Photoswitchable $Cu^{II}_4Mo^{IV}$ and $Cu^{II}_2Mo^{IV}$ cyanido-bridged molecules

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Supplementary information:

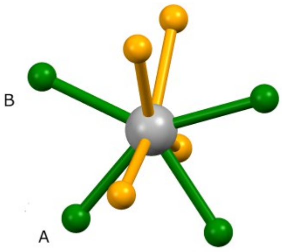

Fig. S1. Vertices naming convention in a dodecahedral complex.

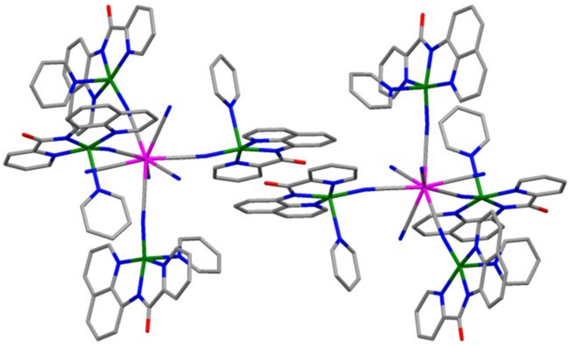

Fig. S2. Hydrophobic π-π stacking interactions in the molecular structure of (1).

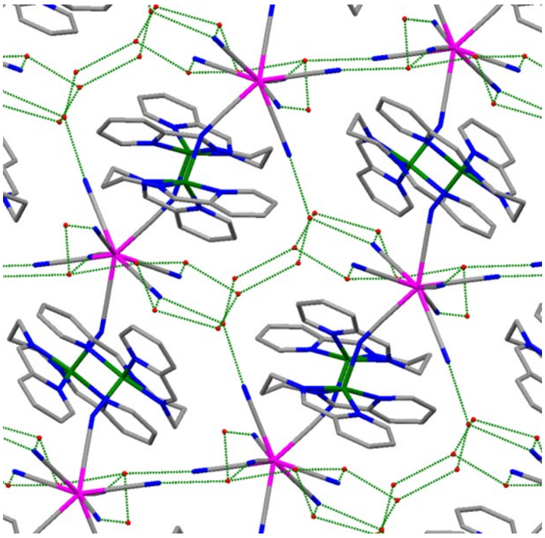

Fig. S3. Hydrogen bond network in the molecular structure of (2)

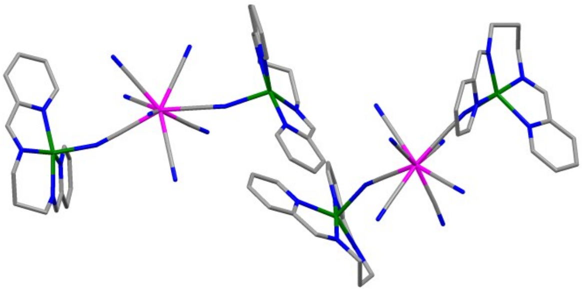

Fig S4. Hydrophobic π-π stacking interactions in the molecular structre of (2).

