Conversion of a porous material based on a Mn^{II}–$TCNQF_4$ honeycomb net to a molecular magnet upon desolvation†

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Removal of methanol molecules from the interstices of a metal-organic framework based on a 2-D hexagonal Mn^{II}-$TCNQF_4$ net results in stronger magnetic interactions and leads to a glassy magnetically ordered state; the magnetic behavior can be reversibly cycled upon solvation-desolvation of the material.

Compounds that contain cyanide bridges have contributed to rapid growth of molecular magnetism over the past decade;[1a] these include magnetic materials based on organocyanide ligands such as 7,7,8,8-tetracyanoquinodimethane (TCNQ) which forms complexes with metal ions that exhibit interesting magnetic[1b,c] and electronic properties.[2,3a] The coordination chemistry of TCNQ is diverse,[4] as illustrated by the formation of 0-D complexes,[5] 1-D chains,[6] and 2-D nets.[3,7] The use of capping ligands that limit the growth of extended structures has led to such interesting compounds as a mononuclear spin crossover complex $[Fe^{II}(abpt)_2(TCNQ^{-\bullet})_2]$ (abpt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole)[5b] and a single-chain magnet $\{[Mn^{III}(5\text{-TMAMsaltmen})(\mu\text{-}TCNQ^{-\bullet})](ClO_4)_2\}_\infty$ (5-TMAMsaltmen = *N*,*N*′-(1,1,2,2-tetramethylethylene)-bis(5-trimethylammoniomethylsalicylideneiminato)).[6a] The use of unprotected metal ions leads to extended coordination frameworks. In this vein, we reported examples of the μ_4-TCNQ binding mode in 2-D networks with Cu^I,[3a] and $[M_2(O_2CCF_3)_4]^+$ (M = Ru, Rh)[7b] ions. We have also investigated the coordination chemistry of the tetrafluoro derivative of TCNQ, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$, Fig. 1(a)), and discovered 2-D frameworks based on μ_4-$TCNQF_4$ coordinated to Ag^I,[3b] and $[Ru_2(O_2CCF_3)_4]^+$,[7c] ions. The diruthenium compound, which was prepared in collaboration with the Miyasaka group, exhibits antiferromagnetic ordering at 95 K.[7c]

As an extension of our work with $TCNQF_4$, herein we report a Mn^{II} material, the structure of which consists of a honeycomb net based on a $[\mu_4\text{-}TCNQF_4]^{2-}$ dianion with free $[TCNQF_4]^{-\bullet}$ radical anions residing between the layers. This material behaves as a glassy magnet upon removal of interstitial solvent, and its magnetic properties can be repeatedly changed upon resolvation-desolvation cycles.

Methanol solutions of $[Mn(CH_3CN)_4(BF_4)_2]$ and $Li(TCNQF_4)$ were layered in a 1 : 1 ratio, and after slow diffusion for two weeks, dark blue crystals of the product‡ $\{[Mn_2(TCNQF_4)(CH_3OH)_{7.5}(H_2O)_{0.5}](TCNQF_4)_2\cdot 7.5CH_3OH\}_\infty$, $\mathbf{1}\supset 7.5CH_3OH$§ were harvested. An X-ray structural determination revealed that $\mathbf{1}\supset 7.5CH_3OH$ crystallizes as a 2-D distorted hexagonal network, in which one type of $TCNQF_4$ units is coordinated *via* all four cyano groups to Mn^{II} ions (Fig. 1(b)) and each Mn^{II} ion is bound to two different $TCNQF_4$ molecules in axial positions. Four methanol molecules in the equatorial sites complete the coordination sphere of each metal ion. The center of each μ_4-bridging $TCNQF_4$ coincides with an inversion center that relates the diagonally opposite Mn^{II} ions bound through the $TCNQF_4$ ligand. The 2-D honeycomb-like net consists of eight-membered rings of alternating Mn^{II} ions and $TCNQF_4$ ligands (Fig. 2(a)). Within each ring, two of the $TCNQF_4$ linkers make a five-atom bridge between metal centers while the other two make a ten-atom bridge, leading to the formation of a large opening, with metal–metal separations of Mn1–Mn1a 7.480 and Mn1a–Mn1b 11.515 Å (Fig. 1(b)). The longest Mn–Mn separation across the center of the eight-membered ring is 13.929 Å.

