Supporting Information

Modulating Noncovalent Cross-links with Molecular Switches

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General Information

5-methoxy-2,3,3-trimethyl-3H-indole was purchased from Biosynth. Cobalt bis(trifluoromethylsulfonyl)imide (Co(NTf₂)₂) and copper bis(trifluoromethylsulfonyl)imide (Cu(NTf₂)₂) were purchased from TCI Chemicals. Sodium bis(trifluoromethylsulfonyl)imide was purchased from Alfa Aesar. All other chemicals and solvents were purchased from either Sigma Aldrich or Alfa Aesar. All chemicals and solvents were used without further purification. NMR spectra were taken on a 500 MHz Carver B500 spectrometer. Gel permeation chromatography (GPC) was performed with a Waters 515 HPLC pump and recorded with Waters 2414 refractive index and Waters 2998 UV absorption detectors. GPC traces were taken of polymer samples dissolved in THF using monodisperse polystyrene as calibration standards.

Synthetic procedures

2,3,3-trimethyl-3H-indol-5-ol: 20 g (105.67 mmol) of 5-methoxy-2,3,3-trimethyl-3H-indole was dissolved in 48% aqueous HBr and refluxed at 140 °C for 2.5 hours under argon. After cooling to room temperature, the solution was added to 600 ml of DI water, partially neutralized with Na₂CO₃ and brought to pH ~7-8 with NaHCO₃. Extracted with CH₂Cl₂ (3 x 200 ml). The combined organics were washed twice with 100 ml of DI water, and concentrated *in vacuo* to yield the product as an off-white solid (16.42 g, 93.7 mmoles, 88.7%). The material was pure by NMR and mass spec, and was used without further purification.

¹H NMR (500 MHz, DMSO-*d*₆) δ 9.27 (s, 1H), 7.18 (d, J = 8.2 Hz, 1H), 6.77 (d, J = 2.4 Hz, 1H), 6.64 (dd, J = 8.2, 2.4 Hz, 1H), 2.12 (s, 3H), 1.18 (s, 6H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 183.93, 155.31, 147.48, 145.85, 119.49, 113.45, 109.17, 53.02, 22.76, 14.81. *Compound* **1**: *5-hydroxy-1,2,3,3-tetramethyl-3H-indol-1-ium iodide*. 16.39 g (93.52 mmol) of *2,3,3-trimethyl-3H-indol-5-ol* was dissolved in 400 ml of 1:1 toluene/acetonitrile in a one-necked round bottom flask. 26.5 g (186.7 mmol, 2 equiv) of iodomethane was added and the solution was refluxed at 90 °C for 14 hours. The precipitated solid was filtered and washed copiously with ethanol and diethyl ether to yield **1** as a white, sand-textured powder (28.914 g, 91.16 mmol, 97.48%). Product was used without further purification.

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.69 (d, J = 8.7 Hz, 1H), 7.12 (d, J = 2.4 Hz, 1H), 6.93 (dd, J = 8.7, 2.4 Hz, 1H), 3.91 (d, J = 1.2 Hz, 3H), 2.70 (d, J = 1.3 Hz, 3H), 1.47 (s, 6H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 191.89, 158.94, 143.72, 134.15, 116.14, 115.01, 110.31, 53.47, 34.79, 21.91, 13.98.

Compound **2**: 1',3',3'-*trimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-ol.* A solution of **1** (4.44 g, 14 mmol), 2-hydroxy-5-nitrobenzaldehyde (2.342, 14 mmol, 1 equiv), and piperidine (2.385 g, ~28 mmol, ~2 equiv) was refluxed in 38 ml of absolute ethanol for 5 hours in an oil bath set to 100 °C. After 5 hours, the solution slowly cooled to room temperature in the oil bath for several hours. The precipitate was filtered, washed with ethanol, diethyl ether and hexanes to yield **2** as dark green crystals (4.25 g, 12.56 mmol, 89.7%). Characterization matched literature values.¹

