Supporting information

for

Multifunctional magnetic material based on a solid solution of Fe(II)/Co(II) complexes with macrocyclic cyclam-based ligand

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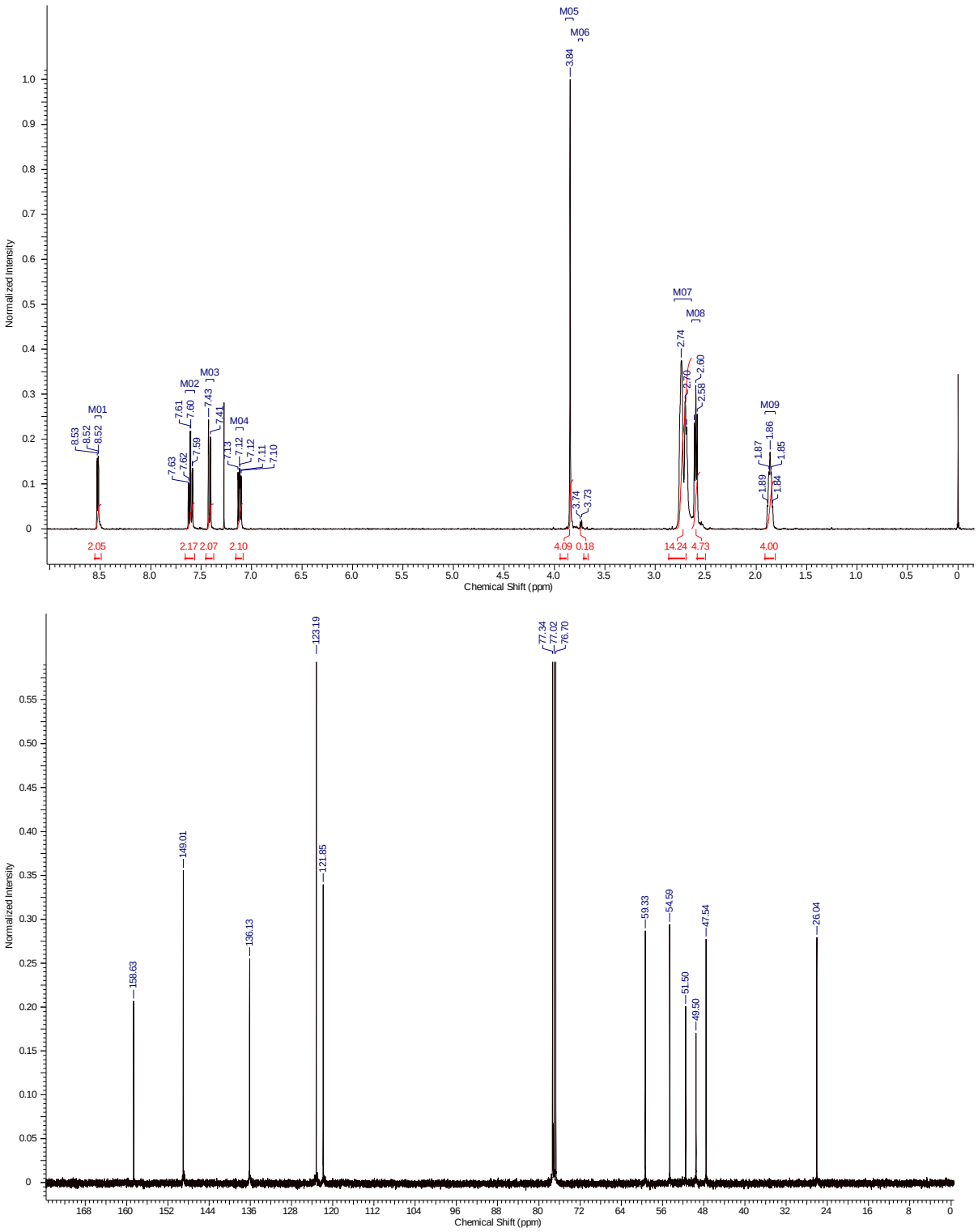

Figure S1 ^{1}H and ^{13}C NMR spectra (400 MHz, $CDCl_3$) of **Py$_2$-C** (*1,8-bis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane*) with the residual peak of $CHCl_3$ at 7.24 ppm (^{1}H) and $CDCl_3$ at 77.0 ppm (^{13}C).

