Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Associated Content:
Electronic Supplementary Information (ESI)

Table S1. Crystallographic data for compounds **1** and **2**.

Compound	1	2
Empirical formula	$C_{176}H_{312}Mn_2Mo_{12}N_{34}O_{61}$	$C_{38}H_{44}Fe_2MnMo_6N_{14}O_{32}$
Formula weight	5141.74	1951.15
Crystal colour	Yellow	Red
Crystal size (mm^3)	0.16×0.10×0.06	0.06×0.05×0.04
Temperature (K)	120(2)	180(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, *Z*	Monoclinic, 2	Monoclinic, 4
Space group	*P* $2_1/n$	*C* 2/*c*
a (Å)	18.6735(2)	24.221(5)
b (Å)	21.7084(2)	16.600(3)
c (Å)	28.6619(4)	16.512(3)
α (°)	90	90
ß (°)	108.8700(10)	97.76(2)
γ (°)	90	90
V ($Å^3$)	10994.3(2)	6578(2)
ρ_{calc} (Mg/m^3)	1.553	1.970
$\mu(Mo_{K\alpha})$ (mm^{-1})	0.853	1.811
θ range (°)	2.807-27.511	2.947-24.667
Reflns collected	233469	13209
Independent reflns (R_{int})	18504(0.0936)	2398(0.1229)
L. S. parameters, *p*/ restraints, *r*	1310 / 0	280 / 2
$R1(F)$,[a] $I > 2\sigma(I)$	0.0436	0.0953
$wR2(F^2)$,[b] all data	0.1083	0.3045
$S(F^2)$,[c] all data	1.034	0.991

[a] $R1(F) = \Sigma||F_O|-|F_C||/\Sigma|F_O|$; [b] $wR2(F^2) = [\Sigma w(F_O^2-F_C^2)^2/\Sigma wF_O^4]^{1/2}$; [c] $S(F^2) = [\Sigma w(F_O^2-F_C^2)^2/(n+r-p)]^{1/2}$

Table S2. High-frequency EPR spectra performed on compound **1**.

ν (GHz)	T (K)	Field range (T)
100	10	0-15
110	10	0-15
180	10	0-15
200	10	0-15
220	10	0-15
240	10	0-15
250	10	0-1
255	10	0-1
260	2, 5, 10, 20, 40	0-15
300	10	0-15
330	2, 5, 10, 20, 40	0-15
370	10	0-15

Table S3. Calculated values from the fitting to an Arrhenius law of the pre-exponential factors (τ_0) and the activation energies (E_a) of **1**, **2**, **3** and **4** under an applied field of 0.5 T.

Compound	τ_0 (s)	E_a (cm^{-1})
1	$7 \pm 1\ 10^{-9}$	13.1 ± 0.4
2	$1.1 \pm 0.5\ 10^{-8}$	13.1 ± 0.3
3	$3 \pm 2\ 10^{-8}$	11.4 ± 2
4	$2 \pm 1\ 10^{-9}$	16 ± 2