SPMA: *1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-yl methacrylate.* 4.23 g (12.5 mmol) of compound **2** and 2 g of DMAP (16.37 mmol, 1.3 equiv) were dissolved in 67 ml of THF. 2.83 g (18.357 mmol, 1.47 equiv) of methacryloyl anhydride was added and the solution stirred at room temperature for 6 hours. A small amount of methanol was then added to quench the reaction. THF was removed *in vacuo* and the crude mixture was redissolved in CH₂Cl₂ and

the product purified by flash chromatography through a silica followed by flash chromatography through basic alumina gel. CH_2Cl_2 was then removed *in vacuo* to yield the product as a brown solid (5.595 g, 11.3 mmol, 90.5%).

¹H NMR (500 MHz, DMSO-*d*₆) δ 8.23 (d, *J* = 2.9 Hz, 1H), 8.01 (dd, *J* = 9.0, 2.8 Hz, 1H), 7.24 (d, *J* = 10.4 Hz, 1H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 1H), 6.92 – 6.90 (m, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.25 (t, *J* = 1.3 Hz, 1H), 6.00 (d, *J* = 10.4 Hz, 1H), 5.87 (t, *J* = 1.6 Hz, 1H), 2.94 (s, 3H), 2.68 (s, 3H), 1.17 (d, *J* = 39.2 Hz, 6H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 165.91, 159.29, 145.15, 143.86, 140.57, 137.04, 135.52, 128.38, 127.31, 125.75, 122.85, 121.18, 120.41, 118.88, 115.84, 115.44, 107.05, 106.40, 79.18, 51.95, 38.60, 28.69, 25.49, 19.50, 18.12. HRMS-ESI (m/z): [M + H]⁺ calcd for C₂₃ H₂₃N₂O₅, 407.1602; found 407.1607

P(DEGMEMA–SPMA): Synthesized by RAFT polymerization. 3.709 g (9.13 mmol) of **SPMA**, 11.394 g (60.54 mmol) of diethylene glycol methyl ether methacrylate (DEGMEMA), 0.181 g (0.09 mmol) of 4-Cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl]pentanoic acid (RAFT agent), and 0.0117 g (.071 mmol) of AIBN was dissolved in 12.5 ml of anhydrous DMF. The monomer solution was degassed by a freeze–thaw cycle, repeated three times, to remove dissolved oxygen. The reaction flask was sealed by Teflon tape and heated at 80 °C for 24 hours. The reaction was stopped by exposure to air. Polymer was precipitated directly into diethyl ether, redissolved in CH₂Cl₂ and precipitated a second time in diethyl ether to yield red colored polymer flakes (10.92 g, 71.4%). $M_n = 25,345$ kDa, $M_w = 30.6675$ kDa (PDI = 1.21) by GPC



Scheme S1. Synthesis of SPMA and P(DEGMEMA–SPMA).



Figure S1. ¹H NMR spectrum of SPMA in CD₃CN.



Figure S2. ¹H NMR spectrum of P(DEGMEMA–SPMA) in DMSO-d6. SPMA concentration (\sim 10.5 mol%) quantified by comparing integrals of aromatic peaks to peak at 4.02 ppm. (b) SEC chromatograms of P(DEGMEMA–SPMA) copolymer (THF- eluent and polystyrene - standard).

UV-Vis data (Fig. 2D) indicates that the degree of crosslinking is likely significantly higher in heat-treated samples than in those equilibrated at room temperature.

