Supporting Information

Solvent Mediated Reversible Solid State Photochromism of $\{Mo_{72}Fe_{30}\}$ Keplerate

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Section 1. IR Spectroscopy

1.1. The IR spectrum was recorded for **regenerated compound 1** after five reversible photochromic cycles. **Regenerated compound 1** showed no structural disintegration after five photo-redox cycles (**Fig. S1**).

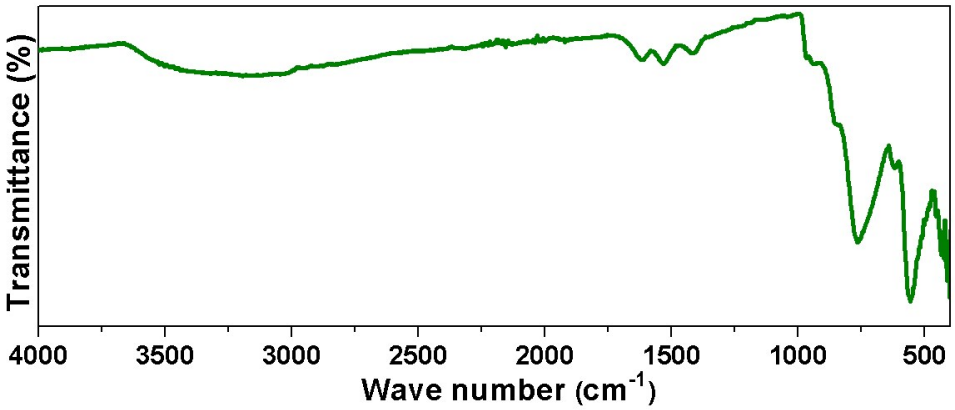

Fig. S1 Infrared spectrum for **regenerated compound 1** after five reversible photo-redox cycles.

Characteristic IR bands: $\bar{\upsilon}$ (cm^{-1}) = 1618 (m, δ (H_2O)), 1533 (m, ν_{as}(COO)), 1414 (s-m, ν_s(COO)), 965 (m, ν(Mo=O)), 857 (m), 768 (s), 626 (m), 558 (s), 418 (m).

Section 2. Diffuse Reflectance Spectroscopy

2.1. Compound **1** was soaked in DMF overnight. The solid state UV-visible spectroscopic study was performed for this wet, yellow coloured crystals of compound **1** prior to its irradiation with sunlight. The diffuse reflectance solid state electronic spectrum for the DMF wetted crystals of compound **1** showed three absorption bands at 305, 415 and 475 nm similar to compound **1** (**Fig. S2**).

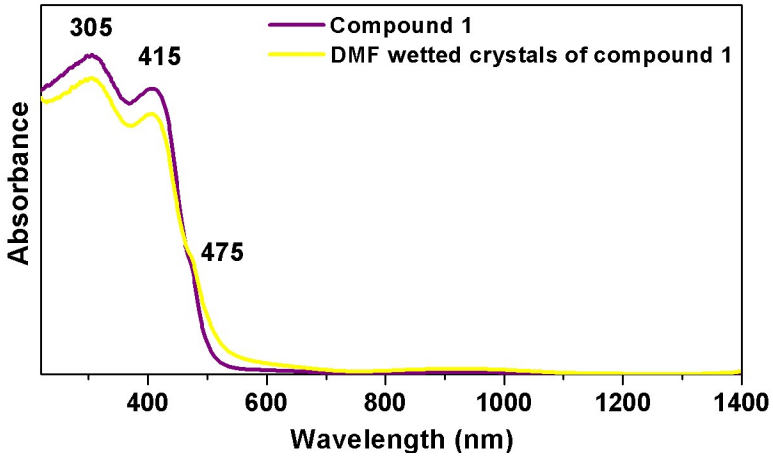

Fig. S2 Diffuse reflectance electronic absorption spectra for compound **1** (purple curve) and overnight DMF wetted crystals of compound **1** (yellow curve).

Section 3. Electron spin resonance (ESR) Spectroscopy

3.1. The room temperature ESR spectra for compound $\mathbf{1}_{red}$ shows a highly intense sharp peak at g~1.98 corresponding to the presence of Mo^{5+} centres of $\mathbf{1}_{red}$ as shown in **Fig. S3**.