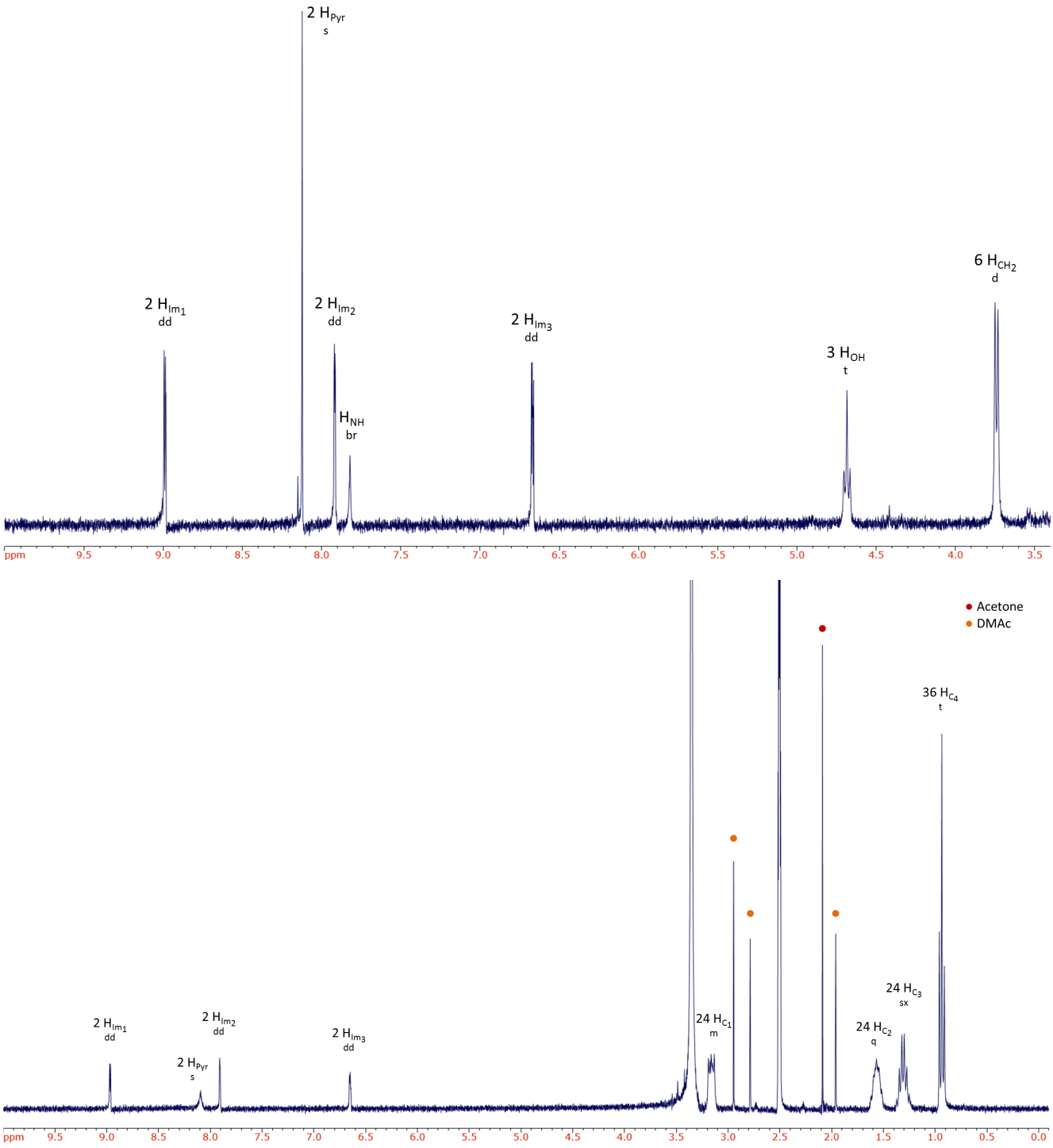


Figure S1. ^{1}H NMR spectra of TRIS-bpp (up) and **1** (bottom).

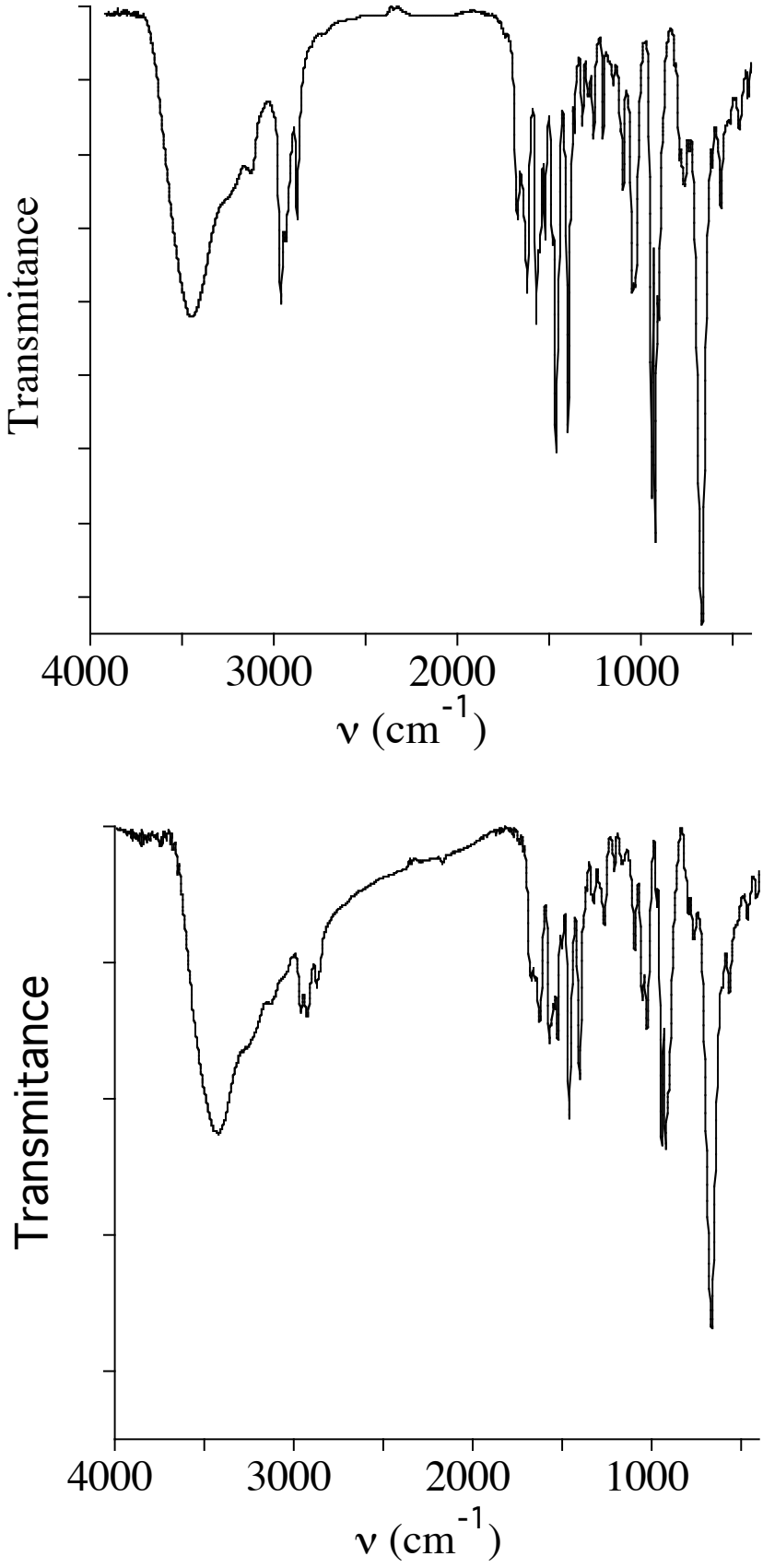


Figure S2. IR spectrum of **1** (top) and **3** (bottom).

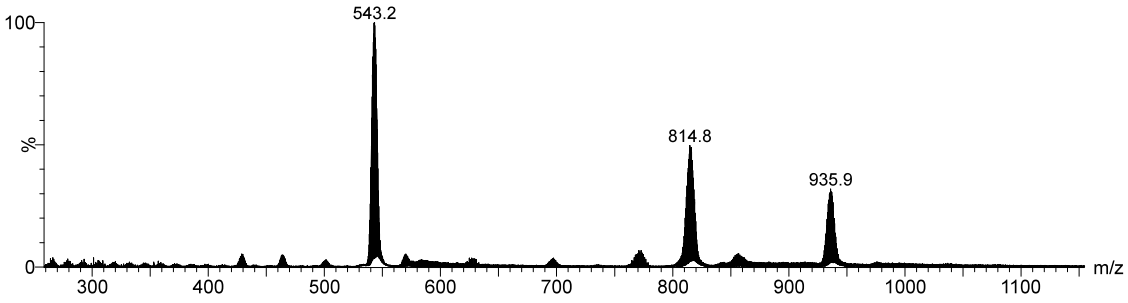


Figure S3. ESI mass spectrum of acetonitrile solutions of compound **1** recorded at Uc = 5 V.

