Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A radical spin on viologen polymers: organic spin crossover materials in water

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Synthesis of Polymer:

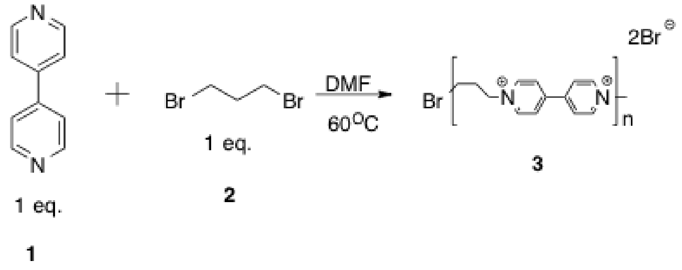

Figure S1. Synthesis of ionene polymer

Synthesis of poly(propyl viologen) (3): The synthesis was adapted from a known procedure.[1] 0.75 g of 4,4'-bipyridine was added to 20 mL of DMF in a 50 mL round bottom flask. The solution was stirred with a stir bar until the bipyridine completely dissolved. To the bipyridine solution was added 0.653 mL of 1,3-dibromopropane and the entire solution was sealed and stirred at 60°C for 5 days. After 5 days, an additional 0.2514 g of bipyridine was dissolved in 10 mL of DMF and added to the solution. This reaction was allowed to continue for one additional day. The solution was then allowed to cool to room temperature. The precipitated solid was filtered and washed with ethyl acetate. After washing, the solid was dissolved in minimal amounts of methanol and poured into a beaker filled with ethyl acetate to precipitate it. This precipitated solid was removed via filtration, washed with ethyl acetate, and allowed to dry under vacuum. ^{1}H-NMR and ^{13}C-NMR were consistent with previously-reported polymers.[1]

Determination of molecular weight: Average molecular weight of the polymer was determined by end group integration in the ^{1}H-NMR. The synthesis of (**3**) resulted in polymers that were terminated by bipyridines, as evidenced by the relatively small peaks related to the CH_2Br hydrogens. Degree of polymerization (X_n) could therefore be determined by the ratio of the peaks attributed to the H in the chain viologen (the aromatic doublets, for a relative integration value of 4 hydrogens per unit each) over twice the doublet at 7.96, assigned to the end bipyridine, with a relative integration value of 4 when accounting for both ends. Polymers synthesized using the above procedure have X_n between 9-20, with the polymers used for all the experiments tested falling around X_n= 15. Multiplying this number by the monomer molecular weight (358.08) gives an average molecular weight between (M_n)=3,200 and 7,100 which was near the range previously reported for this polymer.

UV-Vis studies: The UV-Vis spectrum were collected with the Agilent 8453 UV-Vis spectrometer and Agilent chemstation software. A constant temperature bath equipped with a water pump was used for temperature control.

Temperature switching: A 100 μM solution of the propyl-linked polymer (**3**) dissolved in pH = 9.6 sodium hydroxide/sodium bicarbonate buffer was degassed using argon sparging. Meanwhile, the sodium dithionite was retrieved from a glove box and sealed in a round-bottomed flask to maintain an inert atmosphere. Once sparging was done, the analyte solution was cannulated into the rbf containing the sodium dithionite. Finally, the reduced analyte solution was cannulated into a 1 cm pathlength quartz cuvette fitted with a septum. The cuvette was kept under an argon atmosphere for the duration of the experiments. Spectra were taken every 5°C, allowing 15 minutes for temperature to equilibrate. Decay of signal was monitored at 499nm (figure S4). The new peak growth at 960 required a correction to accommodate the overlapping decay of a broader peak. The correction was made by drawing a straight line from the absorbance at 900nm to the absorbance at 1000 nm and taking the difference in absorbance between the absorbance at 960nm to this new baseline (figure S6).

Jobs Plot Experiment: The Job plot was carried out by titration of 2.5 mL of degassed 100 µM solution of the propyl-linked polymer (**3**) reduced by sodium dithionite in pH = 9.6 sodium hydroxide/sodium bicarbonate buffer using 0.01 M CB[7] solution degassed in the same buffer in a 1 cm path length quartz cuvette. The CB[7] was added to form molar ratios (chi) 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 0.99 through subsequent additions of CB[7] to the same cuvette. This was completed by first scanning **3** then 2.8 µL of the CB[7] solution was added and scanned again. Another 3.5 µL of CB[7] was added for a total volume of 6.3 µL and scanned again. This process was continued with total CB[7] volumes of 10.8, 16.8, 25.1, 37.6, 58.6, 100.6, 220.6, and 660.6 µL for molar ratios 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 0.99, respectively.

