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

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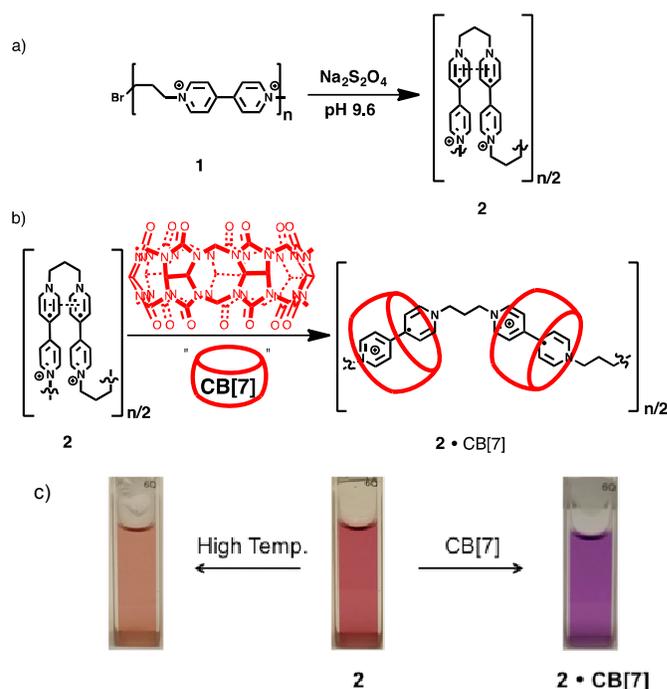
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**A polymer containing viologen radical cation monomer units is shown to reversibly switch between paramagnetic and diamagnetic states via non-covalent host-guest interactions or temperature control in water. Cycling between diamagnetic and paramagnetic forms is accompanied by changes in optical and magnetic properties.**

Organic materials are prized for their broad range of properties and cheap manufacturing protocols on large scales. Yet while organic polymers have a wealth of physical properties available to them, these material properties typically arise from a static structure. Consequently, there has been long-standing interest in developing new organic materials that adapt their properties in response to environmental cues or other external stimuli.<sup>1</sup>

One way of achieving stimuli-responsive properties in organometallic complexes<sup>2-5</sup> is by invoking a change in the spin state of the metal upon a stimulus. Changes in spin states are often accompanied by large changes in materials properties, including changes in color,<sup>6-8</sup> infrared absorption and emission, luminescence,<sup>9-15</sup> crystallinity,<sup>16,17</sup> conductivity, and magnetism.<sup>18-22</sup> As a result of such property changes, spin crossover inorganics that change from low-spin configurations to high-spin configurations upon stimuli such as heating, find use in thermochromic paints<sup>23, 24</sup> and mechanical actuators,<sup>25, 26</sup> and hold promise for use in sensors, displays, and molecular-scale memory storage devices. While such spin-switchable inorganic materials are not uncommon, organic spin-crossover materials are primarily limited to non-polymeric materials,<sup>27-31</sup> Polymers containing paramagnetic building blocks have become increasingly sought after for applications such as molecular electronics, spintronics,<sup>32, 33</sup> bulk ferromagnetic polymers,<sup>34,35</sup> and biological probes for magnetic resonance experiments (e.g. MRI contrast agents<sup>35-37</sup>). We considered the possibility that organic polymers incorporating spin-switchable building blocks could lead to soft materials with similar changes in properties in response to environmental cues that modulate the molecular spin state of the building blocks.

Prior investigations in our lab have demonstrated that a covalently-linked diradical dyad derived from viologen cation radicals could be reversibly switched between a diamagnetic form and a paramagnetic form via non-covalent stimuli or



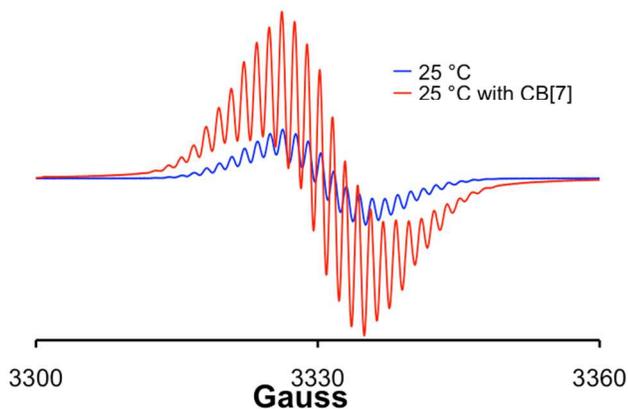
**Fig 1.** (a) Reduction of **1** to the radical dication **2**. (b) Switching between diamagnetic and paramagnetic forms of **2** via binding to a CB[7] host molecule (c) colour changes of **2** in buffered water solution corresponding to a change in temperature or a non-covalent binding event to CB[7].

heating.<sup>38-44</sup> The strategy involved synthesizing two viologen cation radicals tethered with a three carbon linker. This diradical dyad forms a weak pi bond between the two radicals (pimerization), leading to a diamagnetic configuration. Disruption of this weak bond via non-covalent chemistry or heating led to population of a paramagnetic form via disruption of this pi bond. Here, we report that a polymeric material based on this viologen dication diradical building block can be switched between diamagnetic and paramagnetic forms using

non-covalent binding chemistry or by changes in temperature, leading to a bulk organic spin crossover material with stimulus-responsive changes in optical and magnetic properties.