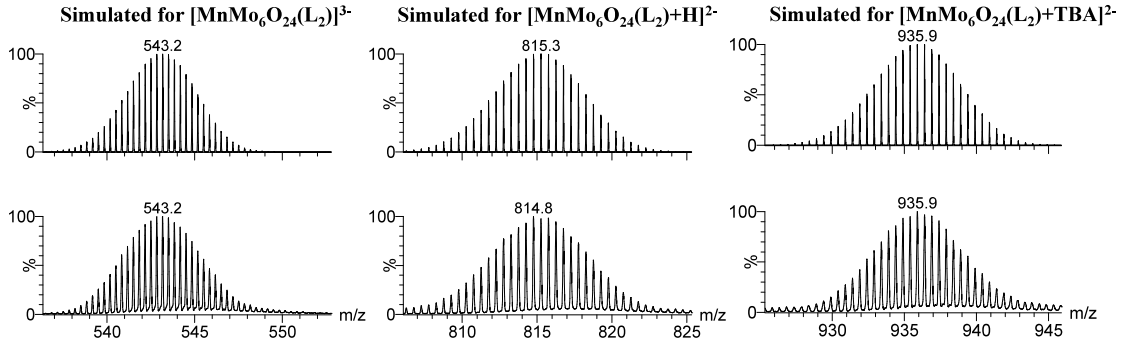


Figure S4. Simulated (top) and experimental (bottom) isotopic distribution for the identified species, $[\mathbf{1}]^{3-}$ (left), $[\mathbf{1} + H]^{2-}$ (center) and $[\mathbf{1} + TBA]^{2-}$ (right).

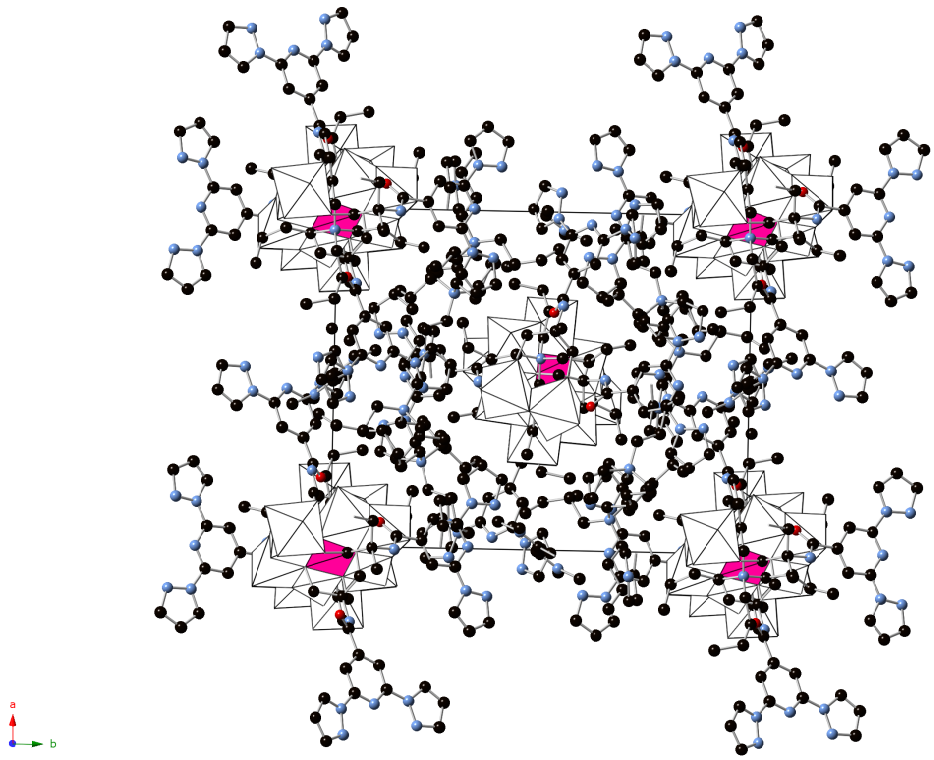


Figure S5. Projection of the structure of **1** in the *ab* plane. (Mn (pink), Mo (white), C (black), N (blue), O (red)). Hydrogen atoms have been omitted for clarity.

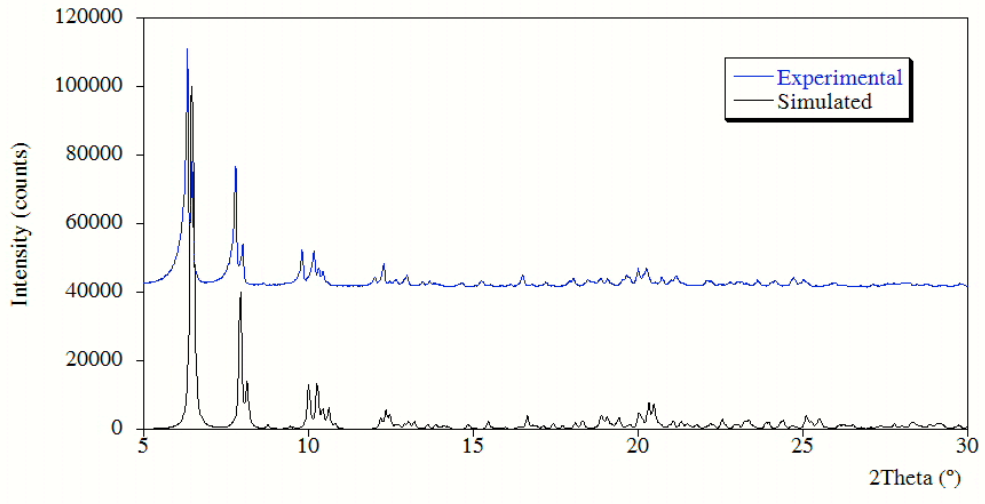


Figure S6. Experimental (top) and simulated (bottom) X-ray powder diffraction patterns of **1**.