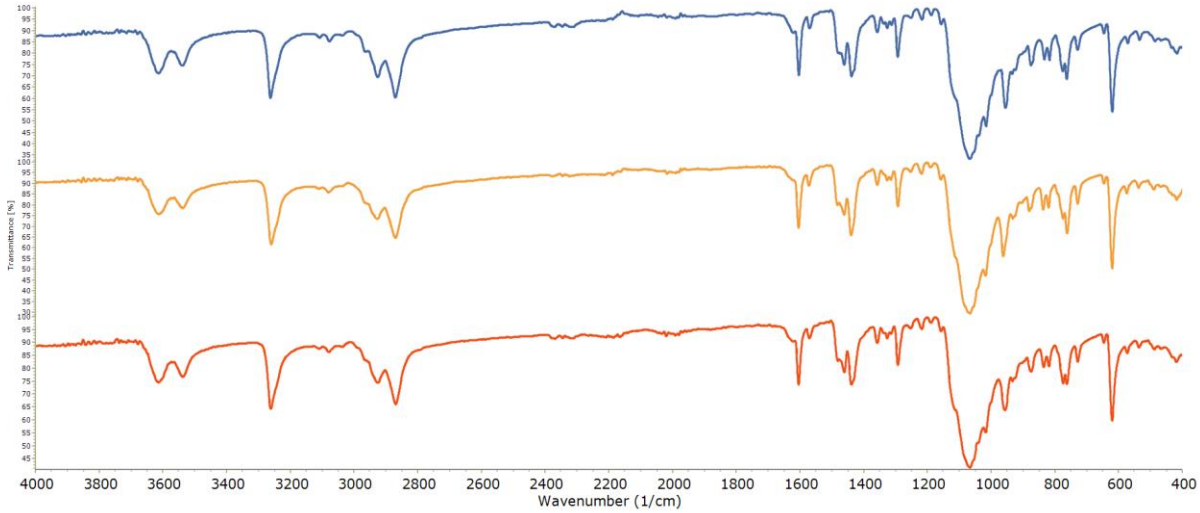

Figure S2 IR spectra of studied complexes **1** (*blue*), **2** (*yellow*) and **3** (*red*).

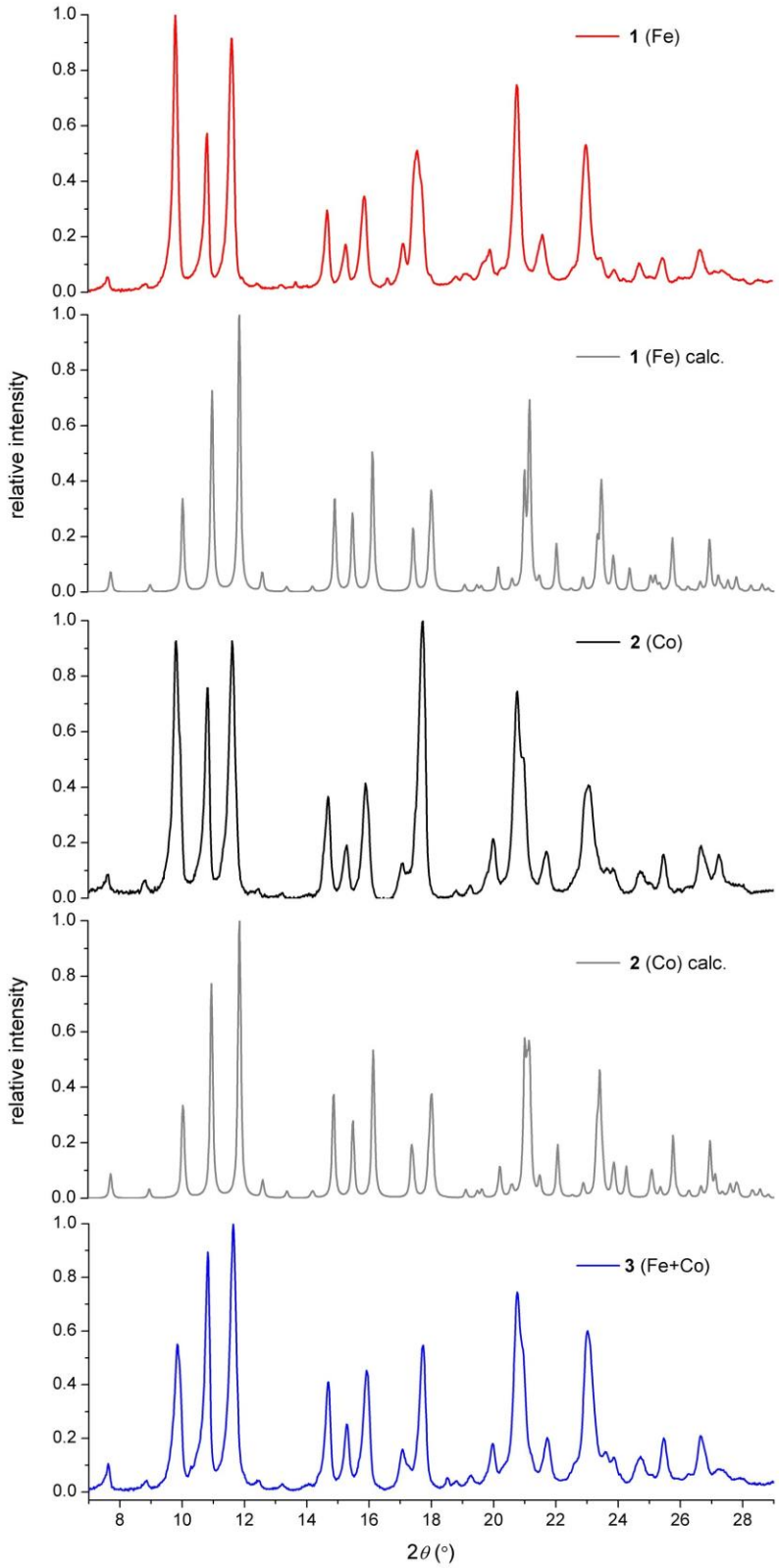

Figure S3 X-ray powder diffraction pattern of studied complexes **1**–**3** together with patterns for **1** (250 K) and **2** (120 K) calculated from the single-crystal data.