EPR Experiments

CB[7] Switching: 3 mL of 10 mM solution of the propyl-linked polymer (**3**) dissolved in pH = 9.6 sodium hydroxide/sodium bicarbonate buffer was degassed using sparging. Meanwhile, the sodium dithionite was retrieved from a glove box and sealed in a round-bottomed flask to maintain an inert atmosphere. 0.034 g of CB[7] was also weighed into a third rbf, sealed with a septum, and degassed. The analyte solution was cannulated into the rbf containing the sodium dithionite and swirled to stir. The reduced solution was cannulated into the CB[7] and swirled to allow for binding. Finally, the reduced analyte solution was cannulated into a custom made EPR tube, 3 mm ID/4 mm OD top and ~30 mm of 1 mm ID/2mm OD bottom, capped by a septum. The solution was then cycled in the EPR using a nitrogen blowoff to maintain the temperature. The spin concentration was calculated via double integration of the signal.

Temperature Switching: A 10 mM solution of the propyl-linked polymer (**3**) dissolved in pH = 9.6 sodium hydroxide/sodium bicarbonate buffer was degassed using sparging. Meanwhile, the sodium dithionite was retrieved from a glove box and sealed in a round-bottomed flask to maintain an inert atmosphere. After sparging, the analyte solution was cannulated into the rbf containing the sodium dithionite. Finally the reduced analyte solution was cannulated into a custom made EPR tube, 3mm ID/4mm OD top and ~30 mm of 1 mm ID/2 mm OD bottom, capped by a septum. The solution was then cycled in the EPR using a nitrogen flow to maintain the heat. The spin concentration was calculated via double integration.

The EPR parameters for all experiments are as follows: Modulation Frequency = 100 kHz, Modulation Amplitude = 1.0 G, Receiver Gain = 50 dB, time constant = .08 ms, conversion time = 20.48 ms, sweep time = 83.89 s, center field = 3335 G, sweep width = 70.0 G, microwave attenuation = 20 dB, microwave power = 1.984 mW, number of points = 4096, and number of averaged scans = 8.

Experiment	Spin Conc. (M)	Percent Radical
25 C with CB[7]	0.002779	27.79
25 C Cycle 1	0.0009395	9.395
90 C Cycle 1	0.001115	11.15
25 C Cycle 2	0.0009394	9.394
90 C Cycle 2	0.001089	10.89
25 C Cycle 3	0.0009317	9.317
90 C Cycle 3	0.00116	11.6
25 C Cycle 4	0.0009263	9.263
90 C Cycle 4	0.00106	10.6

Figure S2. EPR experimental results of the temperature and CB[7] switching. Spin concentration calculated from double integration.