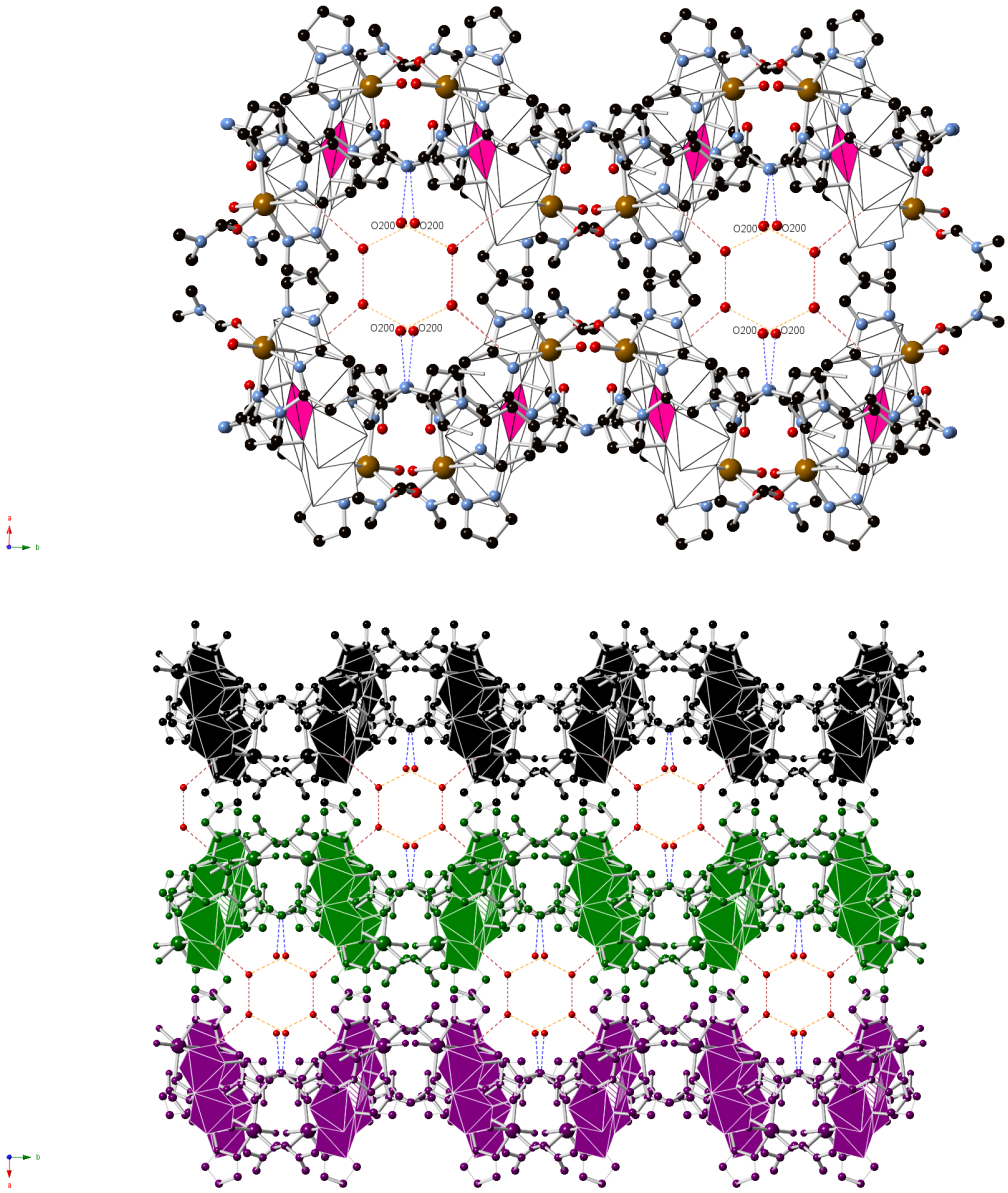
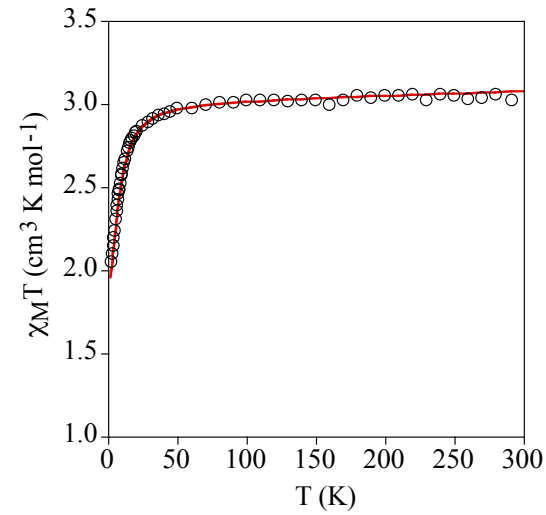
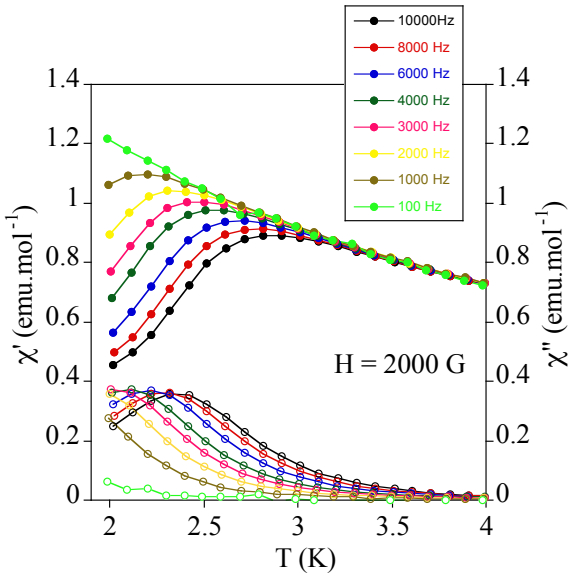