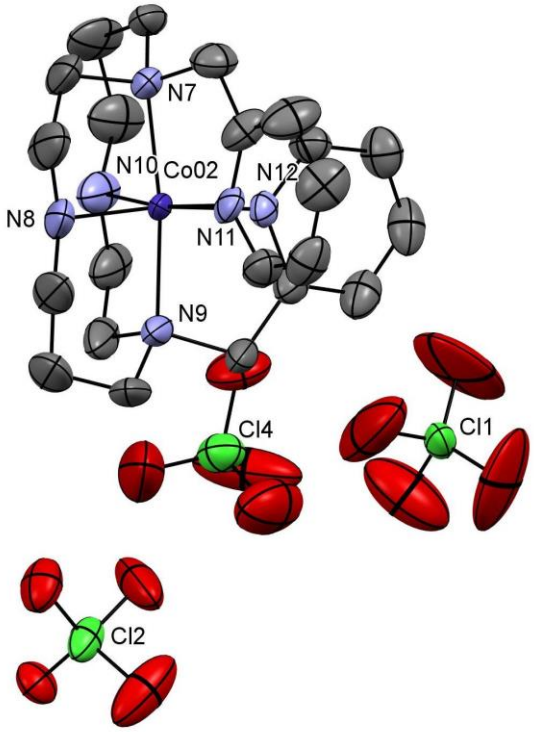

Figure S4 The molecular structure of the complex [Co(**Py2–C**)]$(ClO_4)_3$ (**2b**). Non-hydrogen atoms are drawn as thermal ellipsoids at the 50% probability level. Hydrogen atoms were omitted for clarity. Only one of the two crystallographically independent molecules found in the asymmetric unit is shown.

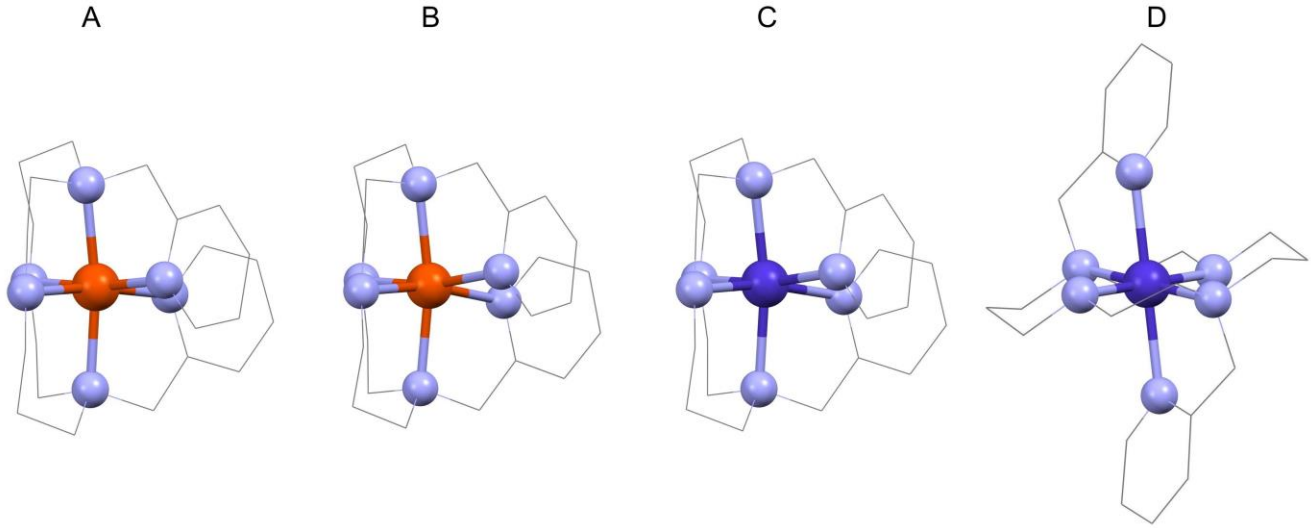

Figure S5 Comparison of the molecular structures of complexes **1** (A – at 120 K, B – at 250 K), **2** (C) and **2a** (D) with the highlighted/visualized chromophore {FeN_6} or {CoN_6}. Hydrogen atoms were omitted for clarity.