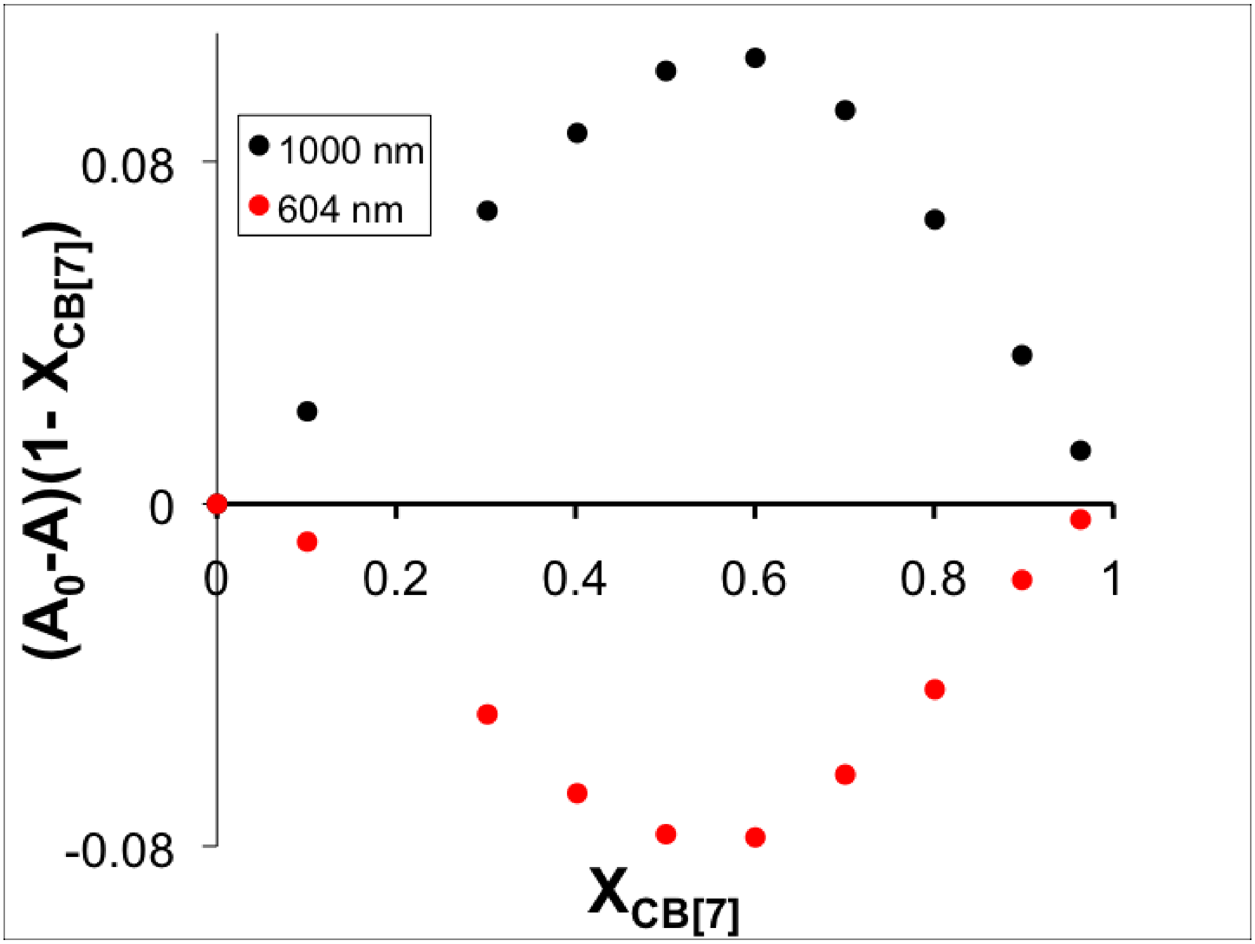

Figure S3. Graphical results of the Job Plot with increasing mole fraction of CB[7] monitored at 604 nm (red) and 100 nm (black).

