

Supporting materials

Conformational and photosensitive adjustment of the 4,4'-bipyridinium in Mn(II) coordination complexes

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1. General Information

The elemental analysis(C, H, N) was performed using a Vario EL III CHNOS elemental analyzer. Diffuse reflectance spectra were recorded on a PerkinElmer Lambda 900 UV/VIS/NIR Spectrometer. The spectrophotometer was calibrated against BaSO₄ surface for 100% reflectance over the wavelength range under consideration. Electron spin resonance (ESR) signals were recorded with a Bruker A300 spectrometer. The variable-temperature magnetic susceptibility data were measured using a Quantum Design MPMS-XL5 SQUID magnetometer.

The structure data were collected on a Rigaku Saturn70 CCD diffractometer for **1**, and a Rigaku Mercury CCD diffractometer for **2** with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at room temperature. All absorption corrections were performed by using the multi-scan method. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXL-97 program package.

2. Synthesis

1-(4-carboxybenzyl)-4,4'-bipyridinium chloride (HBCbpyCl): This compound was synthesized according to the procedure as described previously (Published in CrystEngComm, 2008, 10, 1299).

[Mn(BCbpy)₂(H₂O)₄]·BCbpy·2ClO₄·10H₂O: HBCbpyCl salt (0.033 g, 0.1 mmol) and Mn(ClO₄)₂·6H₂O (0.036g, 0.1 mmol) were dissolved in 7 mL of water and the pH value of the solution was adjusted to 6 with 1 mol/L NaOH solution. After filtration, the filtrate was left for slow evaporation at room temperature. Yellow flake crystals were obtained after two weeks. Yield>40%. Anal. Calc. for C₅₄H₇₀Cl₂MnN₆O₂₈: C, 47.10; H, 5.12; N, 6.10. Found: C, 47.66; H, 5.08; N, 6.14 %.

[Mn₂(BCbpy)₄(H₂O)₃]·4ClO₄·3H₂O: HBCbpyCl salt (0.5g) was dissolved in 10 mL of water with pH = 7 adjusted by 1 mol/L NaOH solution and then the solution was cooled to

5°C. Pure BCbpy deposition was obtain through filtration. After drying, 0.029g (0.1mmol) BCbpy deposition and 0.036 g (0.1mmol) $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 5mL MeOH with three drops of water and then filtered. The filtrate was allowed to evaporate slowly for a week to give yellow prism crystals. Yield: 20% Anal. Calc. for $\text{C}_{72}\text{H}_{80}\text{Cl}_4 \text{Mn}_2\text{N}_8\text{O}_{36}$ (contain 6 non-lattice water molecules): C, 45.87; H, 4.28; N, 5.94. Found: C, 45.69; H, 4.02; N, 5.90 %.

3. The crystallographic information

Crystal data for **1**: $\text{C}_{54}\text{H}_{70}\text{Cl}_2\text{MnN}_6\text{O}_{28}$, $M = 1377.00$, orthorhombic, space group $\text{P2}_1\text{2}_1\text{2}_1$, $a = 18.076(6)$, $b = 18.275(6)$, $c = 18.908(6)$ Å, $V = 6246(3)$ Å³, $T = 293$ K, $Z = 4$, $D_c = 1.434$ g·cm⁻³, $\mu = 0.388$ mm⁻¹, parameters: 820, reffs measured: 49522, unique: 14232, $R_{\text{int}} = 0.0649$, R_1 (wR_2) = 0.0892 (0.2361) and $S = 1.034$ for 10771 reflections with ($I \geq 2\sigma(I)$). Crystal **1** was found to be an inversion twin with Flack parameters of 0.51(3), thus both the left- and right-handed helices exist in separate crystal domains. For **2**: $\text{C}_{72}\text{H}_{68}\text{Cl}_4\text{Mn}_2\text{N}_8\text{O}_{30}$, $M = 1777.03$, Monoclinic, space group $\text{P2}_1/\text{c}$, $a = 15.820(5)$, $b = 27.140(9)$, $c = 23.236(6)$ Å, $\beta = 129.027(15)^\circ$, $V = 7750(4)$ Å³, $T = 293$ K, $Z = 4$, $D_c = 1.493$ g·cm⁻³, $\mu = 0.556$ mm⁻¹, parameters: 1039, reffs measured: 60103, unique: 17735, $R_{\text{int}} = 0.0432$, R_1 (wR_2) = 0.0829 (0.2345) and $S = 1.086$ for 12643 reflections with ($I \geq 2\sigma(I)$) .

