Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2021

Electronic Supplementary Information for:

Chiral porous CN-bridged coordination polymer mimicking MOF-74 and showing magnetization photoswitching

Michał Magott* and Dawid Pinkowicz*

Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Kraków, Poland

Experimental section

Synthesis details

All reagents were used as supplied from commercial sources (Alfa Aesar). Potassium octacyanotungstate(IV) was obtained according to the previously reported procedure.^{S1} Full physicochemical characterization of **1** and **1anh** (except single-crystal X-ray diffraction experiments) was performed on powder samples consisting of a racemic mixture of $P3_121$ and $P3_221$ crystals.

[Mn^{II}(L)]Cl₂·H₂O

Precursor compound $[Mn^{II}(L)]Cl_2 H_2O$ was obtained from $MnCl_2 H_2O$ according to the literature procedure.⁵² Solvate composition was determined by elemental analysis. Anal. found: C:42.92, N:16.47, H:6.68; calc. for $[Mn^{II}(L)]Cl_2 H_2O$: C:42.97, N:16.70, H:6.49.

${[Mn^{II}(L)]_{2}[W^{IV}(CN)_{8}] \cdot 10H_{2}O}_{n}(1)$

Racemate of microcrystalline compound **1** was obtained by mixing $[Mn^{II}(L)]Cl_2 \cdot H_2O$ (63 mg, 0.15 mmol) solution in 13 mL of $H_2O:CH_3CN$ (6:7) with $K_4[W^{IV}(CN)_8]\cdot 2H_2O$ (58 mg, 0.1 mmol) in 13 mL $H_2O:CH_3CN$ (6:7) under constant magnetic stirring. Precipitation of yellow powder is observed immediately, which upon an hour recrystallizes into yellow-orange needles of **1**, that were collected by vacuum filtration. Yield: 50 mg (54%). The purity of the sample was confirmed by powder X-ray diffraction (Figure S6a) and elemental analysis. Anal. found: C:37.15, N:20.43, H:5.41; calc. for $[Mn^{II}(L)]_2[W^{IV}(CN)_8]\cdot 10H_2O$: C:37.02, N:20.45, H:5.72. Single crystals of **1** were prepared in the H-tube, where one arm was filled with $[Mn^{II}(L)]Cl_2\cdot H_2O$ (63 mg, 0.15 mmol) in 1 mL $H_2O:CH_3CN$ (3:4) and the other was filled with $K_4[W^{IV}(CN)_8]\cdot 2H_2O$ (58 mg, 0.1 mmol) in 1 mL $H_2O:CH_3CN$ (3:4). Both arms were connected with $H_2O:CH_3CN$ (1:1) mixture.

${[Mn''(L)]_2[W''(CN)_8]}_n$ (1anh)

Compound **1anh** is obtained by vacuum drying ($p \approx 10^{-2}$ mbar) **1** for 1 hour. In case of singlecrystal X-ray diffraction measurement, crystal of **1** was dried for 1 hour in the stream of dry nitrogen at 300 K. Purity of the bulk sample was confirmed by powder X-ray diffraction (Figure S7a).

[K(crypt-222)]₃[W^{IV}(CN)₇]·4CH₃CN (crypt-222 = [2.2.2]cryptand)

 $[K(crypt-222)]_3[W^{IV}(CN)_7] \cdot 4CH_3CN is synthesized by white light irradiation of the yellow solution$ of K₄[W^{IV}(CN)₈] · 2H₂O (234 mg, 0.4 mmol) and [2.2.2]-cryptand (565 mg, 1.5 mmol) in dryacetonitrile (5 mL) under an inert gas atmosphere (in the oxygen- and water-free glovebox).Upon white light irradiation the initial yellow solution becomes colourless without anyprecipitation. This solution affords colourless crystals after the slow vapor diffusion of diethylether (ca. 2 days). The obtained crystals were recrystallized in acetonitrile/diethyl ether inorder to remove residual [K(crypt-222)]CN byproduct. Purity of the sample was confirmed bypowder X-ray diffraction (Figure S22). Heptacyanotungstate(IV) anion obtained using the $photochemical approach closely resembles that in <math>(n-Bu_4N)_3[W^{IV}(CN)_7]$ prepared by reduction of $(n-Bu_4N)_3[W^{V}(CN)_8].^{S3}$