In addition to the coordinated $TCNQF_4$ molecules, the structure contains uncoordinated $TCNQF_4$ units. A pair of these molecules resides between μ_4-$TCNQF_4$ ligands of the consecutive layers, creating 1-D π–π stacks along the *a* axis (Fig. 2(b)). The interplanar distances are 3.03 Å between uncoordinated $TCNQF_4$ units and 3.24 Å between the uncoordinated $TCNQF_4$ and μ_4-$TCNQF_4$. The structure also contains large channels that run parallel to the *a* axis and are occupied by methanol molecules.

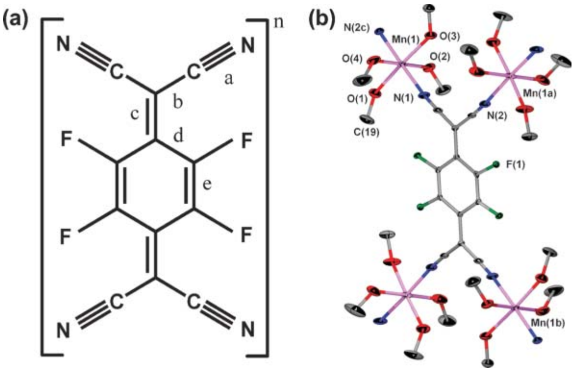

Fig. 1 (a) $TCNQF_4$ (*n* = charge). (b) A fragment of the honeycomb net in the crystal structure of $\mathbf{1}\supset 7.5CH_3OH$ showing a μ_4-$TCNQF_4$ ligand coordinated to four Mn^{II} ions. Hydrogen atoms are omitted for clarity. Mn = pink, C = gray, N = blue, O = red, F = green. Bond angles (°): O3–Mn1–O4 94.5(1), O3–Mn1–N1 86.5(1), O4–Mn1–N1 89.4(1), O3–Mn1–O2 86.1(1), N1–Mn1–O2 90.8(1), O3–Mn1–N2c 91.5(1), O4–Mn1–N2c 89.4(1), O2–Mn1–N2c 90.4(1). Symmetry operations used to generate atoms: Mn1a ($-x$, $y - ½$, $½ - z$), Mn1b ($-x$, $-y$, $1 - z$), N2c ($-x$, $½ + y$, $½ - z$).

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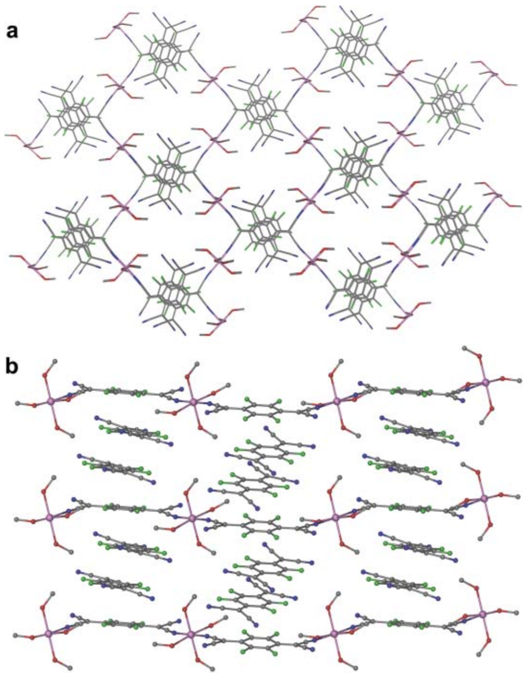

Fig. 2 (a) Crystal structure of **1**$\supset$7.5CH$_3$OH viewed down the *a* axis. (b) A view showing π–π stacking interactions in the crystal structure of **1**$\supset$7.5CH$_3$OH. The interstitial methanol molecules and hydrogen atoms are omitted for the sake of clarity. Colors are the same as in Fig. 1.

