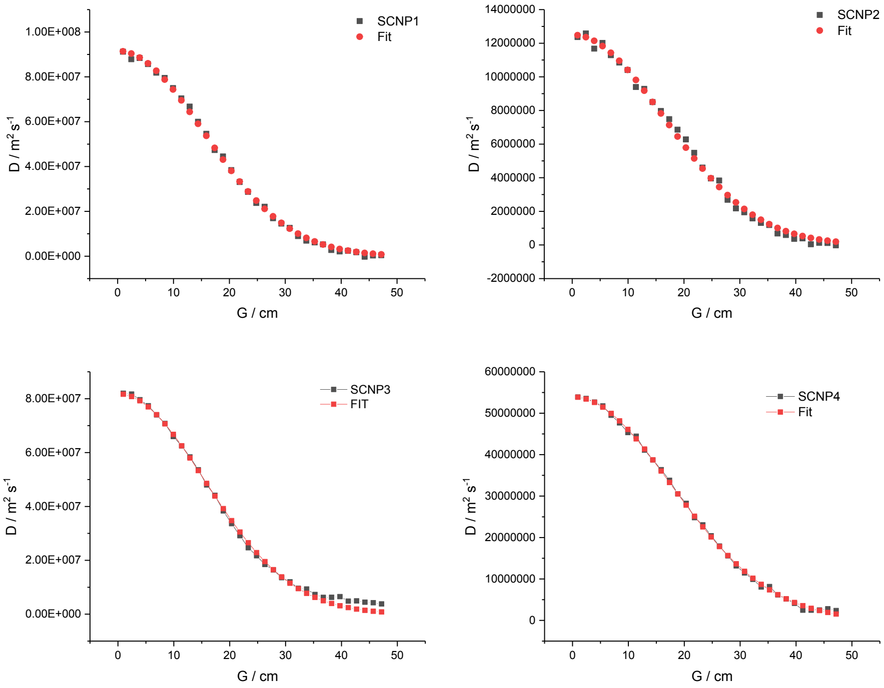


Figure S32: DOSY data fit of the SCNPs (7.09 ppm, polymer backbone signal))

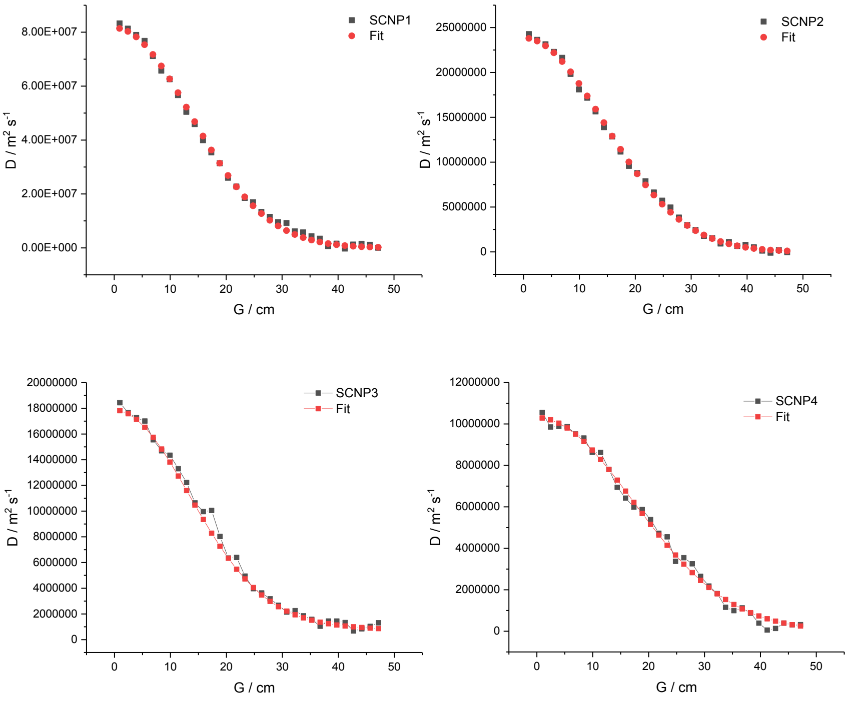


Figure S33: DOSY data fit of the SCNPs (2.66 ppm, tetrazole signal)

Table S3: Diffusion coefficients and diameters of the different polymers and the corresponding SCNPs calculated from DOSY-NMR experiments