Polymers were prepared via a modified procedure based on a previously reported method.<sup>45</sup> Average molecular weights ( $M_n$ ) were determined by <sup>1</sup>H-NMR endgroup analysis (see Supporting Information) to be around 7,000 daltons, consistent with the previously reported ionene complexes. The diamagnetic diradical dimer analogue of the polymer was synthesized by reduction of **1** into **2** using sodium dithionite in buffered water.

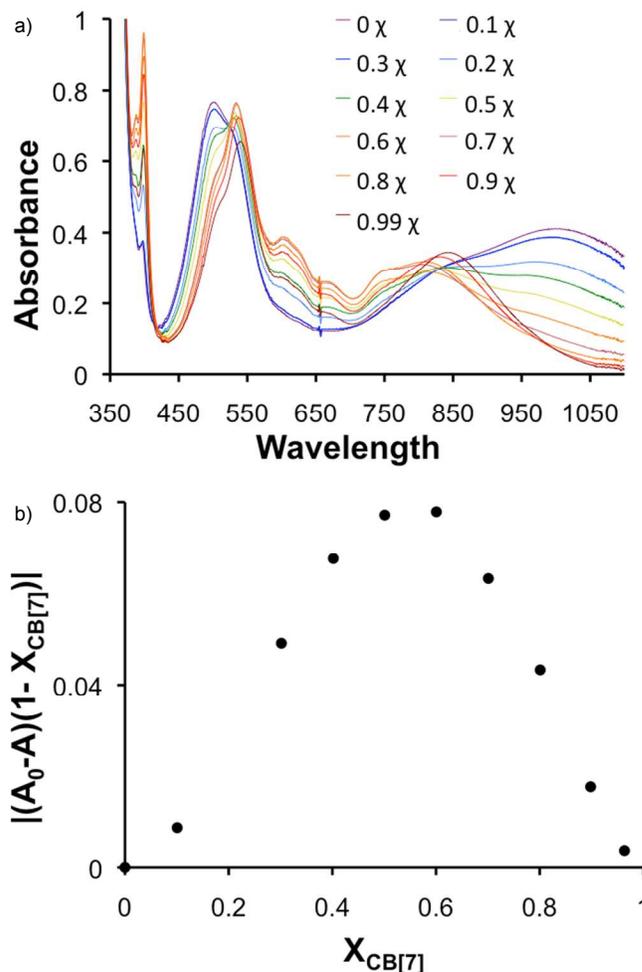
The results of the EPR titration studies and UV-Vis switching studies indicate that the poly(propyl viologen cation radical) is a diamagnetic species (with a small thermal population of a paramagnetic form) that can be switched to a paramagnetic form by formation of a complex with CB[7]. Additionally, an increase in temperature from room temperature correlates with an increase in paramagnetism as seen by EPR measurements. The increase in paramagnetism is fully reversible by decreasing the temperature back to room temperature. Temperature changes can be cycled multiple times with high radical fidelity.



**Fig. 2.** EPR spectrum of **2** (50 mM with respect to the repeat unit) in aqueous buffer solution before binding (blue) and after addition in excess of one equivalent of CB[7] (red).

After reduction of **1** to make **2**, a weak signal in the EPR spectrum, attributable to the viologen radical cation, is detectable (Fig. 2). We attribute this signal to a thermal population of the dissociated paramagnetic diradical at room temperature and/or spin defects in the material (e.g. monomers radical cations lacking a partner). In order to test whether the paramagnetism could be switched on via non-covalent binding chemistry, in excess of 1 equivalent of CB[7] was added to a 1 mM (by repeat unit concentration) solution of the polymer **2** in buffer solution and the change was monitored by EPR (see Fig. 2). We anticipated that CB[7] would thread onto the polymer and bind the cation radical units, leading to a switch-on of EPR signal as the intramolecular dimerization is disrupted (see Fig. 1b for a schematic). Indeed, a 3-fold increase of signal (by integration) was observed after addition of CB[7] (9% spin concentration to 28%), although the lack of complete formation of radical signal by excess CB[7] suggests a low association constant and/or the presence of spin defects. The addition of more CB[7] was hindered by the limits of its solubility in water.