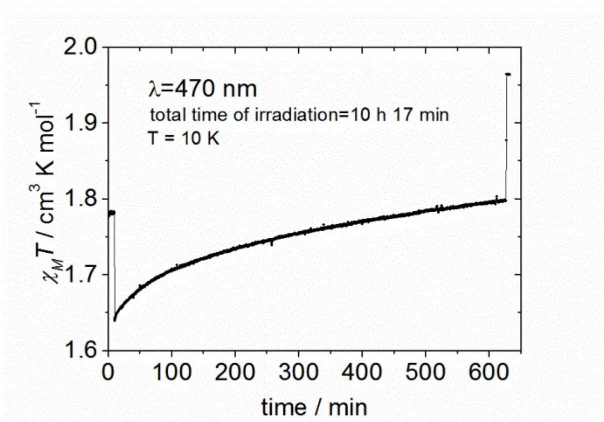

Fig. S5. Time evolution of χT signal upon irradiation for **Cu$_4$Mo**

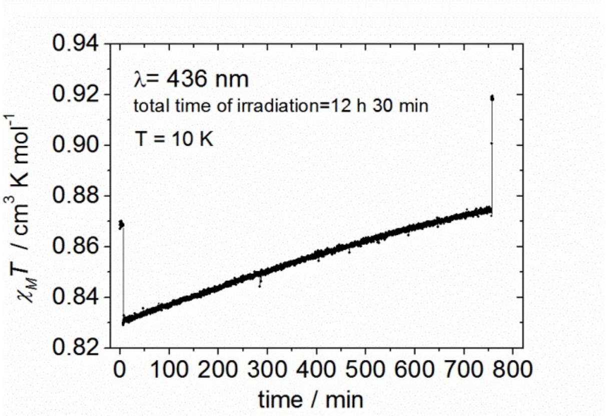

Fig. S6. Time evolution of χT signal upon irradiation for **Cu$_2$Mo**

Tab. S1. Hydrogen bonds lengths and angles in the molecular structure of (2)

D-H-A	D-H [Å]	H-A[Å]	D-A [Å]	D-H-A [°]
O1-H1A-N17	0.79(4)	2.04(4)	2.828(3)	173(3)
O1-H1B-N14	0.81(3)	2.06(3)	2.862(3)	175(3)
O2-H2A-N18	0.77(4)	2.08(4)	2.841(3)	170(3)
O2-H2B-N12	0.82(4)	2.05(4)	2.851(3)	164(3)
O3-H3A-N11	0.72(4)	2.12(4)	2.829(3)	169(4)
O3-H3B-O1	0.82(3)	2.15(4)	2.945(3)	162(3)
O4-H4A-N12	0.86(4)	2.12(4)	2.960(3)	166(3)
O4-H4B-O5	0.77(5)	1.98(5)	2.736(3)	167(5)
O5-H5A-O1	0.82(4)	2.12(4)	2.941(3)	178(4)
O5-H5B-O6	0.82(4)	1.94(4)	2.745(3)	167(4)
O6-H6A-N16	0.83(5)	2.23(5)	3.050(3)	168(4)
O6-H6B-O7	0.70(4)	2.07(4)	2.756(3)	164(4)
O7-H7A-O8	0.71(4)	2.07(4)	2.769(3)	168(4)
O7-H7B-O9	0.84(4)	1.94(5)	2.750(3)	162(4)
O8-H8A-N16	0.73(4)	2.40(4)	3.125(3)	172(4)
O8-H8B-O2	0.81(4)	2.04(4)	2.853(3)	176(4)
O9-H9A-O4	0.75(4)	2.01(4)	2.736(3)	163(4)
O9-H9B-O2	0.81(4)	2.14(5)	2.903(3)	158(4)

Details of calculations of magnetic and photomagnetic properties of (1)

Calculation of magnetic properties of (1) before irradiation

The corresponding Hamiltonian reads

$$\hat{H}_1 = -J_1(\hat{S}_{\mathrm{Cu1}} \cdot \hat{S}_{\mathrm{Cu3}} + \hat{S}_{\mathrm{Cu2}} \cdot \hat{S}_{\mathrm{Cu4}}) + g_{\mathrm{Cu}}\mu_{\mathrm{B}}(\hat{S}_{\mathrm{Cu1}} + \hat{S}_{\mathrm{Cu2}} + \hat{S}_{\mathrm{Cu3}} + \hat{S}_{\mathrm{Cu4}}) \cdot \vec{H}$$

The magnetisation and susceptibility is obtained as appropriate derivatives of the partition function :

$$\begin{aligned} Z_1(H,T) &= 3 + 4\cosh(\beta\mu_{\mathrm{B}} g_{\mathrm{Cu}} H) + 2\cosh(2\beta\mu_{\mathrm{B}} g_{\mathrm{Cu}} H) \\ &\quad + 2\exp(-\beta J_1)(1 + 2\cosh(\beta\mu_{\mathrm{B}} g_{\mathrm{Cu}} H)) + \exp(-2\beta J_1) \end{aligned}$$

where $\beta=1/k_{\mathrm{B}}T$. The magnetisation and susceptibility take the formulas:

$$M_1(H,T) = \frac{N_{\mathrm{A}}}{\beta} \frac{\partial \ln Z_1(H,T)}{\partial H}, \qquad \chi_1 = \frac{N_{\mathrm{A}}}{\beta} \frac{\partial^2 \ln Z_1(H,T)}{\partial H^2}.$$

