Contents

I.   Materials

3,5-Dimethylphenol (Sigma-Aldrich, 98%), caesium carbonate (Acros Organics, 95%), 11-bromo-1-undecanol (Combi-Blocks, 98%), methacryloyl chloride (Sigma-Aldrich, 97%), 1-aminopyrene (Sigma-Aldrich, 97%), 4-Amino-2,6-dichlorophenol (Combi-Blocks, 98%), maleic anhydride (Sigma-Aldrich, 99%), triethylamine (Ajax, 95%), N,N′-dicyclohexylcarbodiimide (DCC, Sigma-Aldrich, 99%), oxalyl chloride (Sigma-Aldrich, 98%), methyl methacrylate (Sigma-Aldrich, 99%), 2-Cyano-2-propyl benzodithioate (Sigma-Aldrich, 97%), hydrogen peroxide (Ajax, 30w% in water), sodium hydrogencarbonate (Sigma-Aldrich, 99.5%), magnesium sulphate (Merck, 98%), and magnesium chloride (anhydrous, Sigma-Aldrich, 98%) were used as received. Azobis-(isobutylonitrile) (AIBN, Sigma-Aldrich, 12w% in acetone) was recrystallised from methanol.

N,N-dimethylformamide (DMF, Ajax), acetone (Ajax), acetonitrile (ACN, RCI labscan), tetrahydrofuran (THF, Ajax), dichloromethane (DCM, Fisher Scientific), toluene (Fisher Scientific), diethyl ether (Ajax), methanol (Ajax), n-hexane (CH, Ajax) and ethyl acetate (EA, Ajax), were used as solvents. Deuterated solvent such as chloroform-d (CDCl$_3$, 99.8%), and DCM-d_2 (CD$_2$Cl$_2$, 99.8%), were purchased from Novachem and used as received.

II.   Characterisation Methods

Nuclear magnetic resonance spectroscopy (NMR)

NMR spectra were recorded on a Bruker System 600 Ascend LH, equipped with a BBO-Probe (5 mm) with z-gradient (1H: 600.13 MHz, 13C: 150.90 MHz,19F: 564.63 MHz, respectively). Chemical shifts are expressed in parts per million (ppm) relative to tetramethylsilane (TMS) and referenced to characteristic residual ^{1}H solvent resonances as internal standards [CDCl$_3$: 7.26 ppm; DCM-d$_2$: 5.32 ppm]. ^{1}H NMR spectra are reported as follows: chemical shift (δ in ppm), multiplicity (s for singlet, d for doublet, t for triplet, q for quartet, p for pentet, m for multiplet, and br for broad signal), coupling constant(s) (Hz), number of protons (concluded from the integrals), specific assignment. ^{13}C-{^{1}H} NMR spectra are reported in terms of chemical shift and specific assignment.

Diffusion Ordered NMR Spectroscopy (DOSY)

DOSY experiments based on ^{1}H NMR were performed in DCM-d_2 at 296 K on a Bruker 400 UltraShield spectrometer equipped with a Quattro Nucleus Probe (QNP) with an operating frequency of 400 MHz (^{1}H). A sequence with longitudinal eddy current delay (LED) using bipolar gradients was employed in order to compensate eddy currents. A bipolar gradient $δ$ = 5 ms and a diffusion delay $Δ$ = 100 ms were used. Gradient strength was linearly incremented from 2% at 0.96 G to 95% at 45.7 G in 64 steps. The obtained data was processed with TopSpin 4.0.6.

After Fourier transform of the 1D spectra, the signal decay along the gradients G was fitted to:

$$f(G) = I_0 * e^{-D * G^2 * \gamma^2 * \delta^2 * \left(\Delta - \frac{\delta}{3}\right)} * 10^4$$

with the gyromagnetic ratio γ and the full signal intensity I_0.

Hydrodynamic radii r_H were calculated from the Stokes-Einstein equation:

$$d_H = \frac{k_B * T}{3 * \pi * \eta * D}$$

Where k_B is the Boltzmann constant, T the temperature and η the solvent viscosity (DCM: 0.413 mPa*s).[1]

Chloroform-Size Exclusion Chromatography (SEC) 'standard mode'
The SEC measurements were conducted on a Waters Breeze QS HPLC system consisting of a Waters 1515 Isocratic HPLC Pump, a Waters 1500 Series Column Heater (35 °C), PSS SDV Column Set (8x150 mm 5 µm Precolumn, 8x300 mm 5 µm Analytical Columns, 100000 Å, 1000 Å and 100 Å), a Waters 2707 Autosampler, a Waters 2414 Refractive Index (RI) Detector (35 °C), and a Waters 2489 UV/Visible Detector (Wavelength A: 254 nm, Wavelength B: 360 nm). Analytical grade chloroform, stabilized with amylene, is used as eluent at a flow rate of 1 mL·min^{-1}. Narrow disperse linear poly(styrene) (M_n: 266 g·mol^{-1} to 2.52x10^6 g·mol^{-1}) and poly(methyl methacrylate) (M_n: 202 g·mol^{-1} to 2.2x10^6 g·mol^{-1}) standards (PSS ReadyCal) were used as calibrants. All samples were passed over 0.22 µm PTFE membrane filters. Molecular weight and dispersity analysis was performed in the Waters Breeze 2 software.

THF-SEC 'triple detection'
The SEC measurements were conducted on a PSS SECurity2 system consisting of a PSS SECurity Degasser, PSS SECurity TCC6000 Column Oven (35 °C), PSS SDV Column Set (8x150 mm 5 µm Precolumn, 8x300 mm 5 µm Analytical Columns, 100000 Å, 1000 Å and 100 Å) and an Agilent 1260 Infinity Isocratic Pump, Agilent 1260 Infinity Standard Autosampler, Agilent 1260 Infinity Diode Array and Multiple Wavelength Detector (A: 254 nm, B: 360 nm), Agilent 1260 Infinity Refractive Index Detector (35 °C), PSS SLD7100 Multiangle Laser Light Scattering (MALLS) Detector and PSS DVD1260 four capillary viscometer. HPLC grade THF, stabilized with BHT, is used as eluent at a flow rate of 1 mL·min-1. All samples were passed over 0.22 µm PTFE membrane filters. Molecular weight and dispersity analysis was performed in PSS WinGPC UniChrom software (version 8.2). Molecular weights were calculated via an iterative algorithm using light scattering and viscosity signals.

Chemiluminescence (CL) Kinetics
Emission intensities of chemiluminescence was investigated using a Tecan Spark multimode microplate reader. CL measurements were performed using an OptiPlate-96

Black Opaque microplate (Polystyrene, PerkinElmer). The investigated SCNP solutions exhibited a concentration of 1 mg·mL^{-1} polymer in DMF. The photon count was measured in luminescence mode in 12 s intervals for 3 h in the range of 360 to 700 nm using an integration time of 1000 ms (software Tecan SparkControl). At the beginning of each interval, the reader plate was shaken mechanically for three seconds at 270 rpm in a double-orbital to ensure sufficient mixing of the solution.

The procedure is as follows: 100 µL of 1 mg·mL^{-1} SCNP in DMF added to a well of the reader plate. Subsequently, 6 µL of a 30% H$_2$O$_2$ solution was added to each well, the well plate was covered with an appropriate cover slide and the measurement was started immediately.

Photoreactor

The samples were irradiated in a Luzchem LZC-4V photoreactor using LZC-UVA lamps, centred at ~350 nm (see spectrum below). Six lamps were installed for side irradiation. Homogeneous irradiation was achieved by stirring the sample solutions during irradiation. The internal chamber was ventilated to maintain ambient temperature during the entire experiment.
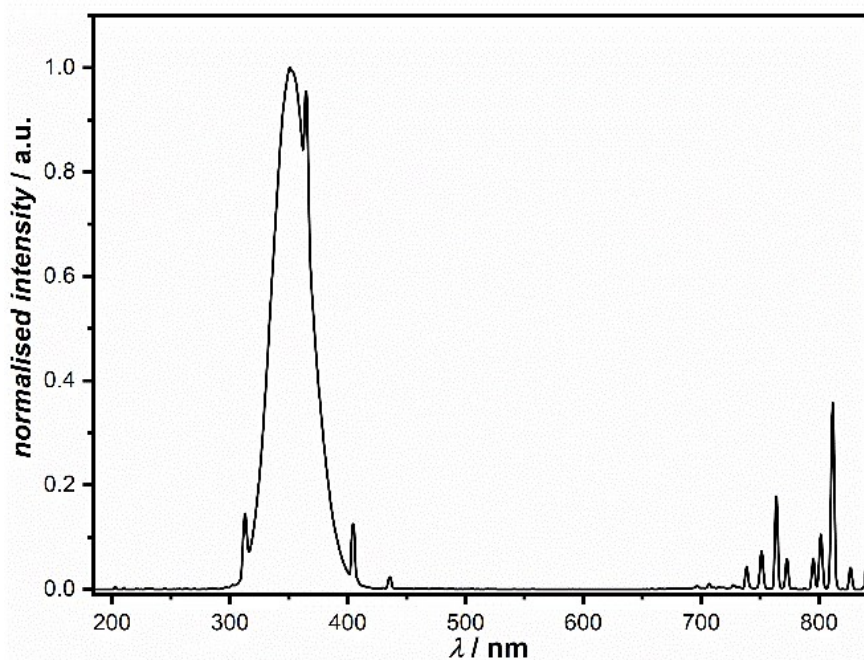

Figure S1. Emission spectrum of the LZC-UVA lamps.

Interchim XS420 + SofTA Model 400 ELSD

Flash chromatography was performed on an Interchim XS420+ flash chromatography system consisting of a SP-in-line filter 20 µm, a UV-VIS detector (200-800 nm) and a SofTA Model 400 ELSD (55 °C drift tube temperature, 25 °C spray chamber temperature, filter 5, EDR gain mode) connected *via* a flow splitter (Interchim Split ELSD F04590). The separations were performed using an Interchim dry load column and an Interchim Puriflash Silica HP 30 µm column.

III. Syntheses

a. Synthesis of the Photo-Enol-Monomer (4)
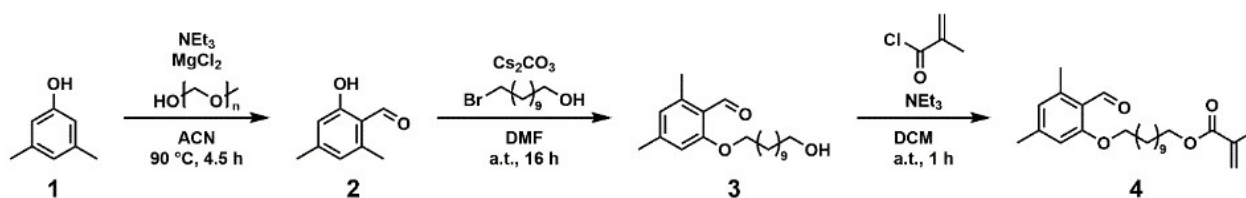
Scheme S1. Synthesis of the photo-enol monomer **4**.

2-hydroxy-4,6-dimethylbenzaldehyde (2)
2 was synthesised according to a literature procedure.[2]
¹H NMR (CDCl$_3$): δ = 11.93 (s, 1H, OH), 10.21 (s, 1H, CHO), 6.60 (s, 1H, CH$_{Ar}$), 6.51 (s, 1H, CH$_{Ar}$), 2.53 (s, 3H, CH$_3$), 2.29 (s, 3H, CH$_3$) ppm. **¹³C NMR** (CDCl$_3$): δ = 195.33, 163.15, 142.15, 141.87, 137.38, 118.52, 116.04, 18.31, 18.03 ppm.

