Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Light-Driven Folding of Single Polymer Chains via Metal-Complexation

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Contents

1 Instrumentation

1.1 Size Exclusion Chromatography

The SEC measurements were conducted on a PSS SECurity2 system containing a PSS SECurity Degasser, PSS SECurity TCC6000 Column Oven (35 °C for THF or 70 °C for DMAc), PSS SDV Column Set (8x50 mm 5 µm precolumn, 8x300 mm 5 µm analytical columns, 100000 Å and 1000 Å) and an Agilent 1260 Infinity II Isocratic Pump, Agilent 1260 Infinity II Standard Autosampler, Agilent 1260 Infinity II Diode Array and Multiple Wavelength Detector, Agilent 1260 Infinity II Refractive Index Detector (35 °C). HPLC grade THF or DMAc were used as eluting solvents at a flow rate of 1 mL min^{-1}. Narrow disperse linear poly(methyl methacrylate) standards (M_n 831 g mol^{-1} to 1.89·106 g mol^{-1}, PSS ReadyCal) were used as calibrants. Molecular weight and dispersity analyses were performed via the PSS WinGPC UniChrom software (version 8.2).

1.2 Bruker 500 MHz NMR

A Bruker Ultrashield Plus 500 spectrometer was used to record both 1D (^{1}H: 500.28 MHz, ^{13}C: 125.81 MHz). The chemical shifts are reported in parts per million (ppm) and referenced to the respective solvent resonances of $CDCl_3$ δ = 7.26 ppm; CD_3CN δ = 1.94 ppm; $DMSO_{d6}$ δ = 2.50 ppm. The abbreviations for the couplings were given as: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet.

1.3 Bruker 400 MHz NMR

A Bruker DRX 400 spectrometer was also used to record both 1D (^{1}H: 500.28 MHz, ^{13}C: 125.81 MHz). The chemical shifts are reported in parts per million (ppm) and referenced to the respective solvent resonances of $CDCl_3$ δ = 7.26 ppm; CD_3CN δ = 1.94 ppm; $DMSO_{d6}$ δ = 2.50 ppm. The abbreviations for the couplings were given as: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet.

1.4 Diffusion Ordered NMR Spectroscopy DOSY

DOSY experiments were performed at 298 K in CD_3CN using a Bruker Avance III 400 MHz spectrometer, with averaged diffusion coefficients given in the experimental section. The Bruker pulse sequence ledbpgp2s using bipolar gradients with longitudinal eddy current delay and two spoil gradients was used. 16 gradient points were recorded in a linear manner ranging from 2 % to 98 % of the maximum

applicable gradient strength. The gradient length (little delta) as well as the diffusion delay (big delta) were optimized prior to each DOSY measurement. The data was processed using Mestrenova (Version 14.1.2)

Hydrodynamic diameters, d_H, were calculated from the Stokes-Einstein equation:

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

Where kB is the Boltzmann constant, T the temperature and η the solvent viscosity (ACN 0.367 Pa·s).[1]

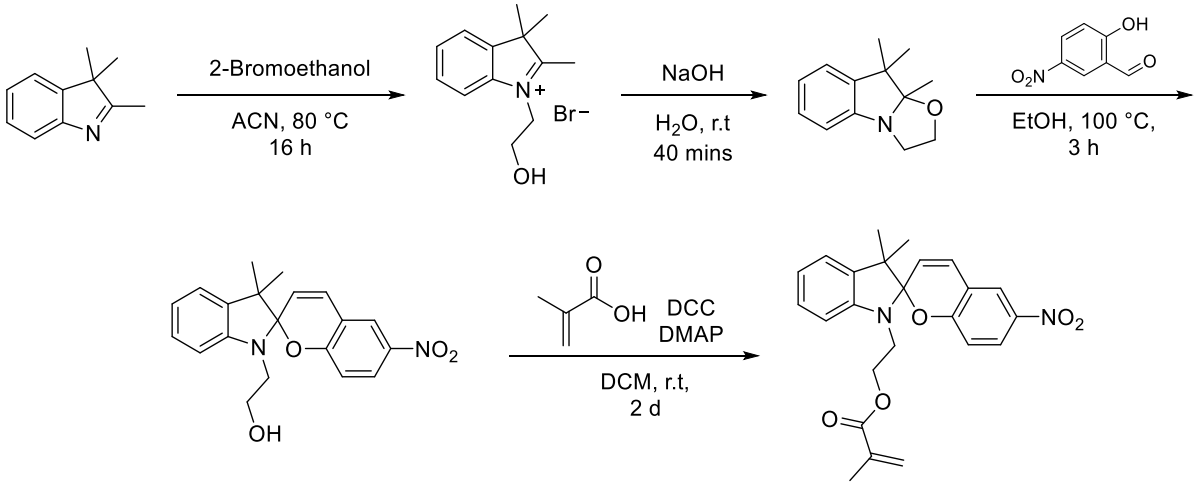
1.5 UV-Vis Spectrometry

UV-vis spectra were recorded on an Agilent Cary 5000 UV-vis-NIR spectrophotometer. Measurements were conducted in a Helma Analytics quartz high precision cell (108-F-10-40) with a path length of 10 mm at room temperature. The settings were: range> 200- 800 nm; interval: 1 nm; scan-rate: 300 nm min-1; SBW = 2; double-beam mode; zero and baseline scan.

1.6 LED Characterisation

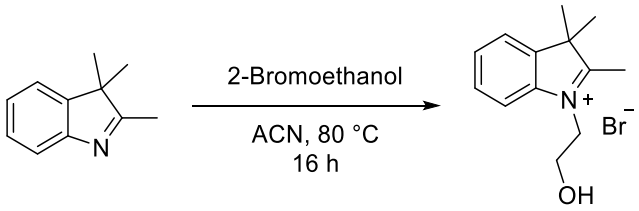
Light-emitting diodes (LEDs) emission spectra and output energies were recorded using an Opsytec Dr. Gröbel Spectoradiometer SR600. The emitted power from each LED was measured for 60 s with an integration time of 5 s at a fixed distance from the sensor (10 mm). LEDs were cooled during the measurement to minimise any thermal effects on the emission power or sensor performance.

2 Small Molecule and Polymer Synthesis



Scheme 1. Synthetic approach to yield the methacrylate functionalised spiropyran monomer.

2.1 Hydroxyethyl Indolenine



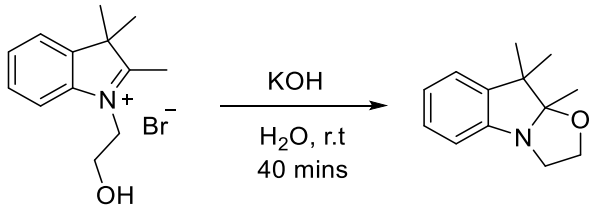
2,3,3 Trimethyl indolenine (2.5 g, 15.7 mmol, 1 eqv) was dissolved in ACN (35 mL) and placed under N_2 atmosphere, to which 2-bromoethanol (2.16 g, 17.27 mmol, 1.1 eqv) was added dropwise. The mixture was subsequently heated to 80 °C overnight, MeOH was added (10 mL) and the reaction was further stirred at 80 °C for 30 minutes. The reaction was then allowed to cool to room temperature before being concentrated to a volume of 10 mL. Cold EtOAc (30 mL) was added and the resulting purple precipitate was filtered and washed with cold EtOAc before being air dried. Affording a purple powder that was used immediately for the next step without further purification.

Yield = 2.58 g (58 %).

^{1}H NMR (400 MHz, DMSO) δ 8.03 – 7.94 (m, 1H), 7.90 – 7.81 (m, 1H), 7.61 (dd, *J* = 5.8, 3.1 Hz, 2H), 4.62 (t, *J* = 5.1 Hz, 2H), 3.88 (t, *J* = 5.1 Hz, 2H), 2.84 (s, 3H), 1.55 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 198.23, 142.31, 141.64, 129.77, 129.28, 123.95, 116.11, 58.25, 54.74, 50.81, 22.52, 14.99.

2.2 Indolenine Oxazole

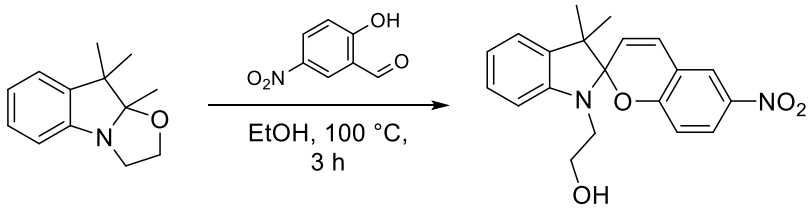


Hydroxyethyl indolenine (2.5 g, 8.8 mmol, 1 eqv) was dissolved in water (50 mL). Separately, potassium hydroxide (0.9 g) was dissolved in water (50 mL) and added to the solution. The combined solutions were stirred at room temperature for 40 minutes. The resulting product was then extracted with DCM (3 x 15 mL) and concentrated under reduced pressure, affording a yellow oil that was used without further purification. Yield = 1.71 g (96 %)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (td, *J* = 7.6, 1.4 Hz, 1H), 7.07 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.92 (td, *J* = 7.4, 1.0 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 3.84 (td, *J* = 7.4, 3.0 Hz, 1H), 3.72 (ddd, *J* = 11.4, 7.1, 3.1 Hz, 1H), 3.63 – 3.48 (m, 2H), 1.43 (s, 3H), 1.39 (s, 3H), 1.18 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.65, 140.13, 127.62, 122.54, 121.83, 112.11, 109.10, 63.11, 50.21, 47.07, 28.22, 20.92, 17.71.

2.3 Hydroxyethyl Spiropyran

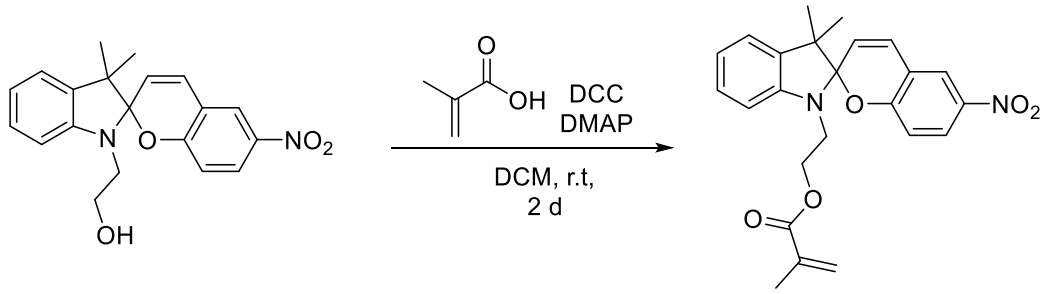


The oxazole (1.2 g, 8.85 mmol, 1 eqv) was dissolved in EtOH (15 mL) and placed under N_2 atmosphere. To this was added 5-nitro salicaldehyde (1.48 g, 8.85 mmol, 1.5 eqv) and the combined reaction mixture was heated to 100 °C for 3 hours. The combined solution was subsequently allowed to cool to room temperature, before being concentrated under reduced pressure. The resulting dark purple solid was purified using a two solvent recrystallization with *n*-hexane and EtOAc (1:1), affording fine purple crystals. Yield = 0.91 g (44 %).