4. Structural drawing and other characterization data

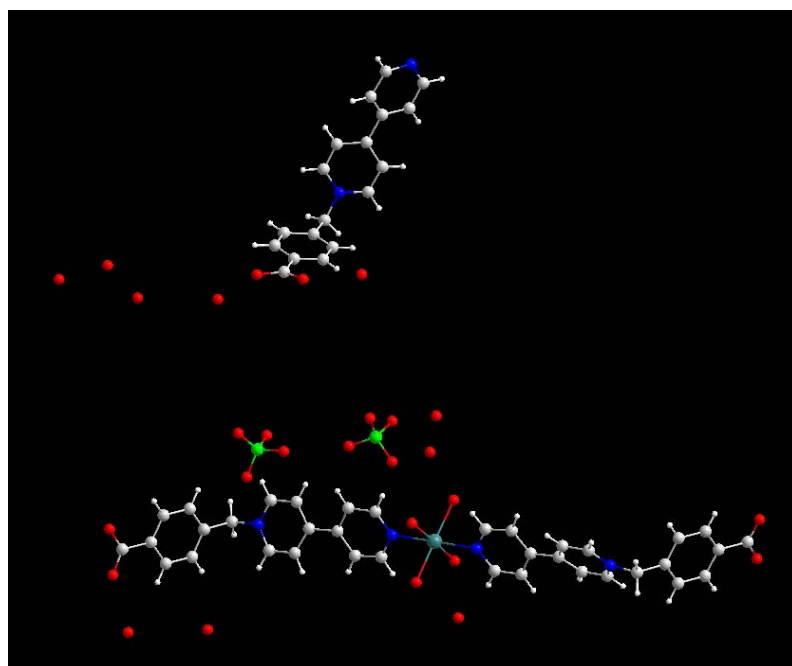


Fig. S1 The asymmetric unit in the crystal structure of complex 1.

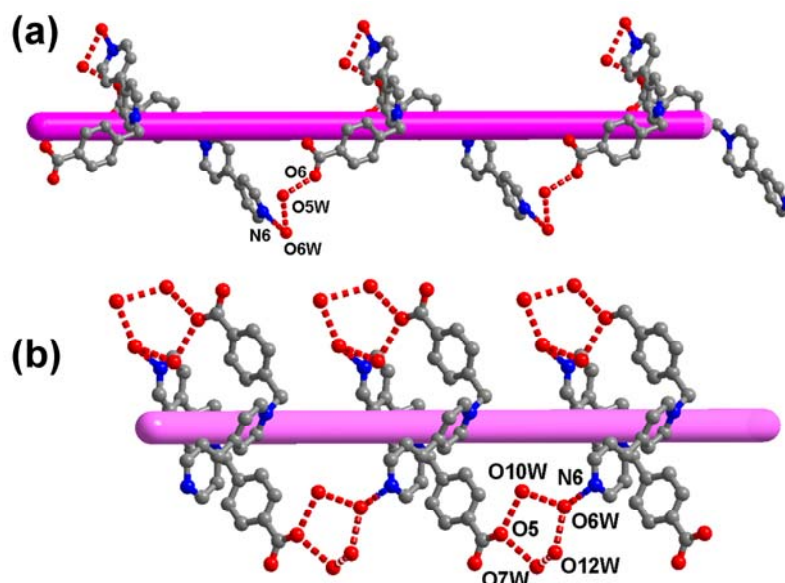


Fig. S2 (a) A-helical chain linked by water dimers via hydrogen bonds. (b) B-helical chain linked by water molecules via hydrogen bonds.

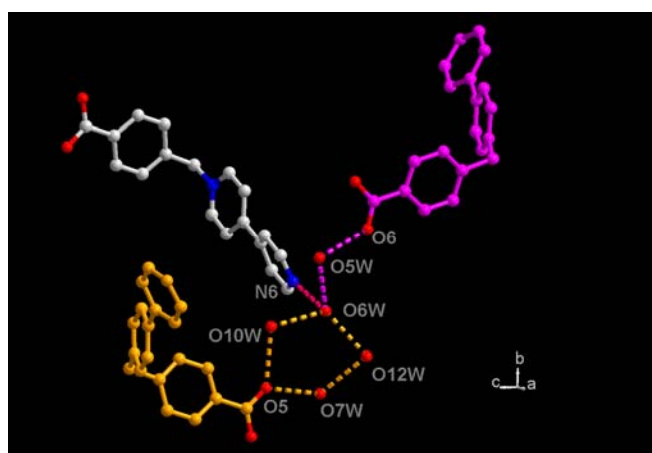


Fig.S3 Hydrogen bonds between lattice waters and adjacent independent BCbpy molecules (O6-O5W 2.773(3)Å, O5W-O6W 2.727(6)Å, O6W-O12W 2.694(7)Å, O12W-O7W 2.732(1)Å, O7W-O5 2.766(3)Å, O5-O10W 2.711(1)Å, O10W-O6W 2.770(4)Å, O6W-N6 2.765(10)Å). BCbpy molecules colored purple and white form A-helical chain through hydrogen bonded water dimer, while BCbpy molecules colored yellow and white form B-helical chain linked by hydrogen bonded pentagon.