2-((11-hydroxyundecyl)oxy)-4,6-dimethylbenzaldehyde (3)
2 (3.00 g, 20.0 mmol, 1.00 eq) and caesium carbonate (7.71 g, 40.0 mmol, 2.00 eq) were dissolved in DMF (200 mL). 1-Bromoundecanol (5.27 g, 21.0 mmol, 1.05 eq) was added and the mixture was allowed to stir at ambient temperature overnight. Subsequently, caesium salts were removed by filtration, the filtrate was diluted with DCM and washed with water. Finally, the solvent was removed under reduced pressure and the crude product was subjected to flash chromatography on silica using n-hexane as the solvent. After removal of the solvent, the pure product **3** was obtained as a colourless oil (6.17 g, 96%).
¹H NMR (CDCl$_3$): δ = 10.60 (s, 1H, CHO), 6.62 (s, 1H, CH$_{Ar}$), 6.59 (s, 1H, CH$_{Ar}$), 4.01 (t, ^3J = 6.3 Hz, 2H, CH$_2$-O), 3.63 (t, ^3J = 6.6 Hz, 2H, **CH$_2$**-OH), 2.53 (s, 3H, CH$_3$), 2.32 (s, 3H, CH$_3$), 1.80 (m, 2H, CH$_2$), 1.56 (m, 2H, CH$_2$), 1.45 (m, 2H, CH$_2$), 1.30 (m, 12H, CH$_2$) ppm. **¹³C NMR** (CDCl$_3$): δ = 192.04, 163.13, 145.74, 141.89, 124.81, 120.99, 110.64, 68.60, 62.89, 32.82, 29.57, 29.51, 29.47, 29.44, 29.30, 29.18, 26.11, 25.78, 22.16, 21.59 ppm. **HR-ESI-MS**: m/z = 321.2430 (M+H$^+$, calculated: 321.2424, Δ_{abs} = 0.0006, Δ_{rel} = 1.87 ppm).

11-(2-formyl-3,5-dimethylphenoxy)undecyl methacrylate (4)
3 (6.17 g, 19.3 mmol, 1.00 eq) and triethylamine (4.03 mL, 2.92 g, 28.9 mmol, 1.50 eq) were dissolved in diethyl ether (100 mL). Methacryloyl chloride (2.26 mL, 2.42 g, 23.1 mmol, 1.50 eq) in diethyl ether (25 mL) was added and the mixture was stirred at ambient temperature for one hour. Subsequently, the mixture was washed with saturated NaHCO$_3$ solution and dried over MgSO$_4$. The solvent was removed under reduced pressure and the crude product was subjected to flash chromatography on silica using n-hexane as the solvent. After removal of the solvent, the pure product **4** was obtained as a colourless oil (6.79 g, 91%).
¹H NMR (CDCl$_3$): δ = 10.61 (s, 1H, CHO), 6.62 (s, 1H, CH$_{Ar}$), 6.60 (s, 1H, CH$_{Ar}$), 6.09 (m, 1H, CH$_{cis}$), 5.54 (m, 1H, CH$_{trans}$), 4.13 (t, ^3J = 6.7 Hz, 2H, CH$_2$-OOC), 4.02 (t, ^3J = 6.4 Hz, 2H, CH$_2$-O), 2.54 (s, 3H, CH$_3$), 2.33 (s, 3H, CH$_3$). 1.94 (s, 3H, CH$_3$), 1.81 (m, 2H, CH$_2$), 1.66 (m, 2H, CH$_2$), 1.47

(m, 2H, CH$_2$), 1.32 (m, 12H, CH$_2$) ppm. ^{13}**C NMR** (CDCl$_3$): δ = 192.04, 163.13, 145.74, 141.89, 124.81, 120.99, 110.64, 68.60, 62.89, 32.82, 29.57, 29.51, 29.47, 29.44, 29.30, 29.18, 26.11, 25.78, 22.16, 21.59 ppm. **HR-ESI-MS**: m/z = 411.2501 (M+Na$^+$, calculated: 411.2506, Δ_{abs} = 0.0005, Δ_{rel} = 1.22 ppm).

b. Synthesis of 1-Pyrenyl Methacrylamide (5)
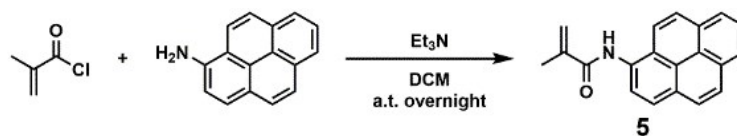
Scheme S2. Synthesis of the 1-pyrenyl methacryloylamide **5**.

Aminopyrene (1.00 g, 4.60 mmol, 1.00 eq) and triethyl amine (770 µL, 559 mg, 5.52 mmol, 1.20 eq) were dissolved in DCM (50 mL) and cooled to 0 °C. Methacryloyl chloride (540 µL, 577 mg, 5.52 mmol, 1.20 eq) was added dropwise and the mixture was allowed to stir overnight. The crude mixture was washed with saturated NaHCO$_3$ solution and dried over MgSO$_4$. The solvent was removed under reduced pressure and the crude product was subjected to flash chromatography on silica using a gradient from 100% n-hexane to 100% ethyl acetate as the eluent. After removal of the solvent, the pure product **5** was obtained as a green solid (1.24 g, 94%).
^{1}**H NMR** (CDCl$_3$): δ = 8.47 (d, ^{3}J = 8.2 Hz, 1H, CHO), 8.19 (m, 4H, CH$_{Ar}$), 8.11 (d, 1H, CH$_{Ar}$), 8.03 (m, 4H, CH$_{Ar}$), 6.05 (m, 1H, CH$_{cis}$), 5.61 (m, 1H, CH$_{trans}$), 2.23 (s, 3H, CH$_3$) ppm. ^{13}**C NMR** (CDCl$_3$): δ = 131.49, 130.92, 130.37, 129.34, 128.21, 127.50, 127.05, 126.33, 125.70, 125.41, 125.33, 125.25, 124.93, 123.68, 122.32, 120.57, 120.15, 19.15 ppm. **HR-ESI-MS**: m/z = 308.1057 (M+Na$^+$, calculated: 308.1046, Δ_{abs} = 0.0011, Δ_{rel} = 3.57 ppm).

c. Synthesis of the crosslinker (MDCPO, 6)
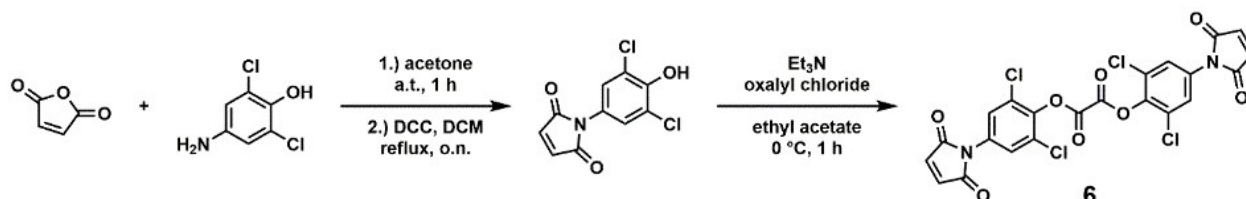
Scheme S3. Synthesis of the the phenyloxalate crosslinker **6**.

MDCPO (6) was synthesised according to a literature procedure.[3]
^{1}**H NMR** (DMSO): δ = 7.63 (s, 4H, CH$_{Ar}$), 6.92 (s, 4H, CH) ppm. ^{13}**C NMR** (DMSO): δ = 169.04, 152.25, 140.84, 135.08, 132.00, 127.37, 127.02 ppm. **HR-ESI-MS**: m/z = 308.1057 (M+Na$^+$, calculated: 308.1046, Δ_{abs} = 0.0011, Δ_{rel} = 3.57 ppm).
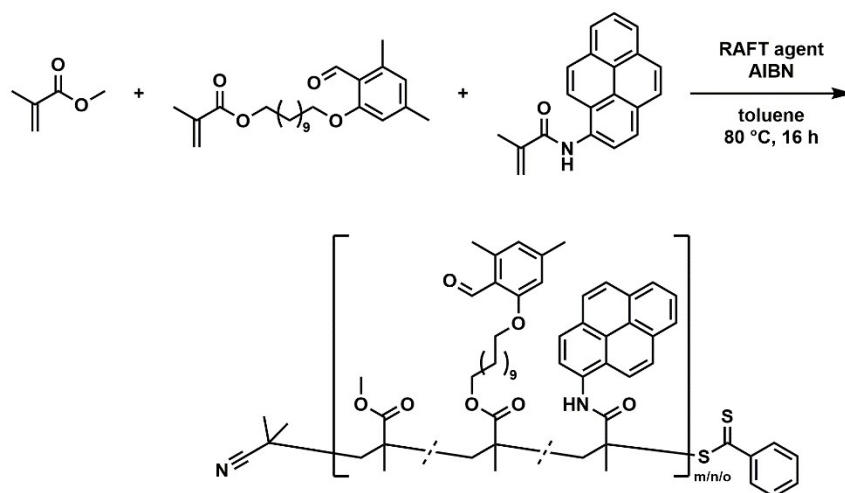
Scheme S4. Standard RAFT polymerisation procedure to obtain **P1-3**.

d. Polymerisation

Monomers (45.2 mmol, 1000 eq different ratios), AIBN (1.48 mg, 9.04 µmol, 0.20 eq) and 2-cyano-2-propyl dithiobenzoate (10.0 mg, 45.2 µmol, 1.00 eq) were dissolved in dry toluene (5 mL) and degassed *via* three consecutive freeze-pump-thaw cycles. The mixture was subsequently immersed into a preheated oil bath at 80 °C and the reaction was allowed to proceed for 16 h. Subsequently, the crude polymers were precipitated first from ice-cold pentane, then from ice-cold methanol and finally dried *in vacuo* to obtain polymers **P1-3**.