The ^{1}H NMR spectrum matched literature.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 7.96 (m, 2H), 7.20 (td, *J* = 7.7, 1.3 Hz, 1H), 7.10 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.94 – 6.87 (m, 2H), 6.76 (d, *J* = 8.9 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 5.89 (d, *J* = 10.4 Hz, 1H), 3.94 – 3.61 (m, 2H), 3.54 – 3.23 (m, 2H), 1.29 (s, 3H), 1.20 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.69, 147.36, 141.55, 136.21, 128.66, 128.25, 126.38, 123.17, 122.31 (d, *J* = 2.2 Hz), 120.40, 118.92, 115.92, 107.30, 61.26, 53.23, 46.51, 26.29, 20.41.

2.4 Methacrylate Spiropyran (**SP-MMA**)

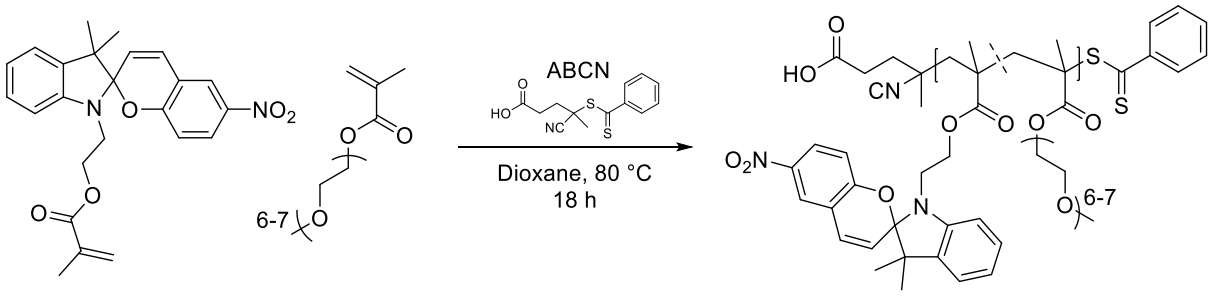


Dicyclohexylcarbodiimide (0.843 g, 4.09 mmol, 1.2 eqv) was dissolved in dry DCM (10 mL) and cooled to 0 °C. Methacrylic acid (0.340 g, 3.95 mmol, 1.16 eqv) was added dropwise, followed by stirring for 10 mins at 0 °C. Subsequently, dimethyl amino pyridine (0.05 g, 0.408 mmol, 0.12 eqv) was added. Separately, hydroxyethyl spiropyran (1.20 g, 3.41 mmol, 1 eqv) was dissolved in dry DCM (10 mL) and subsequently added dropwise to the first solution at 0 °C. The combined solution was then allowed to warm to room temperature and stirred for two days. The reaction mixture was filtered, and the white solid was washed with DCM. The filtrate was collected and concentrated under reduced pressure, affording a purple solid. The product was purified first using silica chromatography (7:3 hexane: EtOAc). The resulting fractions were concentrated and the light-yellow solid was recrystalised from MeOH, affording the product as fine, light-yellow crystals. Yield = 0.572 g (39 %).

The ^{1}H NMR spectrum matched literature.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 7.98 (m, 2H), 7.21 (td, *J* = 7.7, 1.3 Hz, 1H), 7.09 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.93 – 6.87 (m, 2H), 6.75 (d, *J* = 8.8 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.07 (t, *J* = 1.3 Hz, 1H), 5.88 (d, *J* = 10.3 Hz, 1H), 5.57 (q, *J* = 1.5 Hz, 1H), 4.30 (t, *J* = 6.3 Hz, 2H), 3.55 (dt, *J* = 14.9, 6.7 Hz, 1H), 3.43 (dt, *J* = 15.1, 5.9 Hz, 1H), 1.92 (t, *J* = 1.3 Hz, 3H), 1.28 (s, 3H), 1.17 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.35, 159.53, 146.79, 141.21, 136.17, 135.83, 128.44, 127.99, 126.09 (d, *J* = 6.9 Hz), 122.92, 121.94 (d, *J* = 4.2 Hz), 120.07, 118.55, 115.70, 106.89, 106.66, 62.77, 52.94, 42.56, 25.98, 19.97, 18.50.

2.5 RAFT Polymerization of **SP-X-PEGMEMA Polymers**



(Refer to **Table S1** for stoichiometries of the respective polymer syntheses) Polyethylene glycol methyl ether methacrylate (PEGMEMA, M_n = 300 g mol^{-1}) and dioxane were purified over a short plug of basic aluminium oxide to remove inhibitors. De-inhibited PEGMEMA (0.748 g, 2.34 mmol, 300 eqv) and dioxane (0.275 mL for **SP-15/36-PEGMEMA**, 0.137 mL for **SP-38-PEGMEMA**) were added to a vial containing chain transfer agent, 4-cyano-4-(phenylcarbonothioylthio)-pentanoic acid (CTP) and **SP-MMA**. Separately, a stock solution of 1,1-azobis-(cyclohexanecarbonitrile) (ABCN, 3.8 mg.mL^{-1}) was prepared in de-inhibited dioxane. An aliquot of the solution was added to the polymerization mixture. The mixture was transferred to a Schlenk tube and subjected to 5 freeze pump thaw cycles before being submerged in an oil bath pre-heated to 80 °C. After stirring for 18 h, the polymerization was quenched by exposure to air and immediate immersion in liquid N_2. The crude polymerization mixture was diluted with a small amount of dioxane and precipitated three times into *n*-hexane: diethyl ether, (2:1) followed by centrifugation. The resulting purple product were dried overnight at room temperature in a vacuum oven.

Table S1 Reagent quantities for the preparing the **SP-X-PEGMEMA** polymers.

Polymer	PEGMEMA	**SP-MMA**	CTP	ABCN
SP-38-PEGMEMA	0.374 g, 1.17mmol, 150 eqv	0.176 g, 0.42 mmol, 54 eqv	0.00185 g, 0.0035 mmol, 1 eqv	0.05 mL of a 3.8 mg mL^{-1} solution
SP-36-PEGMEMA	0.748 g, 2.34 mmol, 300 eqv	0.353 g, 0.841 mmol 100 eqv	0.00217 g, 0.007 mmol, 1 eqv	0.1 mL of a 3.8 mg mL^{-1} solution
SP-15-PEGMEMA	0.748 g, 2.34 mmol, 300 eqv	0.185 g, 0.441 mmol 50 eqv	0.00217 g, 0.007 mmol, 1 eqv	0.1 mL of a 3.8 mg mL^{-1} solution

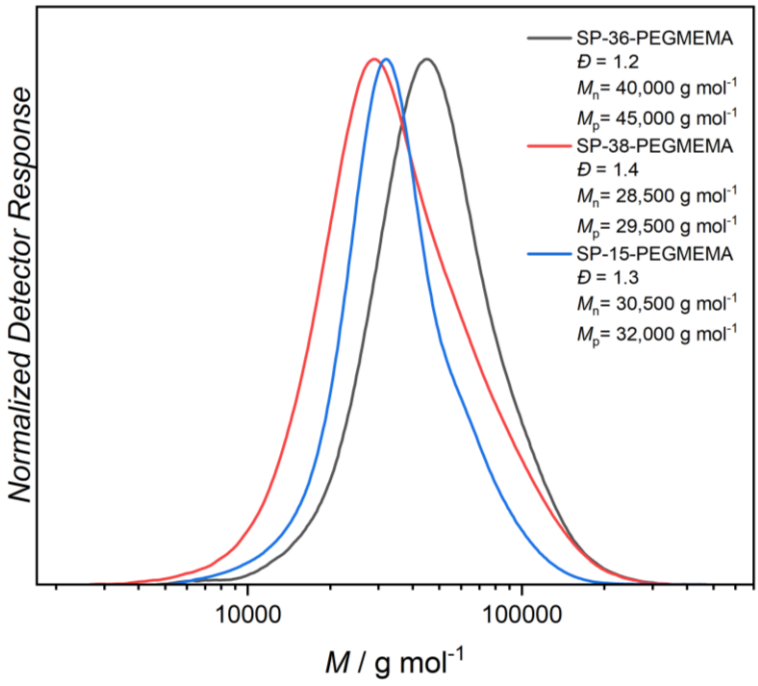
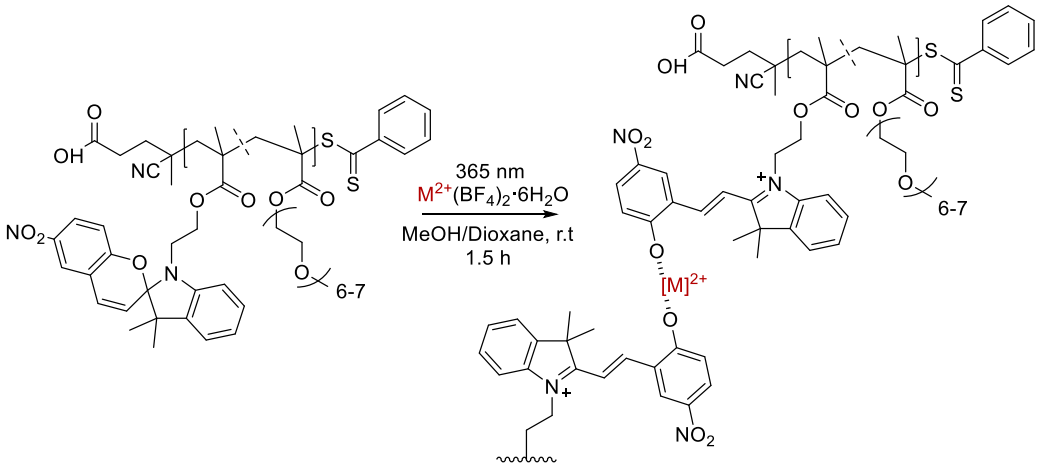


Figure S1. SEC Chromatograms of all **SP-X-PEGMEMA** polymers reporting number average molecular weight (M_n), peak molecular weight (M_p) and Dispersity ($Đ$). Recorded in THF (PMMA calibration standards)

3 Photoinduced $M^{2+}(BF_4)_2$ SCNP Synthesis

3.1 General Procedure and Analysis



2 mg of polymer was placed under inert N_2 atmosphere in a photo vial, to which initially 0.8 mL of dry dioxane were added, followed by 3.8 mL of dry and degassed MeOH. Separately, 4 eqv of the tetrafluoroborate salt (4 eqv per spiropyran, 0.0029 g, 0.00851 mmol) were dissolved in dry and degassed MeOH (0.4mL) in a photovial under N_2 atmosphere. The tetrafluoroborate solution was subsequently added dropwise over a period of 90 mins to the polymer solution. Irradiation with a 365 nm LED was conducted with pulse irradiations of 1 min followed by 30 min of darkness over the same period totalling three times 1 min irradiations with 365 nm light.