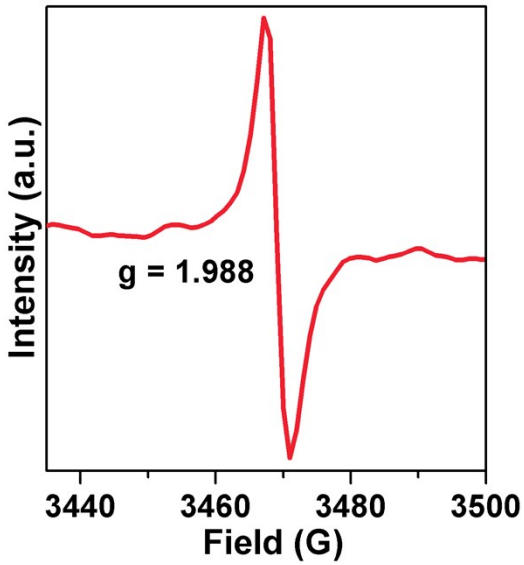

Fig. S3 ESR spectrum for compound $\mathbf{1}_{red}$.

Section 4. Thermogravimetric Analysis (TGA)

4.1. The thermograms, obtained for compounds **1** and $\mathbf{1}_{red}$, show the loss of crystal water in the temperature range of 100˚-250˚C (**Fig. S4-S6**).

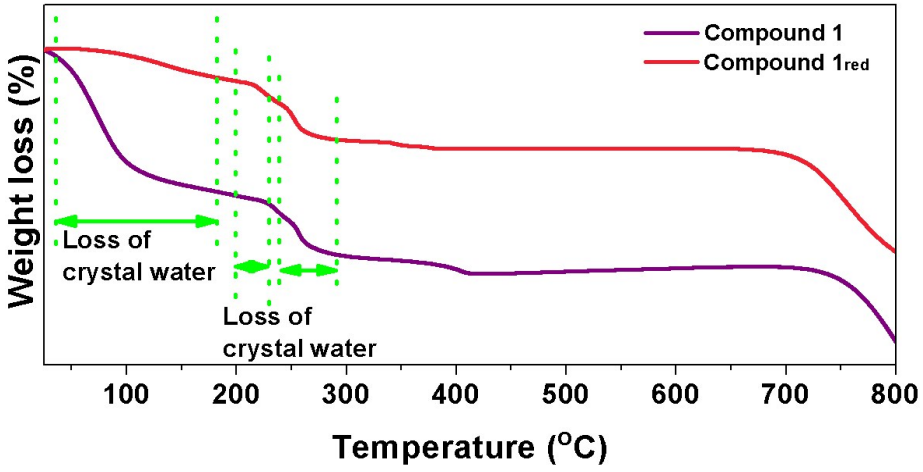

Fig. S4 Comparative thermograms for compound **1** (purple curve) and compound $\mathbf{1}_{red}$; (red curve).

As shown in **Fig. S4** and **S5**, compound **1** loses water in three stages.[1] The first stage of water loss is observed from ~30˚C to ~180˚C (weight loss of ~14%). The second and third stages of water loss are observed at 220˚C and 250˚C respectively (combined weight loss of ~ 6.7%). The weight loss of ~1% observed at 370˚C, corresponds to the loss of CO_2 molecules which are formed due to the decomposition of compound **1**. For compound $\mathbf{1_{red}}$, weight loss before 190˚C (~ 3.4%) corresponding to crystal water as observed from **Fig. S6** is lower in comparison to parent compound **1**. This is possibly due to the exposure to sunlight which results in the partial removal of water molecules from the internal cavity of **1**. Further weight losses of ~6.2% and ~1% at temperatures between 220˚-250˚C and 370˚C respectively are similar to the patterns shown by parent compound **1**. The similarity in the thermograms of compound **1** and $\mathbf{1_{red}}$ is another indication towards the non-incorporation of the DMF solvent into the crystal lattice of compound **1**.