¹H NMR (CDCl$_3$): δ = 10.63 (s, br, CHO), 8.61-7.98 (m, CH$_{Pyr}$), 6.64 (s, br, CH$_{Ar}$), 6.61 (s, br, CH$_{Ar}$), 4.03 (s, br, CH$_2$-O), 3.95 (s, br, CH$_2$-O), 3.61 (s, br, O-CH$_3$), 2.55 (s, br, CH$_3$), 2.34 (s, br, CH$_3$), 2.11-0.76 (m, aliphatic H) ppm. **Chloroform-SEC** (PMMA cal.): P1 = 33.7 kg·mol^{-1}, Đ 1.90; P2 = 33.1 kg·mol^{-1}, Đ 1.46; P1 = 28.3 kg·mol^{-1}, Đ 1.59; **Triple-**
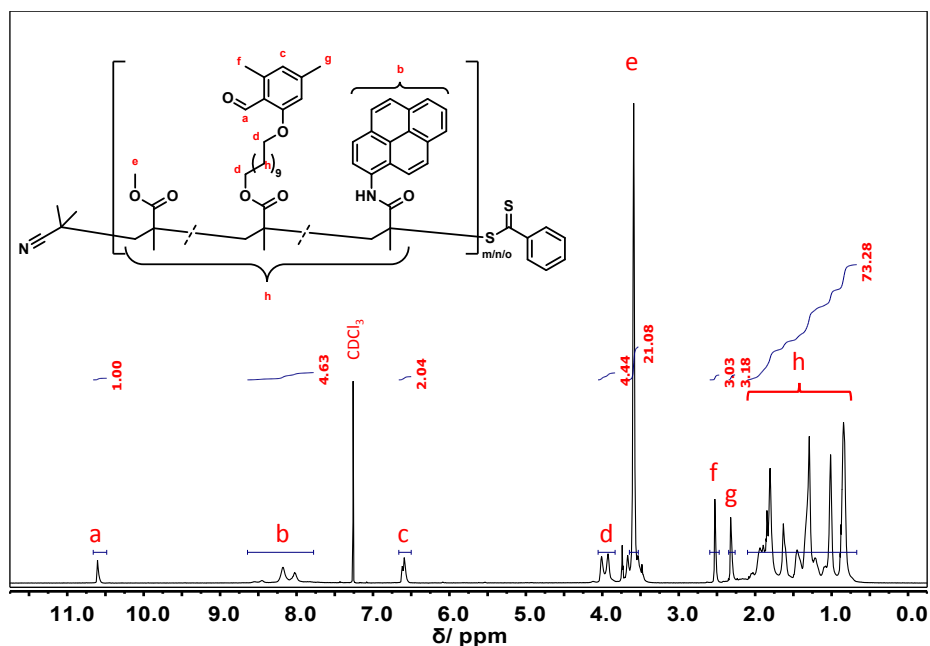
Figure S2. ¹H NMR spectrum (CDCl$_3$, 600 MHz) of **P1**.

detection-SEC (PMMA cal.): P1 = 41.9 kg·mol⁻¹, Đ 1.62; P2 = 39.2 kg·mol⁻¹, Đ 1.63; P1 = 41.3 kg·mol⁻¹, Đ 1.20;
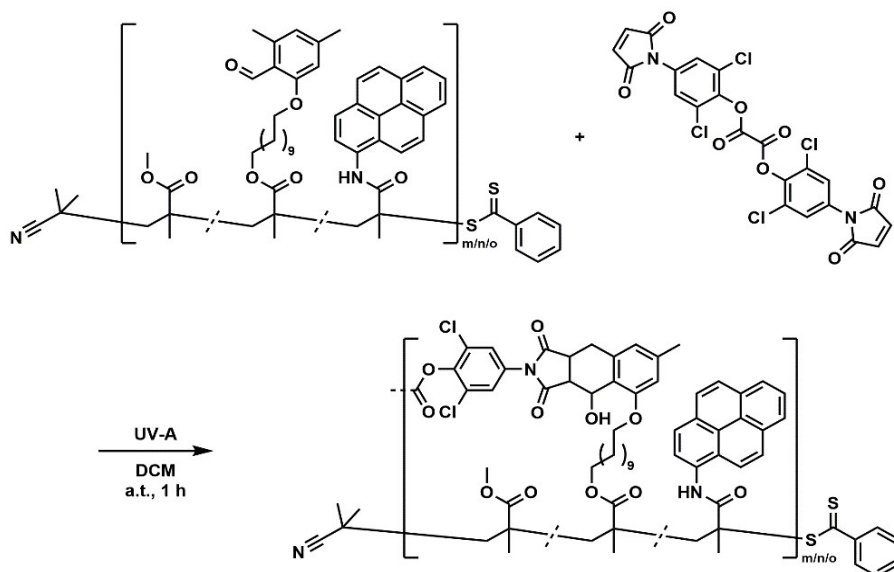
Scheme S5. Light-induced crosslinker-mediated folding procedure to obtain SCN**P1-3**.

e. SCNP folding

P1-3 (50 mg) and bis-maleimide linker (5.00 eq per photo-enol moiety in the backbone) were dissolved in dry DCM (500 mL). After purging with argon for 15 min, the mixture was irradiated with UV-A light (centred at 350 nm) for 60 min at ambient temperature (a.t.). Subsequently, the solvent was removed under reduced pressure and the polymer separated from the linker *via* a sephadex® LH20 column using THF as the eluent.

¹H NMR (CD₂Cl₂): δ = 8.35-7.89 (m, CH$_{Pyr}$), 7.59 (s, br, CH$_{Ar,linker}$), 6.72-6.54 (m, CH$_{Ar}$), 5.89 (s, br, OH), 4.01-3.84 (m, CH$_2$-O), 3.56 (s, br, O-CH$_3$),), 3.42-3.03 (m, CH$_{indol}$), 2.32 (s, br, CH$_3$), 2.05-0.74 (m, aliphatic H) ppm. **Chloroform-SEC** (PMMA cal.): P1 = 22.9 kg·mol⁻¹, Đ 1.65; P2 = 22.1 kg·mol⁻¹, Đ 1.1.64; P1 = 22.5 kg·mol⁻¹, Đ 1.53;
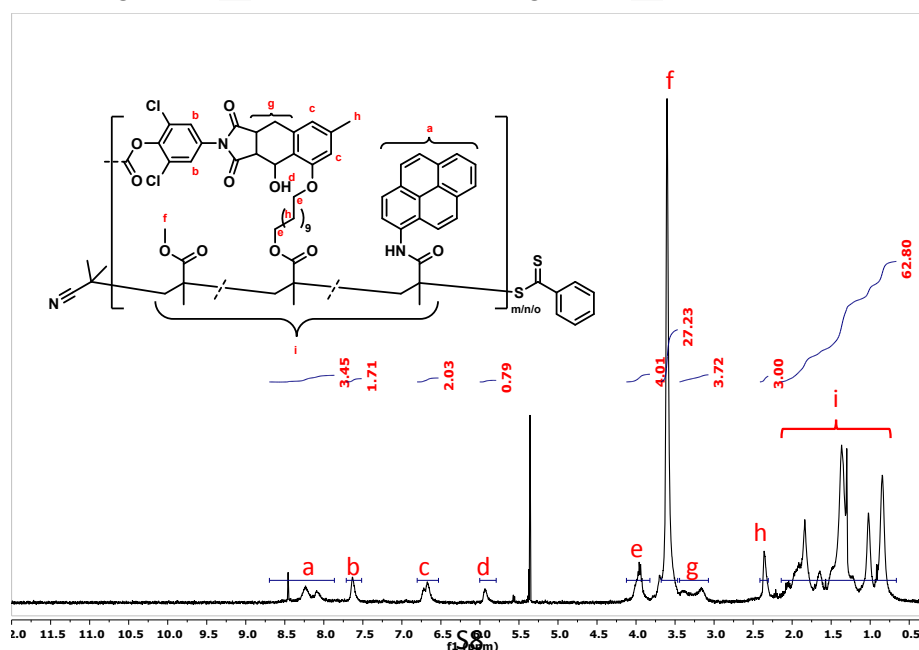
Figure S3. ¹H NMR spectrum (CD₂Cl₂, 600 MHz) of **SCNP1**.

f. SCNP unfolding

SCNP1-3 (10 mg, 201-355 nmol crosslinker) were dissolved in dry DMF (1 mL). An aliquot of the solution (100 μL) was added to the well reader plate and 30% H_2O_2 (6 μL, 58.8 μmol) was added. The reaction was allowed to proceed at ambient temperature for 1 h, then a second portion of 30% H_2O_2 (6 μL, 58.8 μmol) was added and allowed to react to ensure complete unfolding.

^{1}H NMR (CD_2Cl_2): δ = 8.43-7.95 (m, CH_{Pyr}), 7.28 (s, br, $CH_{Ar,linker}$), 6.67-6.63 (m, CH_{Ar}), 5.88 (s, br, OH), 3.92 (s, br, CH_2-O), 3.57 (s, br, O-CH_3), 3.34-3.03 (m, CH_{indol}), 2.31 (s, br, CH_3), 2.05-0.74 (m, aliphatic H) ppm. **Chloroform-SEC** (PMMA cal.): P1 = 12.6 kg·mol^{-1}, Đ 2.72; P2 = 17.6 kg·mol^{-1}, Đ 1.2.09; P1 = 14.7 kg·mol^{-1}, Đ 2.26;
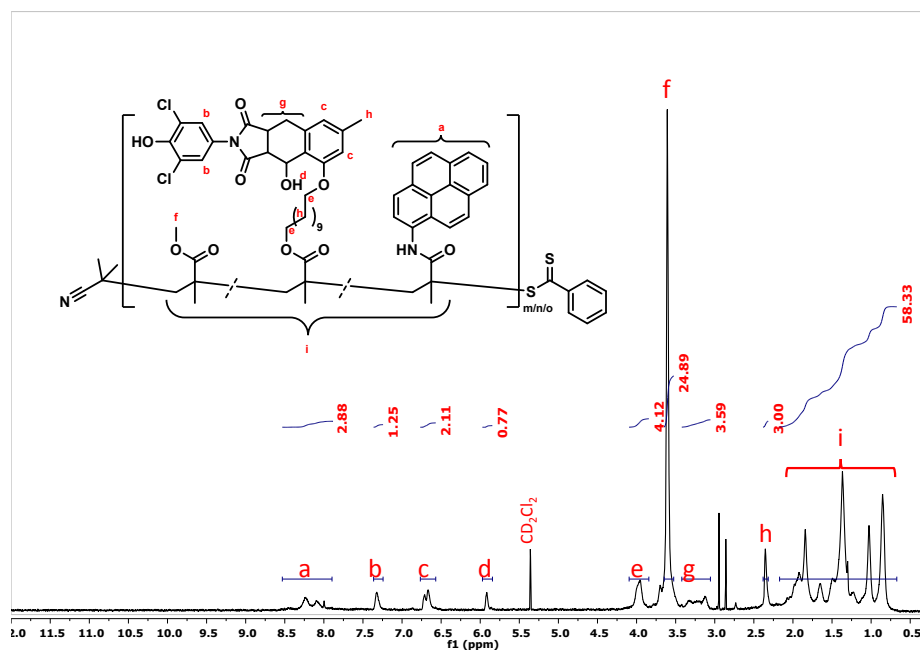
Figure S4. ^{1}H NMR spectrum (CD_2Cl_2, 600 MHz) of **uSCNP1**.

