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An Organic Spin Crossover Material in Water from a Covalently Linked Radical Dyad

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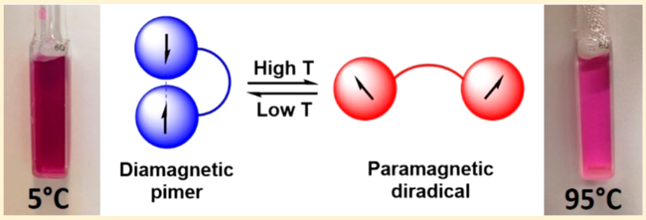
S *Supporting Information*

ABSTRACT: A covalently linked viologen radical cation dyad acts as a reversible thermomagnetic switch in water. Cycling between diamagnetic and paramagnetic forms by heating and cooling is accompanied by changes in optical and magnetic properties with high radical fidelity. Thermomagnetic switches in water may eventually find use as novel biological thermometers and in temperature-responsive organic materials where the changes in properties originate from a change in electronic spin configuration rather than a change in structure.



Changes in molecular spin states of a compound are often associated with large changes in chemical properties,[1−3] including changes in color,[4−6] infrared absorption and emission,[7,8] luminescence,[9−13] crystallinity,[14,15] and magnetism.[16−20] While spin control is a property normally associated with transition metals and organometallic complexes (e.g., "spin-crossover" materials),[21] it is not typically considered for stable organic structures. Some isolated attempts have been made to control spin in organic small molecules,[22−26] including organic spin switching in the solid-state,[27−29] supramolecular organic radical complexes with switchable properties,[30−35] and photochromic organic materials make use of transient spin switching using light as a stimulus.[36−39] Further, [*n.n*]-quinquethiophenophanes and α,ω-bis(quinquethienyl)alkanes have also been studied as π-dimer models.[40,41] More relevant to this study, some intriguing recent reports have also shown that vinyl-linked tritylthiafullvene radicals can form intermolecular dimers[42] that can switch spin with temperature changes in organic solution[43] or via reversible encapsulation in the cavity of a macrocyclic host to stabilize π-dimer form,[44] but a more general strategy for designing organic molecules with stimuli-switchable spin states would be desirable, particularly if this switching is achievable in water to allow for biological applications.

Such spin-switchable organic molecules have a number of possible intriguing applications.[1,45−49] Given the changes in properties that are known to accompany switching of electronic spin states in transition metals and metallic complexes,[50] it is an exciting possibility to consider that soft organic materials incorporating spin-switchable building blocks[51,52] could find use as responsive polymers with large changes in physical properties in response to environmental cues that modulate the molecular spin state of the building blocks. From a biological applications perspective, spin-switchable organic structures could lead to useful switch-on magnetic resonance probes. For such biological applications, it is also necessary for these spin-switchable systems to be compatible with water and be concentration independent. For example, viologen radical cations are known to be in equilibrium with their dimer forms in water.[53]

A recent study from our laboratory[54] demonstrated that a linked viologen dication diradical could be switched reversibly between diamagnetic (spin paired) and paramagnetic (spin unpaired) forms in solution at room temperature via cycling with externally added noncovalent chemical stimuli, providing proof of concept for this idea. The advantage of a covalently linked diradical dyad system is that the extent of intramolecular dimerization is independent of substrate concentration and can exist even in dilute media. In contrast, weak intermolecular dimers dissociate upon dilution. The covalently linked radical cation dyad **2a** forms an intramolecular π-stacked dimer ("pimer") that leads to pairing of the two radical spins. In this study, we demonstrate that the equilibrium between diamagnetic dimer and paramagnetic diradical form of this intramolecularly dimerized diradical **2** can be switched as a function of temperature in water, providing a thermomagnetic switch with changes in magnetic and optical properties.

Propyl-tethered bis(viologen) dication diradical species **2a** was generated in situ by two-electron reduction of the bis(viologen) tetracation **1** in aqueous solution using sodium dithionite as a reducing agent (Figure 1b).[55] While the diamagnetic dimer is favored at room temperature (with a small thermal population of paramagnetic form) we wanted to test whether we could manipulate the equilibrium toward the paramagnetic form by increasing the temperature.

To test whether we could push the equilibrium toward the paramagnetic form by increasing the temperature, variable-temperature EPR studies were performed. At low temperatures, a small EPR signal is observed from the diamagnetic dimer **2a** from a small thermal population of the paramagnetic form, **2b**.