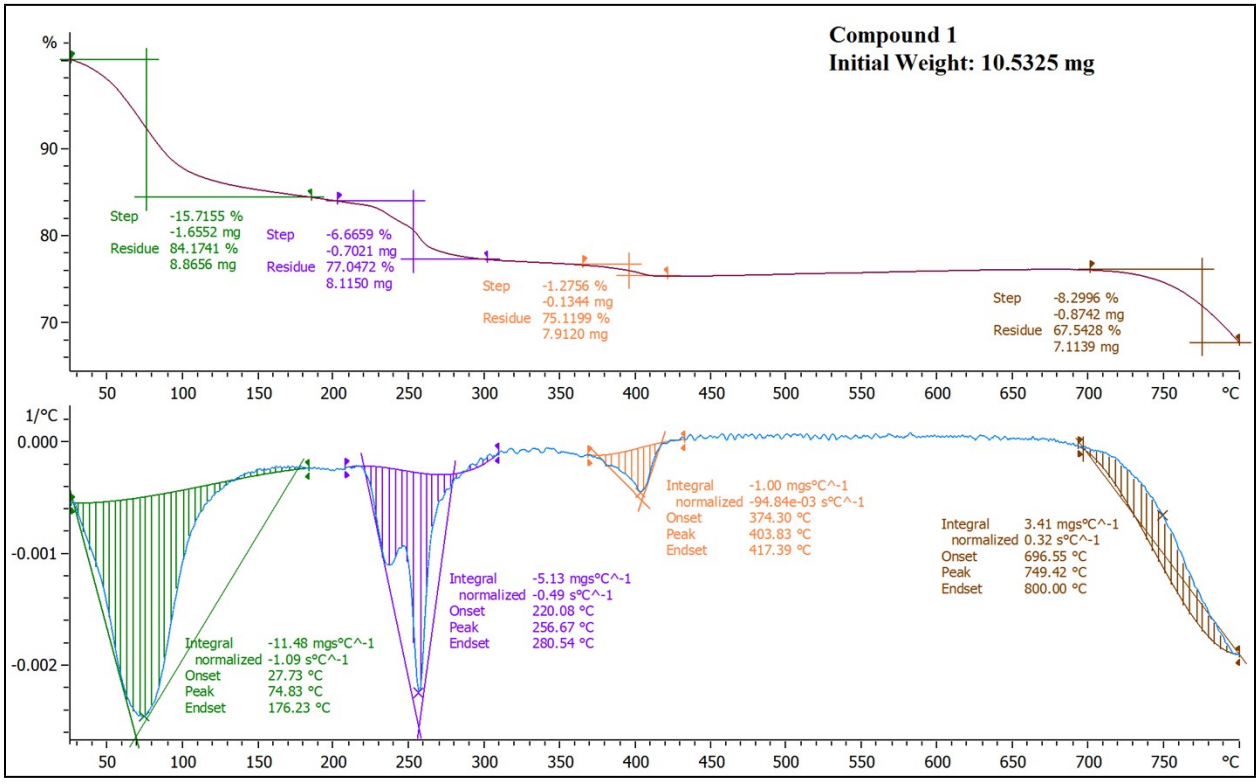

Fig. S5 Thermal analysis plots for compound **1**.