The charge ρ of each independent TCNQF$_4$ unit was estimated from the Kistenmacher relationship, $\rho = A[c/(b + d)] + B$ ($A = -46.729$ and $B = 22.308$; A and B are determined from neutral TCNQF$_4$ ($\rho = 0$)[8] and (n-Bu$_4$N)TCNQF$_4$ ($\rho = -1$)[3b]). The values of c, b and d are the TCNQF$_4$ bond lengths (Fig. 1(a)). The calculated values support the assignment of the bridging units as doubly reduced [TCNQF$_4$]$^{2-}$ ligands ($\rho = -2.09$), and the uncoordinated molecules as singly reduced [TCNQF$_4$]$^{-\bullet}$ radical anions ($\rho = -0.99$). Infrared (IR) spectroscopy is also useful for assigning the oxidation state of TCNQF$_4$ in its compounds.[3b,9,10b] The IR spectrum of the product exhibits three ν(CN) stretching modes at 2211, 2202 and 2161 cm^{-1}, all of which occur at lower frequencies than the corresponding features of neutral TCNQF$_4$ (2227 cm^{-1}). The absorptions at 2211 and 2202 cm^{-1} are in accord with the presence of the [TCNQF$_4$]$^{-\bullet}$ radical anion, whereas the stretch at 2161 cm^{-1} is evidence for the presence of the [TCNQF$_4$]$^{2-}$ dianion, as indicated by the similarity to the previously reported data for the doubly reduced species (2167 cm^{-1}).[10b] Therefore, as established by the structural and IR data, the present compound consists of an unusual combination of the cationic 2-D layer $\{[(\mathrm{Mn^{II}})_2(\mu_4\text{-}[\mathrm{TCNQF_4}]^{2-})(\mathrm{CH_3OH})_{7.5}(\mathrm{H_2O})_{0.5}]^{2+}\}_\infty$ co-crystallized with the radical anion [TCNQF$_4$]$^{-\bullet}$ (Fig. 2(b)). It should be mentioned that there is no evidence of the presence of the dianion in the starting material, Li(TCNQF$_4$), based on the IR data that revealed only a ν(CN) stretch at 2198 cm^{-1}, which corresponds to the radical anion. Clearly the dianion was generated by disproportionation of the radical [TCNQF$_4$]$^{-\bullet}$, as previously observed by others.[11,12]

In general, instances of fully characterized [TCNQF$_x$]$^{2-}$ dianions (x = 0–4) are rare. Previously reported structurally characterized examples include the charge-transfer salts ([Cp*$_2$M]$^{+\bullet}$)$_2$[TCNQF$_x$]$^{2-}$ (M = Co, Fe; x = 0, 4),[10] discrete complexes ([Cp$_2$V]$^{+\bullet}$)$_2$[TCNQ]$^{2-}$[B(C$_6$F$_5$)$_3$]$_2$ and {[Cp$_2$V]$^{2+}$[TCNQ]$^{2-}$[B(C$_6$F$_5$)$_3$]$_2$}$_2$,[13] an infinite chain [Mn$^{\mathrm{III}}$(salen)(TCNQ^{2-})$_{0.5}$][Mn$^{\mathrm{III}}$(salen)(TCNQ^{2-})$_{0.5}$(CH$_3$OH)],[6b] and a 3-D framework {[Zn$^{\mathrm{II}}$(μ_4-TCNQ^{2-})bpy]}$_\infty$.[11]

The 2-D net in **1**$\supset$7.5CH$_3$OH is topologically identical to that found in {[M$_2$(O$_2$CCF$_3$)$_4$]$_2$(TCNQ)·3(C$_7$H$_8$)}$_\infty$ (M = Ru, Rh).[7b] The latter structures contain partially reduced μ_4-TCNQ$^{\delta-}$, with $\delta = -0.42$ and -0.63, respectively. The μ_4-TCNQ linkers are σ-bonded to the axial positions of the dimetal units, in a similar fashion to the binding of μ_4-TCNQF$_4$ to the axial positions of octahedral Mn$^{\mathrm{II}}$ ions in **1**$\supset$7.5CH$_3$OH.

To prevent the loss of interstitial solvent, magnetic susceptibility measurements of **1**$\supset$7.5CH$_3$OH were performed on a sample covered with methanol in a sealed tube. Measurements were performed at 1000 Oe from 1.8 to 300 K with the use of a SQUID magnetometer. The value of χT at 300 K is 9.5 emu mol^{-1} K, which corresponds to the expected spin-only value for two non-interacting Mn$^{\mathrm{II}}$ ions (S = 5/2, g = 2.0) and two [TCNQF$_4$]$^{-\bullet}$ radicals (S = 1/2, g = 2.0). As the temperature is lowered, the χT value decreases smoothly, indicating the presence of a weak antiferromagnetic interaction (Fig. 3). The data were fitted to the Curie–Weiss law with parameters $\theta = -1.7$ K and C = 9.5 emu mol^{-1} K, values which indicate that the magnetic coupling between Mn$^{\mathrm{II}}$ ions propagated by the [TCNQ]$^{2-}$ dianions is, as expected, very weak.