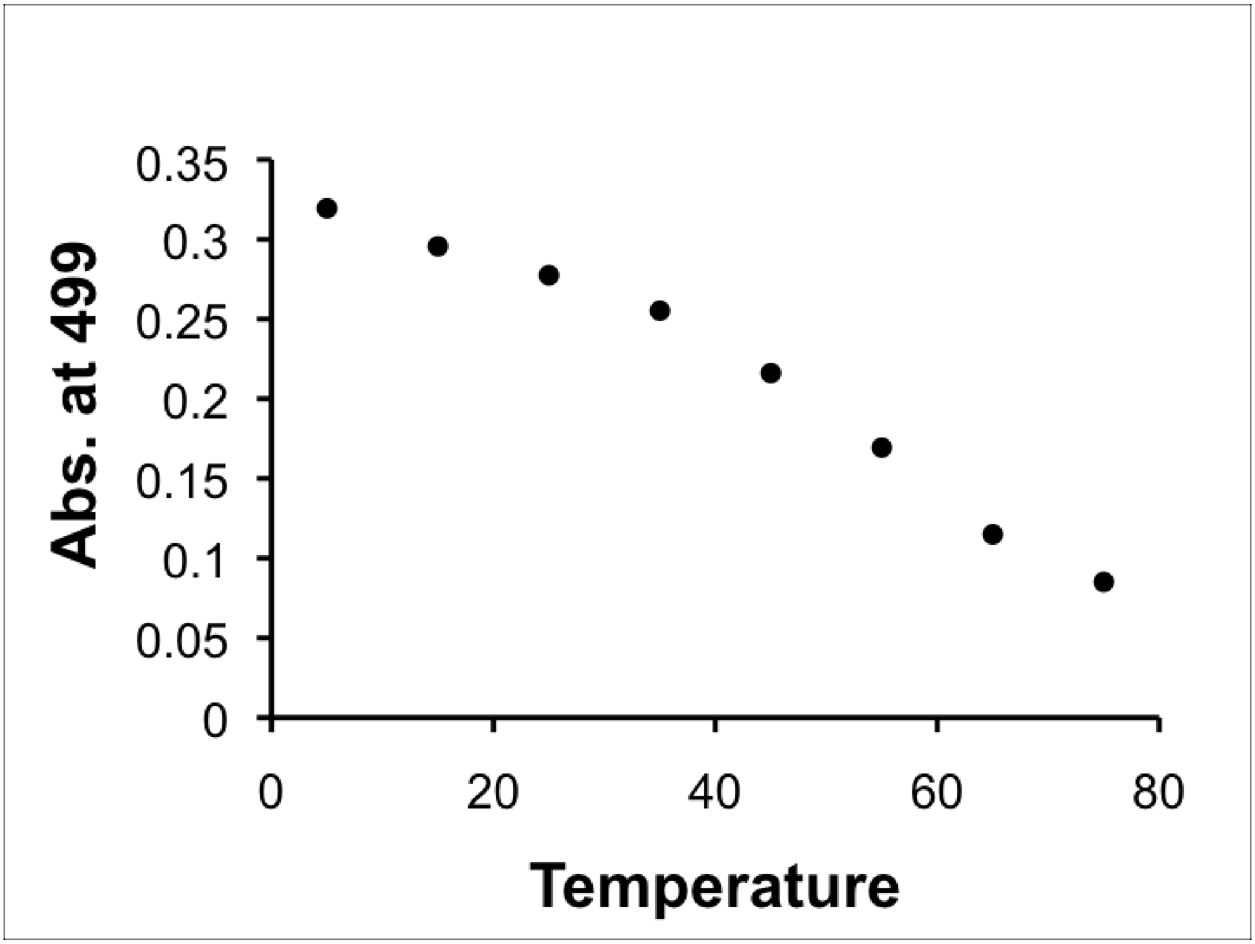

Figure S4. Plot of UV-Vis absorbance of the reduced version of **3** at 499 nm with increasing temperature from 5°C-65°C

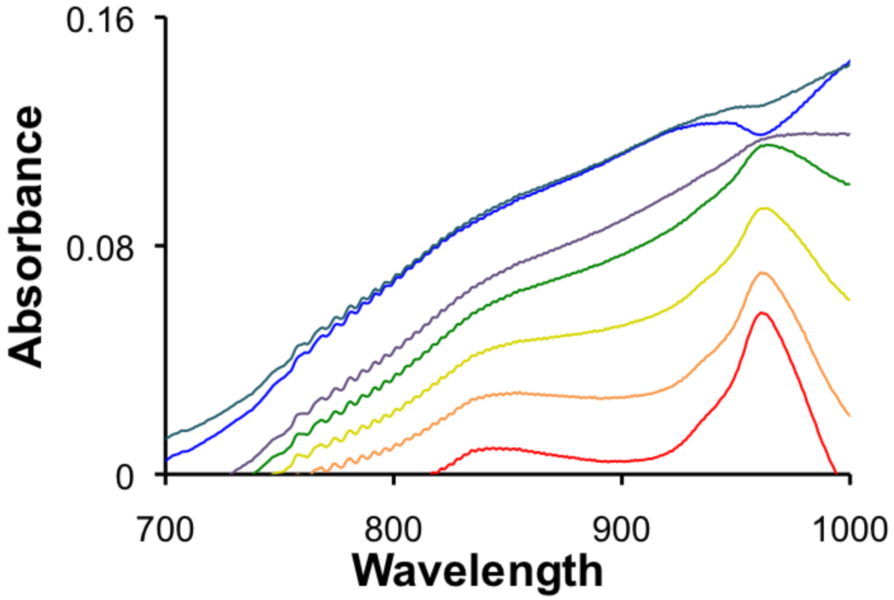

Figure S5. UV-vis of the reduced form of **3** in buffered aqueous solution at 100 μM, highlighting the growth of the 960 nm peak (figure 4b).

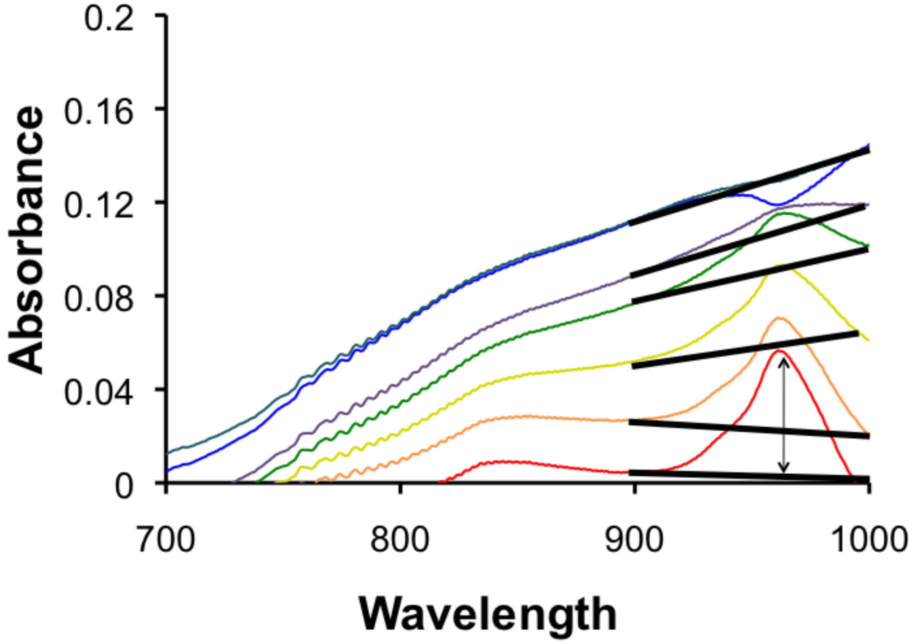

Figure S6. UV-vis of figure S5 showing the straight-line correction for the growth of the peak at 960nm.