IV. Chloroform-SEC Data 'standard mode'
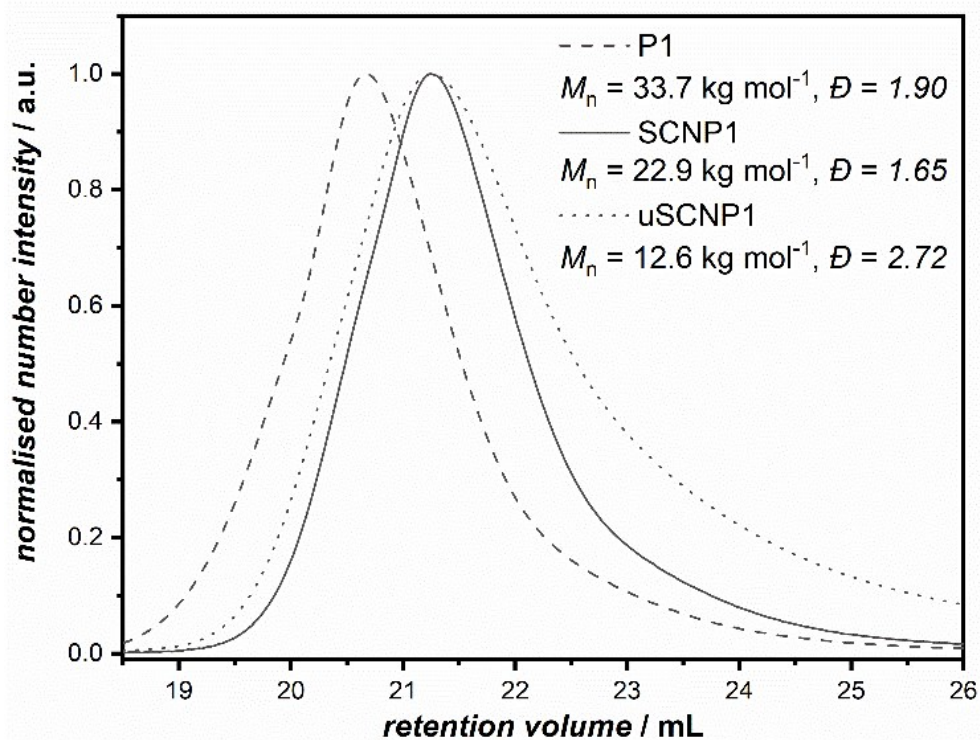
Figure S5. SEC chromatogram of **P1** (dashed), **SCNP1** (solid) and **uSCNP1** (dotted).
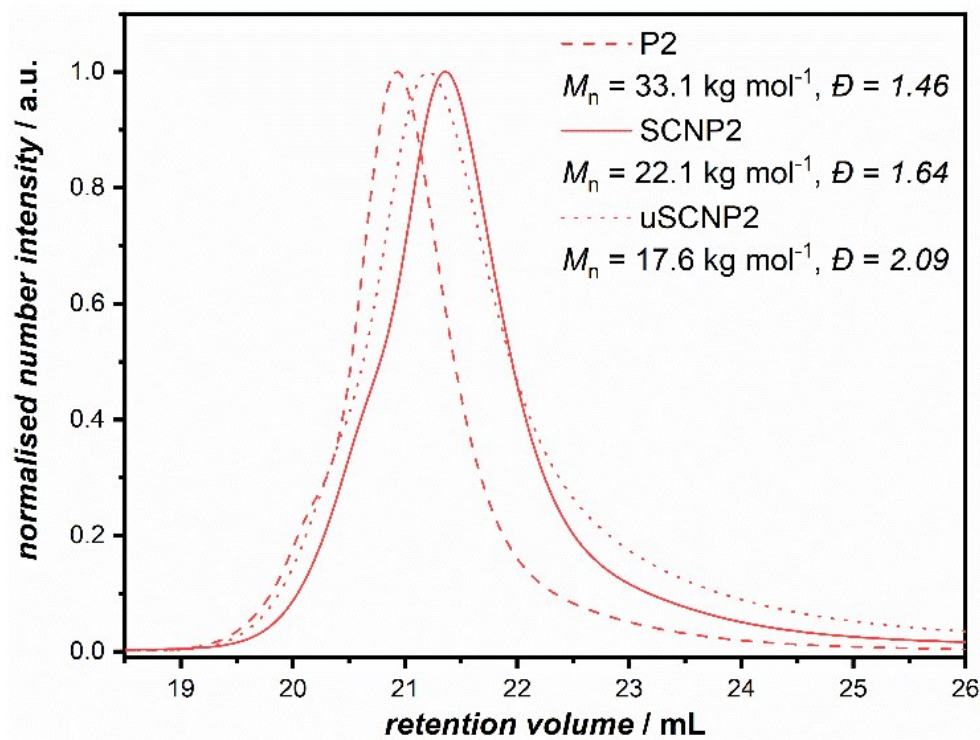
Figure S6. SEC chromatogram of **P2** (dashed), **SCNP2** (solid) and **uSCNP3** (dotted).
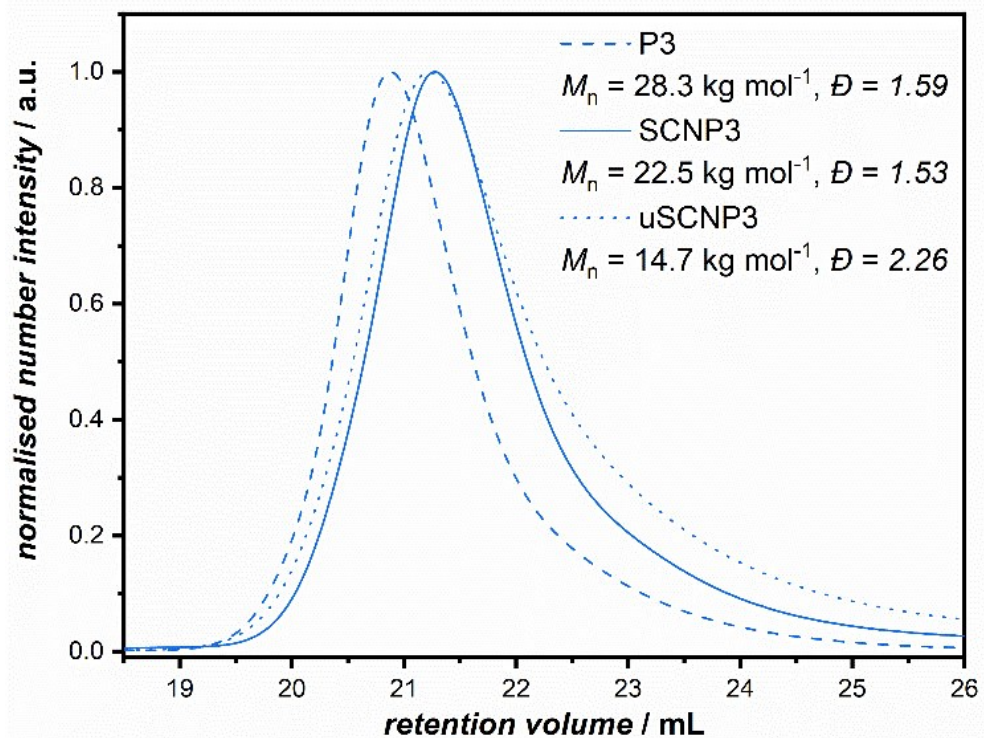
Figure S7. SEC chromatogram of **P3** (dashed), **SCNP3** (solid) and **uSCNP3** (dotted).

V.   DOSY Data
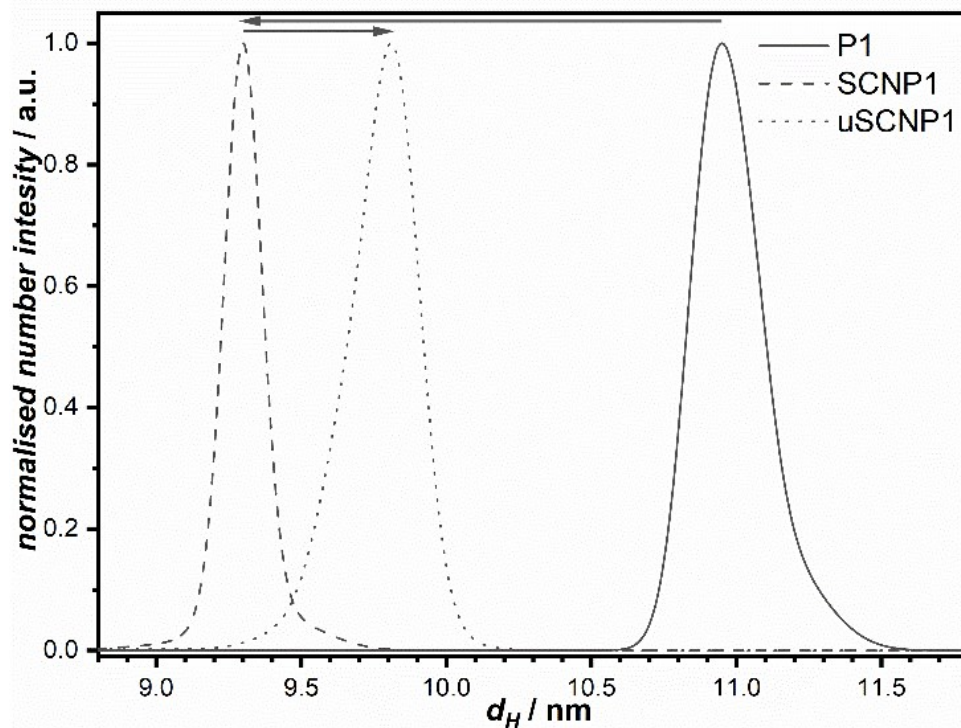
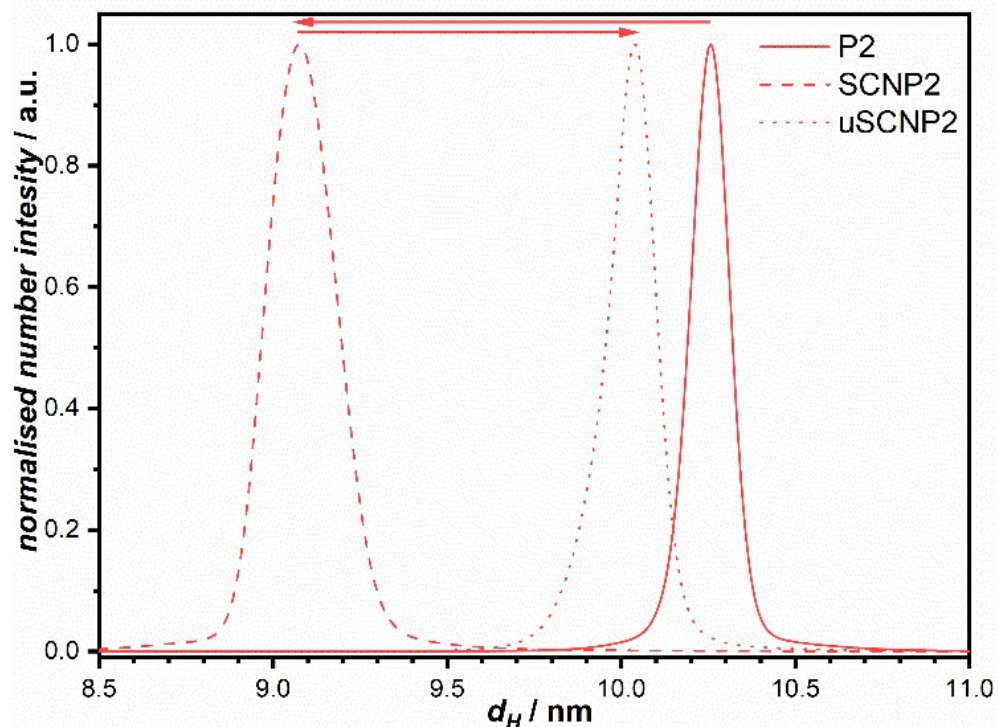**Figure S8.** ^{1}H DOSY NMR projection in the diffusion dimension of **P1** (solid), **SCNP1** (dashed) and **uSCNP1** (dotted).
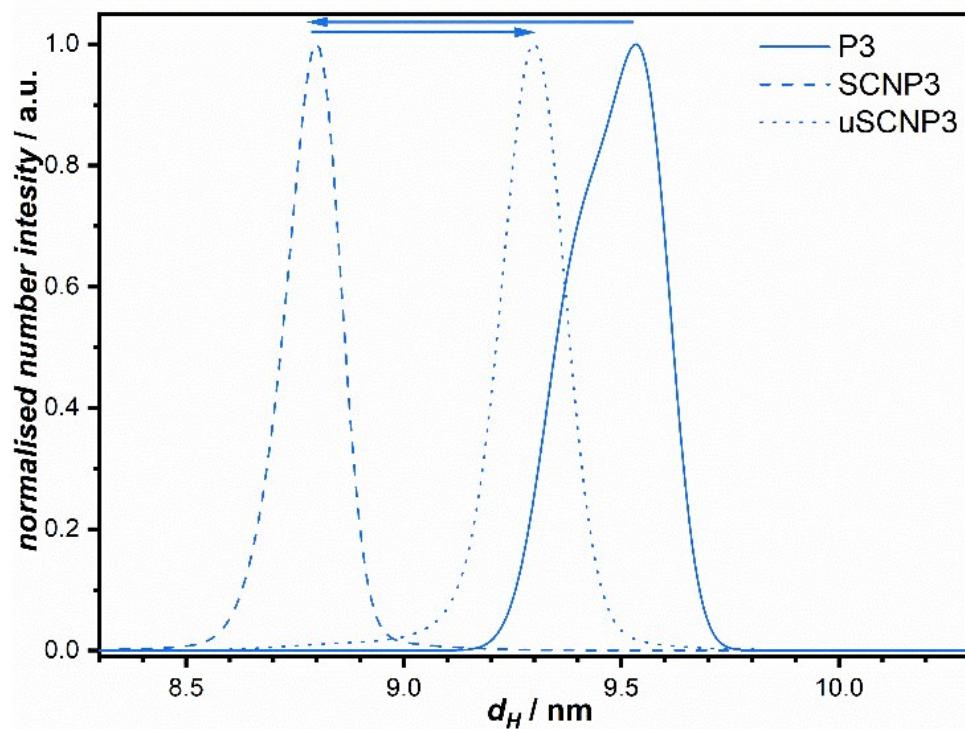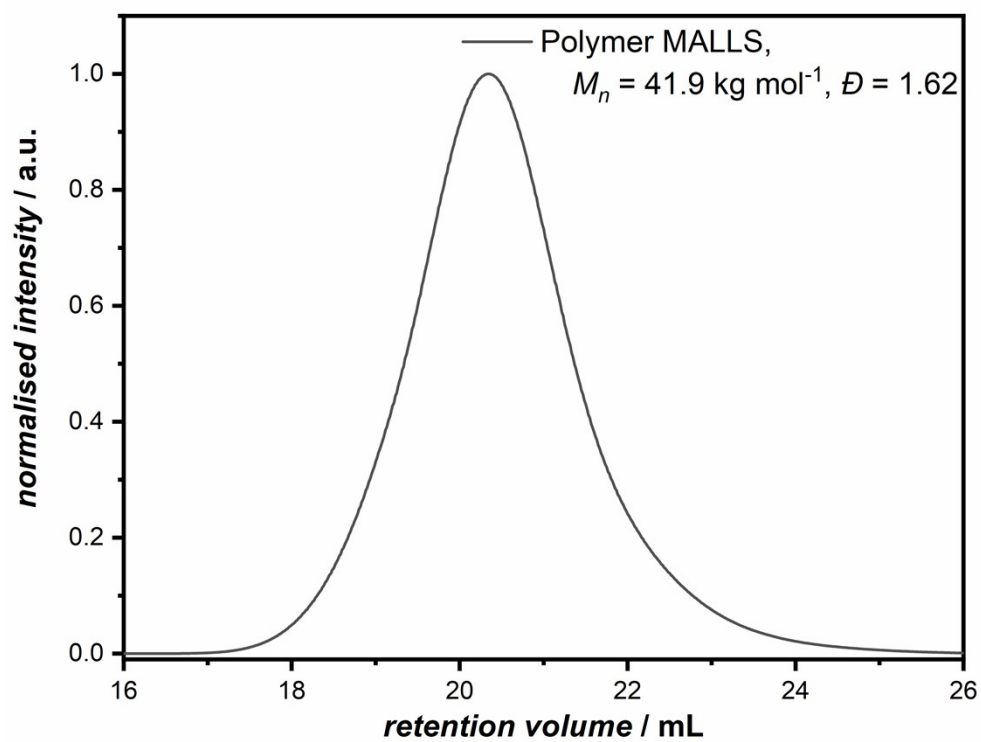
Figure S9. ^{1}H DOSY NMR projection in the diffusion dimension of **P2** (solid), **SCNP2** (dashed) and **uSCNP2** (dotted).