Next, the polycrystalline sample was filtered and dried *in vacuo* for 4 h. The magnetic behavior of this dry sample (**1a**) was found to be remarkably different. When the temperature is decreased, the χT value gradually increases from 9.5 emu mol^{-1} K at 300 K to a maximum of 18 emu mol^{-1} K at ~11 K (Fig. 3), which indicates the presence of ferromagnetic interactions. Below 10 K, χT abruptly decreases, suggesting the possibility of a magnetic phase transition. Evidence for the phase transition was obtained by ac susceptibility and field-cooled (FC) - zero-field-cooled (ZFC) magnetization measurements. FC and ZFC dependences coincide down to T_c = 5 K (Fig. 3, inset), below which temperature they diverge, suggesting spin-glass behavior. The zero-field AC susceptibility measurements performed in the range of frequencies from 1 to 1000 Hz at H_{AC} = 3 Oe show a broad frequency-dependent out-of-phase signal below T_c (Fig. 4). The Mydosh

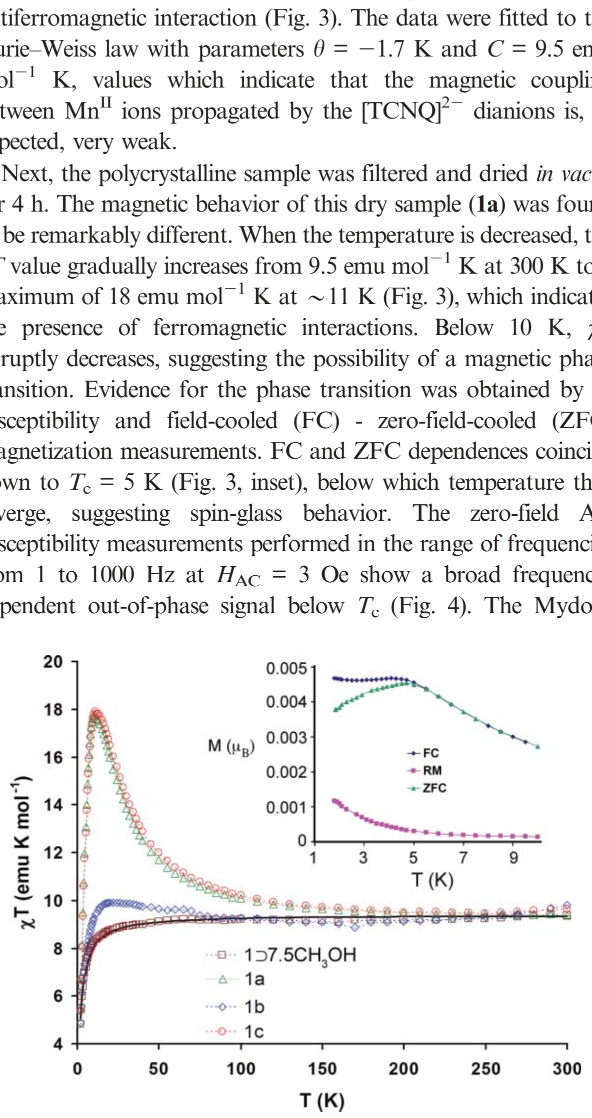

Fig. 3 Temperature dependence of the χT product for **1**$\supset$7.5CH$_3$OH and **1a–c**. The solid black line is the best fit to the Curie–Weiss law for **1**$\supset$7.5CH$_3$OH. Inset: FC and ZFC curves for **1a**.

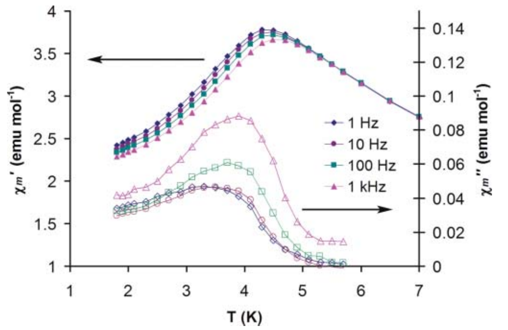

Fig. 4 Temperature dependences of the real χ' and imaginary χ'' components of the ac magnetic susceptibility of **1a** measured in an oscillating field of 3 Oe at different frequencies.

parameter estimated from this dependence, ϕ = 0.023, is characteristic of a spin-glass phase.[14] Hysteresis was observed at 1.8 K with coercivity of ~100 Oe and remnant magnetization of 0.06 μ_B (ESI,† Fig. S1).