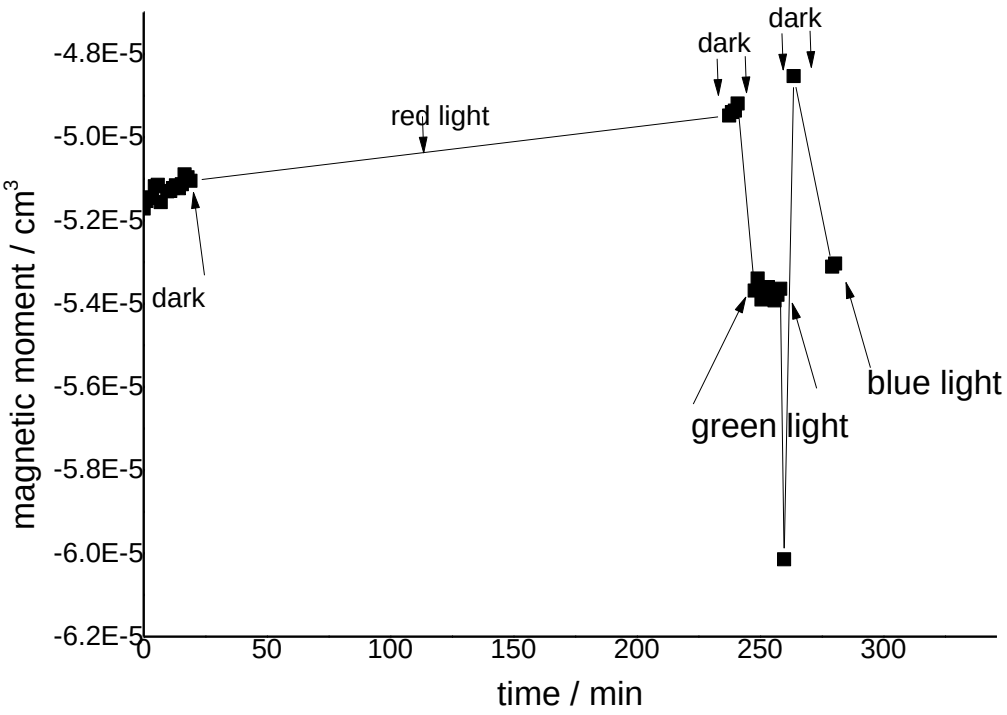

Figure S6 Photomagnetic experiments with **1** at 5 K and B_{DC} = 0.1T. Red (637 nm), green (532 nm) or blue (405 nm) laser light was used for the irradiation of sample, the power of light was adjusted to 10 mW/cm^2.

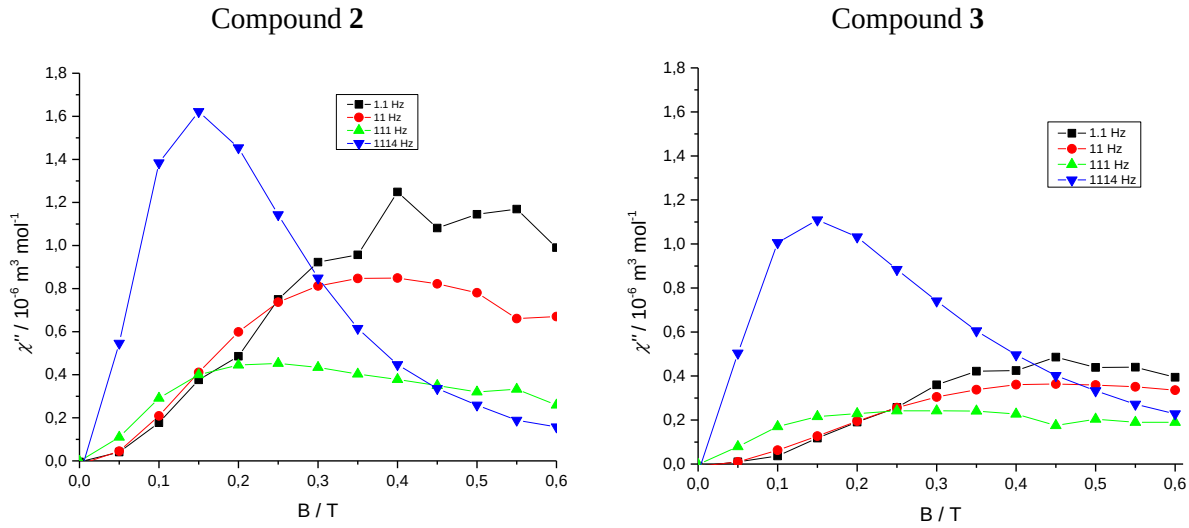

Figure S7 The mapping of the magnetic susceptibility components as functions of the applied external DC field for a set of four frequencies of the AC field (f = 1.1, 11, 111, and 1114 Hz) at T = 2.0 K for compounds **2** and **3**. Solid lines are only guides for the eyes.