The intermolecular interactions are accounted for within the framework of the molecular field approximation leading to an equation for the molar magnetisation of the coupled clusters:

$$M_{1\mathrm{C}}(H,T) = M_1\left(H + \frac{zJ_1'}{N_{\mathrm{A}}\mu_{\mathrm{B}}^2 g_{\mathrm{Cu}}^2} M_1(H,T), T \right)$$

where z denotes the number of the nearest neighbours and J_1' is the intermolecular coupling constant. The molar magnetic susceptibility of the interacting (coupled) cluster $\chi_{1\mathrm{C}}$ was calculated according to the following formula:

$$\chi_{1\mathrm{C}} = \frac{\chi_1}{1 - \dfrac{zJ_1'\chi_1}{N_{\mathrm{A}}\mu_{\mathrm{B}}^2 g_{\mathrm{Cu}}^2}}$$

Calculation of magnetic properties of (1) after irradiation

The corresponding Hamiltonian acquires the following form:

$$\hat{H}_2 = -J_2\hat{S}_{\mathrm{Mo}} \cdot (\hat{S}_{\mathrm{Cu1}} + \hat{S}_{\mathrm{Cu2}} + \hat{S}_{\mathrm{Cu3}}) + g_{\mathrm{Cu}}\mu_{\mathrm{B}}(\hat{S}_{\mathrm{Cu1}} + \hat{S}_{\mathrm{Cu2}} + \hat{S}_{\mathrm{Cu3}}) \cdot \hat{H} + g_{\mathrm{Mo}}\mu_{\mathrm{B}}\hat{S}_{\mathrm{Mo}} \cdot \hat{H}$$

It is straightforward to derive the field- and temperature dependent partition function Z_2 related to Hamiltonian $\hat{H}_2$:

$$\begin{aligned} Z_2(H,T) &= 2\exp(\beta J_2)\cosh\left[\frac{1}{2}\beta\mu_{\mathrm{B}}(3g_{\mathrm{Cu}} + g_{\mathrm{Mo}})H\right] \\ &\quad + 4\exp\left(\frac{1}{2}\beta J_2\right)\cosh\left[\frac{1}{2}\beta\mu_{\mathrm{B}}(g_{\mathrm{Cu}} + g_{\mathrm{Mo}})H\right] \\ &\quad + 4\cosh\left[\frac{1}{2}\beta\sqrt{\mu_{\mathrm{B}}^2(g_{\mathrm{Cu}} - g_{\mathrm{Mo}})^2 H^2 + J_2^2}\right] \\ &\quad + 2\cosh\left[\frac{1}{2}\beta\sqrt{\mu_{\mathrm{B}}^2(g_{\mathrm{Cu}} - g_{\mathrm{Mo}})^2 H^2 + 4J_2^2}\right] \\ &\quad + 2\exp(-\beta\mu_{\mathrm{B}} g_{\mathrm{Cu}} H)\cosh\left[\frac{1}{2}\beta\sqrt{\mu_{\mathrm{B}}^2(g_{\mathrm{Cu}} - g_{\mathrm{Mo}})^2 H^2 + 2\mu_{\mathrm{B}}(g_{\mathrm{Cu}} - g_{\mathrm{Mo}})HJ_2 + 4J_2^2}\right] \\ &\quad + 2\exp(\beta\mu_{\mathrm{B}} g_{\mathrm{Cu}} H)\cosh\left[\frac{1}{2}\beta\sqrt{\mu_{\mathrm{B}}^2(g_{\mathrm{Cu}} - g_{\mathrm{Mo}})^2 H^2 - 2\mu_{\mathrm{B}}(g_{\mathrm{Cu}} - g_{\mathrm{Mo}})HJ_2 + 4J_2^2}\right] \end{aligned}$$

where $\beta=1/k_BT$. The molar magnetisation and susceptibility is obtained as appropriate derivatives of the partition function, i.e.

$$M_2(H,T)=\frac{N_A}{\beta}\frac{\partial \ln Z_2(H,T)}{\partial H}, \qquad \chi_2=\frac{N_A}{\beta}\frac{\partial^2 \ln Z_2(H,T)}{\partial H^2}.$$