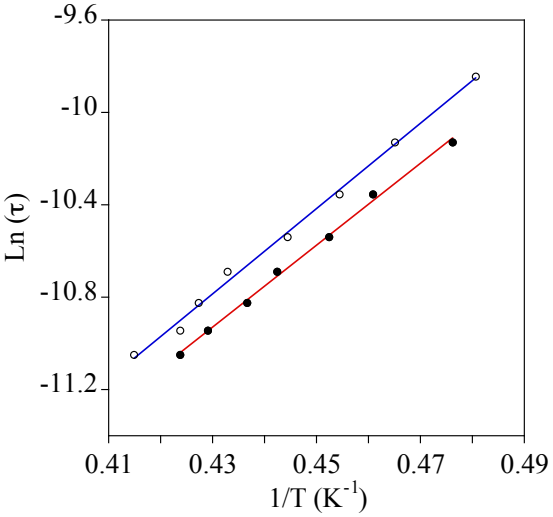
Figure S7. Projection of the structure of **2** in the *ab* plane (Mn (pink), Mo (white), Fe (yellow), C (black), N (blue), O (red)) (top) and view of three covalently-bonded layers with different colours (bottom). Hydrogen atoms have been omitted for clarity. Dashed lines correspond to the hydrogen bonds. O200 is the OH^- group.



(a)

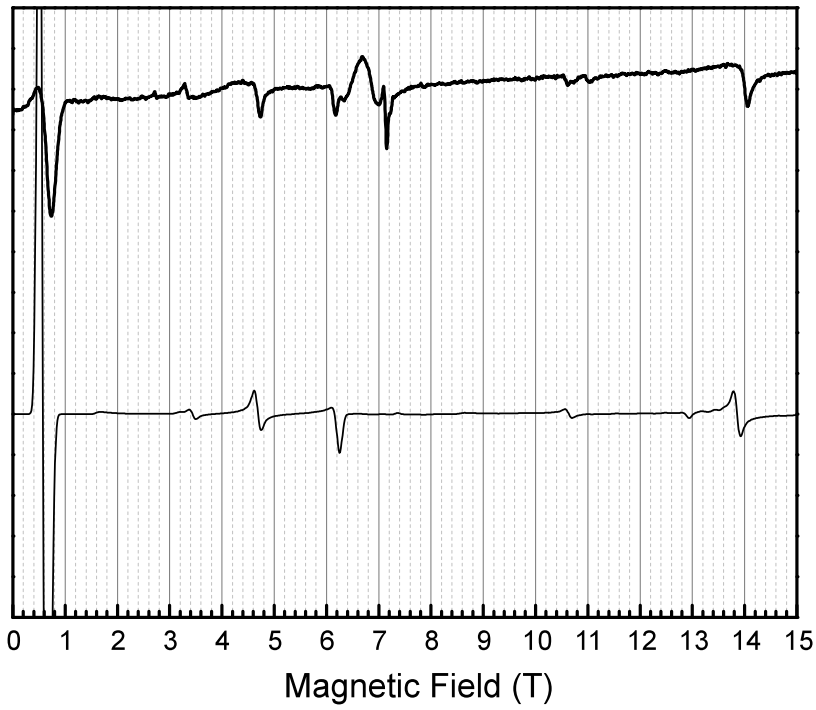


(b)

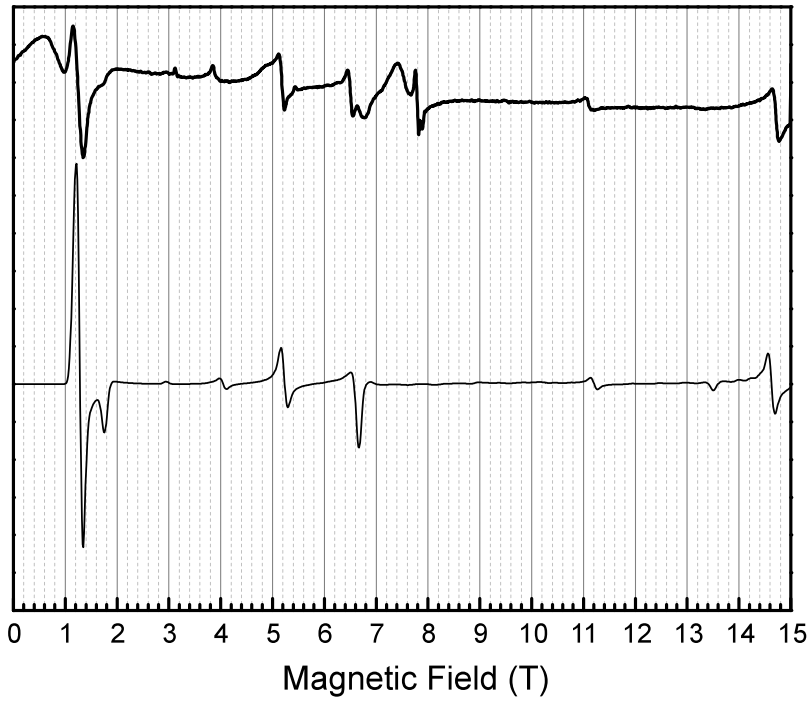


(c)