Polymer	***Diffusion coefficient [m^2 s^{-1}]***	***Signal [ppm]***	***Diameter [nm]***
P1	$1.30\ 10^{-10}$	7.09	6.26
	$1.35\ 10^{-10}$	5.26	6.03
	$1.29\ 10^{-10}$	2.66	6.31
SCNP1	$2.77\ 10^{-10}$	7.09	2.94
	$2.73\ 10^{-10}$	6.48	2.98
	$2.89\ 10^{-10}$	2.65	2.81
P2	$1.50\ 10^{-10}$	7.09	5.42
	$1.51\ 10^{-10}$	5.05	5.39
	$1.44\ 10^{-10}$	4.39	5.65
SCNP2	$2.92\ 10^{-10}$	6.59	2.78
	$2.93\ 10^{-10}$	4.10	2.77
	3.1110^{-10}	2.65	2.61
P3	$7.66\ 10^{-11}$	7.09	10.6
	$7.52\ 10^{-11}$	6.58	10.8
	$7.74\ 10^{-11}$	2.65	10.5
SCNP3	$1.60\ 10^{-10}$	7.07	5.05
	$1.56\ 10^{-10}$	6.50	5.22
	$1.72\ 10^{-10}$	2.66	4.73
SCNP4	$2.09\ 10^{-10}$	7.05	3.89
	$2.12\ 10^{-10}$	6.50	3.84
	$2.18\ 10^{-10}$	2.65	3.73