Sample preparation for:

SEC Analysis – An aliquot of the M^{2+} SCNP solution (0.5 mL) was diluted with THF (0.5 mL) and subsequently filtered into a SEC vial for subsequent injection and analysis.

H NMR/DOSY Analysis – The M^{2+} SCNP solution was diluted with 4.6 mL of toluene and placed on a rotary evaporator and set to 25 °C. Solvent was removed until approximately only 0.5 mL of solvent was left or until the solution became cloudy. The solution was then transferred to a centrifuge vial and centrifuged, resulting in a small off-white pellet and a yellow supernatant. The supernatant was carefully collected and concentrated under reduced pressure to afford the M^{2+} SCNP as a yellow solid. CD_3CN_{-d3} was subsequently added and the solution passed through a PTFE filter directly into an NMR tube for analysis.

UV-Vis Analysis – An aliquot of the M^{2+} SCNP solution (0.2 mL) was taken and diluted with MeOH (0.7 mL) before being inserted into a UV-vis spectrophotometer for analysis.

3.2 Photoinduced $M^{2+}(BF_4)_2$ SCNP Synthesis - Irradiation Setup

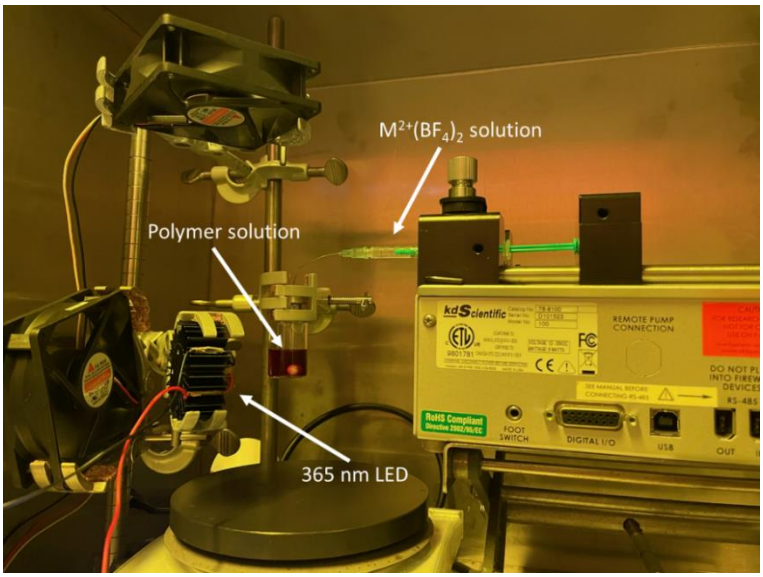


Figure S2. LED setup for the photo-induced $M^{2+}(BF_4)_2$ based single chain polymer folding.

3.3 Photoinduced $M^{2+}(BF_4)_2$ SCNP Synthesis – Irradiation Scheme

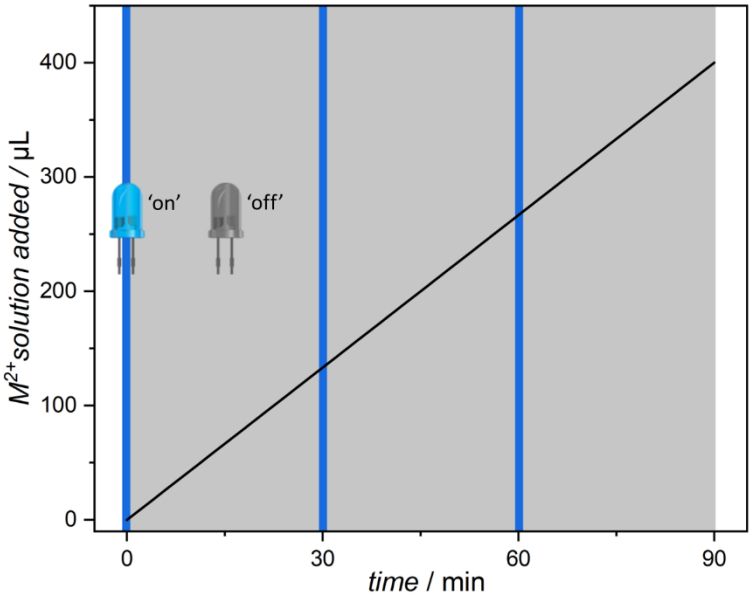
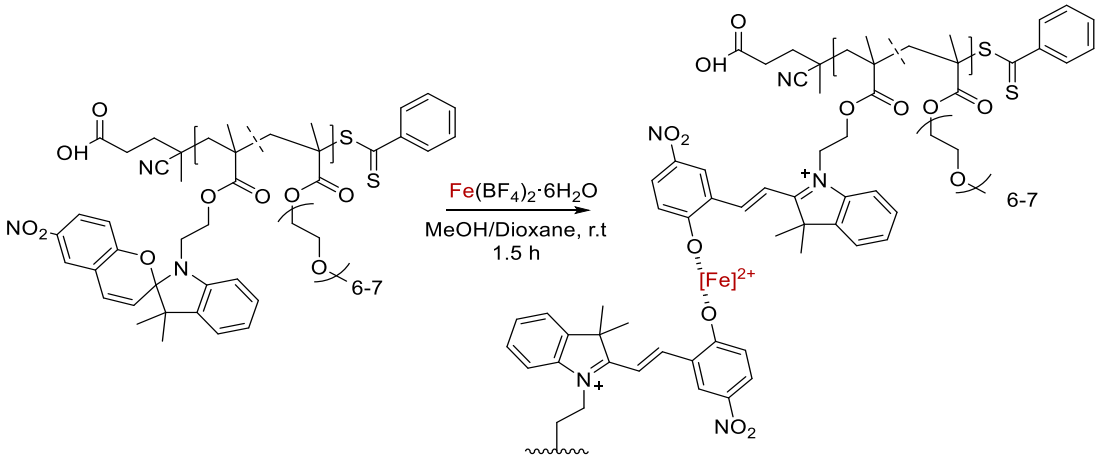


Figure S3. Addition of the $M^{2+}(BF_4)_2$ solution to the polymer solution within the photo vial occurs over a 90 min period at a rate of 4.4 µL min^{-1} (rate of addition = to the gradient of the **black line**), interrupted by short 1 min pulse irradiations (blue) occurring at *t* = 0, 30 and 60 min, separated by dark periods of 30 min (grey).

3.4 Control Experiment in the Dark



The procedure for the $Fe(BF_4)\cdot 6H_2O$ control experiment was followed according to the general SCNP synthesis procedure (refer to section **3.1**), without irradiation cycles.

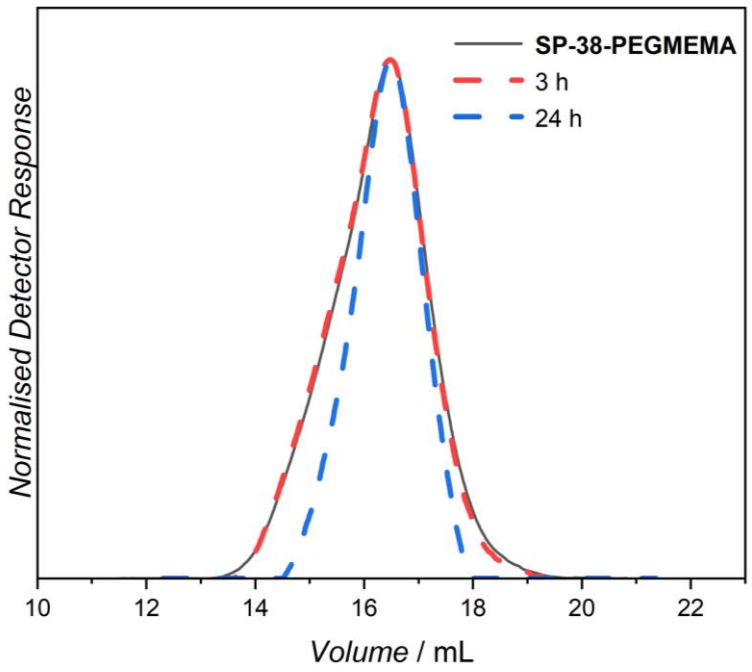
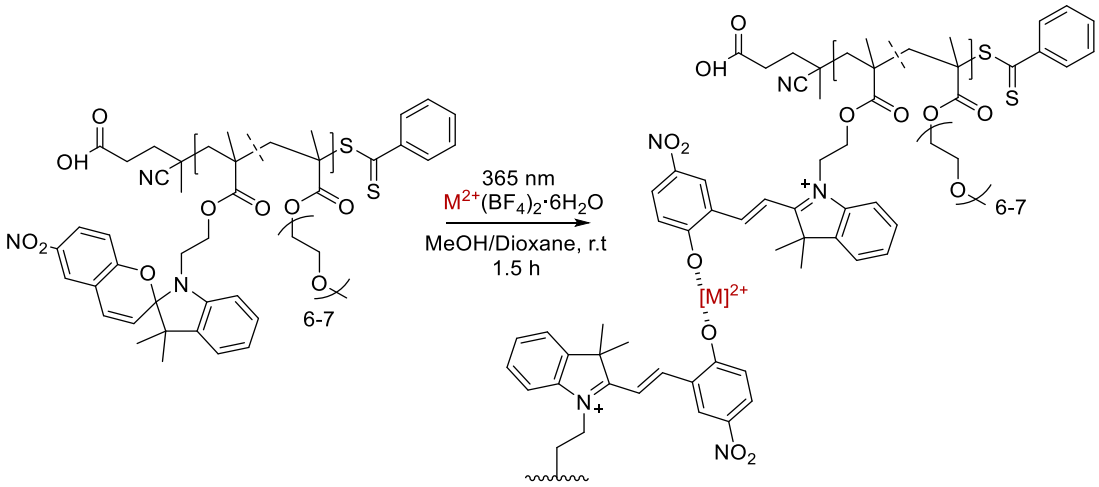


Figure S4. SEC elugram of **SP-38-PEGMEMA** (black) without $Fe(BF_4)\cdot 6H_2O$ addition, 3 h post $Fe(BF_4)\cdot 6H_2O$ addition (red) and 24 h post $Fe(BF_4)\cdot 6H_2O$ addition. Recorded in THF using PMMA calibration standards.

3.5 **SP-15-PEGMEMA** Folding Attempts



The procedure for **SP-15-PEGMEMA** folding experiments was followed according to the general SCNP synthesis procedure (refer to section **3.1**) using amounts for the respective $M^{2+}(BF_4)_2$ salts modified according to the mol % of spiropyran on the polymer (4 eqv per spiropyran, 0.0012 g, 0.0035 mmol).