UV-Vis absorption spectroscopy

For UV-Vis absorption spectra of concentrated polymer solutions (see Fig. 2), 24.5 wt% solutions of P(DEGMEMA-SPMA) with and with Co(NTf₂)₂ in a ratio of 2:1 SP: Co(NTf₂)₂ were prepared in the manner described above. Polymer solutions were sandwiched between glass coverslips using an epoxy-adhered, ~100 µm thick washer as a spacer. The absorption spectra of Figure 2 were measured using an Axio Observer D1 inverted microscope with a Halogen illumination light source, coupled via multi-mode fiber optic cables to a Control Development 2DMPP, thermoelectrically-cooled optical spectrometer ($\lambda = 420-779$ nm detection range). Heating was conducted in the dark using a standard hot plate. Samples were heated to 80 °C for 1 hour and immediately transferred to the spectrometer for measurements. UV exposure was conducted using a 100 W, 365 nm peak wavelength UV light source positioned approximately 6 inches from the sample surface. 3 minutes of UV exposure was used for all UV excitation experiments, as this was determined to maximize the conversion of SP to MC under these conditions. The solution was exposed to visible light using a high current white LED spotlight (Advanced Illumination SL073), which was positioned ~ 6 cm from the surface of the sample. According to the specifications of the manufacturer, the LED spotlight emits wavelengths between approximately 420 to 750 nm, and the irradiance at normal incidence 10 cm from the source varies from 79.6 to 93.7 W/m^2 .

Absorption spectra of dilute solutions (total concentration $[SP] + [Co(NTf_2)_2] = 0.5 \text{ mM}$) (see Fig. S5) were measured in 1 mm path length glass cuvettes using a Shimadzu UV-2401 PC UV-Vis spectrophotometer. Samples were irradiated with a 100 W, 365 nm peak wavelength UV lamp positioned approximately 10 inches from the cuvette. 90 seconds of UV exposure was used for all UV excitation experiments, as this was determined to maximize the conversion of SP to MC under these conditions.



Figure S3. UV-Vis absorption spectra of P(DEGMEMA-SPMA)/Co(NTf₂)₂ solutions in PC. Total concentration [SP] + [Co(NTf₂)₂] = 0.5 mM. (A) Spectra of solutions containing varying ratios of SP/Co(NTf₂)₂. As more Co(NTf₂)₂ is added, the peak centered at λ = 564 nm, (characteristic of MC) gives way to a new peak centered at λ = 506 nm, corresponding to MC-Co complexes. The broad, asymmetric shape of the MC-Co peak suggests that multiple MC-Co isomers may be present. (B) Absorption spectra of solution containing approximately 2:1 molar ratio of SP:Co(NTf₂)₂ before heating, after heating to 80 °C for 4 hours, and after 90 seconds of exposure to UV light at room temperature.

Preparation of polymer solutions for rheology

A stock solution of 27.5 wt% P(DEGMEMA–SPMA) in PC was prepared. Stock solutions of $Co(NTf_2)_2$, $Cu(NTf_2)_2$ and $Na(NTf_2)$ in PC were prepared in separate vials. For each experiment a particular salt solution and the 27.5 wt% P(DEGMEMA–SPMA) solution were combined to

achieve a targeted SPMA:metal stoichiometric ratio. In all cases the polymer solution was diluted to 21 wt% P(DEGMEMA–SPMA) after addition of the metal salt solution. The viscous mixture was vortexed until the solution became homogeneous and then held under high vacuum (50-80 mTorr) for approximately two hours until a final concentration of 24.5 ± 0.3 wt% P(DEGMEMA–SPMA) was attained. Polymer solutions at different concentrations were prepared in a similar manner.



Figure S4. Vial inversion tests demonstrate transient network formation of P(DEGMEMA–SPMA) polymer solutions crosslinked with (A) $Co(NTf_2)_2$ and (B) $Cu(NTf_2)_2$. Heating on a hot plate set to 90 °C causes network formation in under an hour. Network formation also occurs when leaving vials in the dark for several days.