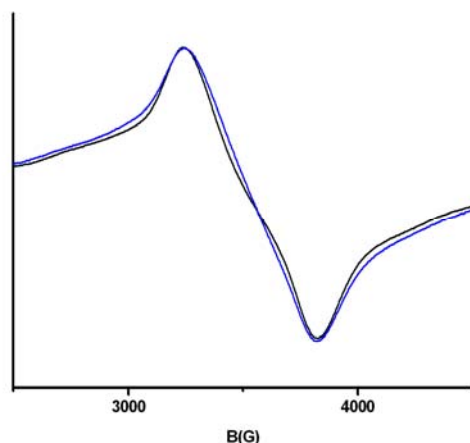


Fig. S4 Change in the ESR spectra of **1** upon photoirradiation : black line = sample before irradiation, blue line = sample irradiated for half an hour.

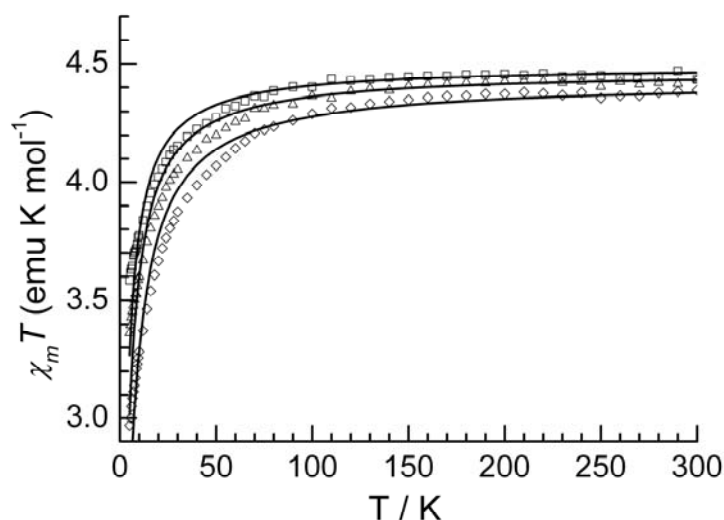


Fig. S5 The variable-temperature magnetic susceptibility data in the $\chi_m T$ product versus T plots measured at 1000 Oe for **1** after irradiation (χ_m being molar magnetic susceptibility per formula unit), $\square$ = blue sample (excited state), Δ = green sample (intermediate state), $\diamond$ = yellow sample (decolored state), the solid lines represent the Curie-Weiss fit. After the continuous irradiation with a Xenon lamp for one hour, the magnetic susceptibility data in the high-temperature region increase by a factor of 1.7%. Based on a simple Curie-Weiss fitting [$\chi_m T = CT/(T-\theta)$], an increase of 0.06 emu K mol⁻¹ in Curie constant can be found (the θ value : -1.86 K for blue sample, -3.47 K for yellow sample), which corresponds to the contribution of ca. 0.16 molar equivalents of free radicals.