3.5.1 $Co(BF_4)_2{\cdot}6H_2O$

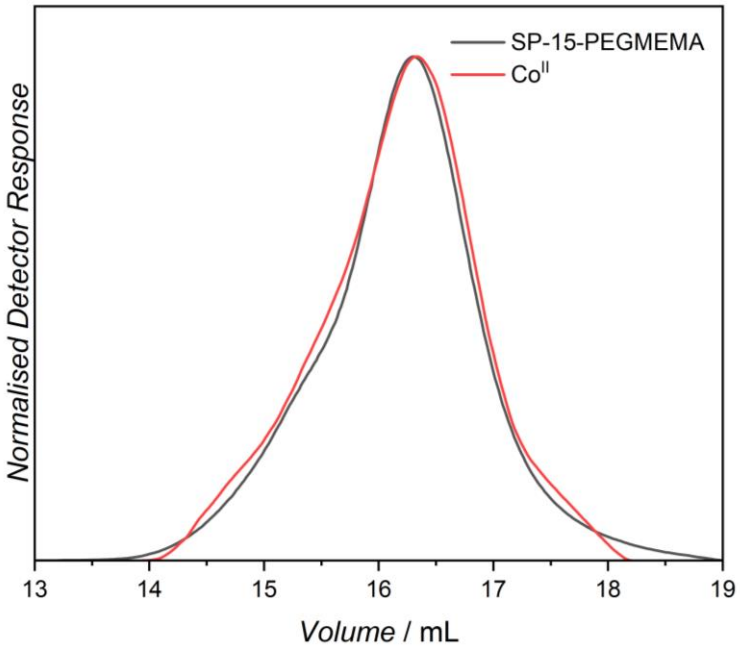


Figure S5. SEC elugram of **SP-15-PEGMEMA** before (black) and after (red) irradiation and addition of $Co(BF_4)_2{\cdot}6H_2O$ measured in THF using PMMA calibration standards.

3.5.2 $Fe(BF_4)_2 \cdot 6H_2O$

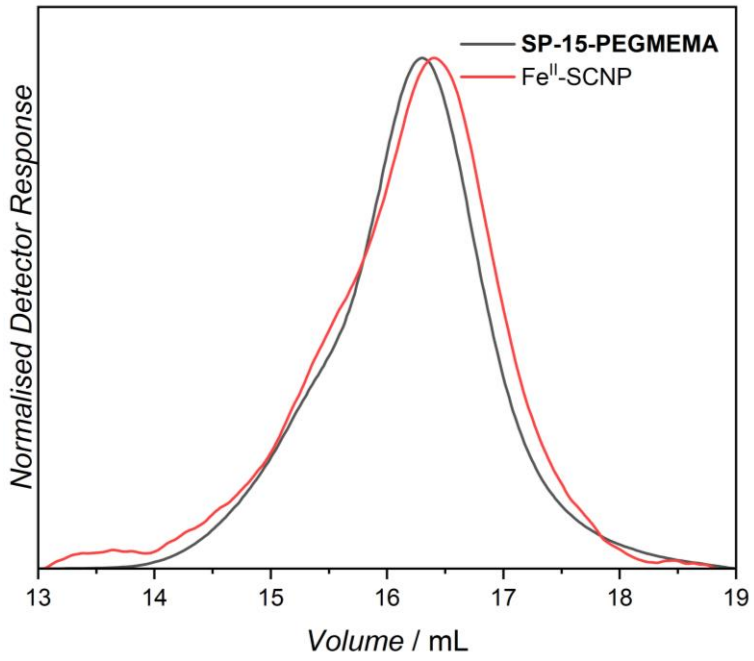
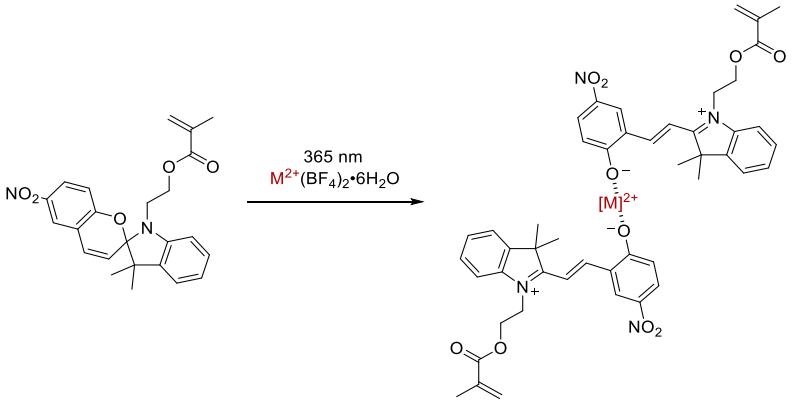


Figure S6. SEC elugram of **SP-15-PEGMEMA** before (black) and after (red) irradiation and addition of $Fe(BF_4)_2 \cdot 6H_2O$ recorded in THF using PMMA calibration standards.

4 Small molecule and Polymer NMR Data (^{13}C and ^{1}H)

4.1 ^{1}H NMR Analysis of Spiropyran-MMA and $M^{2+}(BF_4)_2.6H_2O$ Salts



SP-MMA was added to a photo vial with CD_3OD. The solution was allowed to stir for 15 min in the dark while being bubbled with N_2. Separately, the respective metal tetrafluoroborate salt was dissolved in CD_3OD and the resulting solution bubbled with N_2. The **SP-MMA** solution was subsequently irradiated with a 365 nm LED for 1 min followed by the immediate addition of the metal tetrafluoroborate solution. The combined solutions were allowed to stir in the dark for 30 min. Subsequently, the solution was transferred into an NMR tube and analysed via ^{1}H NMR spectroscopy.

4.1.1 Spiropyran-MMA, 365 nm and No Metal

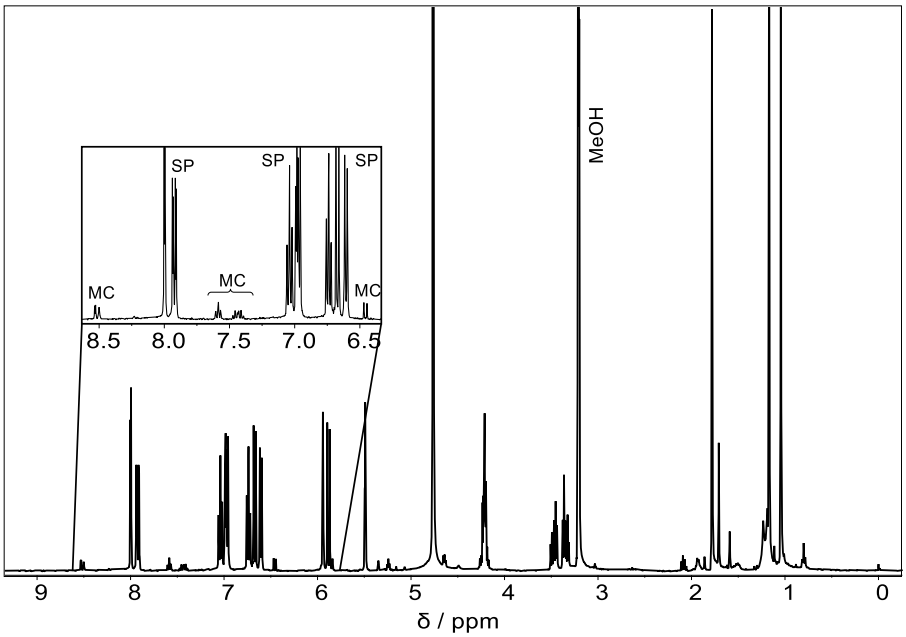


Figure S7. ^{1}H NMR spectrum of **SP-MMA** in CD_3OD after 365 nm irradiation for 1 min. Note that in the above NMR spectrum, less open isomer is formed as the irradiation time was only 1 min, compared to the SCNP folding experiments, which follow an irradiation sequence (Figure S3).

4.1.2 Spiropyran-MMA, 365 nm and $Fe(BF_4)_2.6H_2O$

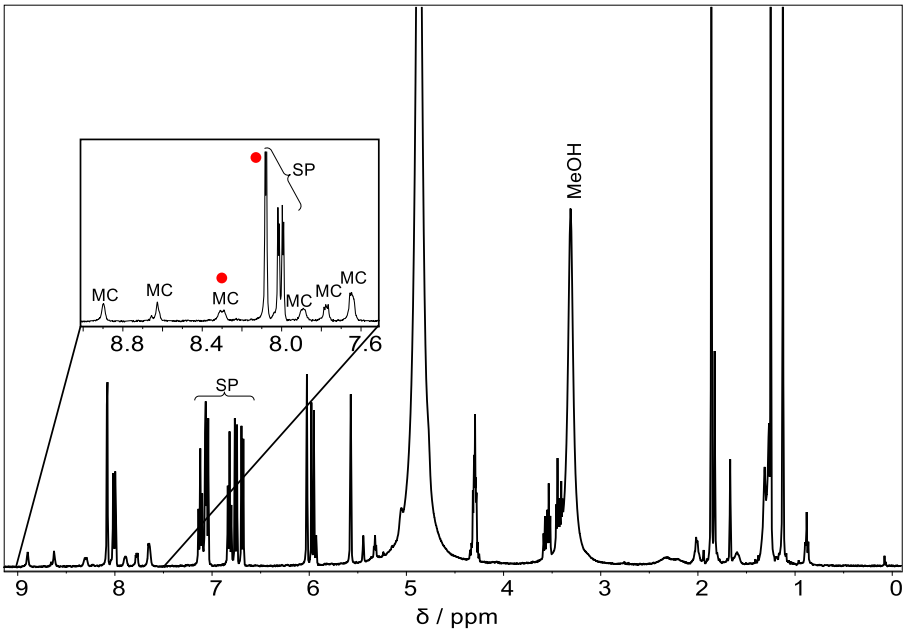


Figure S8. ^1H NMR spectrum of **SP-MMA** in CD_3OD after 365 nm irradiation for 1 min and addition of 0.004 mmol of $Fe(BF_4)_2.6H_2O$. Resonances used for the determination of percentage composition are labelled with a red sphere.