Rheology

Experiments were performed on a stress-controlled (single-head) rotational rheometer (Discovery Series Hybrid Rheometer (DHR), model HR-3, TA Instruments). The instrument has an oscillatory minimum torque $T_{min} = 0.5$ nN·m and inertia $I_{inst} = 21.0044 \ \mu$ N·m·s². A custom

made, glass parallel plate geometry of 25 mm diameter was used. The measured geometry inertia was $I_{geom} = 5.1747 \ \mu \text{N} \cdot \text{m} \cdot \text{s}^2$. In all oscillatory experiments the resolution was limited by inertia of the instrument and geometry.² The inertial limit may be approximated as²

$$G_{\min} > \frac{\left(I_{inst} + I_{geom}\right)F_{\tau}}{F_{\gamma}}\omega^2$$
(S1)

where G_{\min} is the minimum dynamic modulus (Pa) that can be resolved by the instrument, F_r and F_γ are the stress and strain constants of the geometry, which equal 40743.7 m⁻³ and 74.6269, respectively, and ω is the angular frequency of oscillation (rad·s⁻¹). The inertial limit is plotted as grey regions in plots in which data points approach or fall below the limit. The initial gap height at the start of each experiment was ~ 410 ± 15 μ m. Temperature was controlled using a Peltier plate bottom geometry, and three high current, white LED spotlights (Advanced Illumination SL073) were positioned ~ 6 cm from the surface of the top plate and were maintained at approximately the same distance for each experiment. According to the specifications of the manufacturer, the LED spotlight emits wavelengths between approximately 420 to 750 nm, and the irradiance at normal incidence 10 cm from the source varies from 79.6 to 93.7 W/m². Thermal expansion of the geometry was accounted for automatically by the software by performing a calibration prior to all measurements. During the "lights off" stages of experiments (e.g. during crosslinking), the LEDs were turned off and an opaque solvent trap was placed around the geometry to further reduce light exposure.

1. Modeling the linear viscoelastic responses

The linear viscoelastic responses are fit to a three-parameter model of a continuous relaxation spectrum, $H(\tau)$ (a viscosity density on relaxation time, with dimensions of Pa·s/s in SI units), derived from a log-normal distribution of relaxation times:^{3,4}

$$H(\tau) = H_{\rm p} \cdot e^{-\frac{1}{2} \left[\frac{\ln(\tau) - \ln(\tau_{\rm p})}{\sigma}\right]^2}$$
(S2)

where τ_p is the log-median relaxation timescale, H_p is the peak of the spectrum, and σ is the standard deviation of the log-normal distribution. The viscoelastic moduli are related to the spectrum through the equations⁵

$$G'(\omega) = \int_{0}^{\infty} \frac{H(\tau)}{\tau} \cdot \frac{(\omega\tau)^{2}}{1 + (\omega\tau)^{2}} d\tau$$

$$G''(\omega) = \int_{0}^{\infty} H(\tau) \cdot \frac{\omega}{1 + (\omega\tau)^{2}} d\tau$$
(S3)

The apparent plateau modulus, G_0 , is related to the spectrum as

$$G_0 = \lim_{\omega \to \infty} G'(\omega) = \int_0^\infty \frac{H(\tau)}{\tau} d\tau = H_p \sigma \sqrt{2\pi}$$
(S4)

which we use to estimate the crosslink density of the networks. The spectrum is also used to calculate the so-called "number-average" relaxation time, $5-7 \tau_n$,

$$\tau_{\rm n} = \frac{\int_{0}^{\infty} H(\tau) d\tau}{\int_{0}^{\infty} \frac{H(\tau)}{\tau} d\tau} = \tau_{\rm p} e^{\frac{1}{2}\sigma^2}$$
(S5)

and the so-called "weight-average" relaxation time,⁴⁻⁷ or longest characteristic timescale for viscoelastic liquids,⁸⁻¹¹ τ_w ,

$$\tau_{\rm w} = \frac{\int\limits_{0}^{\infty} \tau H(\tau) d\tau}{\int\limits_{0}^{\infty} H(\tau) d\tau} = \tau_{\rm p} e^{\frac{3}{2}\sigma^2}.$$
 (S6)