The intermolecular interactions are accounted for within the framework of the molecular field approximation leading to an equation for the molar magnetisation of the coupled pentamer units

$$M_{2C}(H,T)=M_2\left(H+\frac{zJ_2'}{N_A\mu_B^2 g_{Cu}g_{Mo}}M_2(H,T),T\right)$$

where *z* denotes the number of the nearest neighbours and J_2' is the intermolecular coupling constant. The equation was solved iteratively in a specially designed notebook of the *Mathematica8.0* environment. The direct output of the procedure was the total magnetisation as a function of external magnetic field and temperature. The molar magnetic susceptibility of the interacting (coupled) clusters was calculated with the use of the formula

$$\chi_{2C}=\frac{\chi_2}{1-\dfrac{zJ_2'\chi_2}{N_A\mu_B^2 g_{Cu}g_{Mo}}},$$

In order to study the influence of the relaxation process on the magnetic properties of the photogenerated state we have calculated a fraction of the excited pentamer units in the sample *f* in the function of temperature T during heating from T_{min} to T_{max} in time of Δt_m:

$$f=f_0\exp\left[-e^{-\frac{\Delta}{k_BT}}\frac{T-T_{min}}{T_{max}-T_{min}}\rho\right]$$

where f_0 is the initial fraction of the photogenerated state (t=0) and Δ is the relaxation energy barrier and $\rho=\Delta t_m/\tau_0$. Keeping in mind that the susceptibility of the sample before irradiation χ_{BI} is given by

$$\chi_{BI}(H,T)=\frac{m}{\mu}\chi_{1C}(J_1,zJ_1',g_{Cu},H,T)$$

the susceptibility signal detected just upon irradiation χ_{UI} can be described as a combination of signals inferred from model I (uncoupled pentamer units) and model II (coupled pentamer units):

$$\chi_{UI}(H,T)=\frac{m}{\mu}\{[1-f(f_0,\Delta,\rho,T)]\chi_{1C}(J_1,zJ_1',g_{Cu},H,T)+f(f_0,\Delta,\rho,T)\chi_{2C}(J_2,zJ_2',g_{Cu},g_{Mo},H,T)\}$$

where *m* denotes the mass of the sample, μ is the molar mass of compound **1**, and all the parameters and variables are given explicitly.

In order to analyze the data the product $\chi_{BI}(H,T)T$ with parameters J_1, zJ_1', and g_{Cu} fixed at their bulk values was fitted (green solid line, Fig. 12.) to the experimental points (black symbols) and yielded the agreement quotient $R_{\chi T}=3.5\cdot10^{-5}$. The resultant values were used to simulate the magnetisation vs. field data satisfactorily.

The main step of the analysis was the modeling of the susceptibility signal observed upon irradiation. The product $\chi_{UI}(H,T)T$ was fitted (blue solid line in Fig. 12.) to the experimental data (red symbols) with parameters J_1, zJ_1', g_{Cu}, *m* fixed at the previously found values. Additionally, to reduce the number of free parameters, we fixed the value of the Landé factor g_{Mo} at the plausible value of 2.0.

Details of calculations of magnetic and photomagnetic properties of (2)

Calculation of magnetic properties of (2) before irradiation

The interaction is described by the Hamiltonian:

$$\hat{H}_1 = -J_1 \hat{S}_{\mathrm{Cu1}} \cdot \hat{S}_{\mathrm{Cu2}} + g_{\mathrm{Cu}} \mu_{\mathrm{B}} (\hat{S}_{\mathrm{Cu1}} + \hat{S}_{\mathrm{Cu2}}) \cdot \vec{H}$$

where the only superexchange coupling constant is denoted by J_1. The magnetisation and susceptibility are obtained as appropriate derivatives of the partition function

$Z_1(H,T) = 1 + \exp(\beta J_1)[1 + 2\cosh(\beta \mu_{\mathrm{B}} g_{\mathrm{Cu}} H)]$, where $\beta = 1/k_{\mathrm{B}}T$

and take the formulas:

$$M_1(H,T) = \frac{N_{\mathrm{A}}}{\beta} \frac{\partial \ln Z_1(H,T)}{\partial H}, \qquad \chi_1 = \frac{N_{\mathrm{A}}}{\beta} \frac{\partial^2 \ln Z_1(H,T)}{\partial H^2}.$$