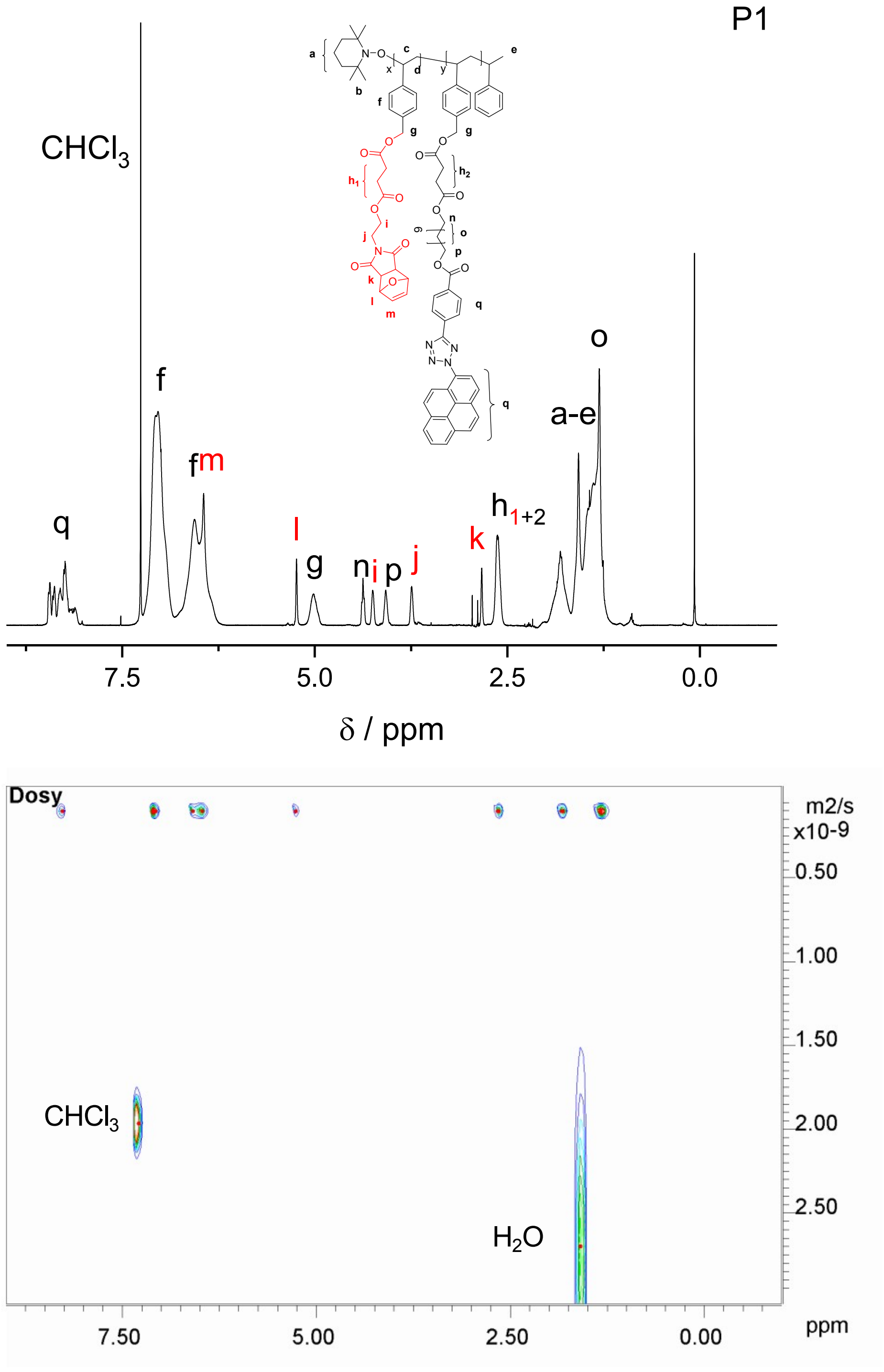


Figure S34: 2D DOSY spectrum of polymer **P1**

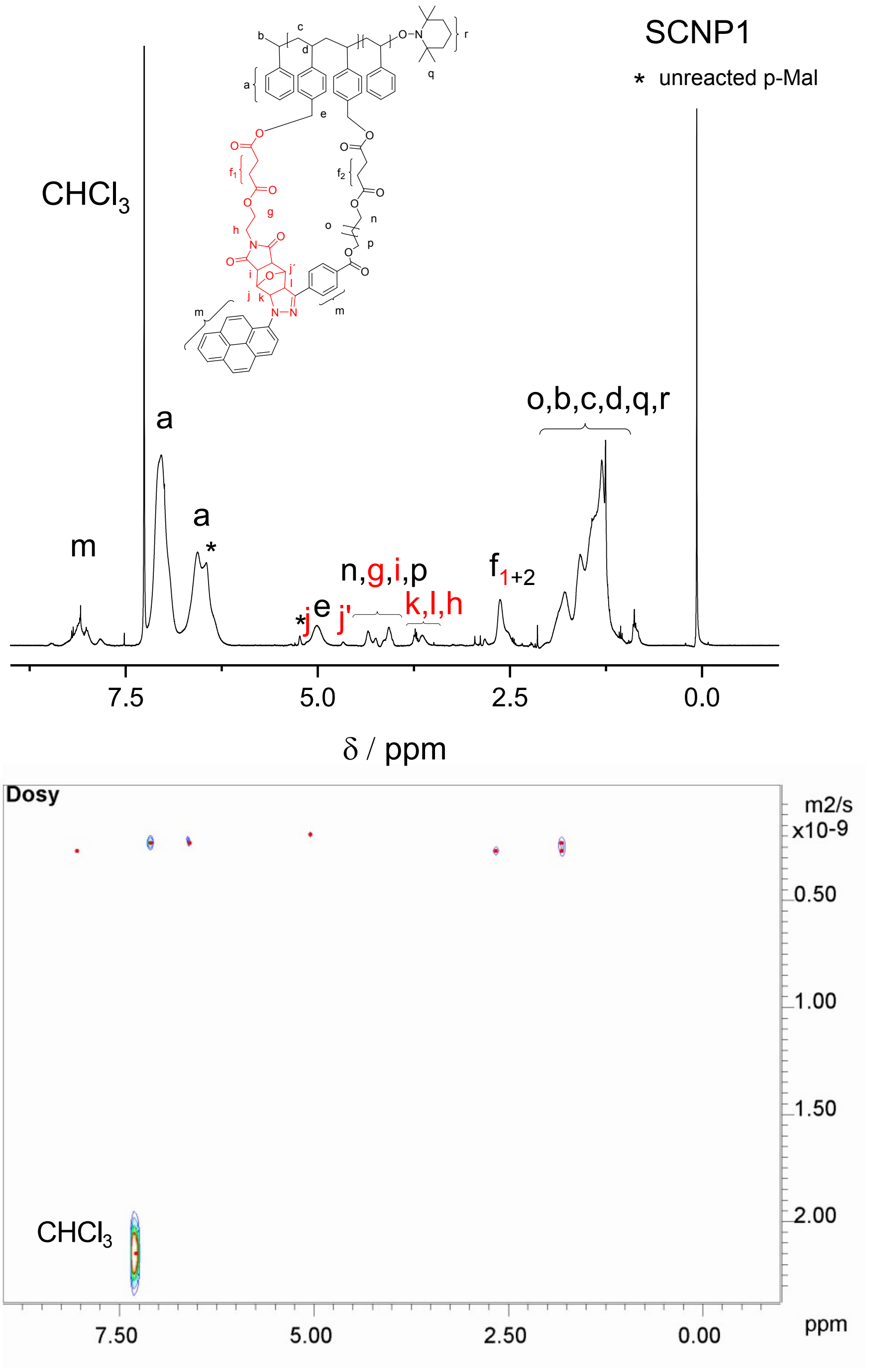


Figure S35: 2D DOSY spectrum of polymer **SCNP1**

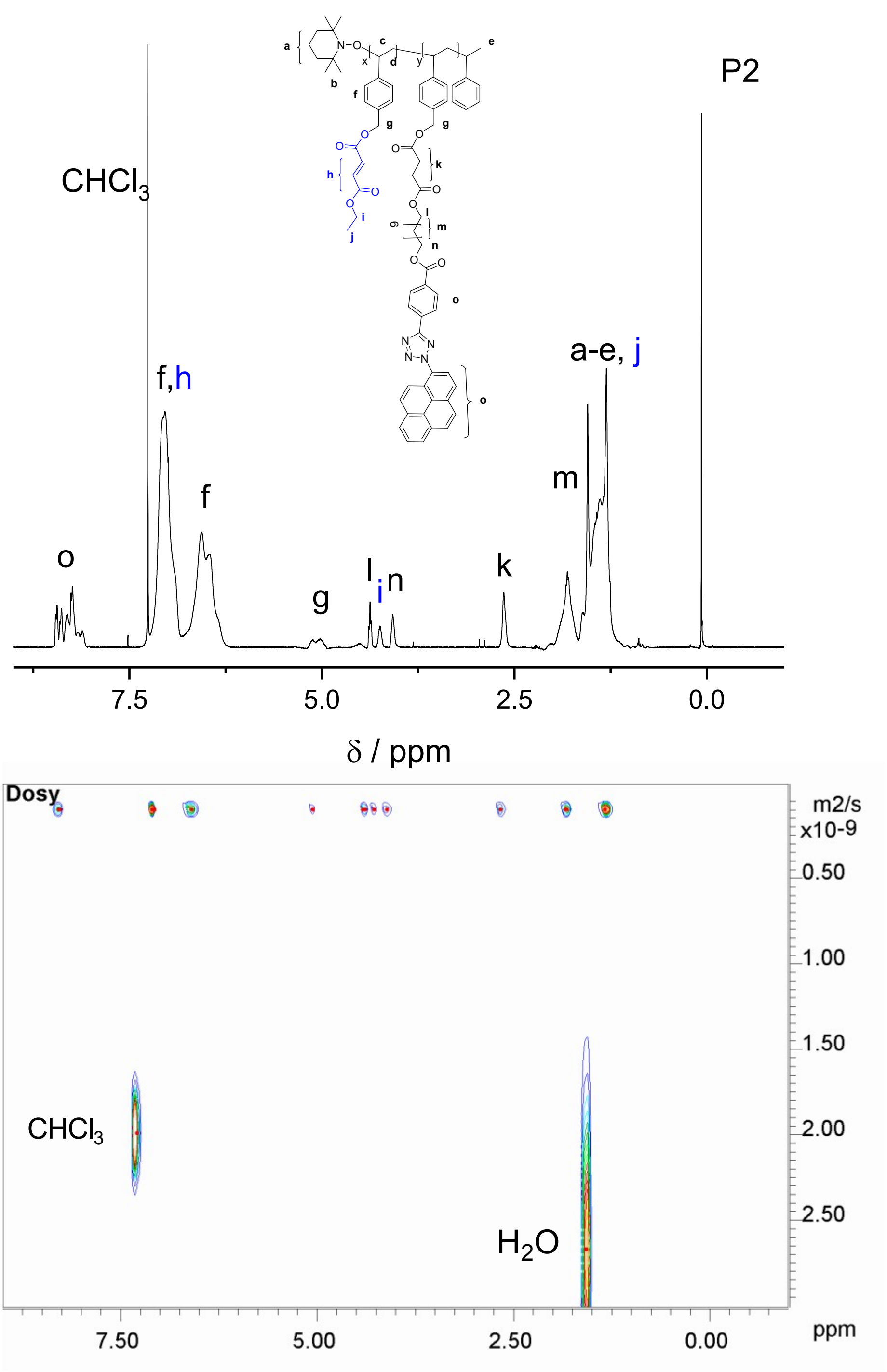


Figure S36: 2D DOSY spectrum of polymer **P2**