Considering the frequency range over which experimental data have been collected, and the decay of the relaxation spectrum (Eq. (S2)) at short time scales, the calculated τ_n and τ_w are to be interpreted as characteristic times of the terminal dispersion of the transient networks.⁸A measure of the spread of this terminal dispersion is given by the so-called polydispersity index (PDI) of relaxation times,⁶⁻⁸

$$PDI = \frac{\tau_{w}}{\tau_{n}} = e^{\sigma^{2}} .$$
 (S7)

The three-parameter model is fit numerically to the data using Eq. (S3) with a custom-written non-linear regression routine in MATLAB. The fit routine minimizes the difference between data and the model using a residual sum of squares (RSS) defined as

$$RSS = \sum_{i} \left(\log_{10} \left(\left| Y_{i}^{\text{model}} \right| \right) - \log_{10} \left(\left| Y_{i}^{\text{exp}} \right| \right) \right)^{2}.$$
(S8)

The elements of the variance-covariance matrix (in linear space), $\sigma_{x_i x_j}^2$ (where $x_i = \{\tau_p, H_p, \sigma\}$), are used to estimate the error, σ_z^2 (where $z = f(x_i)$), on the spectrum $H(\tau)$ and related quantities (G_0 , τ_n , τ_w , PDI) through the following error propagation equation¹¹

$$\sigma_z^2 = \sum_{m=1}^P \sigma_{x_m}^2 \left(\frac{\partial z}{\partial x_m}\right)^2 + 2\sum_{m=1}^P \sum_{n=m+1}^P \sigma_{x_m x_n}^2 \frac{\partial z}{\partial x_m} \frac{\partial z}{\partial x_n}$$
(S9)

where P = 3 is the number of fit parameters. The fit parameters are given in Table S1. Based on these fit parameters, the number-average relaxation time, the longest characteristic relaxation time, the polydispersity index of relaxation times, the plateau modulus, and the crosslink density are calculated, as given in Table S2.



Figure S5. Control experiment showing rheological changes of a 24.5 wt% solution of P(DEGMEMA-SPMA) in PC without any metal salt. No measurable changes in elasticity were observed as the storage modulus remains below the inertial limit. The small change in G'' after heating and cooling is primarily attributed to solvent evaporation.



Figure S6. Reversible changes in dynamic moduli of P(DEGMEMA–SPMA) with Na(NTf₂) salt. (A) Reversible changes of G'' at $\omega = 0.5 \text{ rad} \cdot \text{s}^{-1}$ upon heat treatment and subsequent exposure to visible light. The polymer solution exhibits no measurable change in elasticity, indicating that crosslinks do not form in the presence of monovalent salt. (B) Frequency sweeps showing Newtonian behavior at all observed deformation timescales both before and after activation of MC-Na. This data should be compared to the frequency sweeps of Fig. 5A in the main text. Heating at 80 °C results in a > 2-fold increase of η' . After visible light irradiation, η' decreases. The irreversible viscosity shift is attributed to solvent evaporation, and the reversible viscosity change is speculated to be attributed to changes in polymer-solvent affinity due to activation and deactivation of MC-Na complexes.



Figure S7. (A) Frequency sweeps of 3:1 SP:Co(II) comparing the dynamic moduli after the first and second crosslinking events. This data should be compared to the frequency sweeps of Fig. 5 in the main text. Grey region of plot represents the estimated inertial limit of the rheometer.



Figure S8. (A) Kinetics of light-triggered MC deactivation measured by the decay of G''. Residuals (right plot) of bi-exponential data fit show significantly reduced systematic error compared to a mono-exponential fit. (B) Kinetics of heat-triggered growth (inset), and light-triggered decay, of G'' with 1:1 SP:Co(II). Both growth and decay of G'' fit well with a bi-exponential kinetic model, as judged by the randomly distributed residuals of the data fits (right plot). The behavior of P(DEGMEMA–SPMA) with 2:1 SP:Na(I) and 1:1 SP:Co(II) are strikingly similar. Both samples exhibit a small increase in G'' and no observable change in G', and upon exposure to white light, G'' in both samples undergoes bi-exponential decay. The similarities between the two samples suggests that the reversible G'' shift is due to the same underlying chemical mechanism; namely molecular stacking of MC. Yellow shaded area indicates data acquired during visible light exposure.