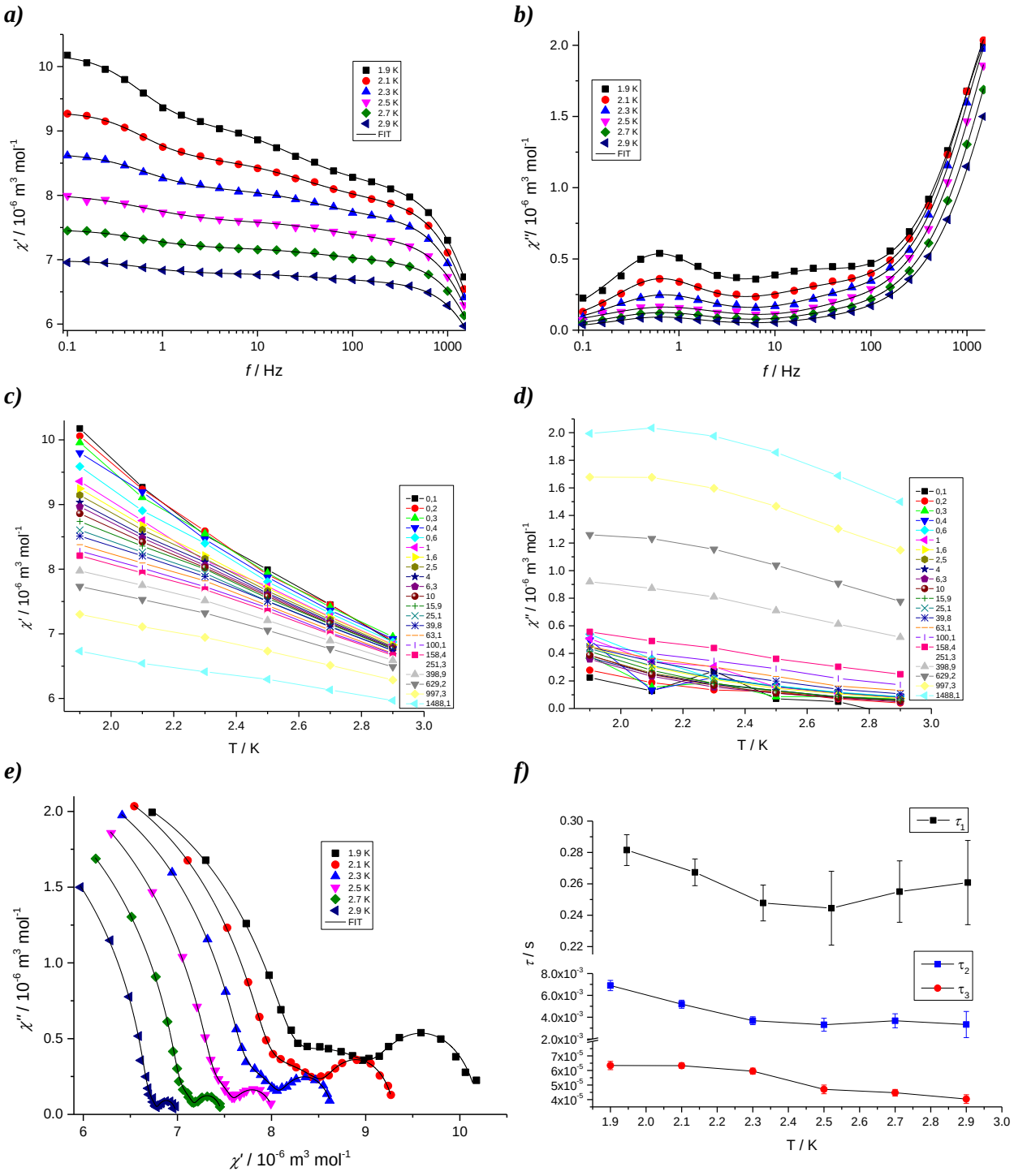

Figure S8 AC susceptibility data for **2** recorded at B_{DC}=0.15 T: Frequency (***a***, ***b***) and temperature (***c***, ***d****;* solid lines are guides for eyes only) dependent in-phase χ' and out-of-phase χ'' components of AC susceptibility, Cole-cole diagram (***e***), temperature dependency of τ_1- τ_3 (***f***).