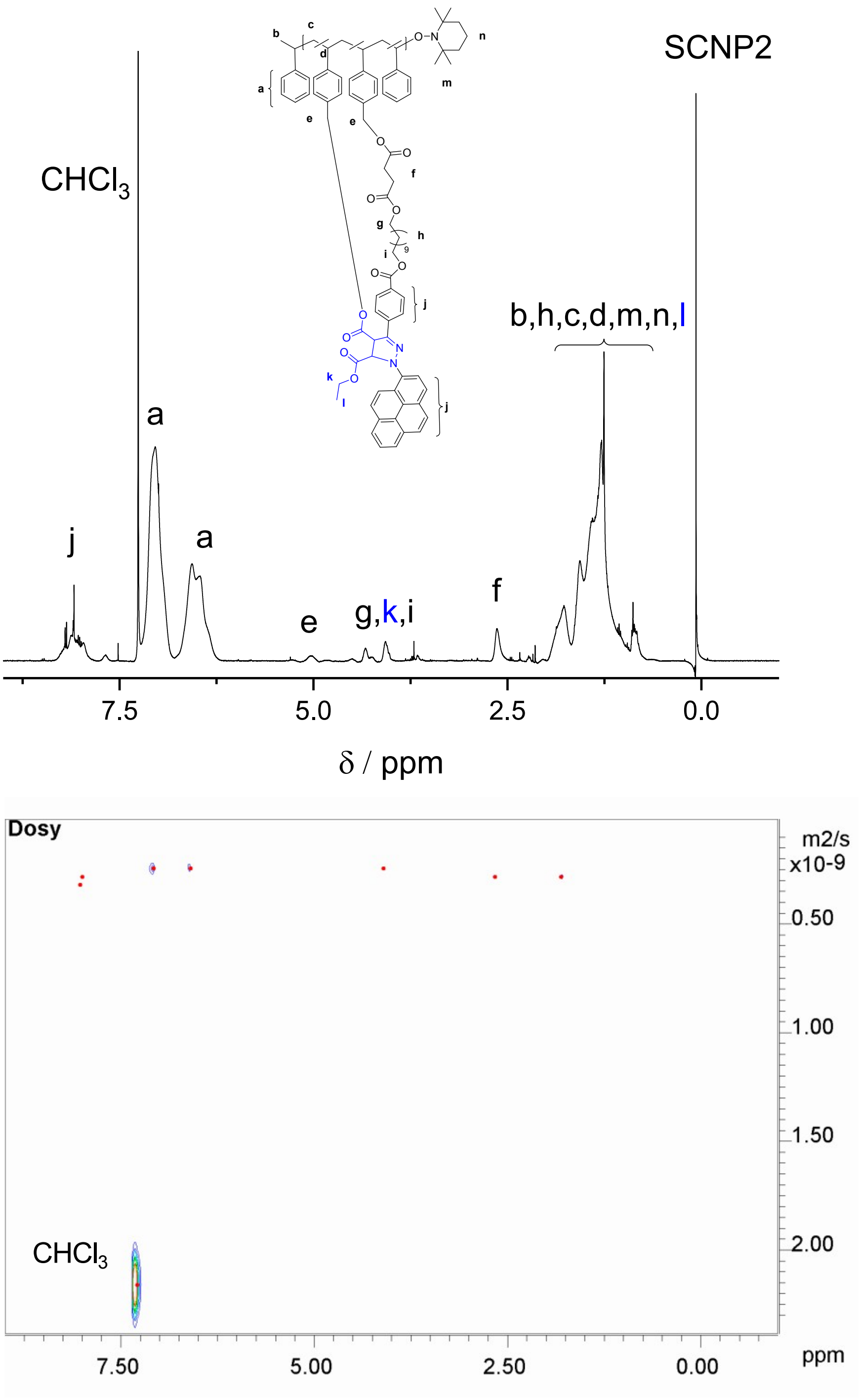


Figure S37: 2D DOSY spectrum of polymer **SCNP2**

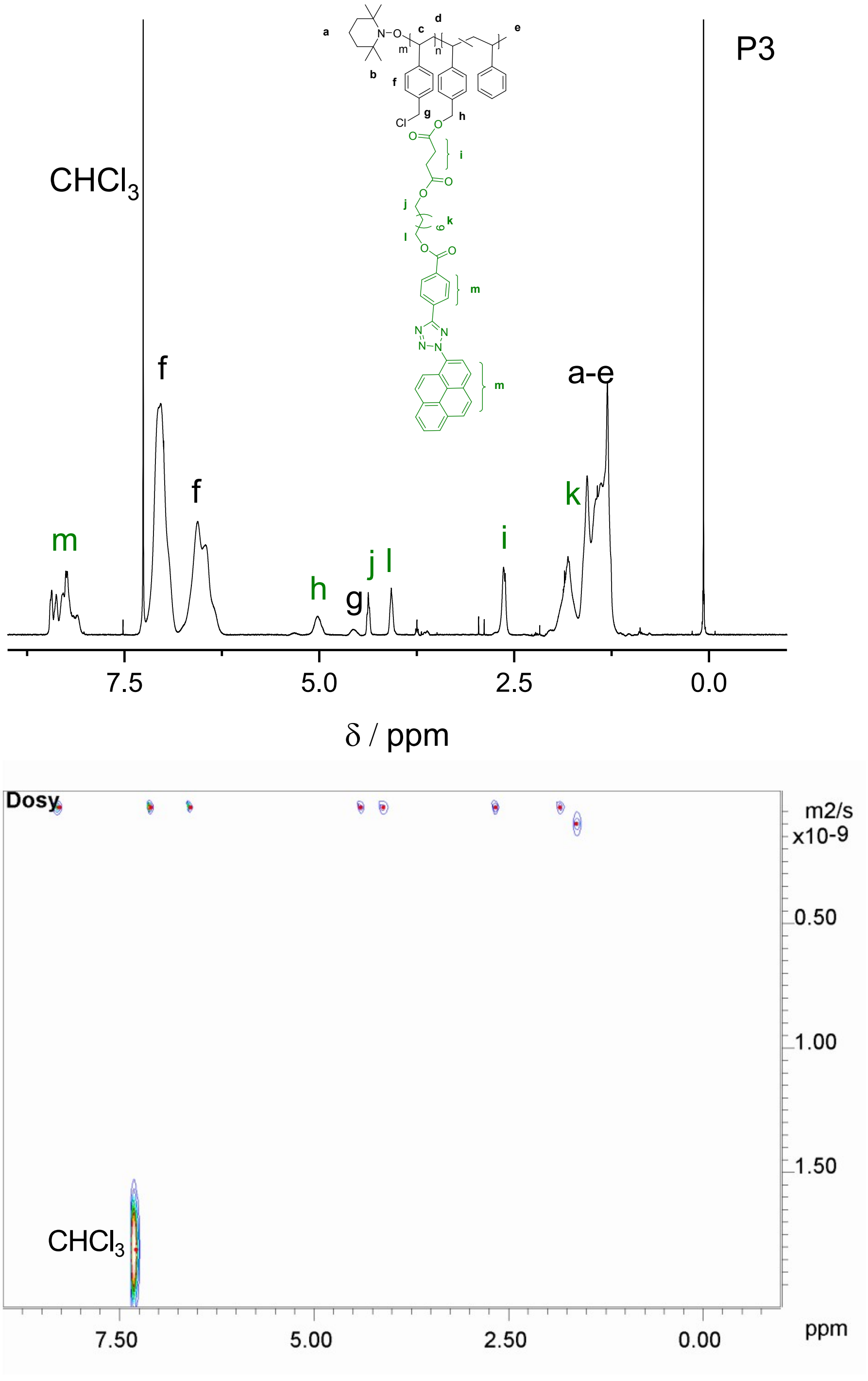


Figure S38: 2D DOSY spectrum of polymer **P3**

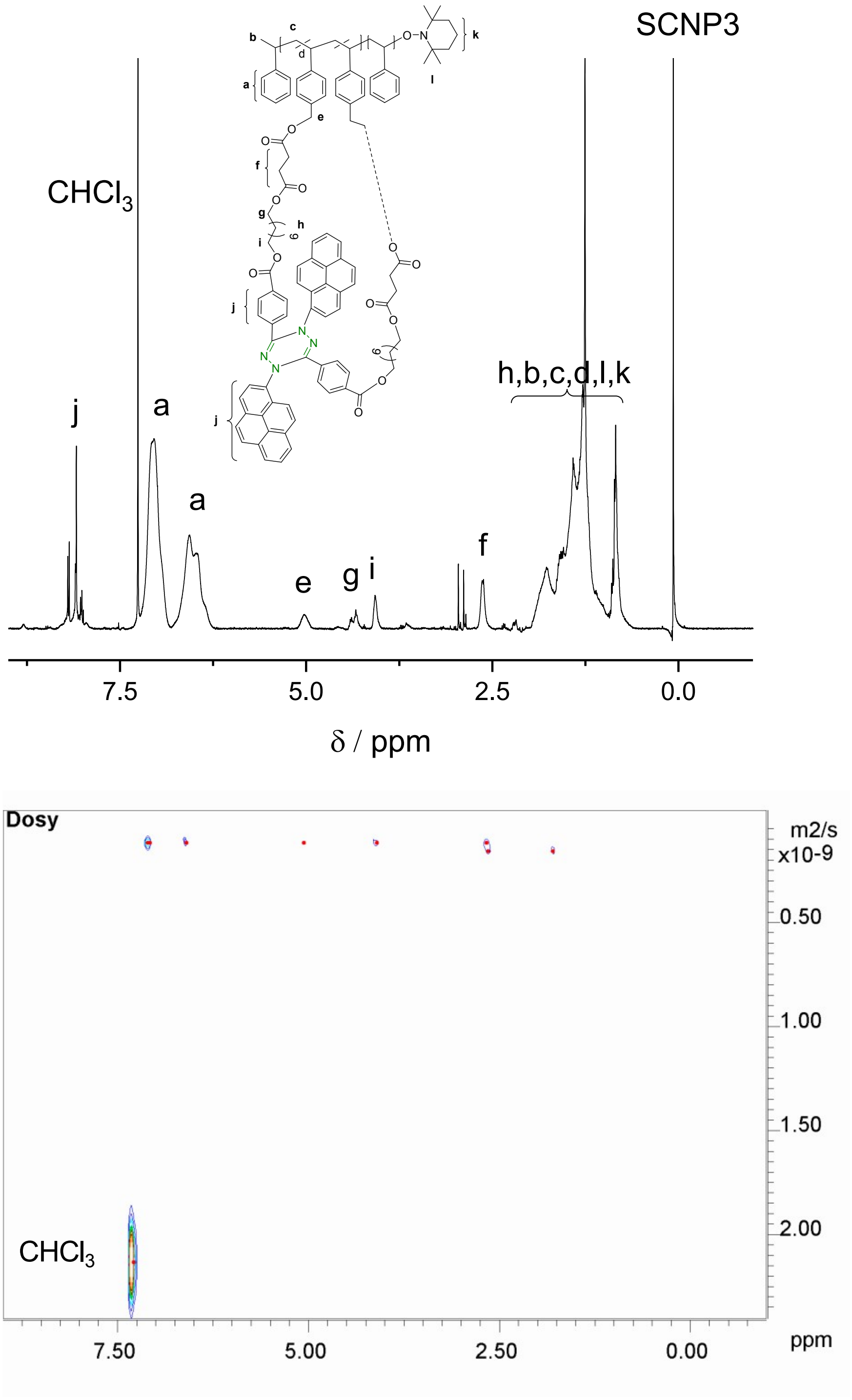