Single crystal X-ray diffraction

SCXRD experiments were performed for **1** and [K(crypt-222)]₃[W^{IV}(CN)₇]·4CH₃CN at 100 K using Bruker D8 Quest Eco diffractometer (Mo K α radiation, Triumph[®] monochromator). Single crystals were moved directly from mother liquor into the cryoprotectant to avoid loss of crystallization solvent. Absorption corrections, data reduction and unit cell refinements were performed using SADABS and SAINT programs included in the Apex3 suite. SCXRD experiments for **1anh** were performed at 30 K using synchrotron X-ray source (Diamond Light Source, United Kingdom) at the I19 beamline (EH2) equipped with Newport 4-circle κ -diffractometer, monochromatic X-ray synchrotron radiation ($\lambda = 0.6889$ Å) and Pilatus 300 K detector.⁵⁴ Absorption corrections, data reduction and unit cell refinement were performed using Xia2 and CrysAlisPRO software (Rigaku Oxford Diffraction, 2019).⁵⁵ The structures were solved using direct methods and refined anisotropically using weighted full-matrix least-squares on F^{2} .^{56,57} Hydrogen atoms of the ligands were placed in calculated positions and refined as riding on the parent atoms. Structural diagrams were prepared using Mercury CSD 2020.3.0.⁵⁸ Photocrystallography experiments were performed at 30 K using 453 nm laser as a light source. CCDC 2094734 (**1** right-handed), 2094735 (**1** left-handed), 2094736 (**1anh** right-handed) contain the supplementary crystallographic data for this paper which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Powder X-ray diffraction

PXRD data were obtained using Bruker D8 Advance diffractometer (Cu K α radiation, graphite monochromator) at room temperature for ground crystalline samples loaded into glass capillaries (0.7 mm in diameter). Results were subjected to background correction using the DIFFRAC algorithm implemented in the DIFFRAC.EVA V5 software. Pawley refinement of PXRD patterns was performed using GSAS-II software.⁵⁹

Thermogravimetric analysis

TGA was performed using a NETZSCH TG 209 F1 Libra under a flow of nitrogen (20 mL/min) and temperature scanning rate of 2°C/min.

Nitrogen adsorption measurements

Nitrogen adsorption experiment was performed at 77 K using Micromeritics 3Flex Adsorption Analyzer for 76 mg sample degassed in vacuum at 60 °C. BET surface was obtained for $0.008 < p/p_0 < 0.07$ range, while *t*-plot curve used for microporosity determination was constructed by applying Harkins-Jura isotherm to the $0.16 < p/p_0 < 0.43$ data.

Infrared spectroscopy

Infrared spectra were recorded using a Nicolet iN10 MX FT-IR microscope in the transmission mode (a small amount of powdered sample was spread on a BaF_2 pellet). Dehydration-rehydration experiments were performed with the use of a Linkam THMS350V temperature-controlled stage. For the sample dehydration it was purged with dry nitrogen at 60 °C and rehydration was performed by passing the water vapour over sample at 20 °C.

UV-Vis spectroscopy

UV-Vis spectra were measured in transmission mode for samples mixed with paraffin oil between two quartz slides using a Shimadzu UV-3600i Plus spectrophotometer equipped with an integrating sphere.

Magnetic and photomagnetic measurements

Magnetic susceptibility measurements were performed using a Quantum Design MPMS-3 Evercool magnetometer in magnetic fields up to 7 T for samples packed into Delrin sample holders.⁵¹⁰ The experimental data were corrected for the diamagnetism of the sample and the sample holder. Photomagnetic measurements were performed for samples placed between two layers of scotch tape and inserted into the plastic straw. **1anh** was prepared for photomagnetic measurements in the oxygen- and water-free glovebox to prevent its rehydration and **1** was inserted into the magnetometer and vacuum pumped below 240 K to avoid its dehydration. Irradiation was performed using 450 nm light produced by a laser diode (L450P1600MM; power at the sample position 6-10 mW/cm²).



Figure S1. Schematic representation of $[Mn(L)]^{2+}$ building unit used in synthesis of 1.