4.1.3 Spiropyran-MMA, 365 nm and $Co(BF_4)_2.6H_2O$

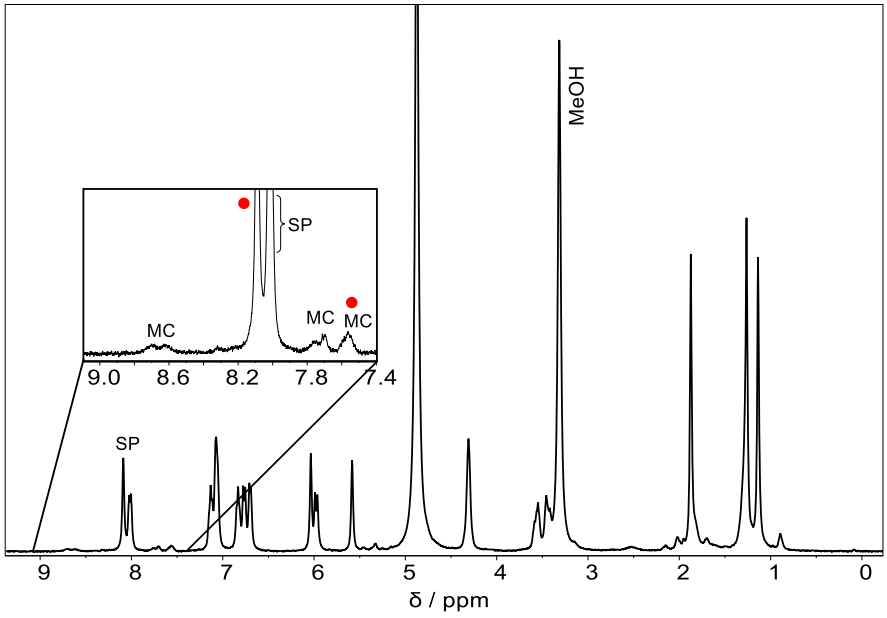


Figure S9. ^1H NMR spectrum of **SP-MMA** in CD_3OD after 365 nm irradiation for 1 min and addition of 0.004 mmol of $Co(BF_4)_2.6H_2O$. Resonances used for the determination of the percentage composition are labelled with a red sphere.

4.1.4 Spiropyran-MMA, 365 nm and $Cu(BF_4)_2.6H_2O$

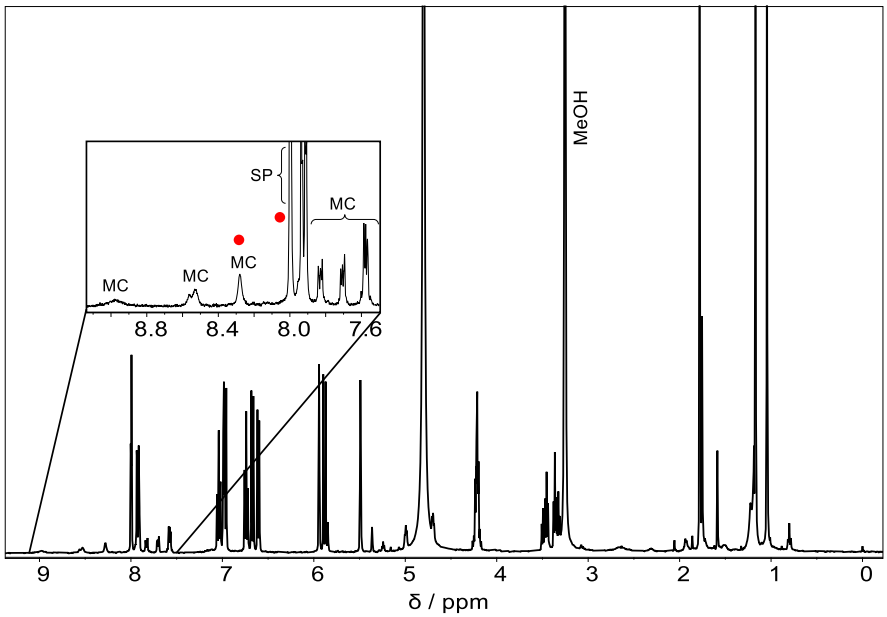


Figure S10. ^1H NMR spectrum of **SP-MMA** in CD_3OD after 365 nm irradiation for 1 min and addition of 0.004 mmol of $Cu(BF_4)_2.6H_2O$. Resonances used for the determination of percentage composition are labelled with a red sphere.

4.2 Monomer and Polymer NMR Analysis

4.2.1 Hydroxyethyl indolenine

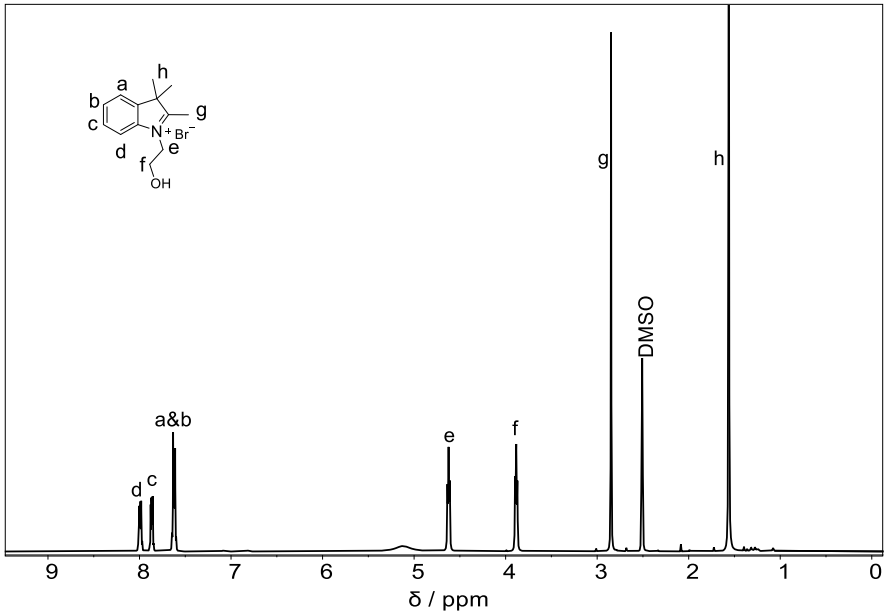


Figure S11. ^{1}H NMR spectrum of hydroxyethyl indolenine recorded in DMSO$_{d8}$.

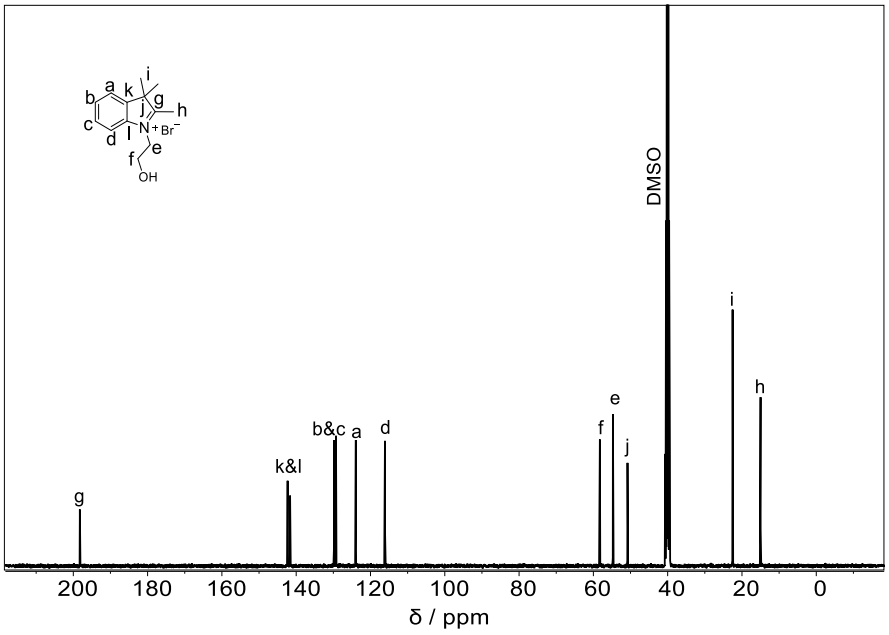


Figure S12. ^{13}C NMR spectrum of hydroxyethyl indolenine recorded in DMSO$_{d8}$.

4.2.2 Indolenine Oxazole

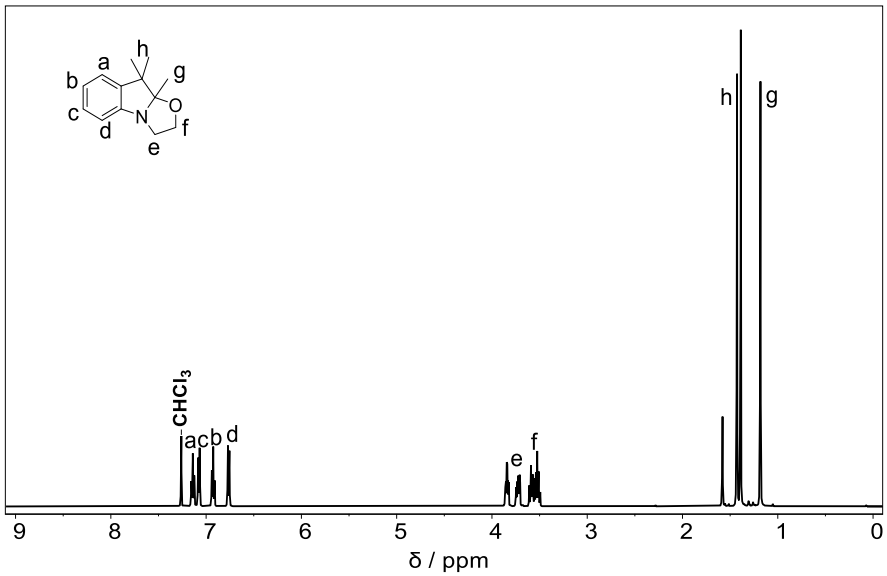


Figure S13. ^{1}H NMR spectrum of indolenine oxazole recorded in $CDCl_3$.

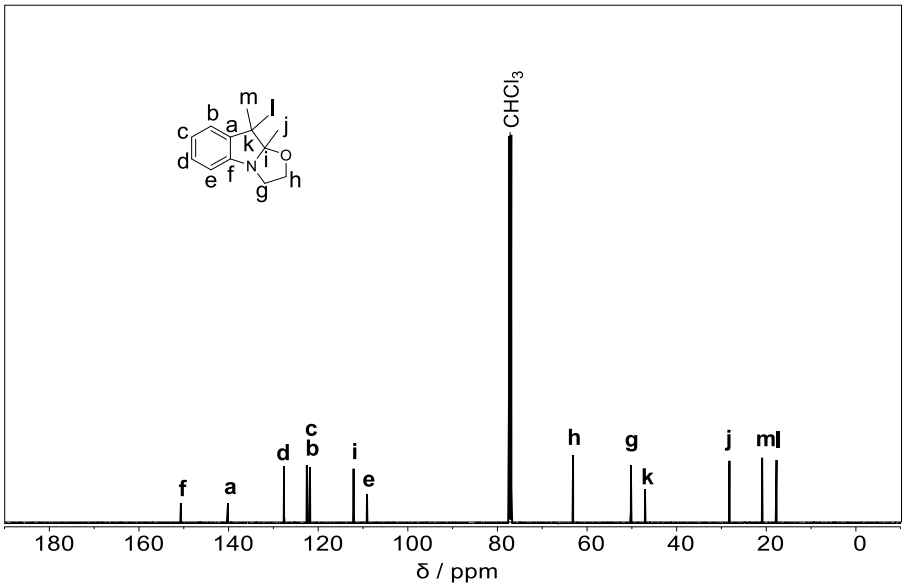


Figure S14. ^{13}C NMR spectrum of indolenine oxazole recorded in $CDCl_3$.