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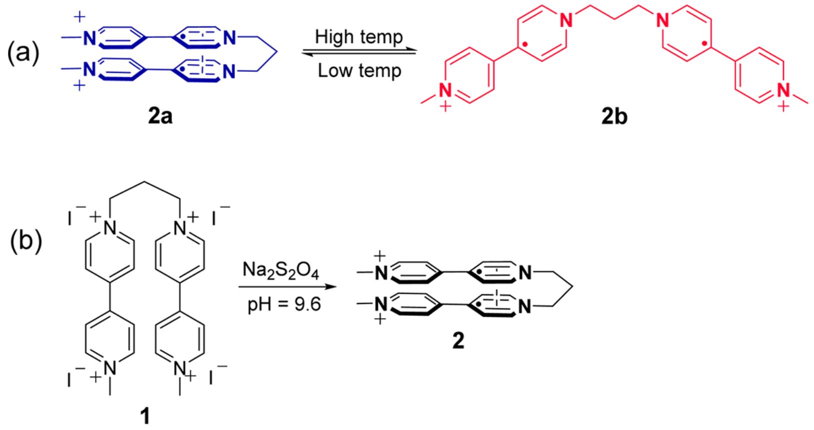

Figure 1. (a) Schematic demonstrating reversible thermomagnetic switching from diamagnetic diradical dication pimer **2a** to paramagnetic diradical dication **2b** in water. (b) Reduction of propyl-linked bis(viologen) tetracation **1** to diradical dication **2a** using sodium dithionite.

Elevating the temperature from 5 to 25 °C leads to an increase in the EPR signal, and a further increase is seen upon elevating the temperature to 90 °C (see Figure 2).

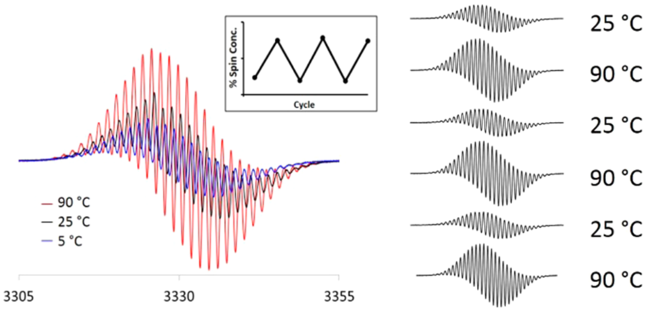

Figure 2. EPR spectra of 2 mM aqueous solution of **2a** in buffer at 5, 25, and 90 °C. Inset: three subsequent cycles at 25 and 90 °C are shown.

We attribute this increase in EPR signal intensity to an increasing population of the paramagnetic form **2b**. Furthermore, EPR studies for multiple subsequent temperature cycles show that this thermomagnetic switching is reversible. Alternating between high and low temperatures leads to increases in the spin concentration and return to the initial spin concentration, respectively. See the inset in Figure 2. Remarkably, we did not observe any major deterioration of the EPR signal upon temperature cycling, suggesting that the diradical **2** is fairly robust to temperature changes (Figure 2).

Variable-temperature EPR studies were also performed in DMSO as a supplementary data set for wider range of temperatures (up to 130 °C, Figure 3). Above 130 °C, we observe loss of EPR signal as a likely result of radical decomposition. The studies demonstrate that the established trend continues over 100 °C (limit for water solution temperature range) with a near-linear increase in the spin concentration over this temperature range.

We also monitored the changes in the optical properties of **2a** upon temperature cycling. UV–vis spectra of the aqueous solution of **2a** were taken in the 5–95 °C range (Figure 4). Upon heating **2** from 5 to 90 °C we observe a decrease in the absorption intensities for the bands at 535 and 837 nm. A new band grows in at 958 nm, attributed to the paramagnetic diradical form. This band at 958 nm was partially overlapped with a shoulder of the more intense absorption at 837 nm.