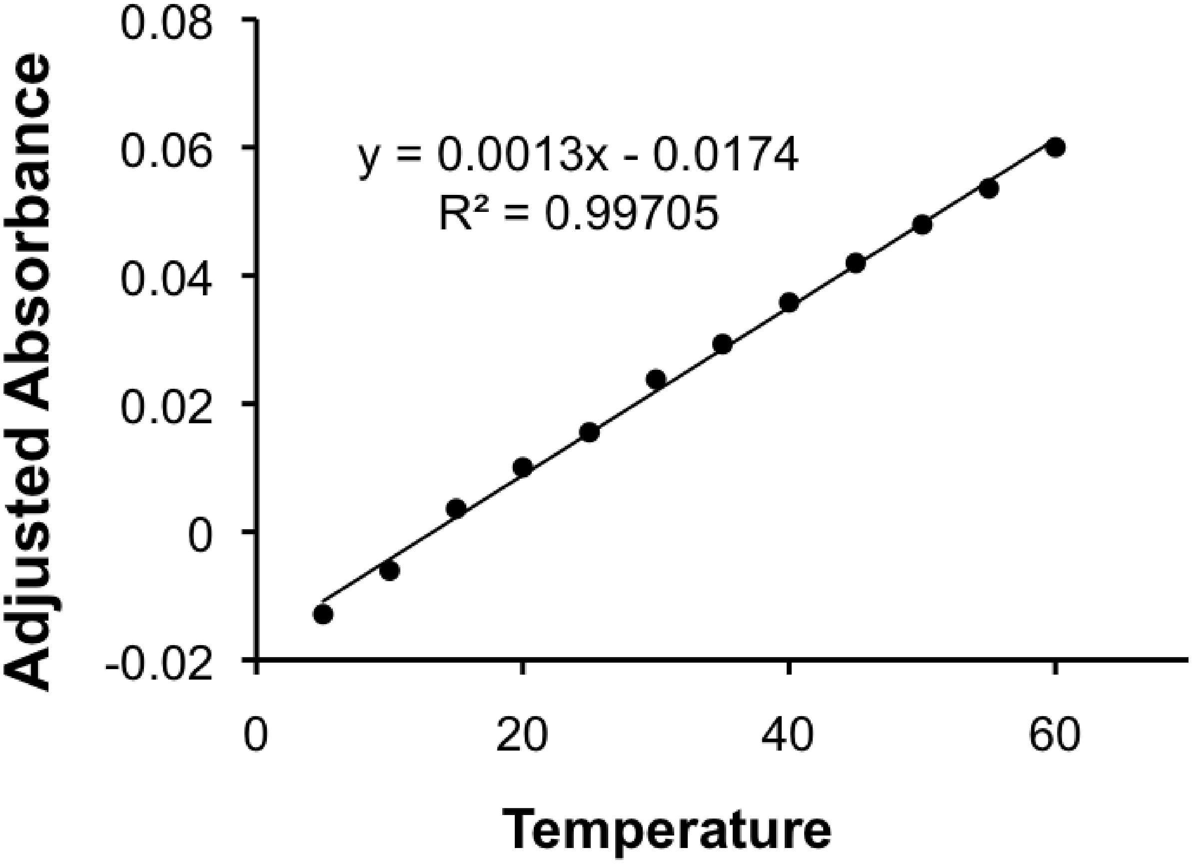

Figure S7. Plot of the absorbance (from the baseline linear correction of figure S6 of the reduced form of **3** at increasing temperatures.