4.2.3 Hydroxyethyl Spiropyran

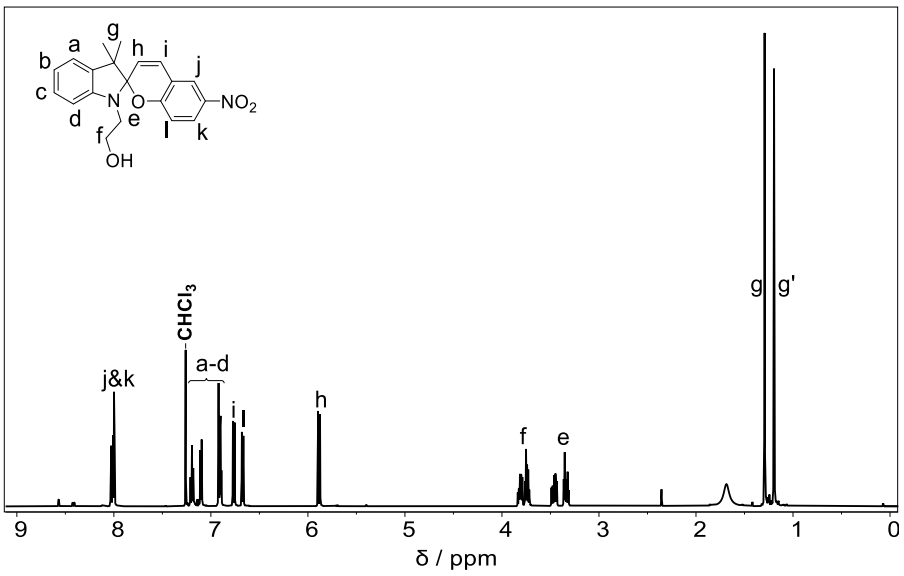


Figure S15. ^{1}H NMR spectrum of hydroxyethyl spiropyran in $CDCl_3$.

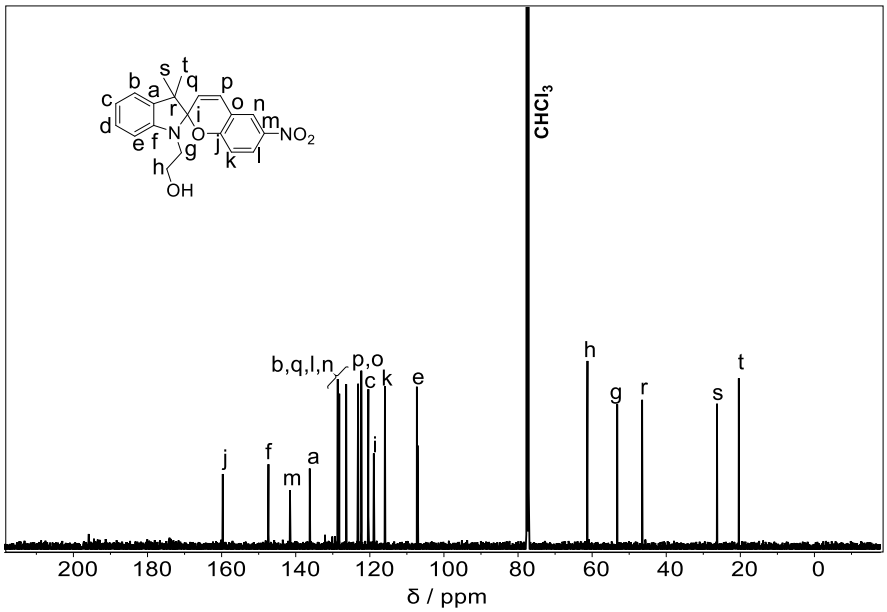


Figure S16. ^{13}C NMR spectrum of hydroxyethyl spiropyran in $CDCl_3$.

4.2.4 Methacrylate Spiropyran (**SP-MMA**)

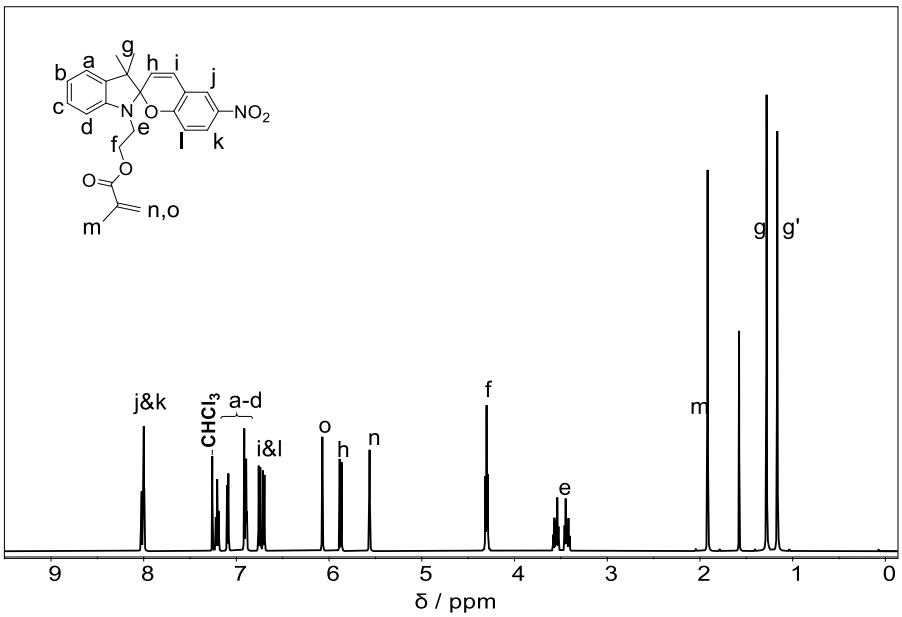


Figure S17. ^{1}H NMR spectrum of methyl methacrylate spiropyran (**SP-MMA**) in $CDCl_3$.

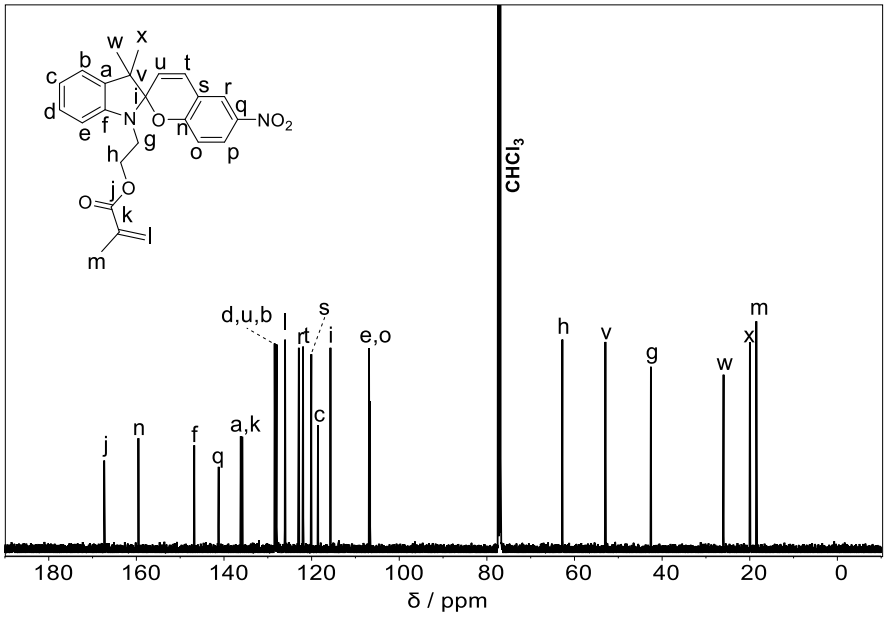


Figure S18. ^{13}C NMR spectrum of methyl methacrylate spiropyran (**SP-MMA**) in $CDCl_3$.

4.3 **SP-X-PEGMEMA** Polymer ^{1}H NMR

4.3.1 **SP-15-PEGMEMA**

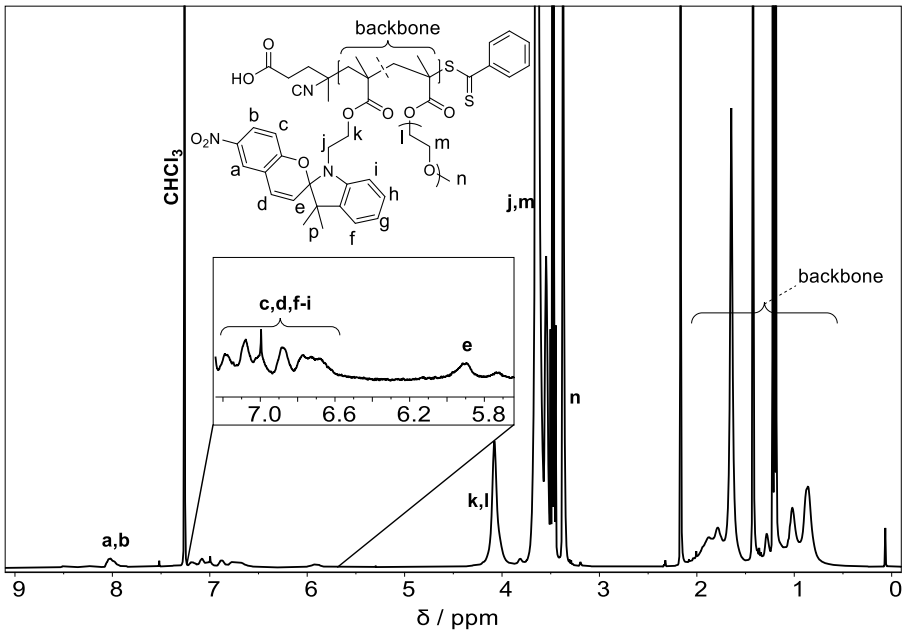


Figure S19. ^{1}H NMR spectrum of **SP-15-PEGMEMA** in $CDCl_3$.