Like with the EPR studies described above, cycling between **2a** and **2b** can be followed by UV–vis spectroscopy (Figure 4, inset). A sample of **2a** was heated and cooled sequentially within a cuvette between 5 and 65 °C. The band at 837 nm was associated with diamagnetic pimer and the band at 958 nm indicates the presence of paramagnetic diradical. These bands exhibit reversible behavior and are opposite to each other in the

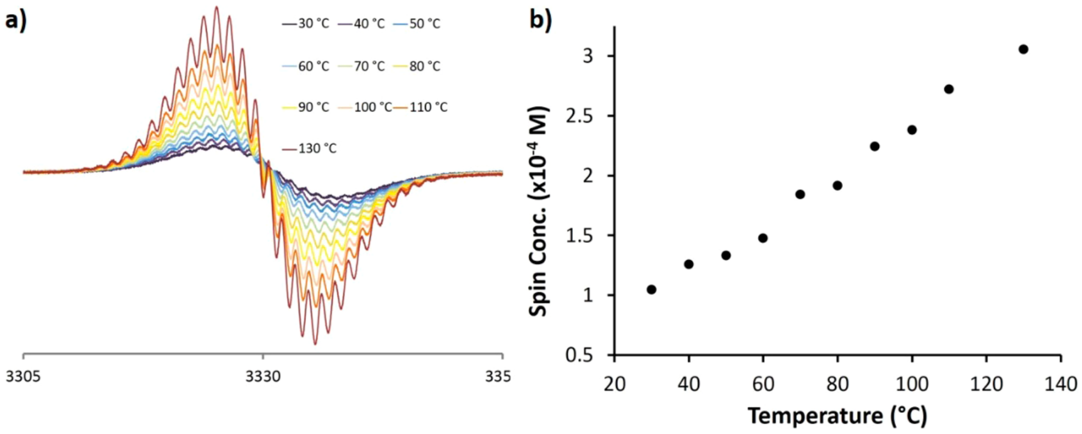

Figure 3. (a) EPR spectra of 1 mM DMSO solution of **2a** at 30–130 °C temperature range. (b) Spin concentration of 1 mM DMSO solution of **2a** in the 30–130 °C temperature range.

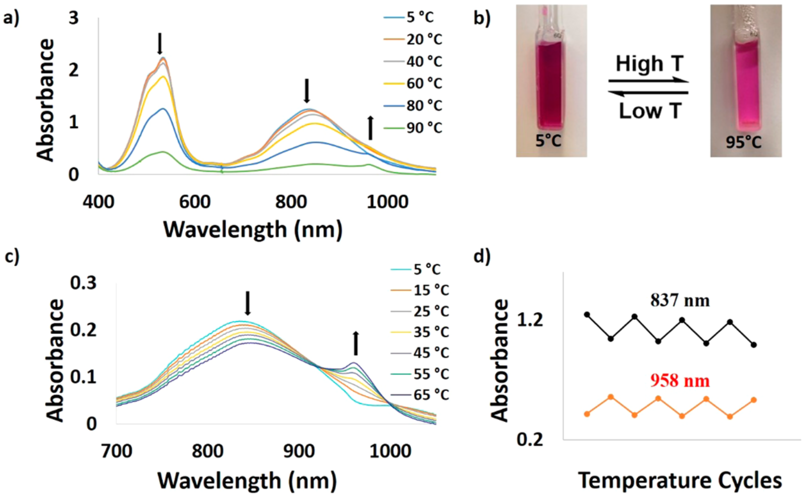

Figure 4. (a) UV−vis spectra of 100 μM aqueous solution of **2a** in buffer at 5, 20, 40, 60, 80, and 90 °C. (b) Color changes of the solution at 5 °C (dark fuchsia) and 90 °C (pink). (c) UV−vis spectra of 20 μM aqueous solution of **2a** in buffer at 5, 15, 25, 35, 45, 55, and 65 °C. (d) Reversibility studies of 100 μM solution of **2a** in buffer. Four sequential heating and cooling cycles for one sample are shown: 837 nm (black line) and 958 nm (red line).

direction of the absorbance change upon temperature cycling. Because the optical changes upon increasing the population of the diradical form involves loss of the visible bands and growth of a new band at 958 nm (outside of the visible wavelengths), the color change of the solution is mostly observed as a lightening from a dark fuchsia to pink upon heating (Figure 4, inset).