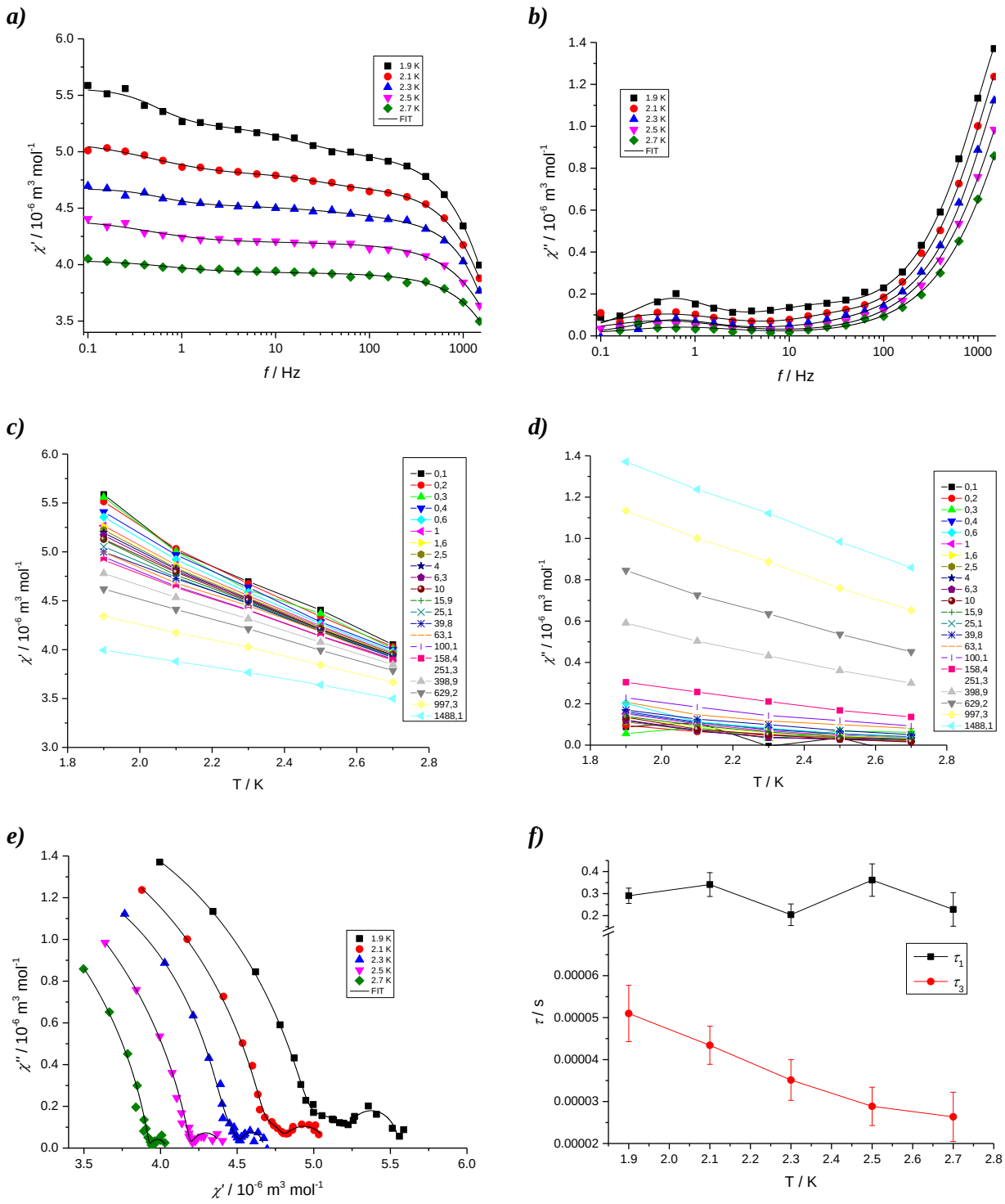

Figure S9 AC susceptibility data for **3** recorded at B_{DC}=0.15 T: Frequency (***a***, ***b***) and temperature (***c***, ***d****;* solid lines are guides for eyes only) dependent in-phase χ' and out-of-phase χ'' components of AC susceptibility, Cole-cole diagram (***e***), temperature dependency of τ_1 and τ_3 (***f***).

Table S1 Crystal data and structure refinements for studied complexes **1**, **2** and **2a**.

Compound	**1**	**1**	**2**	**2a**
Formula	$C_{22}H_{36}Cl_2FeN_6O_9$	$C_{22}H_{36}Cl_2FeN_6O_9$	$C_{22}H_{36}Cl_2CoN_6O_9$	$C_{22}H_{34}Cl_2CoN_6O_8$
M_r	655.32	655.32	658.40	640.38
Temperature (K)	120(2)	250(2)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	9.8497(14)	9.9415(6)	9.8295(8)	9.2833(6)
b (Å)	14.052(2)	14.1336(8)	14.0388(11)	14.1761(10)
c (Å)	19.649(3)	19.9165(12)	19.7163(16)	10.5176(7)
α (°)	90	90	90	90
β (°)	90.004(4)	90.212(2)	90.258(3)	110.258(2)
γ (°)	90	90	90	90
V, Å^3	2719.5(7)	2798.4(3)	2720.7(4)	1298.51(15)
Z	4	4	4	2
D_{calc} (g cm^{-3})	1.601	1.555	1.607	1.638
μ (mm^{-1})	0.814	0.791	0.890	0.927
F(000)	1368	1368	1372	666
R(int)[a]	0.0445	0.0367	0.0408	0.0232
Data/restrains/parameters	4499/ 71/ 385	5506/ 60/ 420	5335/80/401	2993/0/199
Completeness to θ (%)	99.2	99.6	99.8	99.9
Goodness-of-fit on F^2	1.228	1.121	1.173	1.037
R_1, wR_2 ($I>2\sigma(I)$[b]	0.0696/ 0.1497	0.0449/ 0.1101	0.0500/ 0.1153	0.0234/0.0608
R_1, wR_2 (all data)[b]	0.0783/ 0.1547	0.0510/ 0.1145	0.0528/ 0.1170	0.0247/0.0615
Largest diff. peak and hole (A^{-3})	0.716 and – 0.653	0.707 and – 0.538	0.922 and –0.508	0.420 and –0.371
CCDC number	2057933	2057935	2057936	2057934

[a] $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$, [b] $R_1 = \Sigma(\left| \left| F_o \right| - \left| F_c \right| \right|) / \Sigma \left| F_o \right|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$