	1 (right-handed)	1 (left-handed)	1anh (right-handed)
CCDC	2094734	2094735	2094736
Formula	$C_{114}H_{150}Mn_6N_{54}O_{30}W_3$	$C_{114}H_{150}Mn_6N_{54}O_{30}W_3$	$C_{22.8}H_{30}Mn_{1.2}N_{10.8}W_{0.6}$
FW / g mol ⁻¹	3638.06	3638.06	631.61
Temperature / K	100(2)	100(2)	30(2)
Crystal system	Trigonal	Trigonal	Trigonal
Space group	P3 ₁ 21	P3221	P3 ₁ 21
a = b / Å	19.0123(5)	19.0231(5)	18.3685(4)
c / Å	12.4699(4)	12.4374(4)	12.3021(3)
V / ų	3903.6(2)	3897.8(2)	3701.1(2)
Z	1	1	5
$ ho_{ m calc}$ / g cm 3	1.55	1.55	1.42
Abs. coeff. / mm ⁻¹	2.75	2.75	2.63
F(000)	1824	1824	1584
Radiation source	Μο Κα	Μο Κα	Synchrotron
			(λ = 0.6889 Å)
Crystal size / mm	0.45 x 0.05 x 0.03	0.45 x 0.05 x 0.03	0.05 x 0.01 x 0.01
heta range / °	2.7-26.7	2.7-27.6	2.0-29.9
Reflections collected	16182	45889	29185
R _{int}	0.069	0.058	0.073
Parameters/restraints	316/163	316/175	255/176
GOF on F ²	1.04	1.08	1.06
R_1 (refl. with I > 2 σ (I))	0.053	0.040	0.063
wR ₂ (all reflections)	0.113	0.093	0.176
Largest diff. peak and hole / e Å ⁻³	1.42/-1.25	1.61/-1.67	1.42/-1.46
Flack parameter	0.020(8)	0.014(5)	-0.019(10)

 Table S1. Crystallographic data obtained from SCXRD for 1 and 1anh.

Table S2. Comparison of coordination bond lengths formed by manganese(II) in the structures of **1**, **1anh** and $[Mn^{II}(L)]Cl_2 \cdot 1.78EtOH \cdot 0.22H_2O$.

	1 (100 K)	1anh (30 K)	[Mn ^{II} (L)]Cl ₂ ·1.78EtOH·0.22H ₂ O (100 K; CCDC 646955)
Mn-N _{pyridine} / Å	2.300(12)	2.400(9)	2.347(2)
Mn-N _{imine1} / Å	2.328(11)	2.322(16)	2.345(2)
Mn-N _{imine2} /Å	2.364(12)	2.45(2)	2.349(2)
Mn-N _{amine1} /Å	2.410(16)	2.47(2)	2.428(2)
Mn-N _{amine2} /Å	2.350(10)	2.371(16)	2.394(2)
Mn-NC / Å	2.254(10)	2.211(11)	n/a
Mn-Cl / Å	n/a	n/a	2.5072(7), 2.6277(6)



Figure S2. Fragments of crystal structure of **1** showing manganese(II) coordination sphere in $P3_121$ crystal (a) and $P3_221$ crystal (b), as well as coordination helix in the framework of **1** in $P3_121$ crystal (c) and $P3_221$ crystal (d). W – red, Mn – purple, N – dark blue, C – grey.

Figure S3. TGA curve obtained for 1 at temperature scanning rate of 2°C/min.

Figure S4. Fragment of structure of compound **1** as seen along crystallographic *c* axis (water molecules and hydrogen atoms were omitted for clarity).

Figure S5. Fragment of structure of compound **1anh** as seen along crystallographic *c* axis (hydrogen atoms were omitted for clarity).

Figure S6. a) Comparison of experimental powder X-ray diffraction pattern for **1** (orange line) and the powder pattern calculated from the crystal structure (grey line). b) Experimental powder X-ray diffraction pattern at room temperature for **1** (orange points), Pawley refinement obtained for a = b = 19.1708(9) Å and c = 12.5857(4) Å unit cell, and the difference between the observed and the calculated powder pattern (blue line).

Figure S7. a) Comparison of experimental powder X-ray diffraction pattern for **1anh** (red line) and the powder pattern calculated from the crystal structure (grey line). b) Experimental powder X-ray diffraction pattern at room temperature for **1anh** (red points), Pawley refinement obtained for a = b = 18.770(3) Å and c = 12.409(1) Å unit cell, and the difference between the observed and the calculated powder pattern (blue line).

Figure S8. Evolution of the experimental PXRD pattern of **1** upon repetitive dehydration at 80°C (ambient atmosphere) and rehydration at room temperature (saturated water vapour).