4.3.2 **SP-38-PEGMEMA**

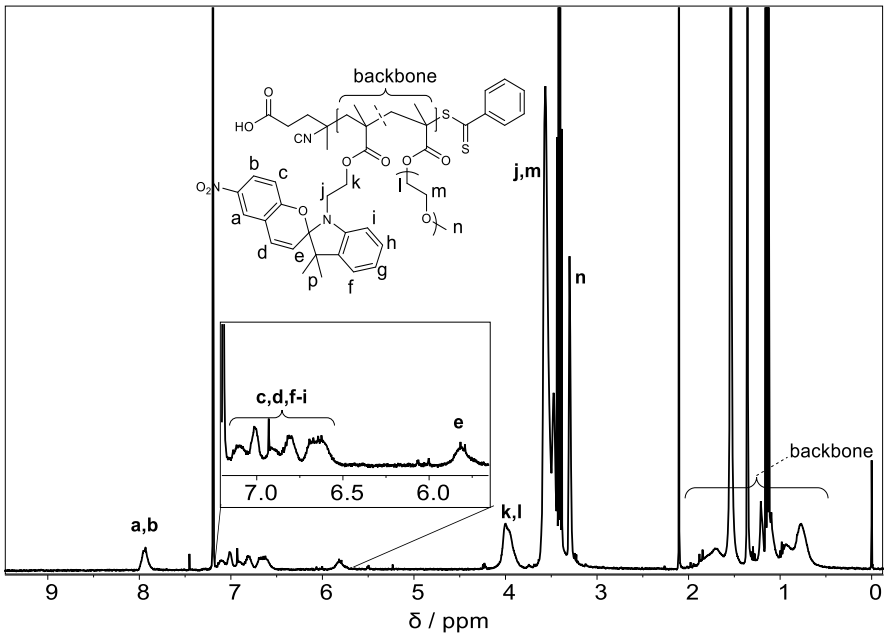


Figure S20. ^{1}H NMR spectrum of **SP-38-PEGMEMA** in $CDCl_3$.

4.4 Calculation of the Number of Spiropyran Units Per Chain

$$n(monomers) = \frac{M_n\ (Polymer)}{M_{Average}\ (monomer)}$$

$$M_{Average} = X(M1) \times M(M1) + X(M2) \times M(M2)$$

$$n(monomers) = \left(\frac{M_n\ (Polymer)}{X(M1) \times M(M1) + X(M2) \times M(M2)}\right) \times X(M1)$$

4.4.1 **SP-38-PEGMEMA**

SP content by ^{1}H NMR = 38%

$\frac{28\ 500\ g\ mol^{-1}}{0.38(420.47\ g\ mol^{-1})+0.62(300\ g\ mol^{-1})} * 0.38$ = 31 units of spiropyran

4.4.2 **SP-36-PEGMEMA**

SP content by ^{1}H NMR = 36%

$\frac{40000\ g\ mol^{-1}}{0.36(420.47\ g\ mol^{-1})+0.64(300\ g\ mol^{-1})} * 0.36$ = 42 units of spiropyran

4.4.3 **SP-15-PEGMEMA**

SP content by ^{1}H NMR = 15%

$\frac{30500\ g\ mol^{-1}}{0.15(420.47\ g\ mol^{-1})+0.85(300\ g\ mol^{-1})} * 0.15$ = 14 units of spiropyran

5 LED Emission Spectra

5.1 365 LED

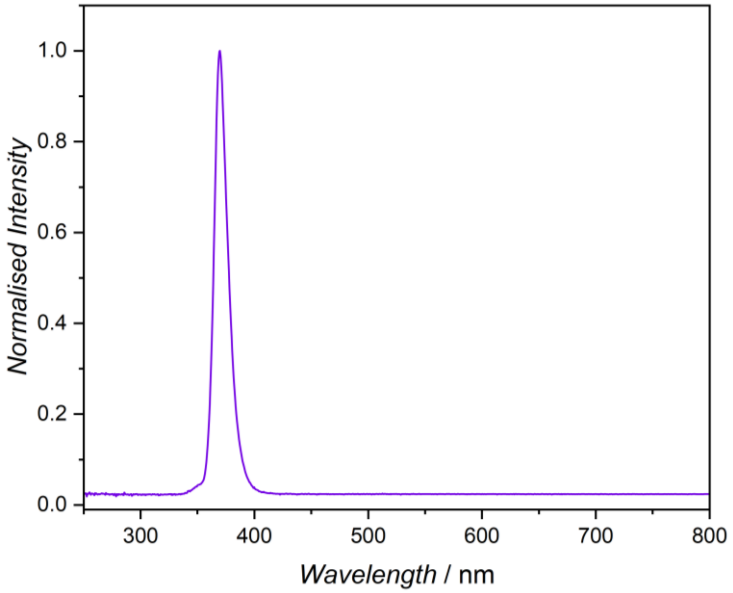


Figure S21. Emission spectrum of the 365 nm LED (7 W, λ_{max} = 365 nm) used to switch the spiropyran species from the closed spiro isomer to the merocyanine open isomer.

5.2 White Light LED

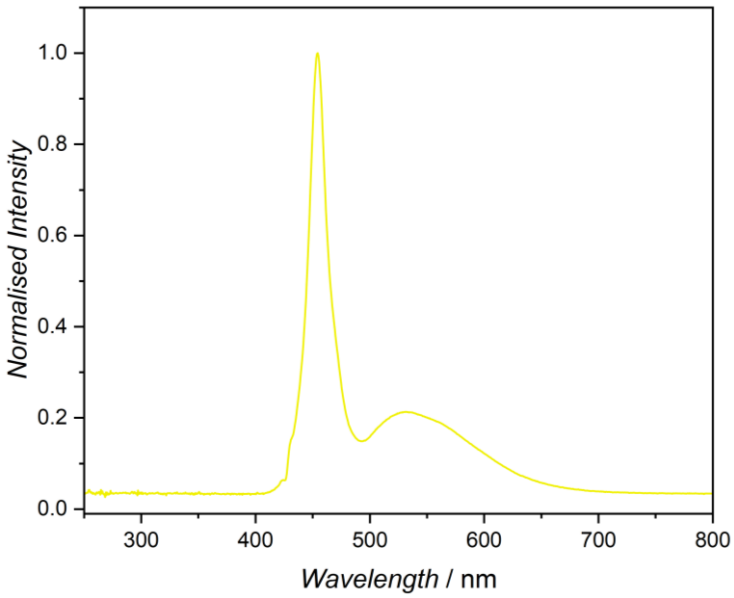
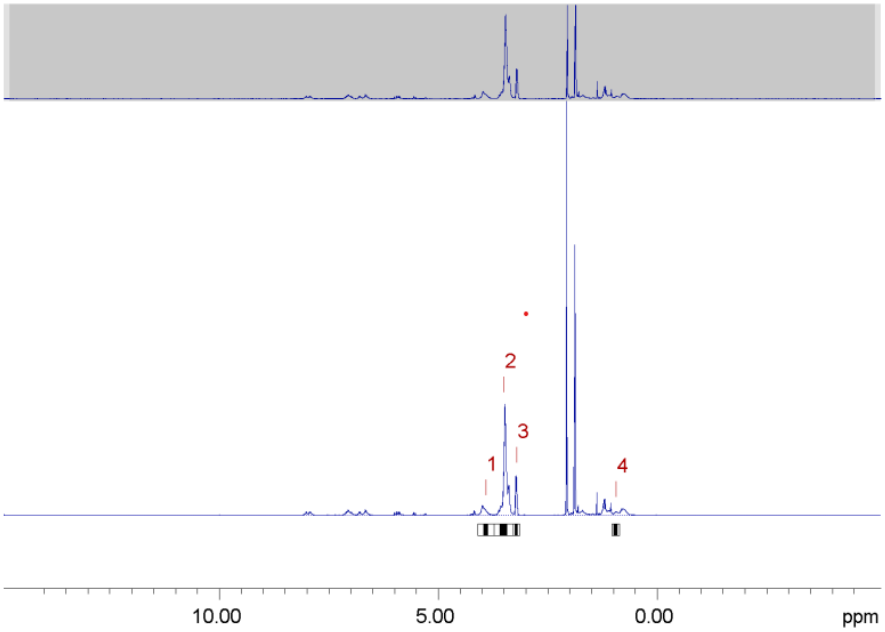
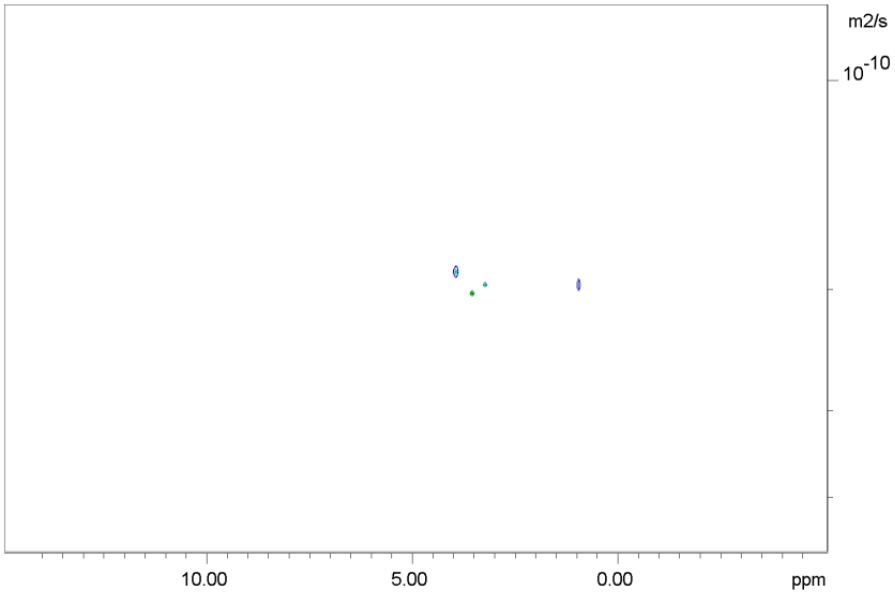


Figure S22. Emission spectrum of the white light LED (10 W, λ_{max} = 455 nm) used to switch the merocyanine open isomer to the closed spiro isomer.