Table S2 Selected interatomic angles [°] for compounds **1**, **2** and **2a**.

angles	**1** (120 K)	**1** (250 K)	**2**	**2a**	
N1-Fe/Co-N3	171.7(2)	169.34(12)	170.81(15)	N1-Co-N1	180.0
N2-Fe/Co-N1	81.2(3)	81.25(13)	81.10(16)	N1-Co-N3	99.71(4)
N2-Fe/Co-N3	92.7(3)	91.24(14)	92.11(17)	N1-Co-N3	80.29(4)
N2-Fe/Co-N4	95.2(2)	95.94(11)	97.24(13)	N1-Co-N3	80.29(4)
N5-Fe/Co-N1	81.6(2)	79.04(12)	79.84(15)	N1-Co-N3	99.71(4)
N5-Fe/Co-N2	87.9(2)	88.20(11)	87.92(13)	N2-Co-N1	93.58(4)
N5-Fe/Co-N3	103.8(2)	108.46(12)	106.26(15)	N2-Co-N1	86.42(4)
N5-Fe/Co-N4	172.6(2)	169.02(13)	170.18(15)	N2-Co-N1	93.58(4)
N5-Fe/Co-N6	88.3(2)	87.83(11)	86.58(14)	N2-Co-N1	86.42(4)
N4-Fe/Co-N1	92.2(3)	91.51(12)	92.67(15)	N2-Co-N2	180.00(5)
N4-Fe/Co-N3	82.8(2)	81.69(12)	81.98(15)	N2-Co-N3	91.35(4)
N6-Fe/Co-N1	105.7(3)	110.14(13)	108.77(16)	N2-Co-N3	91.35(4)
N6-Fe/Co-N2	171.5(3)	166.95(14)	167.61(17)	N2-Co-N3	88.65(4)
N6-Fe/Co-N3	80.9(3)	78.26(13)	78.82(17)	N2-Co-N3	88.65(4)
N6-Fe/Co-N4	89.5(2)	90.24(11)	89.90(13)	N3-Co-N3	180.0

Details of AC susceptibility measurements

Parameters of AC magnetic susceptibility measurements of **2** and **3** are listed in Table S3. In-phase (χ') and out-of-phase (χ'') components of AC susceptibility have been recorded at the given temperatures upon the oscillating magnetic field of different frequency.

Table S3 Conditions of AC magnetic experiments for compounds **2** and **3.**

	B_{DC} / T	B_{AC} / mT	Temperature range	Frequency range
2	0.15	3.8	1.9-2.9 K (7 steps)	0.1 Hz -1488.1 Hz (22 steps)
3	0.15	3.8	1.9-2.7 K (6 steps)	0.1 Hz -1488.1 Hz (22 steps)

Collected sets of χ' and χ'' susceptibilities (22 χ' and 22 χ'') at each temperature (**2**: 1.9 K-2.9 K; **3**: 1.9 K-2.3 K) were fitted using the formulas for three-set Debye model (eq. S1 and S2). Additionally, the suppression of the second relaxation channel in **3** allowed to use two-set Debye model (eq. S3 and S4) for isotherms at 2.5 K and 2.7 K.

$$\chi'(\omega) = \chi_S + (\chi_{T1} - \chi_S)\frac{1+(\omega\tau_1)^{(1-\alpha_1)}\sin(\pi\alpha_1/2)}{1+2(\omega\tau_1)^{(1-\alpha_1)}\sin(\pi\alpha_1/2)+(\omega\tau_1)^{(2-2\alpha_1)}} + (\chi_{T2} - \chi_{T1})\frac{1+(\omega\tau_2)^{(1-\alpha_2)}\sin(\pi\alpha_2/2)}{1+2(\omega\tau_2)^{(1-\alpha_2)}\sin(\pi\alpha_2/2)+(\omega\tau_2)^{(2-2\alpha_2)}} + (\chi_{T3} - \chi_{T2})\frac{1+(\omega\tau_3)^{(1-\alpha_3)}\sin(\pi\alpha_3/2)}{1+2(\omega\tau_3)^{(1-\alpha_3)}\sin(\pi\alpha_3/2)+(\omega\tau_3)^{(2-2\alpha_3)}} \quad \textbf{(S1)}$$

$$\chi''(\omega) = (\chi_{T1} - \chi_S)\frac{(\omega\tau_1)^{(1-\alpha_1)}\cos(\pi\alpha_1/2)}{1+2(\omega\tau_1)^{(1-\alpha_1)}\sin(\pi\alpha_1/2)+(\omega\tau_1)^{(2-2\alpha_1)}} + (\chi_{T2} - \chi_{T1})\frac{(\omega\tau_2)^{(1-\alpha_2)}\cos(\pi\alpha_2/2)}{1+2(\omega\tau_2)^{(1-\alpha_2)}\sin(\pi\alpha_2/2)+(\omega\tau_2)^{(2-2\alpha_2)}} + (\chi_{T3} - \chi_{T2})\frac{(\omega\tau_3)^{(1-\alpha_3)}\cos(\pi\alpha_3/2)}{1+2(\omega\tau_3)^{(1-\alpha_3)}\sin(\pi\alpha_3/2)+(\omega\tau_3)^{(2-2\alpha_3)}} \quad \textbf{(S2)}$$