Figure S9. Comparison of (41¹) peak broadening for **1** (orange points) and **1anh** (red points). The black line shows best fits to the pseudo-Voigt line profile $y = y_0 + A \left[\eta \cdot \frac{1}{\pi} \cdot \frac{\left(\frac{\Gamma}{2}\right)}{\left(x - x_0\right)^2 + \left(\frac{\Gamma}{2}\right)^2} + (1 - \eta) \cdot \sqrt{\frac{\ln 2}{\pi} \cdot \frac{2}{\Gamma} \cdot e^{\frac{4\ln 2\left(x - x_0\right)^2}{\Gamma^2}}} \right]$ with the following FWHM

parameters: a) Γ = 0.115(1) and b) Γ = 0.174(4).

Figure S10. Evolution of the IR spectrum of **1** upon repetitive dehydration at 60°C (dry nitrogen atmosphere) and rehydration at room temperature (saturated water vapour).

Figure S11. Comparison of room-temperature IR spectra for 1 (solid orange line) and $[Mn^{II}(L)]Cl_2 \cdot H_2O$ (dashed yellow line).

Figure S12. Nitrogen adsorption (full circles) and desorption (open circles) isotherms recorded for **1anh** at 77 K.

Figure S13. Solid state UV-Vis spectrum of $K_4[W^{IV}(CN)_8] \cdot 2H_2O$.

Figure S14. $\chi T(T)$ curves obtained for **1** (orange) and **1anh** (red) under $H_{DC} = 0.1$ T. Both **1** and **1anh** are characterised by similar room temperature χT values of 8.9 cm³ K mol⁻¹ expected for two non-interacting Mn^{II} centres per formula unit, but reach 7.5 and 7.1 cm³ K mol⁻¹ at 2.0 K for **1** and **1anh**, respectively. This is most probably caused by weak antiferromagnetic interactions between Mn^{II} ions. Solid black lines demonstrate the best fits to the Curie-Weiss law, which afford Weiss constant $\theta = -0.38$ K for **1** and $\theta = -0.56$ K for **1anh**.

Figure S15. M(H) curves for **1** (orange points) and **1** anh (red points) at T = 2.0 K. Both curves reach a saturation value of 9.9 N β , expected for non-interaction or weakly interacting Mn^{II} centres. Solid lines are guides for an eye.

Figure S16. $\chi T(t)$ curves obtained for **1** (orange) and **1anh** (red) upon 450 nm irradiation at T = 10 K and $H_{DC} = 0.1$ T.

Figure S17. Field-cooled magnetization curve for **1** before irradiation (black) and after 450 nm light irradiation (red).

Figure S18. Magnetic hysteresis recorded at T = 2.0 K for **1** after 450 nm irradiation at 10 K (red points) and after 2 hours of thermal relaxation at 300 K (blue points). Solid lines are guides for an eye.

Figure S19. M(H) curves at T = 2.0 K for **1anh** before light irradiation (black), after 450 nm light irradiation (red) and after 2 hours of thermal relaxation at 300 K (blue). Solid lines are guides for an eye.

Figure S20. $\chi T(T)$ curves obtained for **1anh** before light irradiation (black), after 450 nm light irradiation (red) and after 2 hours of thermal relaxation at 300 K (blue) under $H_{DC} = 0.1$ T.

Photomagnetic irreversibility and preparation of [W^{IV}(CN)₇]³⁻ via photochemical route

Photo-crystallography experiments using synchrotron radiation (Diamond Light Source, beamline 119) were performed on single crystals of **1anh** at 30 K. Despite several attempts, deterioration of a diffraction pattern was observed in all of the 453 nm irradiation experiments with 10-200 minutes irradiation intervals due to the loss of the single crystal integrity. Therefore, based on the slightly irreversible character of the photomagnetic effect in **1anh**, we hypothesize that it might proceed via the photodissociation mechanism proposed for $[Mo^{IV}(CN)_8]$ moiety – the 4*d* metal analogue of the octacyanotungstate(IV).^{S11} This mechanism relies on the reversible photodissociation of one of the CN⁻ ligands from the $[M^{IV}(CN)_8]^{4-}$ moiety to form a S = 1 $[M^{IV}(CN)_7]^{3-}$ species. In the case of **1anh** this photodissociation would be partly irreversible due to the presence of large pores, which may result in partial diffusion of the free cyanide too far away from the photo-induced $[W^{IV}(CN)_7]$ species.