6 Primary DOSY data

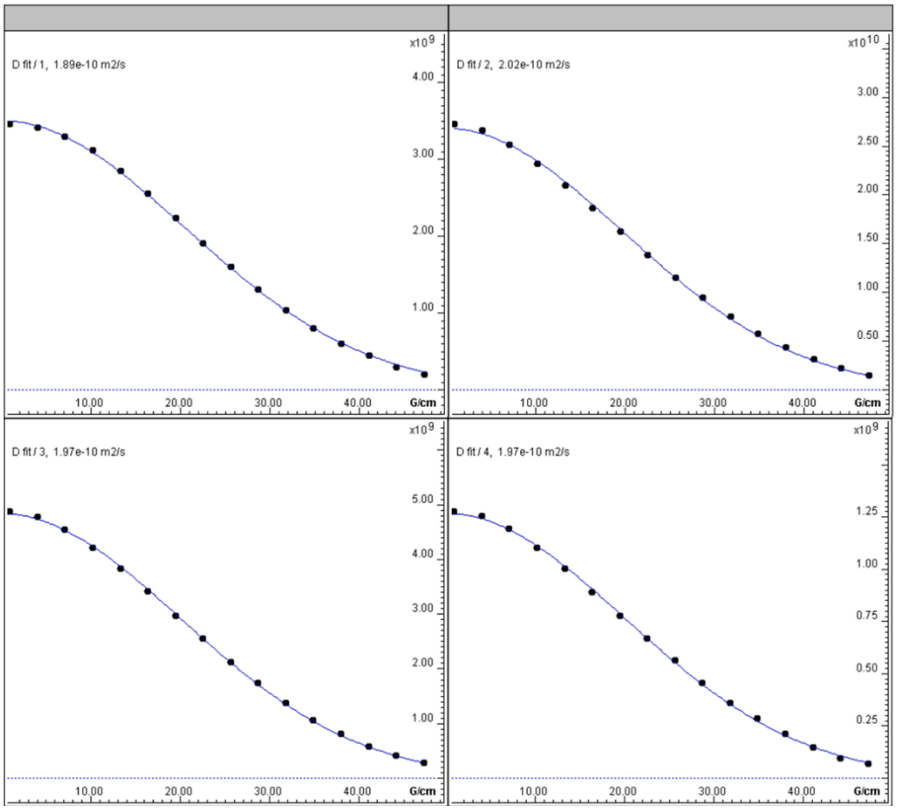
6.1 SP-38-PEGMEMA



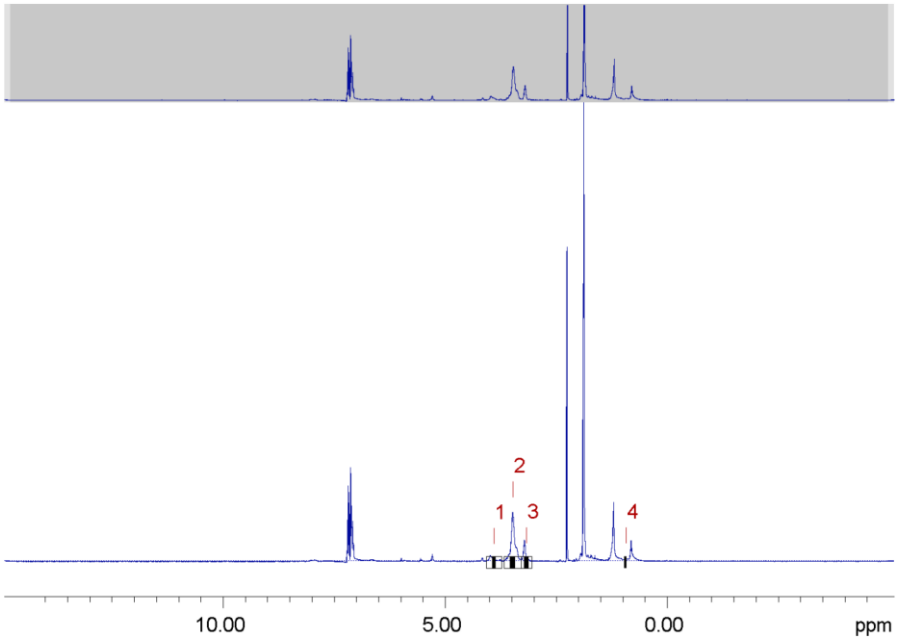


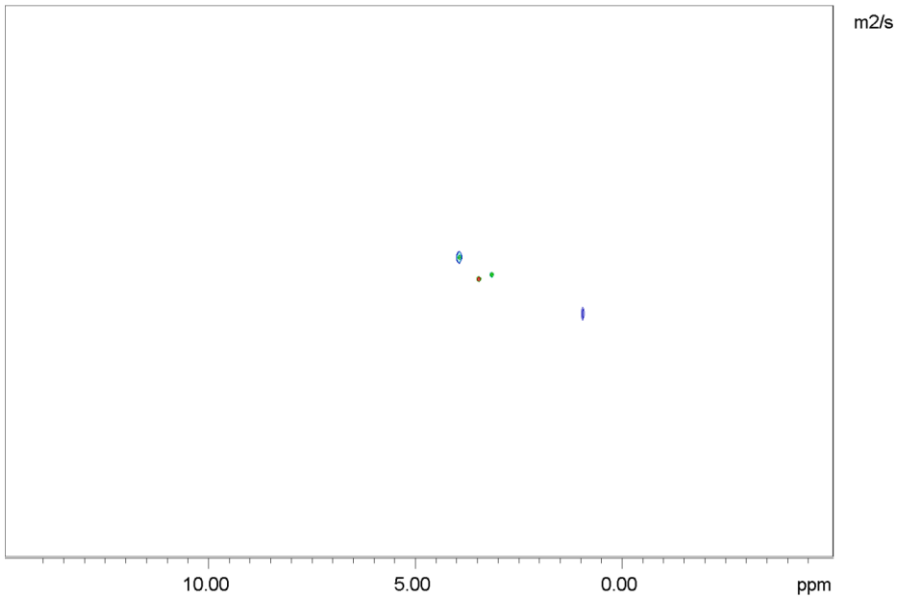
Fitted function:	f (x) = Io * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0030000 s
used big delta:	0.099900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using calculated y uncertainties
Confidence level:	0%
Used peaks:	peaks from C:/Users/aidan/Desktop/DOSY/AEI_186/4/pdata/1/peaklist1D.xml
Used integrals:	area integral

Peak name	F2 [ppm]	Io	error	D [m2/s]	error	fitInfo
1	3.907	3.51e+09	1.113e+06	1.89e-10	1.451e-13	Done
2	3.504	2.69e+10	1.225e+06	2.02e-10	2.216e-14	Done
3	3.211	4.85e+09	7.216e+05	1.97e-10	7.079e-14	Done
4	0.936	1.27e+09	7.712e+05	1.97e-10	2.888e-13	Done



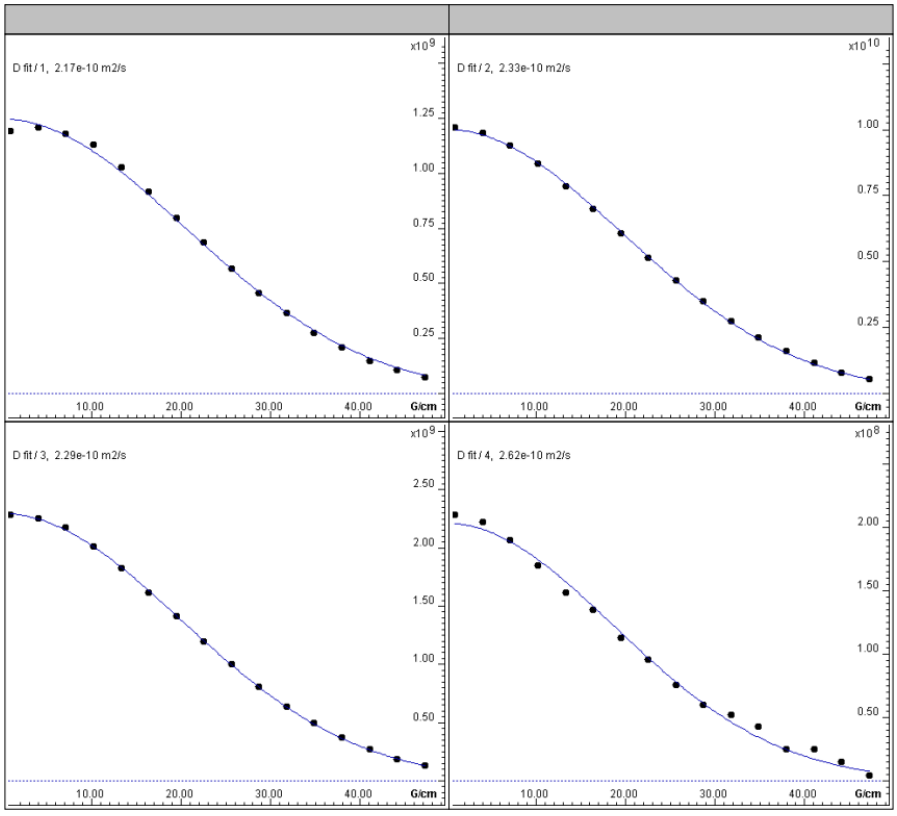
6.2 **SP-38-PEGMEMA**-Fe^{II}





Fitted function:	f (x) = Io * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0028000 s
used big delta:	0.099900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using calculated y uncertainties
Confidence level:	0%
Used peaks:	peaks from C:/Users/aidan/Desktop/DOSY/AEI_1872.0/5/pdata/1/peaklist1D.xml
Used integrals:	area integral

Peak name	F2 [ppm]	Io	error	D [m2/s]	error	fitInfo
1	3.893	1.25e+09	1.069e+06	2.17e-10	4.494e-13	Done
2	3.477	1.00e+10	1.144e+06	2.33e-10	6.404e-14	Done
3	3.164	2.30e+09	9.190e+05	2.29e-10	2.206e-13	Done
4	0.933	2.04e+08	4.165e+05	2.62e-10	1.281e-12	Done



6.3 Correlation of Compaction with Spiropyran Unit Density

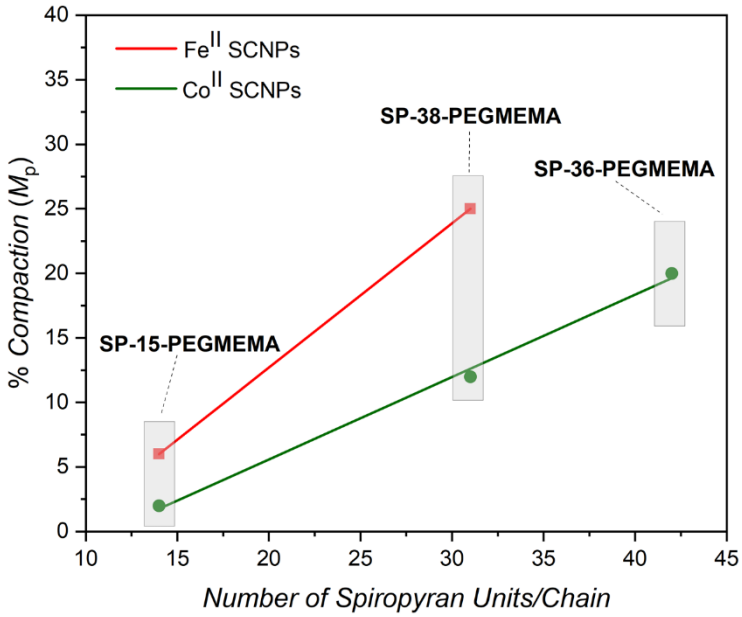


Figure S23. Linear fits of the percentage compaction (based on the change in M_p) of SCNPs vs the number of spiropyran per chain of each precursor polymer (**SP-X-PEGMEMA**) upon photoinduced complexation and compaction with metal ions Fe^{2+} and Co^{2+}.

7 References

1 W. M. Haynes, W. M. Haynes, D. R. Lide and T. J. Bruno, *CRC handbook of chemistry and physics : a ready-reference book of chemical and physical data.*, CRC Press, Boca Raton, Florida ;, Ninety-seven edition., 2017.

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3 J. Chen, W. Zhong, Y. Tang, Z. Wu, Y. Li, P. Yi and J. Jiang, *Macromolecules*, 2015, **48**, 3500–3508.