Figure S9. (A) Comparison of G'' responses during crosslinking with 3:1 and 2:1 SP:Co(II). (B) Comparison of G'' responses during un-crosslinking. Residuals of bi-exponential fits (bottom plots) in (A) and (B) show systematic error, indicating that the changes in G'' due to activation and deactivation of a structured, MC-metal coordinated polymer network is governed by different kinetics than the changes in G'' due to molecular stacking of MC in the presence of metal salts (Fig. S10).



Figure S10. Relaxation spectra of reversible networks at 20 °C after the first (black), second (red), and third (blue) crosslinking sequences. Lines are numerical fits to the experimental data of Fig. 4 B–D of a log-normal distribution of relaxation times with parameters (τ_p , H_p , σ); values indicated by symbols, the horizontal bars are $\tau_p^{-1}e^{\pm\sigma}$. Shaded areas denote the error on the spectra estimated through error propagation, according to Eq. (S9).

Table S1. Values of the parameters of the relaxation spectrum obtained by numerically fitting the frequency sweep data of Fig. 4 B–D in the main text.

	$\tau_{\rm p}$ [ms]	H _p [kPa]	σ [-]
1 st time crosslinked	0.5 ± 0.2	1.5 ± 0.3	2.0 ± 0.07
2 nd time crosslinked	0.17 ± 0.03	3.8 ± 0.4	2.7 ± 0.05
3 rd time crosslinked	0.13 ± 0.06	3.5 ± 0.4	3.0 ± 0.07

Table S2. Number-average relaxation time (τ_n) , longest characteristic relaxation time (τ_w) , polydispersity index of relaxation times (PDI = τ_w/τ_n), plateau modulus (G_0), crosslink density, and estimated percentage of SP molecules in P(DEGMEMA–SPMA) that actively form an elastic polymer network after each crosslinking cycle. Values computed from nonlinear least squares fits of frequency sweep data of Fig. 4 B–D in the main text.

	τ_n [ms]	$ au_{ m w}$ [s]	PDI · 10 ⁻³ [-]	G ₀ [kPa]	$\mu \cdot 10^{-24} [\mathrm{m}^{-3}]$	Elastically active SP [%]
1 st time crosslinked	3.9 ± 0.8	0.2 ± 0.03	0.06 ± 0.02	7.8 ± 1.6	1.9 ± 0.4	4.3 ± 0.9
2 nd time crosslinked	4.4 ± 0.6	5.2 ± 0.8	1.2 ± 0.3	25.6 ± 3.5	6.3 ± 0.9	14.3 ± 2
3 rd time crosslinked	16.9 ± 2.1	169 ± 56	10 ± 4.4	26.4 ± 3.6	6.5 ± 0.9	14.8 ± 2



Figure S11. Crosslinking with $Cu(NTf_2)_2$. (A) Crosslinking of 24.5 wt% P(DEGMEMA–SPMA) solution with 3:1 SP:Cu(II). Cu(II) data (circles) overlays the data of 3:1 SP:Co(II) for comparison. (B) Phase separation (left image) prevented meaningful evaluation of the crosslinked Cu(II) solution at room temperature. However, mixing during visible light irradiation enabled re-dissolution of the polymer back into PC. Right image shows a homogeneous crosslinked Co(II) solution for comparison.



Fig. S12. Strain amplitude sweeps of 2:1 SP:Co(II) polymer solutions monitored at 20 °C (A) before crosslinking, and (B) after crosslinking (third cross-linking cycle). Crosslinked and un-crosslinked polymer solutions exhibit linear viscoelastic responses over a wide range of strain amplitudes.

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