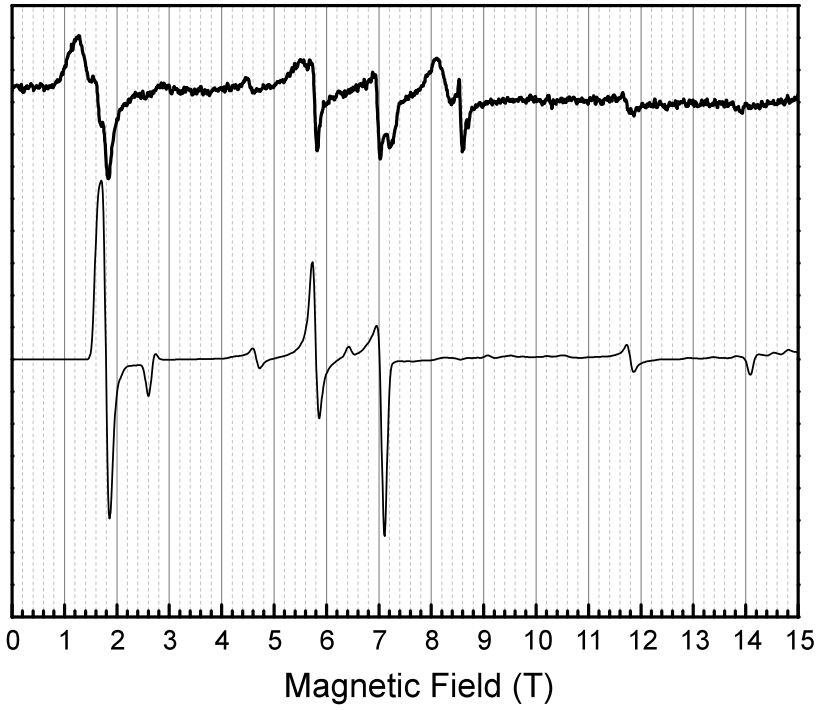
Figure S8. Temperature dependence of $\chi_m T$ of **1** (a). The continuous line corresponds to the fit (see the text for details). Temperature dependence of the in-phase AC susceptibility (χ_m') (filled symbols) and the out-of-phase AC susceptibility (χ_m") (empty symbols) of **1** under an applied field of 0.2 T (b). Arrhenius plots of AC measurements of **1** under an applied field of 0.2 T (full circles) and 0.5 T (empty circles) (c).


0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Magnetic Field (T)

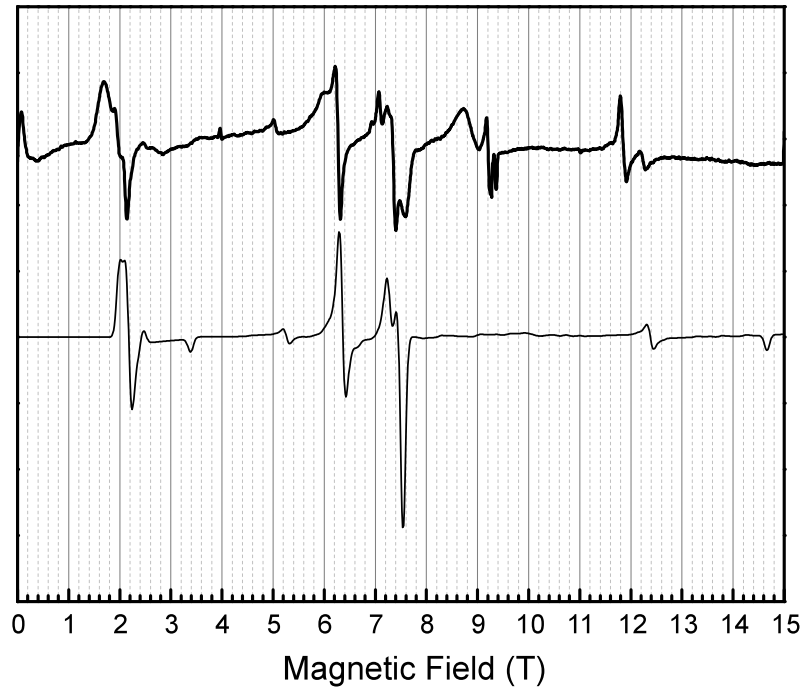
(a)


0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Magnetic Field (T)

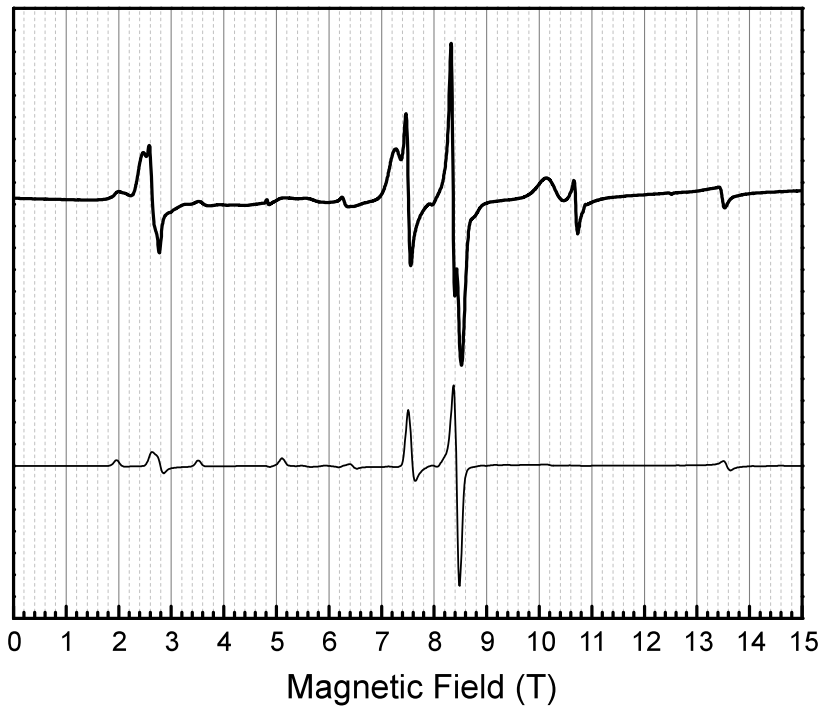
(b)