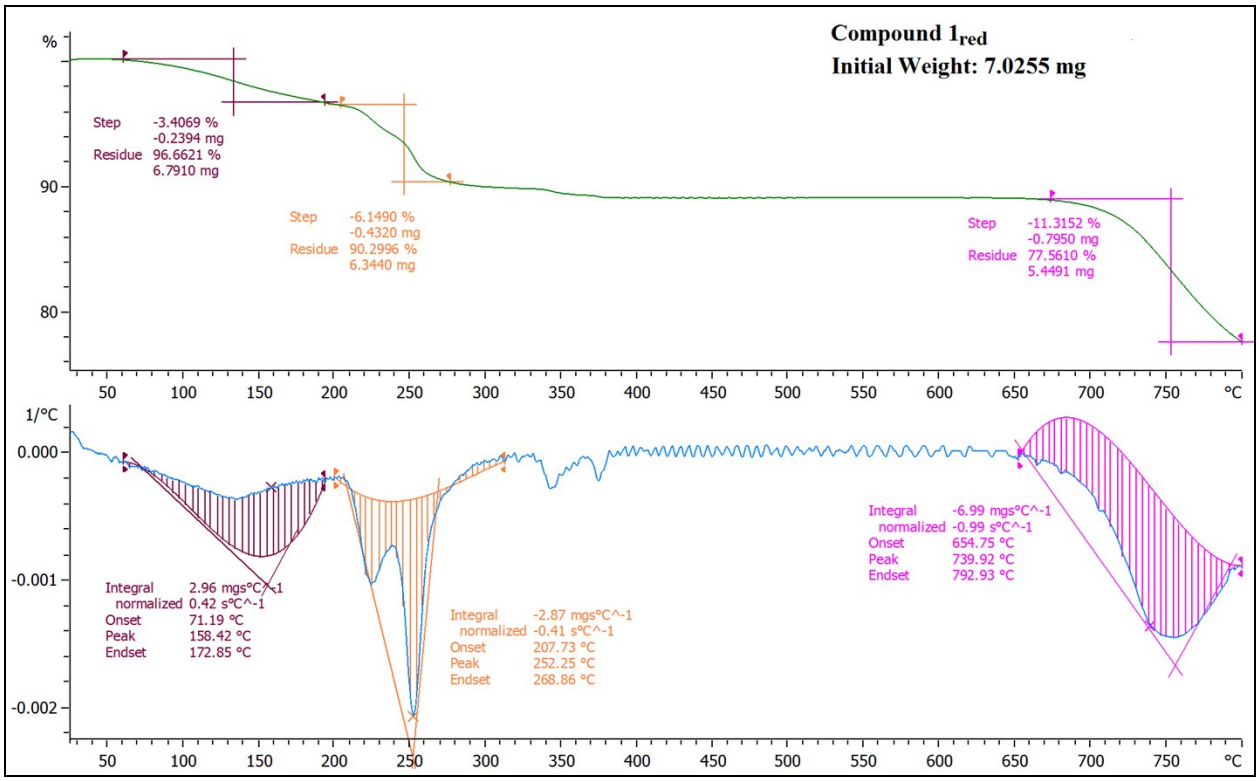

Fig. S6 Thermal analysis plots for compound $\mathbf{1}_{red}$.

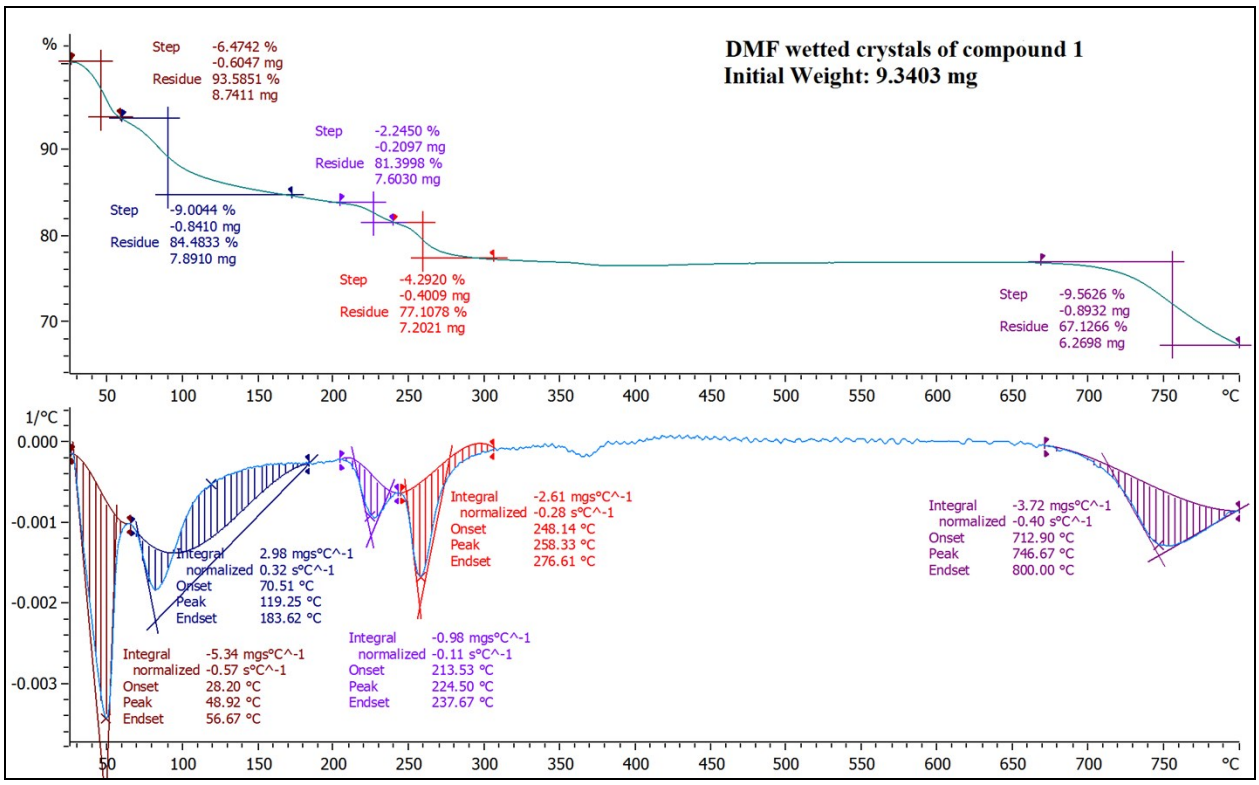

Fig. S7 Thermal analysis plots for overnight DMF wetted crystals of compound **1**.