The intermolecular interactions are accounted for within the framework of the molecular field approximation leading to an equation for the molar magnetisation of the coupled clusters

$$M_{1\mathrm{C}}(H,T) = M_1\left(H + \frac{zJ_1'}{N_{\mathrm{A}} \mu_{\mathrm{B}}^2 g_{\mathrm{Cu}}^2} M_1(H,T), T \right),$$

where z denotes the number of the nearest neighbours and J_1' is the intermolecular coupling constant. The molar magnetic susceptibility of the interacting clusters $\chi_{1\mathrm{C}}$ was calculated according to the following formula:

$$\chi_{1\mathrm{C}} = \frac{\chi_1}{1 - \dfrac{zJ_1' \chi_1}{N_{\mathrm{A}} \mu_{\mathrm{B}}^2 g_{\mathrm{Cu}}^2}},$$

Calculation of magnetic properties of (2) after irradiation

The Hamiltonian used for the calculation takes the form:

$$\hat{H}_2 = -J_2 \hat{S}_{\mathrm{Mo}} \cdot \hat{S}_{\mathrm{Cu1}} - J_3 \hat{S}_{\mathrm{Mo}} \cdot \hat{S}_{\mathrm{Cu2}} + g \mu_{\mathrm{B}} (\hat{S}_{\mathrm{Cu1}} + \hat{S}_{\mathrm{Cu2}} + \hat{S}_{\mathrm{Mo}}) \cdot \vec{H},$$

where for the sake of simplicity a single average Landé factor was assumed.

It is straightforward to derive the field- and temperature dependent partition function Z_2 related to Hamiltonian $\hat{H}_2$:

$$Z_2(H,T) = e^{\frac{3}{4}\beta(J_2+J_3)}[1 + 2\cosh(2\beta\mu_{\mathrm{B}} gH) + 2\cosh(\beta\mu_{\mathrm{B}} gH)] + e^{-\frac{3}{4}\beta(J_2+J_3)} \\ + 2[1 + 2\cosh(\beta\mu_{\mathrm{B}} gH)]\cosh\left(\frac{1}{4}\beta\sqrt{9J_2^2 - 14J_2J_3 + 9J_3^2} \right)$$

where $\beta = 1/k_{\mathrm{B}}T$. The molar magnetisation and susceptibility is obtained as appropriate derivatives of the partition function, i.e.

$$M_2(H,T) = \frac{N_{\mathrm{A}}}{\beta} \frac{\partial \ln Z_2(H,T)}{\partial H}, \qquad \chi_2 = \frac{N_{\mathrm{A}}}{\beta} \frac{\partial^2 \ln Z_2(H,T)}{\partial H^2}.$$

The intermolecular interactions are accounted for within the framework of the molecular field approximation leading to an equation for the molar magnetisation of the coupled trimer units

$$M_{2C}(H,T) = M_2\left(H + \frac{zJ'_2}{N_A \mu_B^2 g^2} M_2(H,T), T\right),$$

where z denotes the number of the nearest neighbours and J'_2 is the intermolecular coupling constant. The equation was solved iteratively in a specially designed notebook of the *Mathematica8.0* environment. The direct output of the procedure was the total magnetisation as a function of external magnetic field and temperature. The molar magnetic susceptibility was calculated approximately using the following formula

$$\chi_{2C} = \frac{\chi_2}{1 - \frac{zJ'_2 \chi_2}{N_A \mu_B^2 g^2}},$$

where χ_{2C} denotes the susceptibility corresponding to the interacting (coupled) clusters.

In order to estimate a fraction f of the sample which undergoes the spin transition process we have taken into account that the excited Mo(IV)* state is a metastable one and the fraction f is expected to diminish in the course of time. However, we have assumed here that within the temperature range of 1.8-50 K this fraction remains constant and is equal to its initial value f_0. The susceptibility of the sample before irradiation χ_{BI} is given by the equation:

$$\chi_{BI}(H,T) = \frac{m}{\mu} \chi_{1C}(J_1, zJ'_1, g_{Cu}, H, T)$$

whereas the susceptibility signal detected just upon irradiation χ_{UI} can be described by an appropriate combination of signals inferred from model I (not excited trimer units) and model II (excited trimer units):

$$\chi_{UI}(H,T) = \frac{m}{\mu}\{[1 - f_0]\chi_{1C}(J_1, zJ'_1, g_{Cu}, H, T) + f_0 \chi_{2C}(J_2, zJ'_2, g, H, T)\}$$

where m denotes the mass of the sample, μ is the molar mass of compound **2**, and all the parameters and variables are given explicitly.