In order to support our claim regarding the photodissociation mechanism of the photomagnetic effect in **1anh** and other $[W^{IV}(CN)_8]^{4-}$ -based compounds we have performed the white light irradiation experiment of the acetonitrile solution of $K_4[W^{IV}(CN)_8]\cdot 2H_2O$ at room temperature (the salt could be dissolved in this solvent in the presence of [2.2.2]-cryptand). After several hours, the yellow solution becomes colourless and the slow vapour diffusion of diethyl ether onto the reaction mixture yields crystals of $[K(crypt-222)]_3[W^{IV}(CN)_7]\cdot 4CH_3CN$ as the sole tungsten-based photoproduct, identified and confirmed by single-crystal and powder X-ray diffraction experiments (Table S3 and Figures S21-S22).

Figure S21. Fragment of the crystal structure of $[K(crypt-222)]_3[W^{IV}(CN)_7]\cdot 4CH_3CN$ showing the distorted pentagonal bipyramidal geometry of the $[W^{IV}(CN)_7]^{3-}$ anion and the three surrounding $[K(crypt-222)]^+$ cations (dimmed). MeCN and H-atoms are omitted or the sake of clarity (W – greenish blue, W – pink, C – grey, N – blue, O – red).

Figure S22. Comparison of the experimental powder X-ray diffraction pattern for $[K(crypt-222)]_3[W^{V}(CN)_7] \cdot 4CH_3CN$ (black line) and the powder pattern calculated from the crystal structure (grey line; please see also the deposited crystal structure file CCDC 2094737 and Table S3).

	[K(crypt-222)] ₃ [W ^{IV} (CN) ₇]·4CH ₃ CN	
CCDC	2094737	
Formula	$C_{34.5}H_{60}K_{1.5}N_{8.5}O_9W_{0.5}$	
FW / g mol ⁻¹	888.48	
Temperature / K	296(2)	
Crystal system	Monoclinic	
Space group	P2/c	
a / Å	14.2356(8)	
b / Å	12.1365(7)	
c / Å	25.4233(15)	
β / °	93.891(2)	
V / Å ³	4382.3(4)	
Z	4	
$ ho_{ m calc}$ / g cm ³	1.347	
Abs. coeff. / mm ⁻¹	1.53	
F(000)	1856	
Radiation source	Μο Κα	
Crystal size / mm	0.36 x 0.27 x 0.12	
heta range / °	2.4-25.7	
Reflections collected	43080	
R _{int}	0.056	
Parameters/restraints	491/12	
GOF on F ²	1.06	
R_1 (refl. with I > 2 σ (I))	0.034	
wR_2 (all reflections)	0.070	
Largest diff. peak and hole / e Å- ³	0.76/-0.53	

Table S3. Selected crystallographic data obtained from the SCXRD structural analysis for $[K(crypt-222)]_3[W^{IV}(CN)_7]\cdot 4CH_3CN$.

Bibliography:

[S1] D. Matoga, J. Szklarzewicz, M. Mikuriya, Inorg. Chem., 2006, 45, 7100–7104

[S2] A. Dees, A. Zahl, R. Puchta, N. J. R. van Eikema Hommes, F. W. Heinemann, I. Ivanović-Burmazović, *Inorg. Chem.*, 2007, **46**, 2459-2470

[S3] F. J. Birk, D. Pinkowicz, K. R. Dunbar, Angew. Chem. Int. Ed., 2016, 55, 11368

[S4] H. Nowell, S. A. Barnett, K. E. Christensen, S. J. Teat, D. R. Allan, *J. Synchrotron. Radiat.*, 2012, **19**, 435-441

[S5] G. Winter, J. App. Crystallogr., 2010, **43**, 186-190

[S6] G. Sheldrick, Acta Crystallogr. A, 2008, 64, 112-122

[S7] G. Sheldrick, Acta Crystallogr. C, 2015, **71**, 3-8

[S8] C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P.

Shields, J. S. Stevens, M. Towler, P. A. Wood, J. Appl. Crystallogr., 2020, 53, 226-235

[S9] B. H. Toby, R. B. Von Dreele, J. Appl. Crystallogr., 2013, 46, 544-549

[S10] M. Arczyński, J. Stanek, B. Sieklucka, K. R. Dunbar, D. Pinkowicz, *J. Am. Chem. Soc.*, 2019, **141**, 19067-19077

[S11] X. Qi, S. Pillet, C. de Graaf, M. Magott, E.-E. Bendeif, P. Guionneau, M. Rouzières, V. Marvaud, O. Stefańczyk, D. Pinkowicz and C. Mathonière, *Angew. Chem. Int. Ed.*, 2020, **59**, 3117-3121.