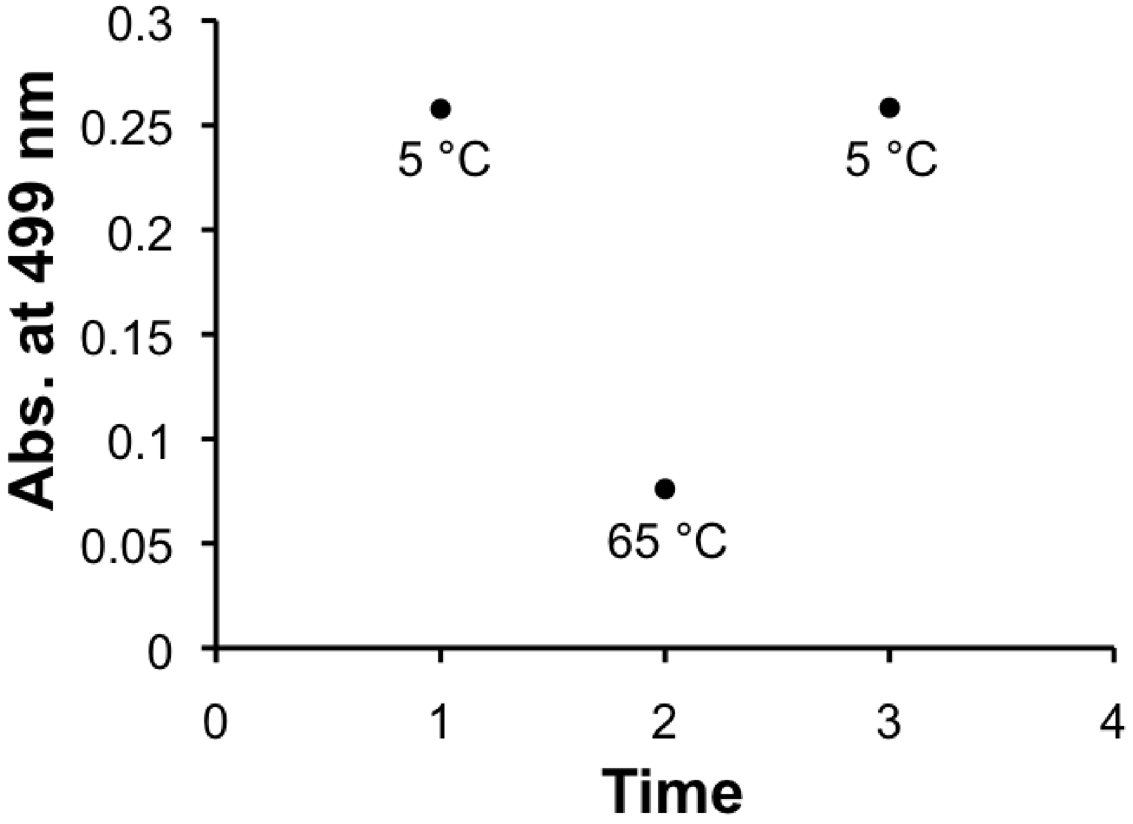

Figure S8. Absorbance of the reduced form of **3** at 5 °C to 65 °C back to 5 °C. Temperatures were maintained until the absorbance stopped changing (~30 minutes for heating, ~3 hours for cooling).