$$\chi'(\omega) = \chi_S + (\chi_{T1} - \chi_S)\frac{1+(\omega\tau_1)^{(1-\alpha_1)}\sin(\pi\alpha_1/2)}{1+2(\omega\tau_1)^{(1-\alpha_1)}\sin(\pi\alpha_1/2)+(\omega\tau_1)^{(2-2\alpha_1)}} + (\chi_{T2} - \chi_{T1})\frac{1+(\omega\tau_2)^{(1-\alpha_2)}\sin(\pi\alpha_2/2)}{1+2(\omega\tau_2)^{(1-\alpha_2)}\sin(\pi\alpha_2/2)+(\omega\tau_2)^{(2-2\alpha_2)}} \quad \textbf{(S3)}$$

$$\chi''(\omega) = (\chi_{T1} - \chi_S)\frac{(\omega\tau_1)^{(1-\alpha_1)}\cos(\pi\alpha_1/2)}{1+2(\omega\tau_1)^{(1-\alpha_1)}\sin(\pi\alpha_1/2)+(\omega\tau_1)^{(2-2\alpha_1)}} + (\chi_{T2} - \chi_{T1})\frac{(\omega\tau_2)^{(1-\alpha_2)}\cos(\pi\alpha_2/2)}{1+2(\omega\tau_2)^{(1-\alpha_2)}\sin(\pi\alpha_2/2)+(\omega\tau_2)^{(2-2\alpha_2)}} \quad \textbf{(S4)}$$

Ten or seven free parameters can be retrieved reliably by using 44 experimental data points for each temperature (Table S4 and S5).

Table S4 Parameters of the three-set Debye model (eq. S1 and S2) for compound **2** (two relaxation processes) at B_{DC} = 0.15 T.

	1.9 K	**2.1 K**	**2.3 K**	**2.5 K**	**2.7 K**	**2.9 K**
χ_S / 10^{-6} m^3 mol^{-1}	3.3(2)	3.1(1)	2.8(1)	2.1(2)	2.1(2)	2.0(3)
χ_{T1} / 10^{-6} m^3 mol^{-1}	4.3(2)	3.8(1)	3.4(1)	2.5(2)	2.4(2)	2.2(2)
χ_{T2} / 10^{-6} m^3 mol^{-1}	5.3(2)	4.5(1)	3.8(2)	2.7(3)	2.6(2)	2.4(3)
χ_{T3} / 10^{-6} m^3 mol^{-1}	10.20(1)	9.30(1)	8.66(1)	8.03(2)	7.47(1)	6.99(1)
α_1	0.07(2)	0.06(2)	0.13(3)	0.24(5)	0.15(5)	0.09(7)
α_2	0.34(4)	0.27(4)	0.20(6)	0.1(1)	0.15(1)	0.2(2)
α_3	0.08(1)	0.05(1)	0.05(1)	0.07(2)	0.05(1)	0.05(2)
τ_1/s	0.28(1)	0.267(9)	0.25(1)	0.24(2)	0.26(2)	0.26(3)
τ_2 / 10^{-3} s	6.9(5)	5.2(4)	3.7(4)	3.3(6)	3.7(6)	3(1)
τ_3 / 10^{-5} s	6.3(2)	6.3(2)	6.0(2)	4.7(3)	4.5(2)	4.0(3)
R^2	0.99999	0.99999	0.99999	0.99999	0.99999	0.99999

Table S5 Parameters of the three-set Debye model (1.9-2.3 K; eq. S1 and S2) and two-set Debye model (2.5-2.7 K; eq. S3 and S4) for compound **3** at B_{DC} = 0.15 T.

	1.9 K	**2.1 K**	**2.3 K**	**2.5 K**	**2.7 K**
χ_S / 10^{-6} m^3 mol^{-1}	1.0(3)	0.8(2)	1.6(3)	0.3(4)	0.3(5)
χ_{T1} / 10^{-6} m^3 mol^{-1}	1.4(3)	1.1(3)	1.7(3)	0.5(4)	0.5(5)
χ_{T2} / 10^{-6} m^3 mol^{-1}	1.6(4)	1.2(3)	2.0(5)	-	-
χ_{T3} / 10^{-6} m^3 mol^{-1}	5.56(1)	5.10(3)	4.67(1)	4.40(2)	4.04(2)
α_1	0	0.27(9)	0	0.36(7)	0.2(2)
α_2	0.2(2)	0	0.4(3)	-	-
α_3	0.12(3)	0.12(2)	0.01(7)	0.14(2)	0.12(2)
τ_1/s	0.29(3)	0.34(5)	0.27(4)	0.36(7)	0.3(3)
τ_2 / 10^{-3} s	9(2)	6(2)	1(3)	-	-
τ_3 / 10^{-5} s	5.1(6)	4.3(5)	5.6(6)	2.9(5)	2.6(6)
R^2	0.99991	0.99996	0.99995	0.99995	0.99992