Fig. S7 shows the thermogram obtained for an overnight soaked sample of compound **1** in DMF. The DMF wetted crystals of compound **1**; prior to their irradiation with sunlight, also show weight losses in three stages: ~15% before 190˚C, ~2.3% and ~4.3% at 220˚C and 250˚C respectively. It is to be noted that for compound **1** and $\mathbf{1_{red}}$ a single weight loss step corresponding to the loss of crystal water is observed before 190˚C. However for compound **1** soaked overnight in DMF an increased weight loss of ~15% (in comparison to ~14% for parent compound **1**) is observed taking place in two overlapping steps. This weight loss may correspond to the loss of DMF adhering on the surface of compound **1** apart from the loss of crystal water.

Section 5. Photochromic conversion of compound 1 to $\mathbf{1_{red}}$

5.1. Fig. S8 shows compound $\mathbf{1_{red}}$ obtained on irradiation of DMF wetted crystals of compound **1** with sunlight.

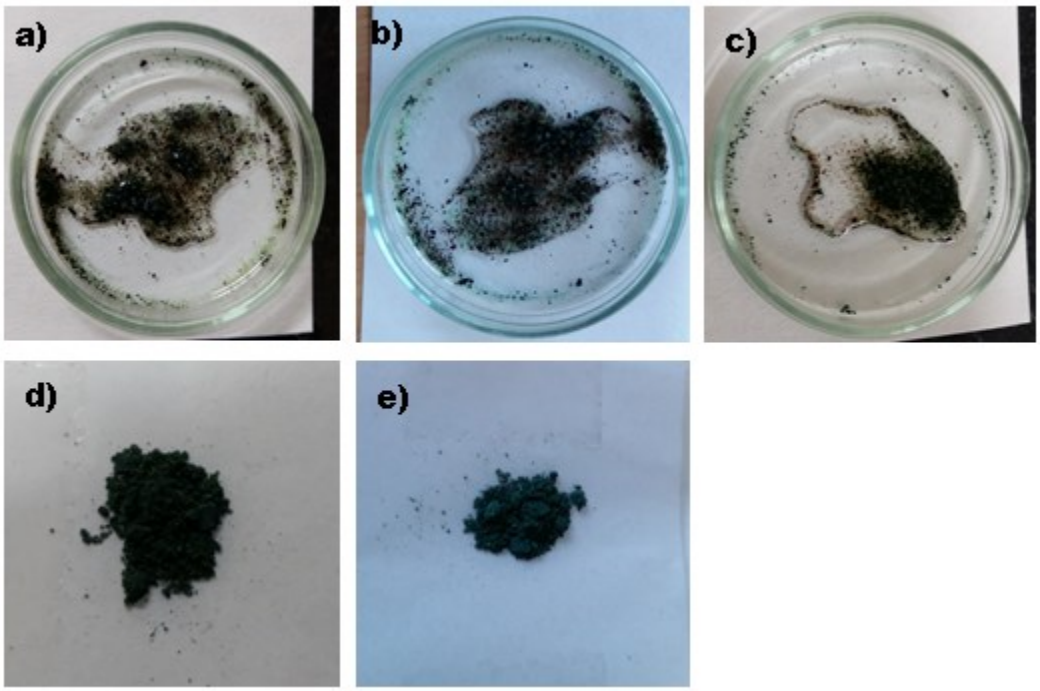

Fig. S8 a-c) Compound $\mathbf{1}_{red}$ obtained when the DMF wetted crystals are exposed to sunlight. The images show compound $\mathbf{1}_{red}$ with DMF on its surface ; d-e) Compound $\mathbf{1}_{red}$ obtained after separation from DMF.

References

1. A. A. Ostroushko, M. O. Tonkushima, A. P. Safronov, V. Y. Korotaev, V. A. Vazhenin, V. Y. Kolosov, N. A, Martynova, I. B. Kutashev, S. G. Bogdanov, A. N. Pirogov, K. B. Grzhegorzhevskii and A. V. Prokof'eva, *Russ. J. Inorg. Chem.*, 2012, **57**, 858-863.