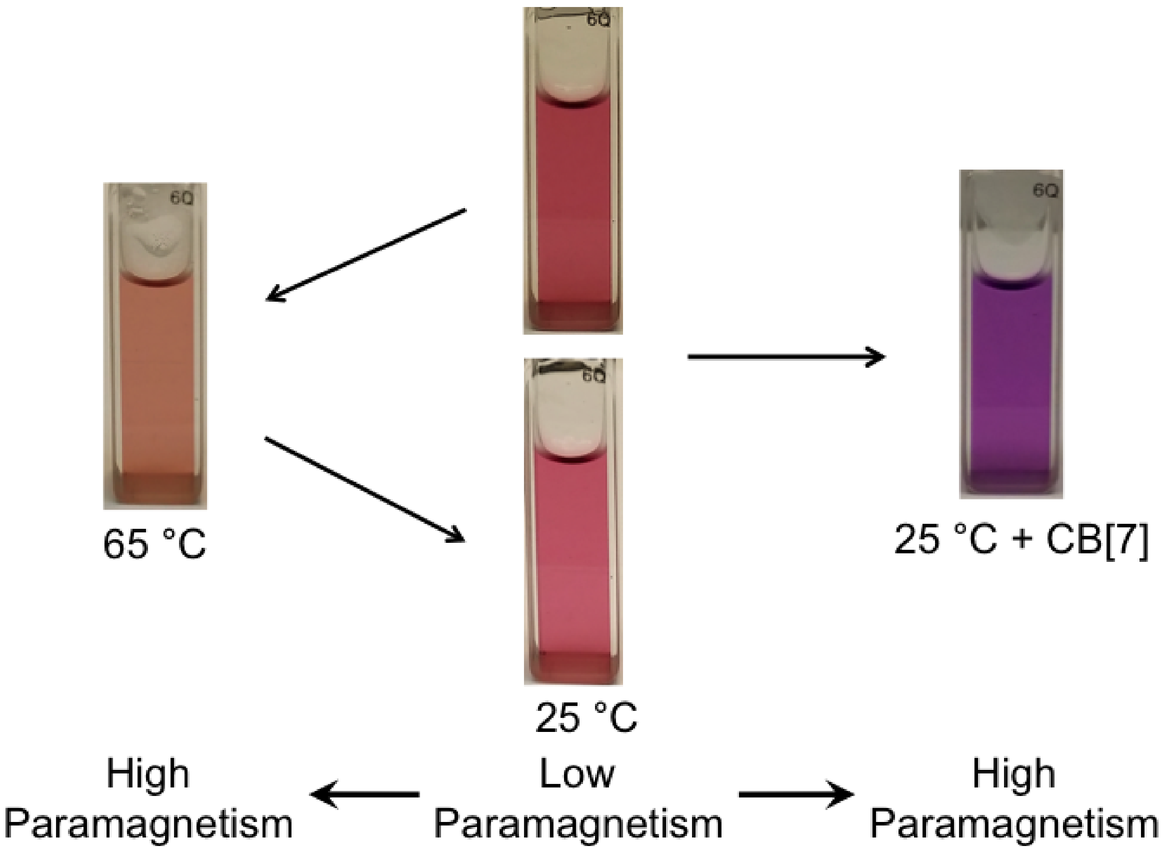

Figure S9. Aqueous buffer solution of the reduced **3** at 25°C (top middle) with color change to dark purple by addition of CB[7] (right) or to peach with heating (left). Color returned to the original fushia upon cooling to room temperature (bottom middle). The middle two and the figure on the right are all from the same experiment. The cuvette on the right is a representative color change from a different experiment.