To determine the binding ratio of CB[7] to the viologens, a Job Plot was performed (Fig. 3). Since binding to the CB[7] corresponded to a darkening of colour, from fuchsia to dark purple (see Fig. 1), UV-Vis was used. A new peak, corresponding to the complex at 604 nm, was monitored as a function of mole fraction of CB[7]. The Job Plot had a maximum at a mole fraction of ~0.5, consistent with a 1:1 CB[7]:viologen repeat unit stoichiometry (see Fig. 3). The binding pocket of CB[7] has been shown to accommodate one viologen unit, and this result was consistent with a single CB[7] binding to each viologen cation radical unit.<sup>38</sup>

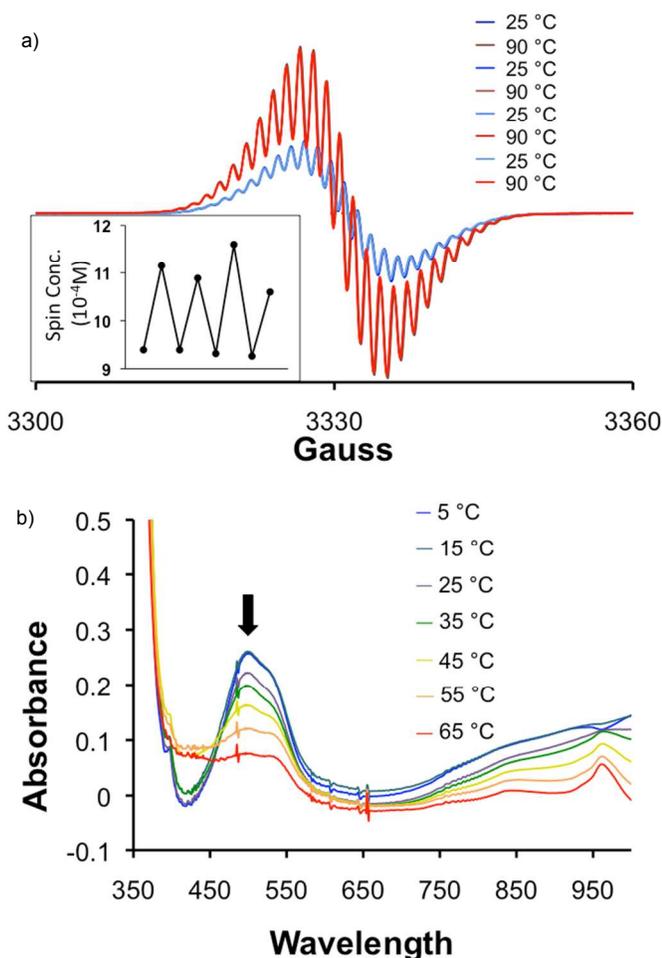


**Fig. 3.** (a) UV-plot of **2** starting at concentration of 100  $\mu$ M with respect to the repeat unit and adding CB[7] to change molar ratio from 0%-99% viologen:CB[7] (b) UV-Vis Job Plot titration of **2** from the data in (a) monitored at 604 nm.

While the diamagnetic dimer is favoured at room temperature, we anticipated that the diradical form could be favoured also by increasing the temperature to demonstrate temperature-dependent spin crossover. To test this idea, variable temperature EPR studies were performed. Accordingly, elevating the temperature from 25°C to 90°C in a buffered water solution leads to a small increase in EPR signal, and this change is highly reversible (Fig. 4). Cycling between high and low temperature reproduced the original spectra with no signs of radical degradation through four iterations. Because no deterioration of signal was detected, these results suggest that **2** is robust to temperature changes, with no apparent radical

degradation. This cycling could also be followed by UV-Vis spectroscopy (see Supporting Information).

The changes in temperature and spin concentration also corresponded to a change in colour that could be monitored by UV-Vis spectroscopy between 5°C and 65°C. Temperature was not increased beyond 65°C to avoid the formation of bubbles in the cuvette, which results in scattering artifacts. Upon heating, we observed a decrease in the absorption band at ~500 nm as well as the broad band between 800-1000 nm. A new band grows in at 958 nm, which we attribute to the paramagnetic diradical. Because of the broad band simultaneously decreasing with the increase of the sharper 958 nm band, a simple straight-line correction was used to monitor the growth of the 958 nm band (see Supporting Information). The result of the decrease in the visible bands (and a growth of a new band in the near-IR) can be visualized as a change in colour from fuchsia to a lighter pink upon heating (see Fig.1).



**Fig. 4.** (a) EPR spectra of 1 mM (by viologen repeat units) of **2** in buffer at 25 and 90°C. Inset: four subsequent cycles at 25°C and 90°C are shown (b) UV-Vis plot of **2** at 100  $\mu$ M with respect to the repeat unit with temperature increasing from 5 to 65°C

## Conclusions

EPR experiments reveal that the diamagnetic form of a reduced poly(propyl viologen) can be reversibly switched between a

diamagnetic form and a paramagnetic form by non-covalent binding or by heating, leading to changes in optical and magnetic properties. Such spin-crossover organic materials may find use in stimuli-responsive bulk materials, where the change in properties of the material arises from a change in the spin configuration of the building blocks.

## Notes and references

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<sup>†</sup> Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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