Figure S10. ^{1}H DOSY NMR projection in the diffusion dimension of **P3** (solid), **SCNP3** (dashed) and **uSCNP3** (dotted).

Figure S11. SEC-MALLS chromatogram of **P1**.

VI. THF-SEC Data 'Triple-Detection'
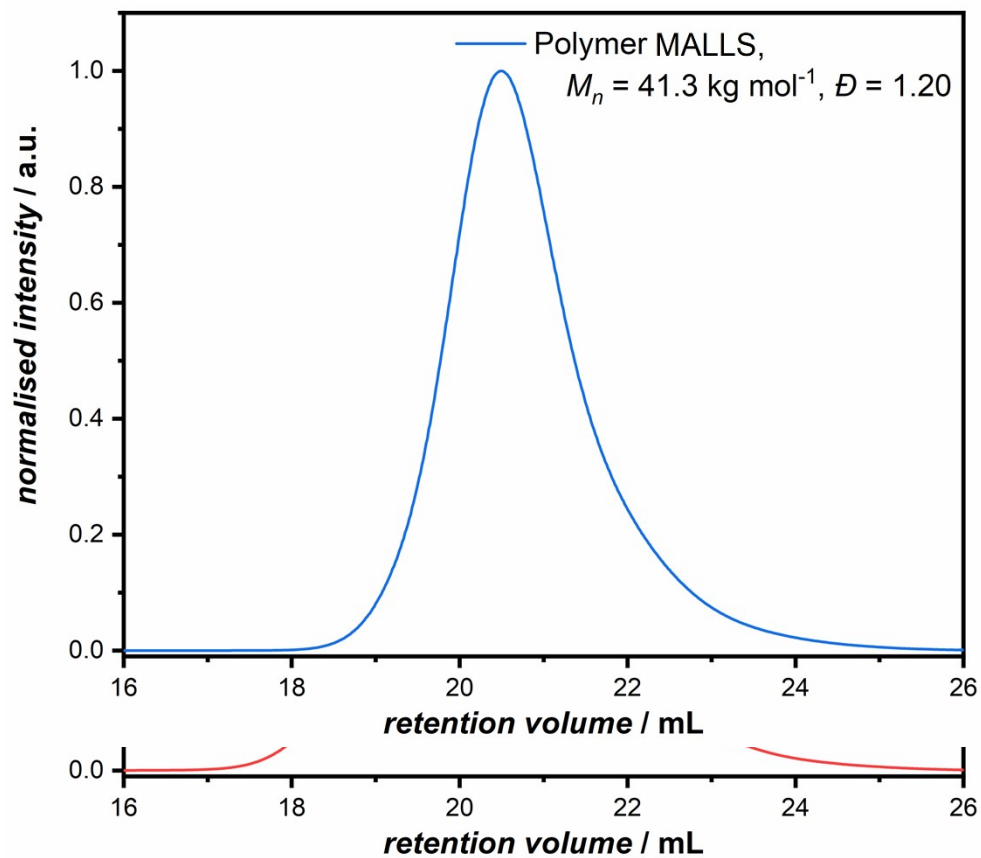
Figure S12. SEC-MALLS chromatogram of **P2**.