0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Magnetic Field (T)

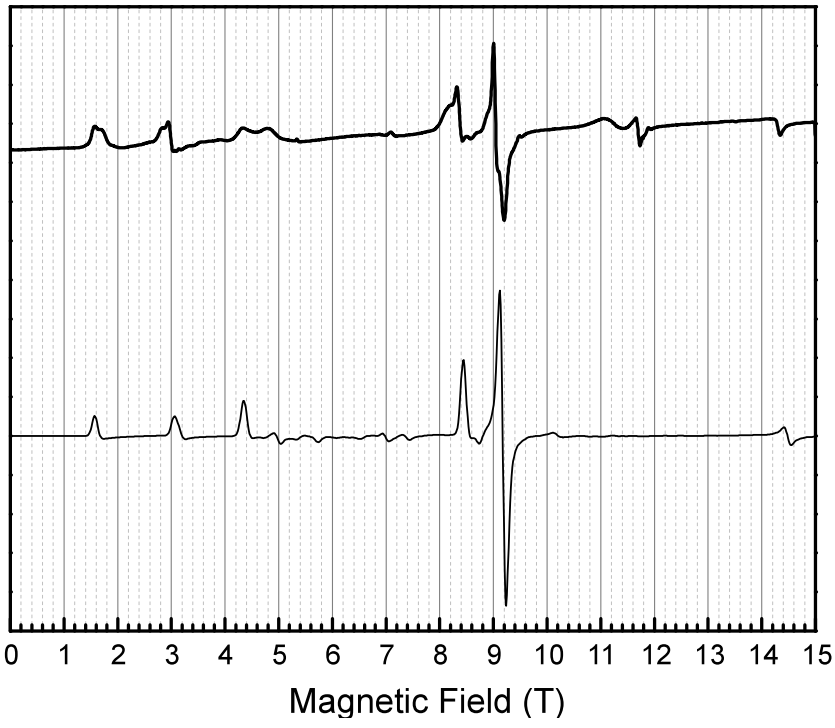
(c)


0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Magnetic Field (T)

(d)



(e)



(f)

Figure S9. HF-EPR spectra of **1** (bold: experiment, thin: simulation) at 200 GHz (a), 220 GHz (b), 240 GHz (c), 260 GHz (d), 300 GHz (e) and 330 GHz (f) and 10 K. Note that the strong signals at 6.8 T (a), 7.6 T (b), 8.3 T (c), 9 T (d), 10.5 T (e) and 11.4 T (f) are at g = 2 and caused by some impurity.

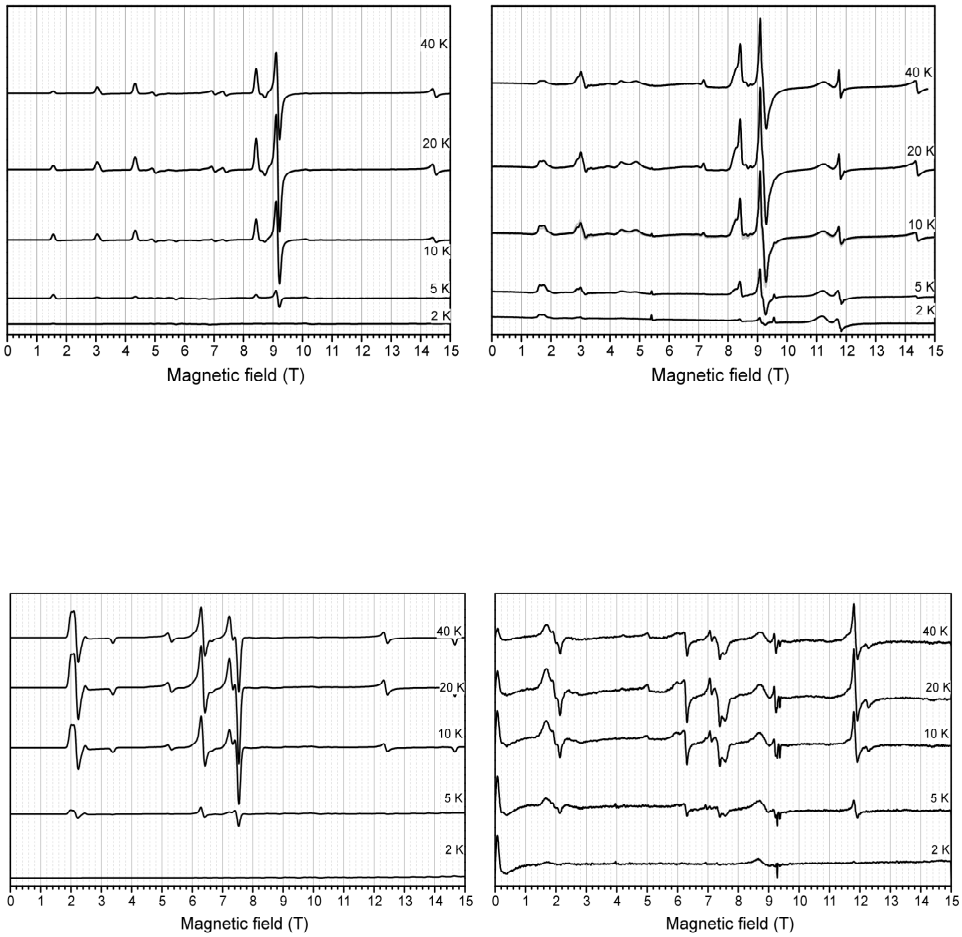


Figure S10. Temperature dependence of the HF-EPR spectra of **1**. The left figures show the simulations for 330 GHz (upper) and 260 GHz (lower). The right figures show the experimental data at the same frequencies.