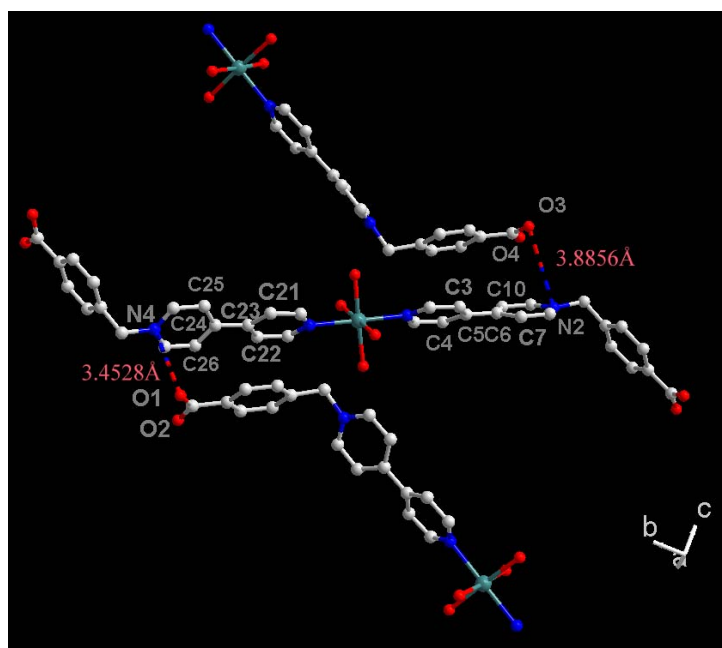


Fig.S6 The distances and orientations of carboxylate oxygen atoms and pyridinium nitrogen atoms between adjacent ribbons of rings in complex 1.

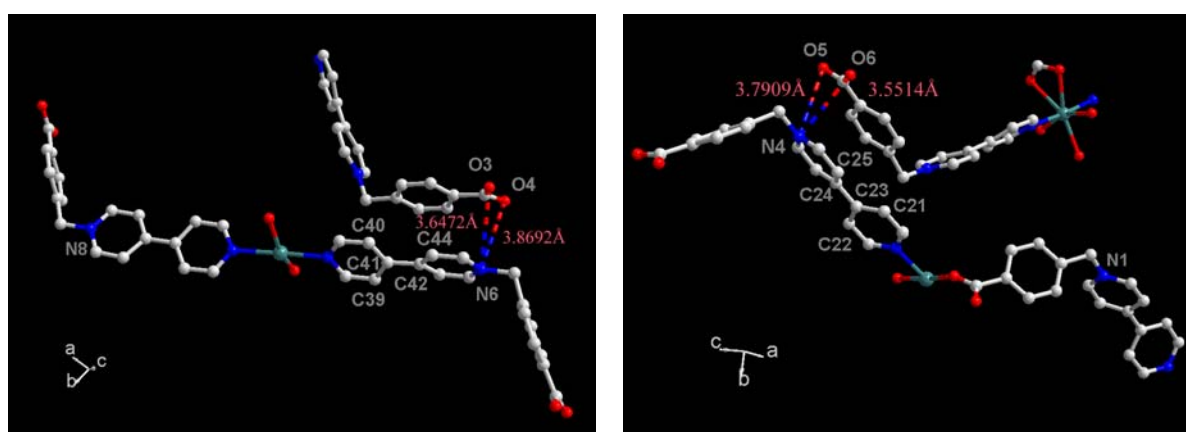
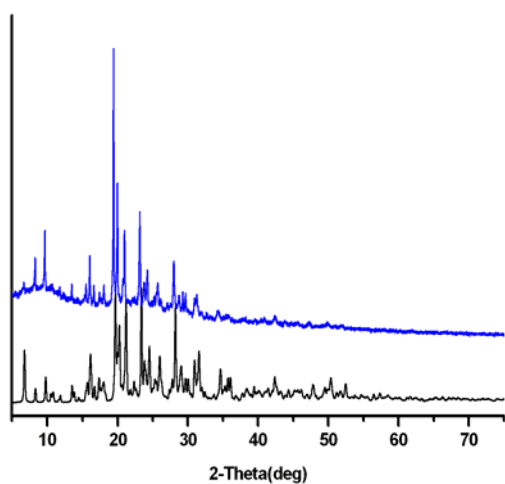
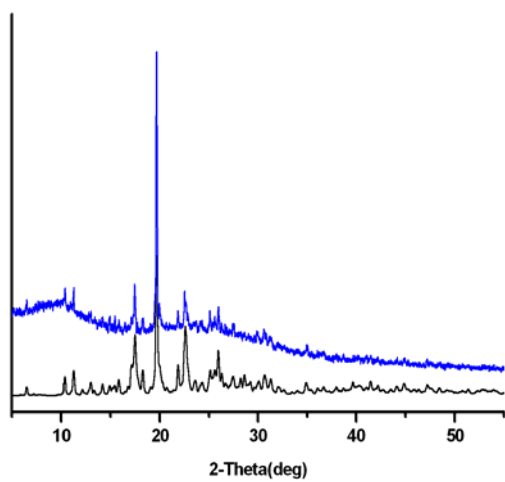


Fig.S7 The distances and orientations of carboxylate oxygen atoms and pyridinium nitrogen atoms in complex 2.



(a)



(b)

Fig. S8 X-ray powder diffraction patterns of **1** (a) and **2** (b). Blue: experimental data; black, simulated patterns from single-crystal X-ray structure data.