Figure S13. SEC-MALLS chromatogram of **P3**.
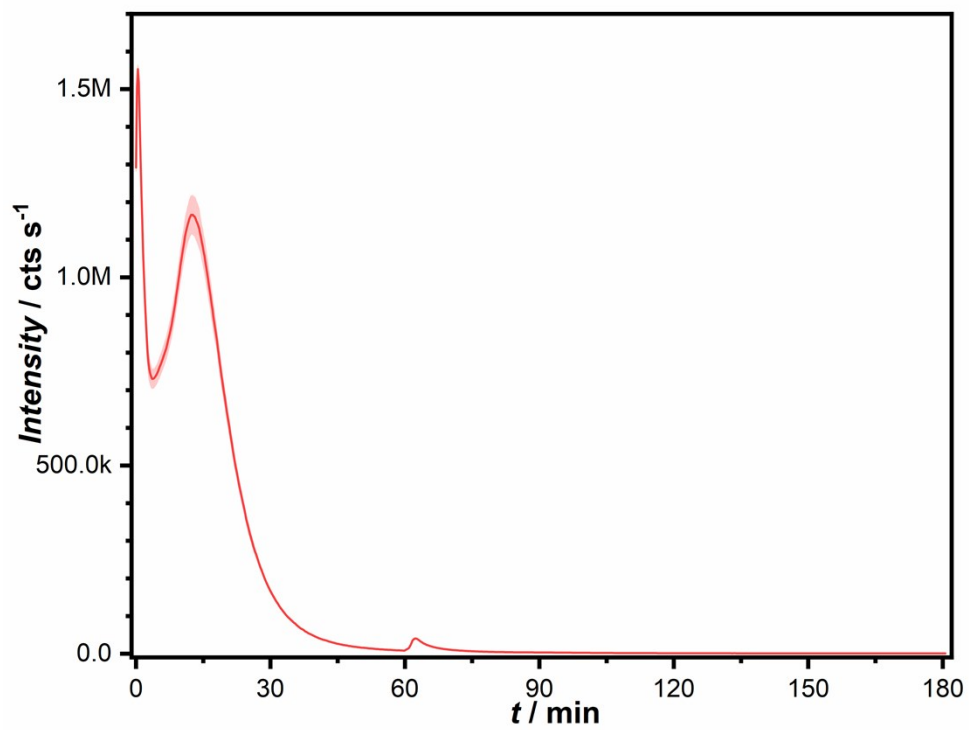
VII. Time-dependant Emission
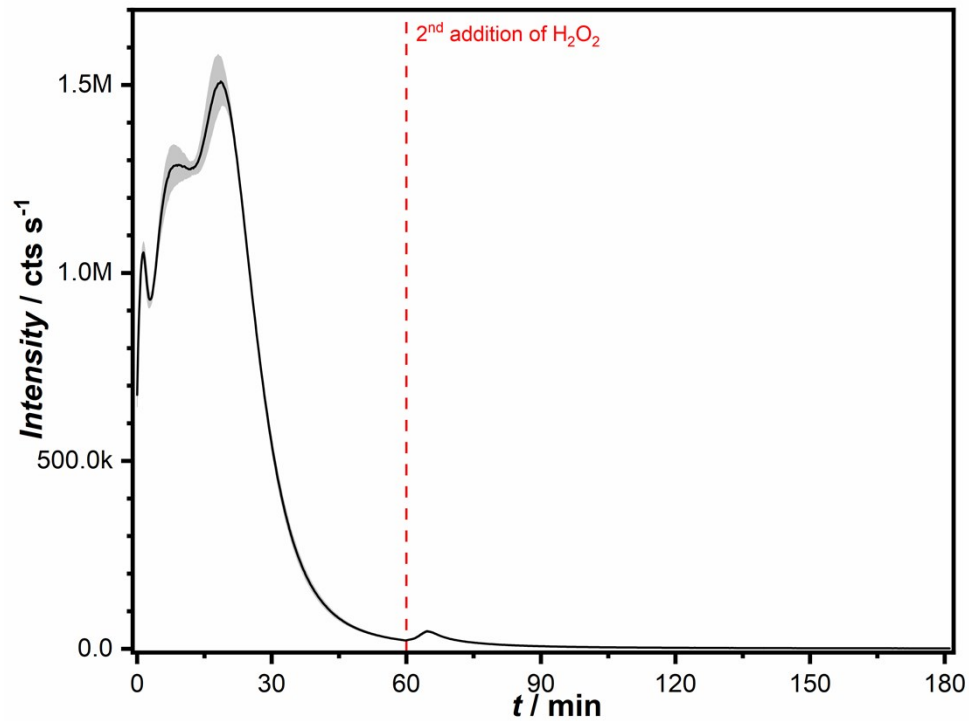
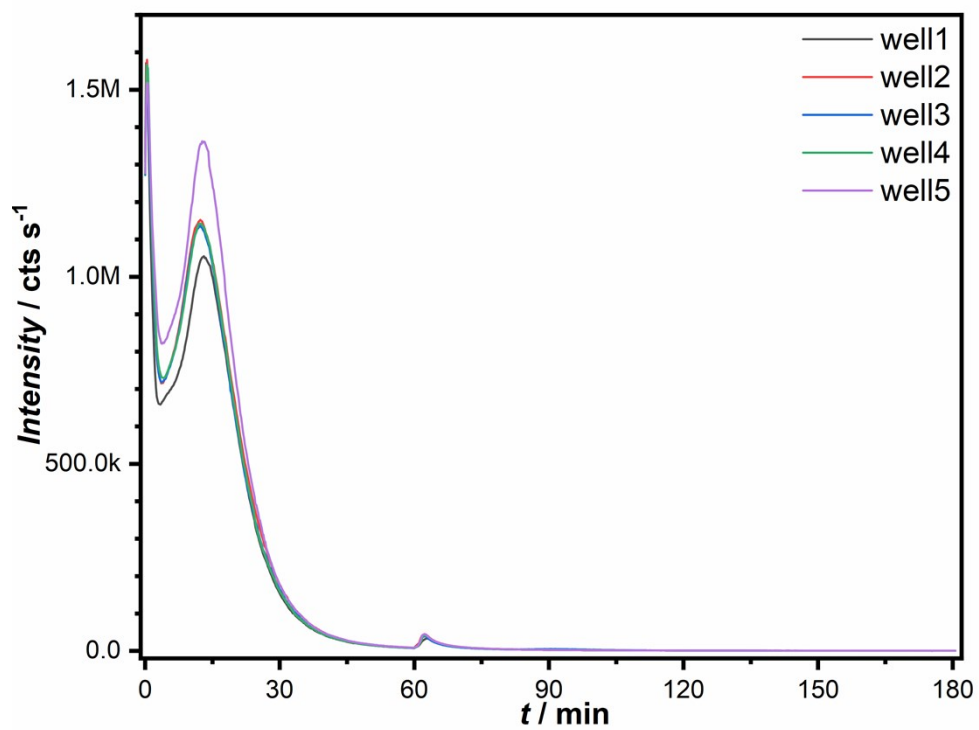**Figure S11.** Averaged time-dependant CL intensity of **P1** over the course of 180 min.
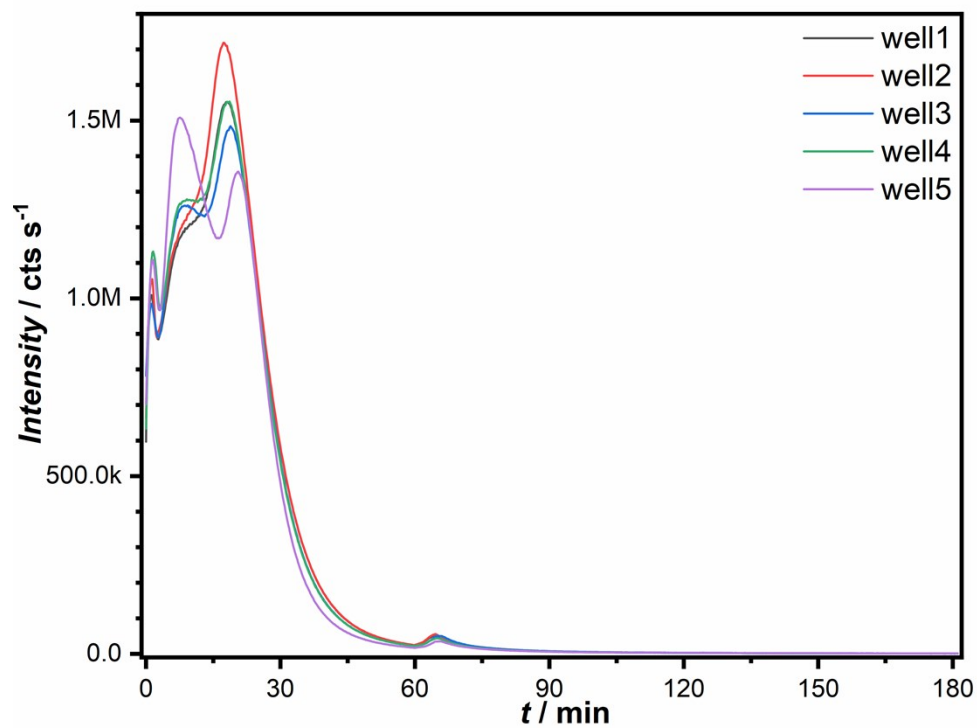
Figure S12. Time-dependant CL intensity of five identical samples of **P1** over the course of 180 min.

Figure S13. Averaged time-dependant CL intensity of **P2** over the course of 180 min.

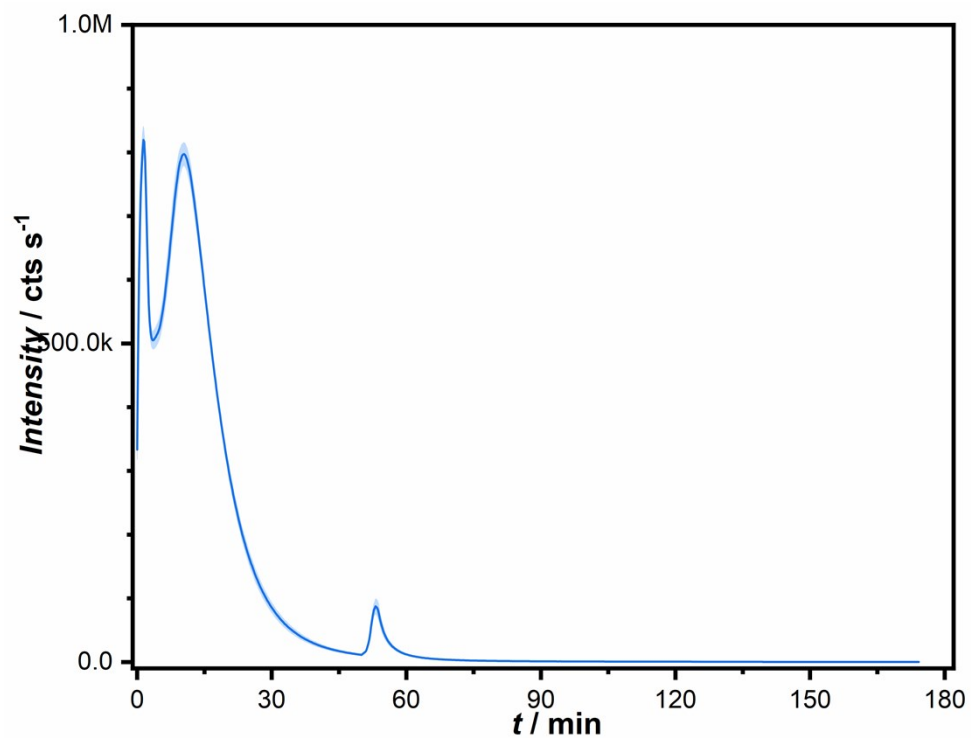**Figure S14.** Time-dependant CL intensity of five identical samples of **P2** over the course of 180 min.

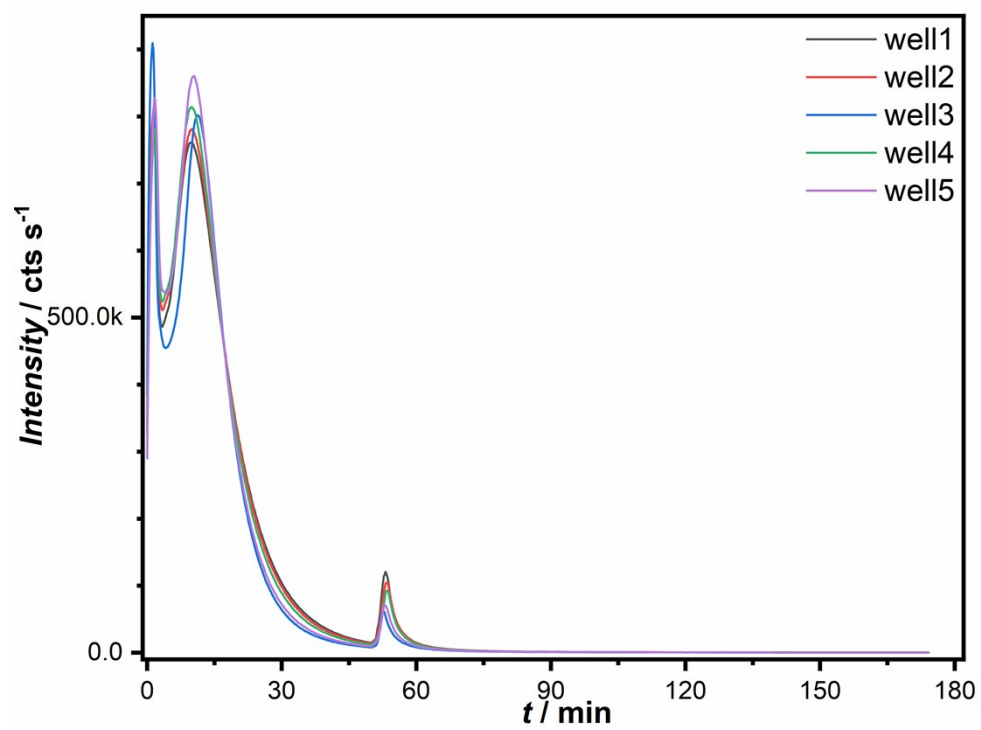**Figure S15.** Averaged time-dependant CL intensity of **P3** over the course of 180 min.


Figure S16. Time-dependant CL intensity of five identical samples of **P3** over the course of 180 min.