Figure S39: 2D DOSY spectrum of polymer **SCNP3**

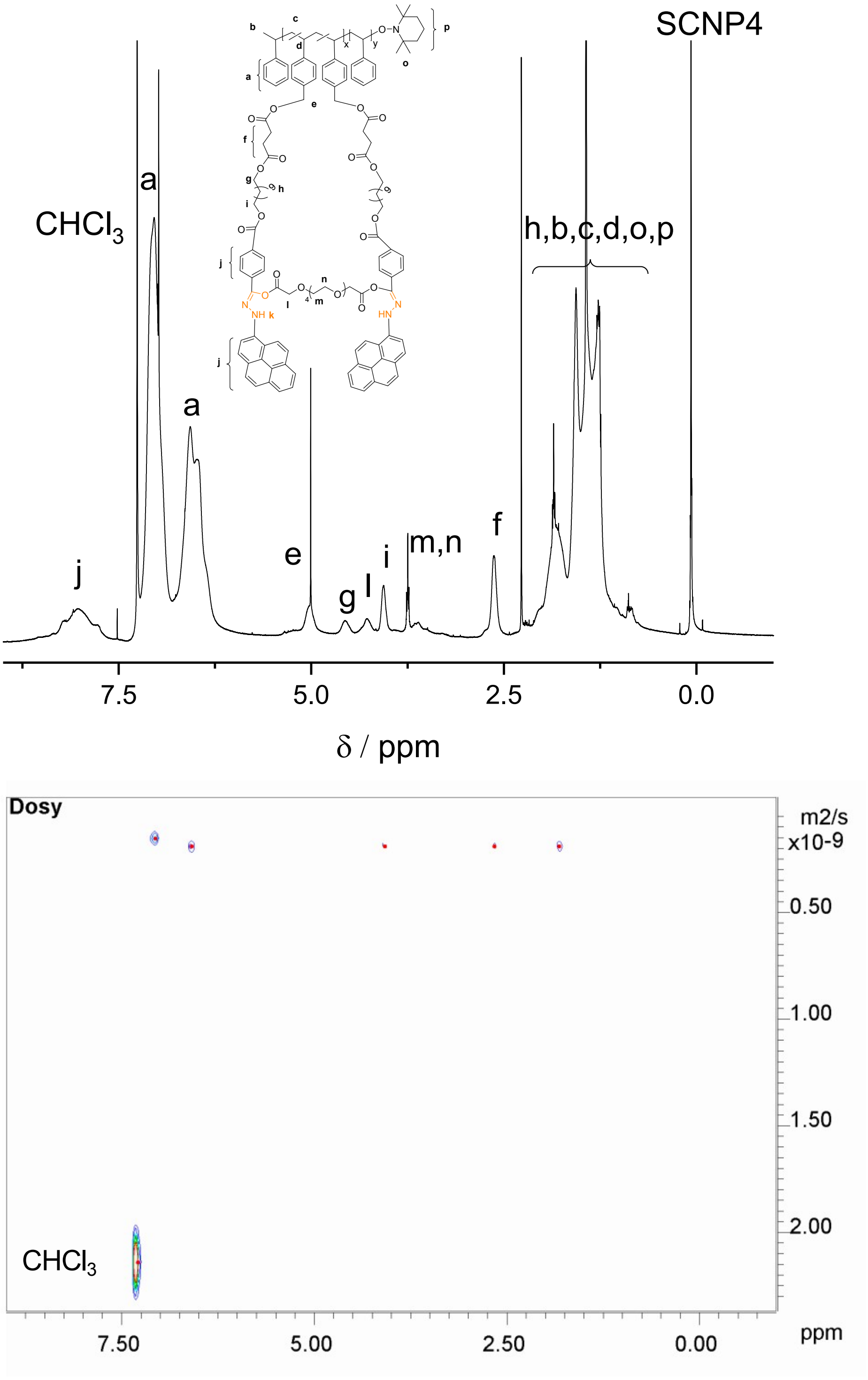


Figure S40: 2D DOSY spectrum of polymer **SCNP4**

4. General procedure for the photo-induced single chain nanoparticle formation

Solutions of the functionalized linear precursor polymers were prepared in DCM (c = 0.017 mg mL^{-1}) and irradiated for 1.5 h with an Avonec LED setup using 3 lamps (Figure S41) with a wavelength emission from 410-420 nm (Figure S42) in a custom build photoreactor The round bottom flask equipped with a stir bar was placed in the middle and 3 Avonec LED lamps were placed in a triangular geometry (Figure S43). The solvent was removed under reduced pressure to afford the fluorescent single-chain polymer nanoparticles, which were directly dissolved in the appropriate solvent for analysis.