The dry sample **1a** was then immersed in methanol for 12 h and the resulting sample (**1b**), covered with methanol in a sealed tube, no longer showed an out-of-phase AC signal (ESI,† Fig. S2). The DC χT values at low temperatures decreased considerably from those observed for **1a**, but did not completely reverse back to the values observed for $\mathbf{1}\supset 7.5CH_3OH$ (Fig. 3). Thus, after re-solvation, the short-range ferromagnetic interactions become much weaker, while the spin-glass ordering is destroyed. Sample **1b** was filtered and once again dried *in vacuo* for 4 h. The obtained dry sample (**1c**) again showed an increase in the χT values below 150 K (Fig. 3) and the presence of a broad frequency-dependent signal in the χ'' *vs.* T dependence (ESI,† Fig. S2), resembling the behavior observed for **1a**. This indicates that upon removal of guest molecules the magnetic glassiness of the host is recovered. Reversible changes in magnetic properties upon desolvation-resolvation of coordination frameworks have been observed in several cases, and the name “magnetic sponges” was proposed for such materials.[15]

The dry sample **1a** is a different phase, as shown by comparison of its X-ray powder diffraction pattern to the theoretically simulated pattern of $\mathbf{1}\supset 7.5CH_3OH$ (ESI,† Fig. S3). The powder diffraction data reveal that, not surprisingly, the material has poor crystallinity in the dried state as well. As was stated above, the $[TCNQF_4]^{2-}$ dianion is a poor mediator of magnetic coupling between Mn^{II} ions. On the other hand, it is known that the $[TCNQF_4]^{-\bullet}$ radical provides an efficient pathway for magnetic superexchange between metal ions.[1b,c,7c] It is possible that desolvation of $\mathbf{1}\supset 7.5CH_3OH$ also leads to the loss of some coordinated methanol molecules with subsequent structural rearrangement and binding of uncoordinated $[TCNQF_4]^{-\bullet}$ radicals to the Mn^{II} ions, which would result in stronger magnetic communication, as observed for samples **1a** and **1c**. The five-atom bridge Mn–N≡C–C–C≡N–Mn involving the $[TCNQF_4]^{-\bullet}$ radical would provide an efficient pathway for ferromagnetic superexchange between Mn^{II} ions. Furthermore, the similarity of the honeycomb nets present in $\mathbf{1}\supset 7.5CH_3OH$ and $\{[M_2(O_2CCF_3)_4]_2\text{-}(TCNQ)\cdot 3(C_7H_8)\}_\infty$ (M = Ru, Rh)[7b] suggests that 2-D structures could be formed with both $[TCNQF_x]^{2-}$ dianions and $[TCNQF_x]^{-\bullet}$ radicals. It would be interesting to prepare other materials with first-row transition metals and μ_4-$[TCNQF_x]^{-\bullet}$ radicals and compare their magnetic properties to those of $\mathbf{1}\supset 7.5CH_3OH$. Efforts to this end are currently in progress.

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Notes and references

‡ $[Mn(CH_3CN)_4(BF_4)_2]$, $TCNQF_4$ and $Li(TCNQF_4)$ were prepared according to the reported procedures.[16] All reactions were performed under nitrogen using standard Schlenk techniques. Single crystals of $\mathbf{1}\supset 7.5CH_3OH$ were obtained by layering a solution of $[Mn(CH_3CN)_4(BF_4)_2]$ (150 mg in 4 mL of distilled methanol) with $Li(TCNQF_4)$ (108 mg in 12 mL of distilled methanol) in a Schlenk tube (yield = 3.4%). IR (Nujol): ν_{max}/cm^{-1} 2211m, 2202s, 2161m (CN).

§ *Crystal data*: $C_{51}H_{61}F_{12}Mn_2N_{12}O_{15.5}$, M = 1428.00, monoclinic, $P2_1/c$, a = 9.538(2), b = 14.957(3), c = 23.021(4) Å, β = 91.399(3)°, V = 3283(1) Å^3, Z = 2, Mo-Kα radiation (λ = 0.71073 Å), 110 K, F_{000} = 1466, GooF = 1.057, a total of 28531 reflections collected, 7962 unique (R_{int} = 0.0744); $R1$ = 0.0768, $wR2$ = 0.1605 for 486 parameters/20 restraints [$I > 2\sigma(I)$]. CCDC 619045. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b710149j

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