VIII.   Parameter Estimation

The unknown rate coefficients k_{HEI} and k_{cat} were estimated via the simulation of three separate experimental CL emission profiles. Within a first approximation step, the kinetic scheme given in **Scheme S6** was fitted to the experimental data given in **Figures S11, S13 and S15** with the parameter estimation function of the PREDICI® simulation package (version 11). This feature allows for the simultaneous fit of individually obtained data sets to a common kinetic scheme. This estimation procedure suggests possible best fit solutions for the rate coefficients that are unknown (in this case k_{HEI} and k_{cat}). It is very important for the estimation process to pre-select appropriate starting values for the rate coefficients that are estimated. The starting values used in this work were obtained by careful consideration of what may be expected for the individual rate coefficients on the basis of the chemistry involved. The starting value of 4.5×10^{-3} s^{-1} for k_{HEI} was selected based on the hydrolysis of phenyloxalates as reported by Catheral et $al.$ and Neuvonen.[4,5] The starting value of 4.2×10^4 for k_{cat} was selected based on values reported by Ciscato et $al.$
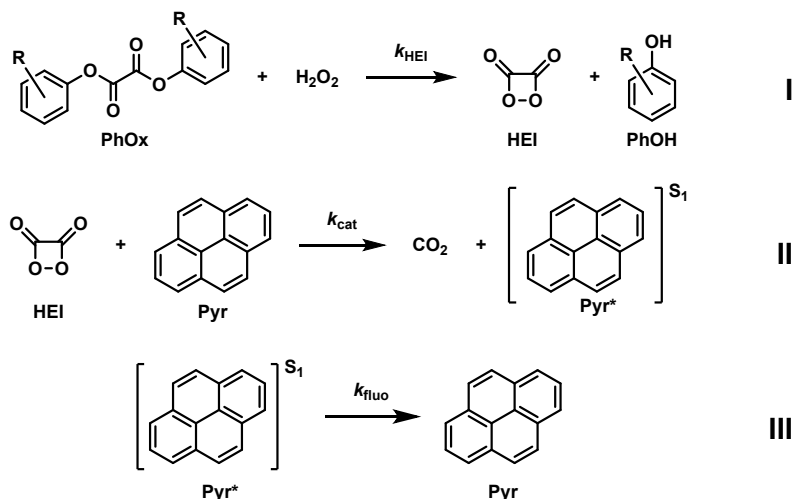
Scheme S6. Overview of the reaction steps involved in the chemiluminescent unfolding **of SCNP2** and simulated in PREDICI®.

$$\frac{d[PhOx]}{dt} = -k_{HEI}[PhOx][H2O2]$$

$$\frac{d[HEI]}{dt} = k_{HEI}[PhOx][H2O2] - k_{cat}[HEI]$$

$$\frac{d[h\nu]}{dt} = k_{cat}[HEI]$$

Table 1: Rate coefficients of HEI formation (k_{HEI}) and catalytic pyrene emission (k_{cat}) leading to qualitative description of CL emission behaviour.

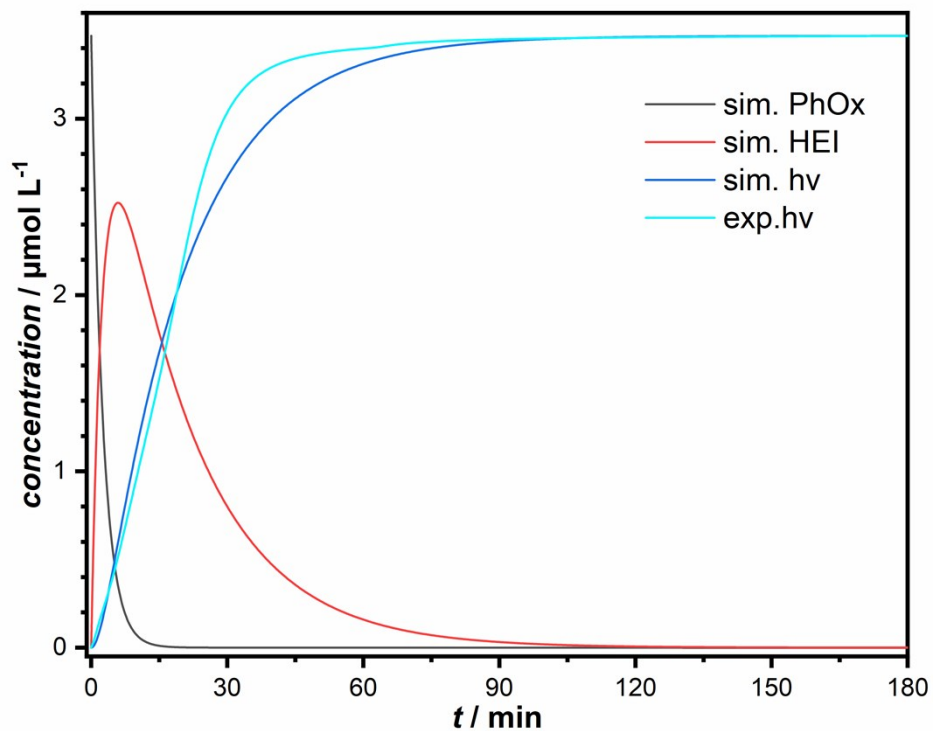|	k_{HEI} / s^{-1}	k_{cat} / s^{-1}
SCNP1	11±5	260±4
SCNP2	160±24	470±4
SCNP3	90±5	470±4

IX. Simulated Emission Data

Figure S17. Simulated concentration of the phenyloxalate crosslinker (black), of the high-energy intermediate (HEI, red) and the photons (black) compared to the experimental concentration of photons (cyan) for the unfolding of **SCNP1**.
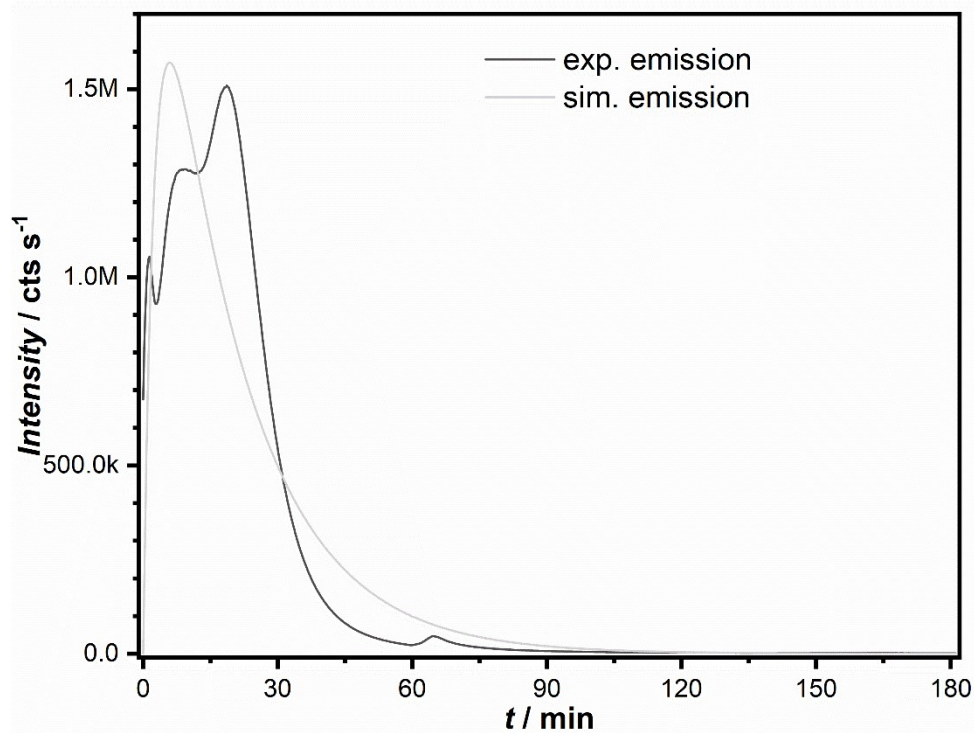

Figure S18. Emission of the chemiluminescent unfolding of **SCNP1** (black) and the simulated emission (grey).
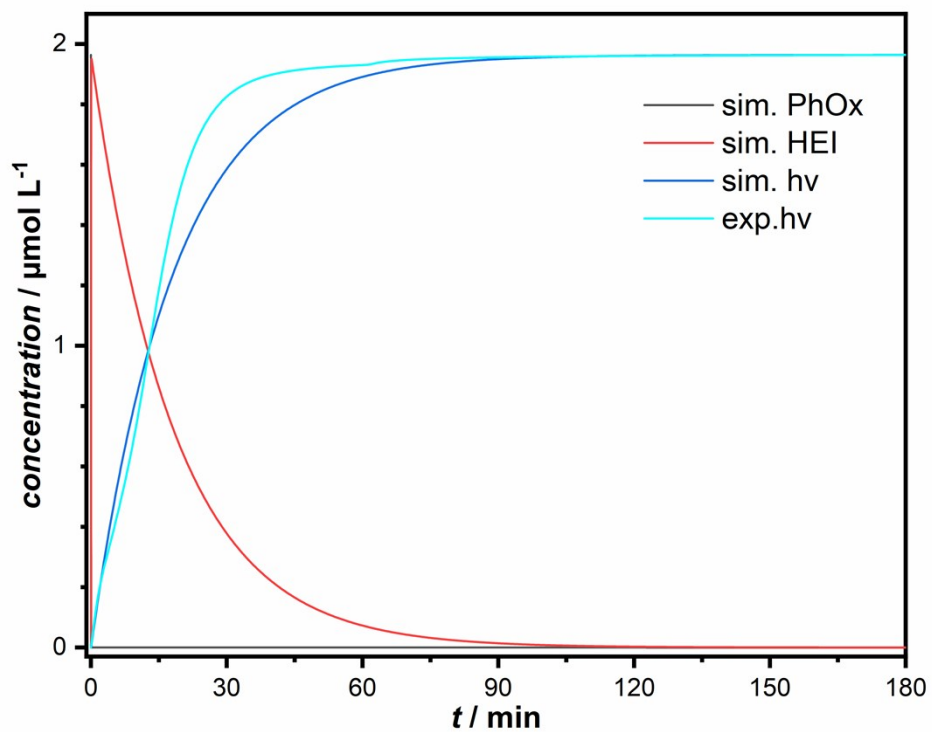
Figure S19. Simulated concentration of the phenyloxalate crosslinker (black), of the high-energy intermediate (HEI, red) and the photons (black) compared to the experimental concentration of photons (cyan) for the unfolding of **SCNP2**.
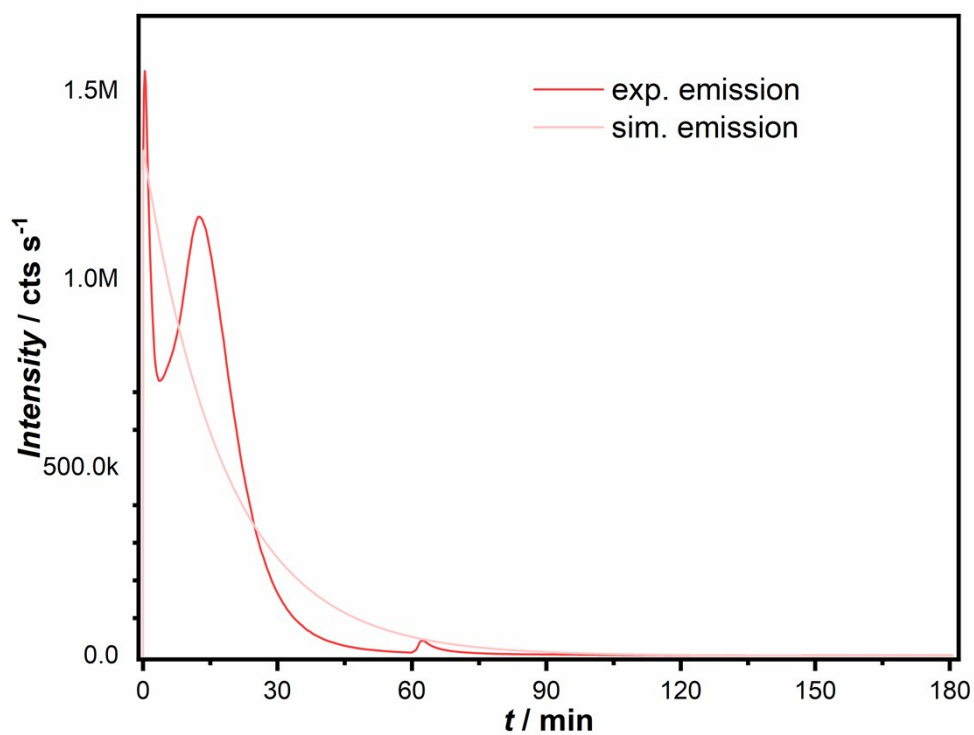