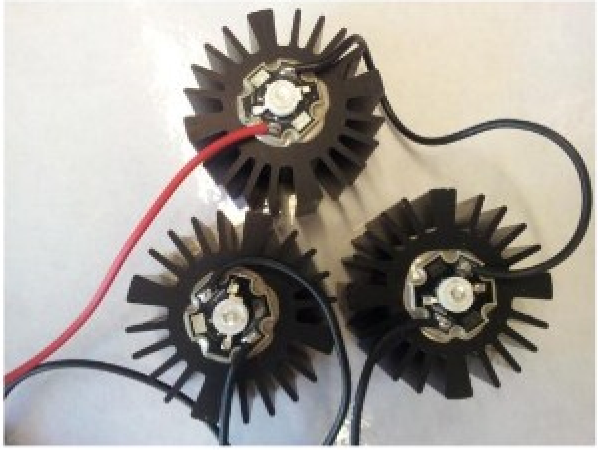


Figure S41: Photograph of the Avonec LED lamps (410-420 nm) (3 x 3 W)

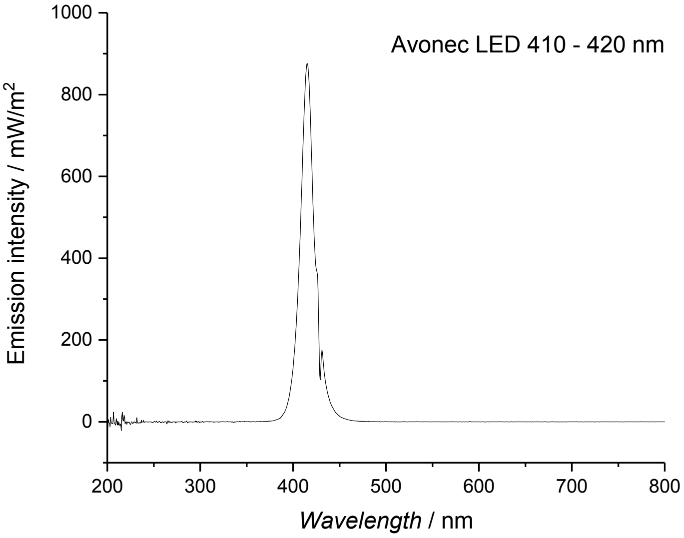


Figure S42: Emission intensity spectrum of the set-up (3xLED) employed

Figure S43: Custom built photoreactor used for the reactions

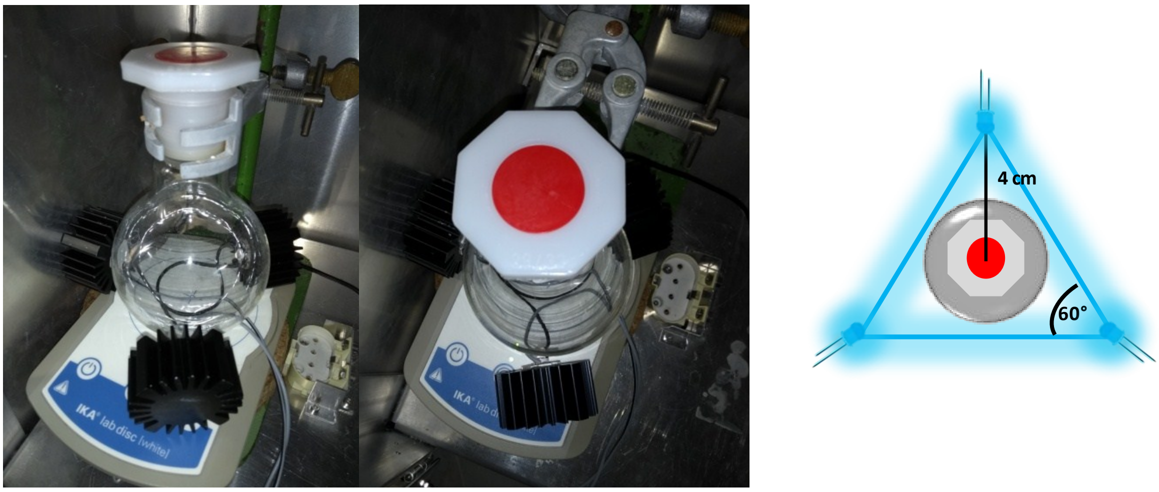


Figure S44: Left: Images of the irradiation setup (frontal and aerial view). Right: Scheme of the geometry of the flask and 3 LED-set-up employed

References

(1) Brandrup J-, Immergut H. E., E. A. G. *Polymer Handbook, 4th Edition*; 2003.

(2) Willenbacher, J.; Wuest, K. N. R.; Mueller, J. O.; Kaupp, M.; Wagenknecht, A.; Barner-Kowollik, C. *ACS Macro Lett.* **2014**, *3*, 574.

(3) Lederhose, P.; Wüst, K. N. R.; Barner-Kowollik, C.; Blinco, J. P. *Chem. Commun.* **2016**, *52*, 5928.

(4) Lederhose, P. *From UV to NIR Light, Photo-Triggered 1,3-Dipolar Cycloadditions as a Modern Ligation Method in Solution and on Surface*; Dissertation **2016**, Karlsruhe,.