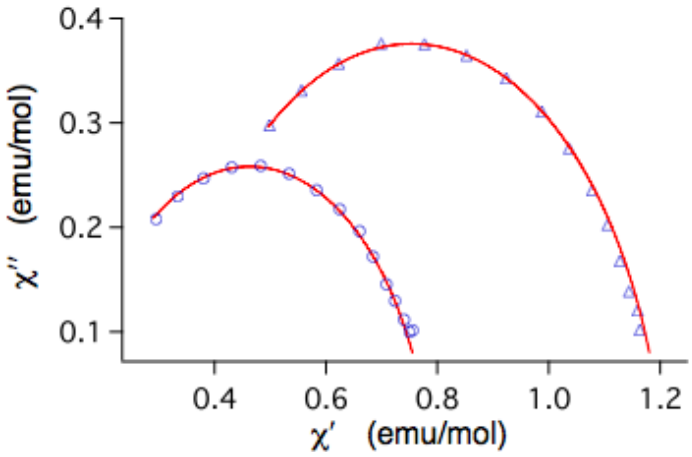
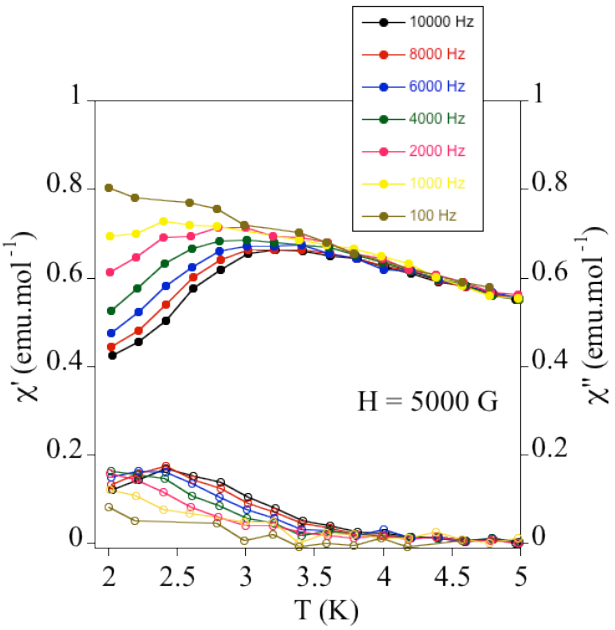
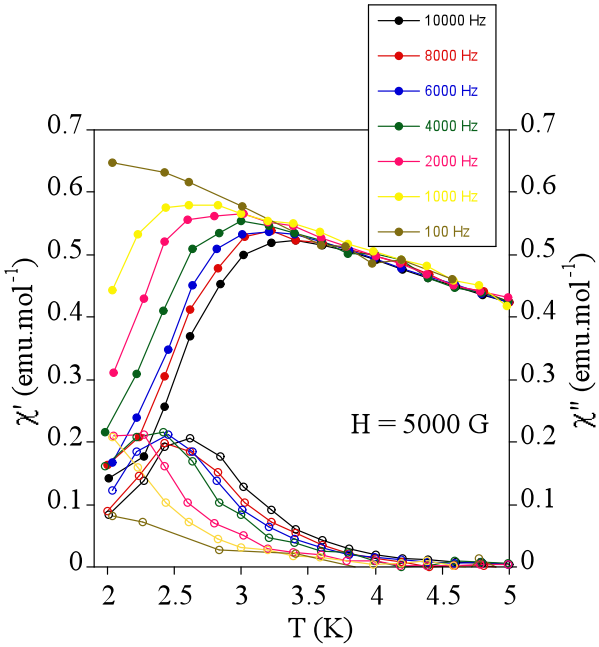


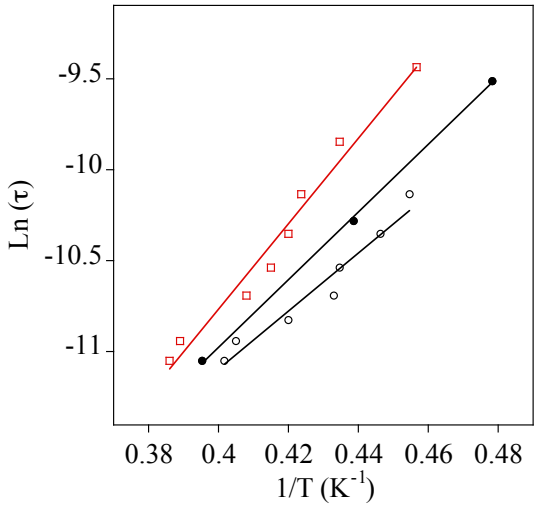
Figure S11. Cole-Cole plots at 2.1 K of **1** under applied magnetic fields of 0.2 T (empty circles) and 0.5 T (empty triangles). The red lines are the best fit-curves.



(a)



(b)



(c)

Figure S12. Temperature dependence of the in-phase AC susceptibility (χ_m') (filled symbols) and the out-of-phase AC susceptibility (χ_m") (empty symbols) of **3** (a) and **4** (b) under an applied field of 0.5 T. Arrhenius plots of **2** (full circles), **3** (empty circles) and **4** (red empty squares) under an applied field of 0.5 T (c).