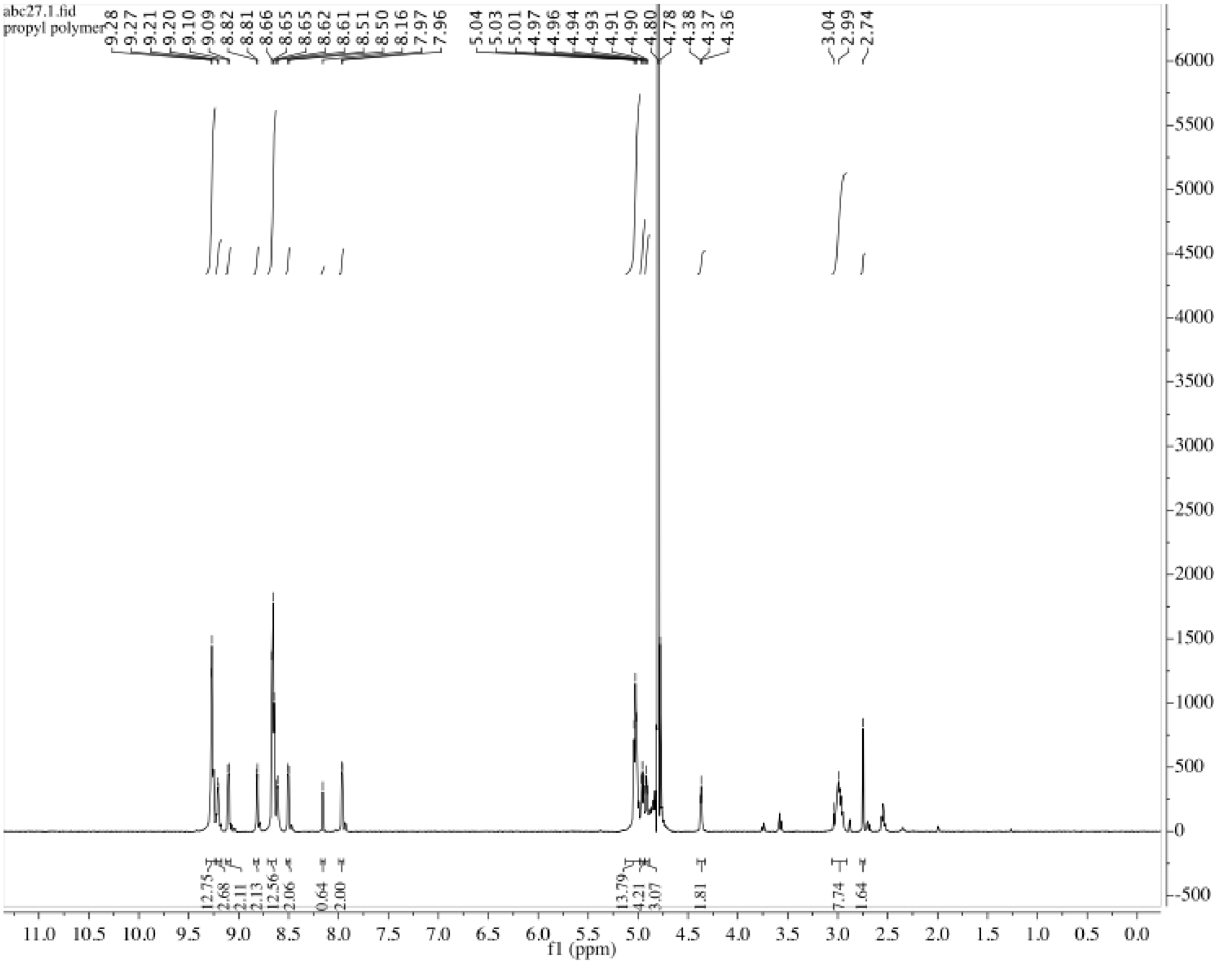

Figure S10. ^{1}H-NMR of **3** in D_2O

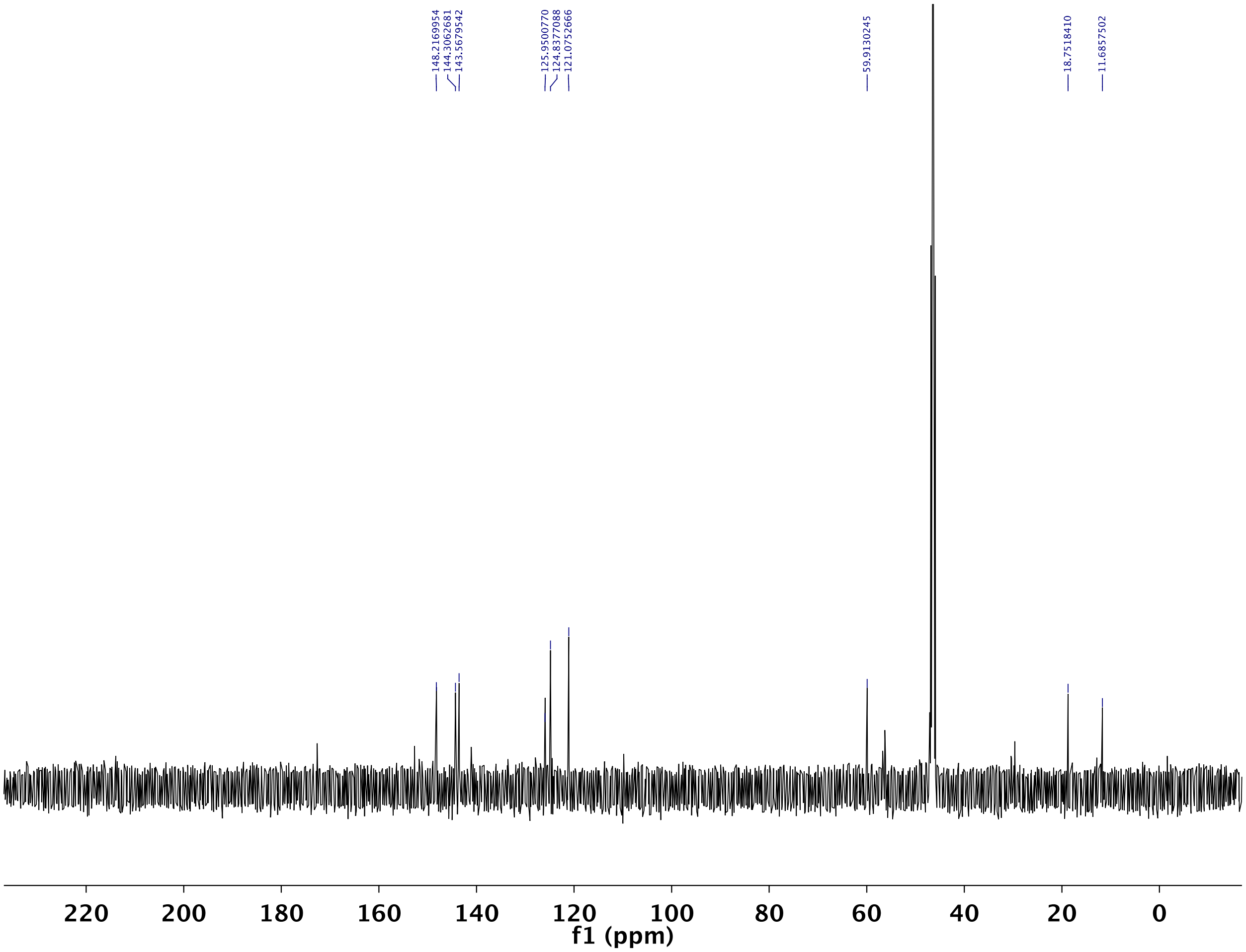

Figure S11. ^{13}C-NMR of **3** in 95% Deuterated methanol 5% water

(1) Shimomura, M.; Utsugi, K.; Horikoshi, J.; Okuyama, K.; Hatozaki, O.; Oyama, N. *Langmuir* **1991**, *7*, 760.