Figure S20. Emission of the chemiluminescent unfolding of **SCNP2** (red) and the simulated emission (light red).
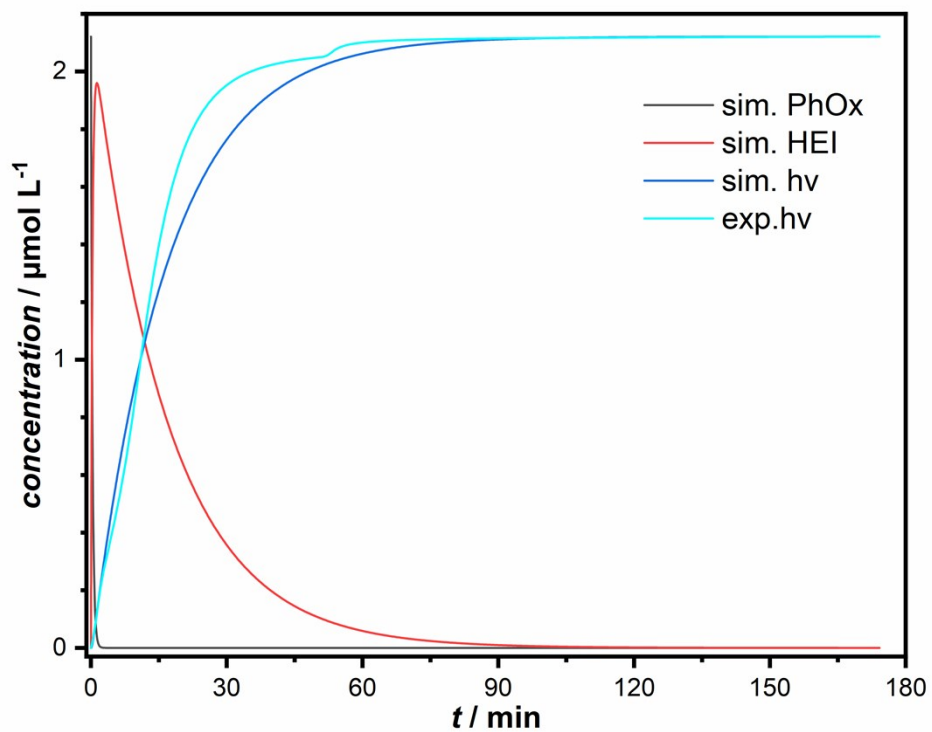
Figure S21. Simulated concentration of the phenyloxalate crosslinker (black), of the high-energy intermediate (HEI, red) and the photons (black) compared to the experimental concentration of photons (cyan) for the unfolding of **SCNP3**.
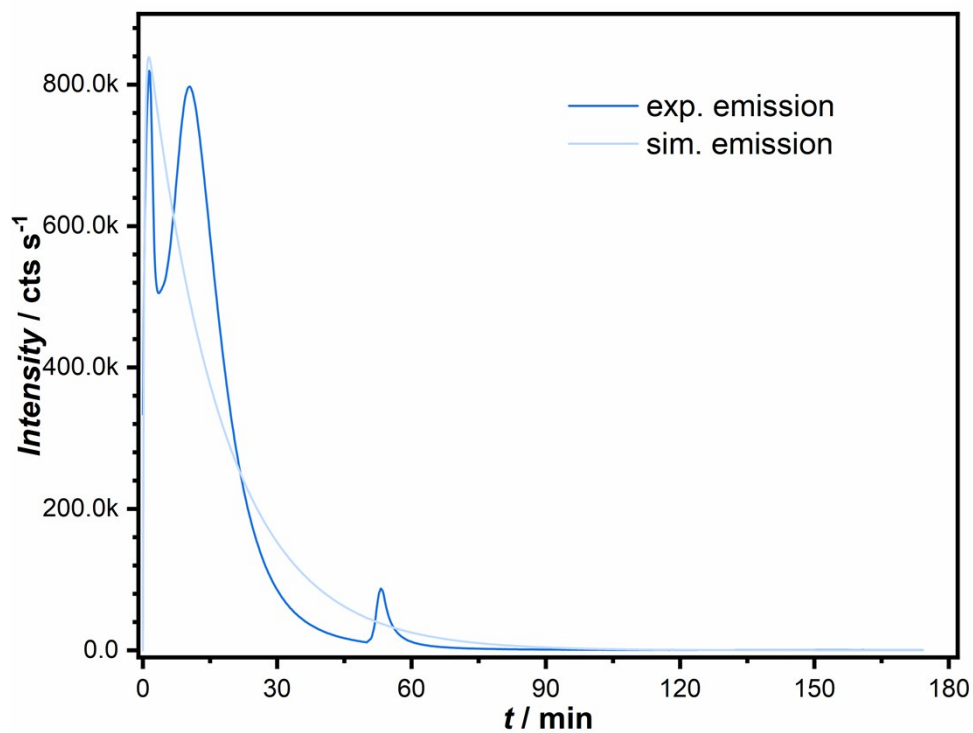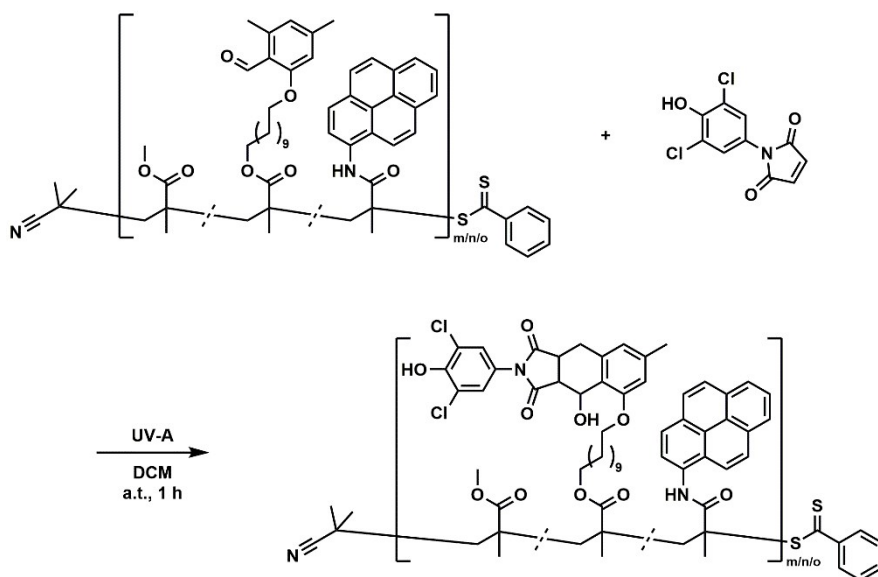

Figure S22. Emission of the chemiluminescent unfolding of **SCNP3** (blue) and the simulated emission (light blue).

X.   Control Experiment

Scheme S7. Light-induced crosslinker-mediated folding procedure to obtain SCN**P1-3**.

To confirm that the decrease in apparent molecular according to chloroform-SEC as well as the incomplete return to initial r_H values can be attributed to polymer-column and polymer-solvent interactions, respectively, a control experiment was performed. Here, parent polymer **P1** was functionalised with 2,6-dichloro-4-maleimidophenol (intermediate in the synthesis of **6**, cf. III.c) to yield side-chain functionalised polymers with an identical structure as the completely unfolded **uSCNP1**. While chloroform-SEC was unavailable due to instrument failure and it was impossible to get replacement parts in the current COVID environment, results from THF-SEC were inconclusive. The hydrodynamic radius of the post-modified **P1** obtained from DOSY, however, was not only lower than the r_H of the parent polymer but even lower than the r_H of **uSCNP1**, thus proving the successful unfolding of the SCNPs despite an apparent decrease in molecular weight according to SEC and despite the incomplete return to initial dH values, and the presence of polymer-column and polymer-solvent interactions.
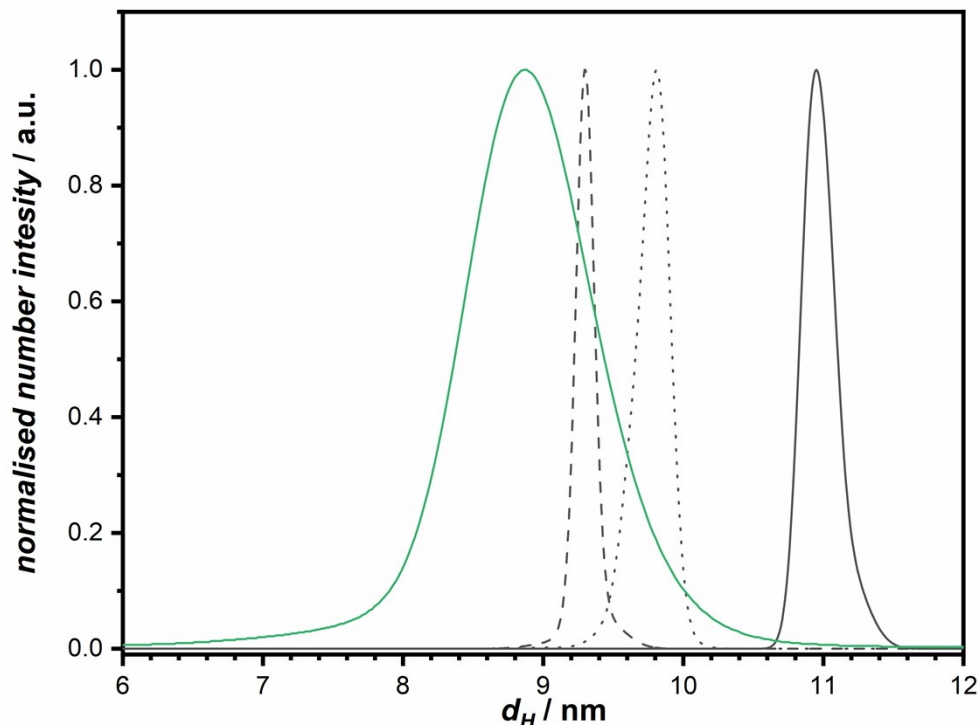
Figure S23. ^{1}H DOSY NMR projection in the diffusion dimension of the post-modified parent polymer (green solid line) as well as **P1** (black solid), **SCNP1** (black dashed) and **uSCNP1** (black dotted).

XI References

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