A practical difficulty should be noted: At elevated temperatures (>70 °C), it is difficult to avoid formation of bubbles in the cuvette. An isosbestic point is clearly seen between the dimer absorption band at 837 nm and the diradical absorption at 958 nm when the temperature is raised in small increments up to 65 °C (see Figure 4c), indicating a clean dimer to diradical transition, but this isosbestic point is obscured in Figure 4a when we raise the temperature up to 90 °C due to bubble-induced light scattering at the higher temperatures. Therefore, additional experiments have been done under similar conditions in DMSO (Supporting Information, Figure S4) where isosbestic points can be clearly seen at elevated temperatures.

In conclusion, both UV−vis and EPR experiments indicate that the diamagnetic pimer/paramagnetic diradical equilibrium can be manipulated reversibly in aqueous solution by changing the temperature, leading to changes in magnetic and optical properties of an organic species **2**. Stimuli-responsive polymers may permit synthetic materials that change their properties in response to temperature changes. The possibility of achieving the responsive changes in physical properties by changes in the quantum mechanical property of the electron spin of a material is an intriguing one. Additionally, spin-switchable organic species may find use as switch-on magnetic resonance biological probes. We look forward to exploring these possibilities in future work.

■ EXPERIMENTAL SECTION

Preparation of 1,1″-(Propane-1,3-diyl)bis(([4,4′-bipyridin]-1-ium)) Iodide and 1′,1‴-(Propane-1,3-diyl)bis(1-methyl-[4,4′-bipyridine]-1,1′-dium) Iodide (1). 1,1″-(Propane-1,3-diyl)bis(([4,4′-bipyridin]-1-ium)) iodide and 1′,1‴-(propane-1,3-diyl)bis(1-methyl-[4,4′-bipyridine]-1,1′-dium) iodide (**1**)were synthesized from a modification of a known method[56] that we previously reported.[54]

UV−vis Thermomagnetic Cycling Experiments. *Preparation of Propyl-Linked Bis(viologen) Dication Diradical **2a**.* A modified chemical reduction of Komers was used to prepare dication diradical **2a**.[57] Propyl-linked bis(viologen) tetracation **1** (0.9 mg) was dissolved in 10 mL of pH 9.6 water (0.045 M $NaHCO_3$/0.009 M NaOH buffer) giving a 100 μM solution. This solution was purged with argon gas in a round-bottom flask fitted with a rubber septa and a cannula needle as an out needle for about 50 min. Sodium dithionite was weighed (1.3 mg, 0.007 mmol) and placed into a quartz cuvette (1 cm path length) in a glovebox followed by sealing the cuvette with a rubber septa before being removed from the glovebox. Degassed 100 μM solution (about 2.5 mL) was cannulated into the sealed quartz cuvette with sodium dithionite to prepare the aqueous solution of dication diradical **2a**. UV−vis scans of propyl-linked bis(viologen) dication diradical **2a** water solution were taken at 5 and 65 °C using a calibrated UV−vis temperature controller for five sequential cycles of heating from 5 to 65 °C followed by cooling from 65 to 5 °C. Moreover, a separate experiment was performed to take UV−vis scans at different temperatures in 5−95 °C range with an interval of 5 °C. This procedure was repeated for 20−100 μM solution range concentrations as these concentrations allowed to obtain appropriate absorbance range.

EPR Thermomagnetic Cycling Experiments. The EPR parameters for all experiments are as follows: modulation frequency = 100 kHz, modulation amplitude = 1.0 G, receiver gain = 50 dB, time constant = 0.16 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 = 1.990 mW, no. of points = 4096, and no. of averaged scans = 8.

The 2 mM solution of propyl-linked bis(viologen) tetracation **1** in pH = 9.6 water (0.045 M $NaHCO_3$/0.009 M NaOH buffer) was degassed using sparging. Meanwhile, the sodium dithionite (2.2 mg) was retrieved from a glovebox and sealed in a round-bottomed flask to maintain an inert atmosphere. After sparging, the 2 mM analyte solution was cannulated into the round-bottom flask containing the sodium dithionite. Finally the reduced analyte solution was cannulated into a custom-made quartz EPR tube, 3 mm i.d./4 mm o.d. top and ~30 mm of 1 mm i.d./2 mm o.d. bottom, capped by a septum. The solution was then cycled in the EPR instrument using a nitrogen flow to maintain the heat. The spin concentration was calculated via double integration. Temperature switching of 1 mM solution of dication diradical **2a** in pure DMSO was done in the same manner as the aqueous solution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supplementary UV−vis and EPR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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