Supplementary material

Mixed-valence heptanuclear iron complexes with ferromagnetic interaction

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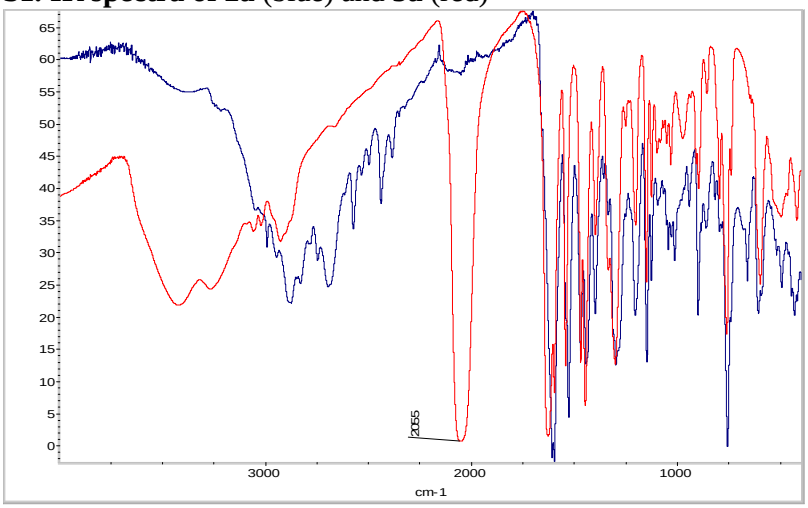
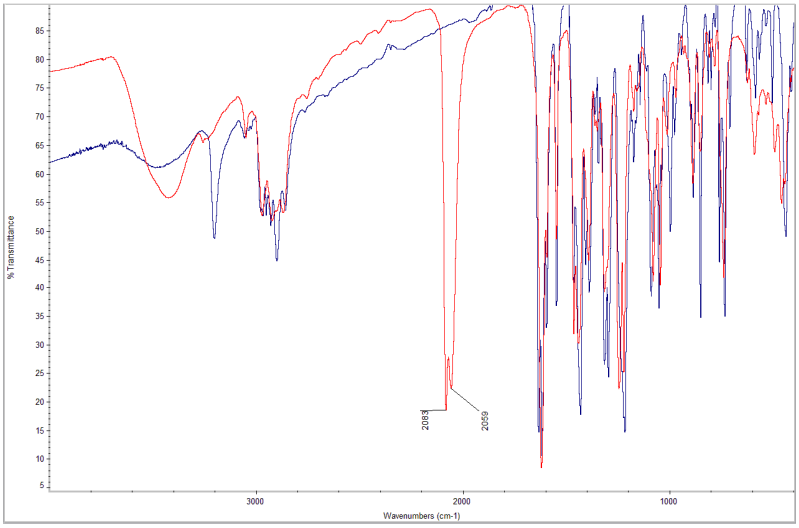
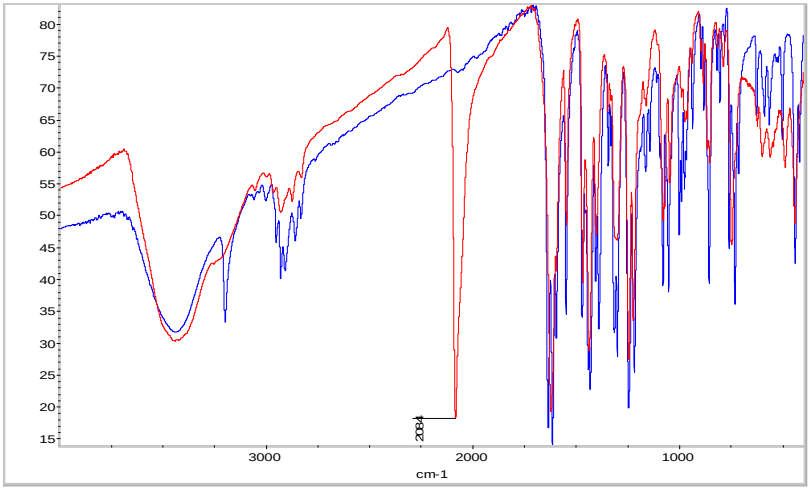
S1. IR spectra of 2a (blue) and **3a** (red)



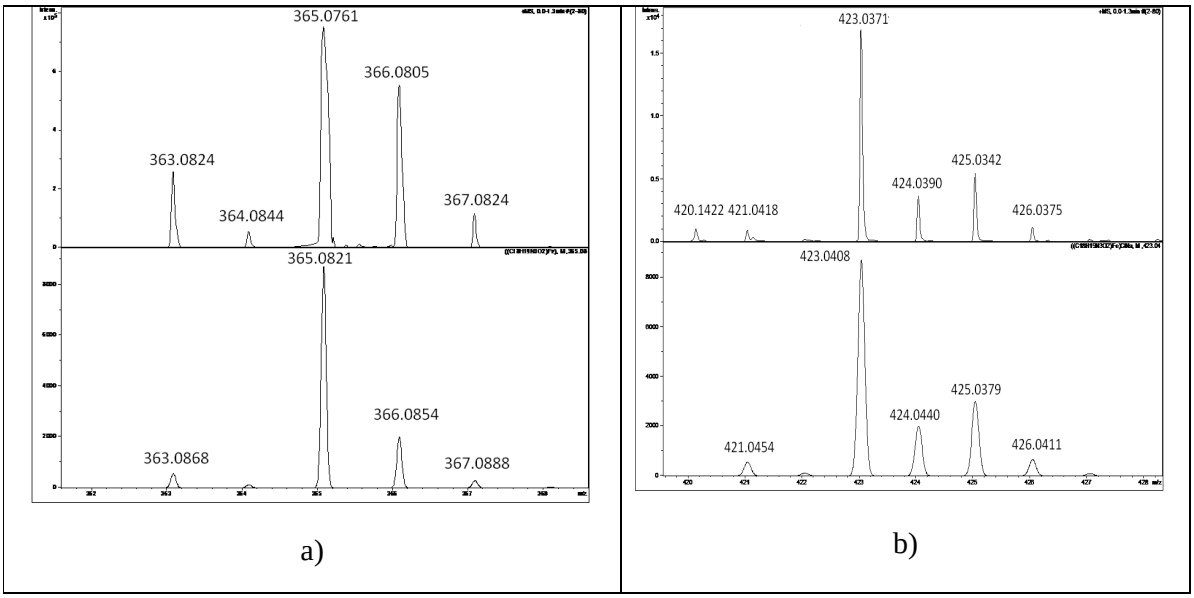
S2. IR spectra of **2b** (blue) and **3b** (red)

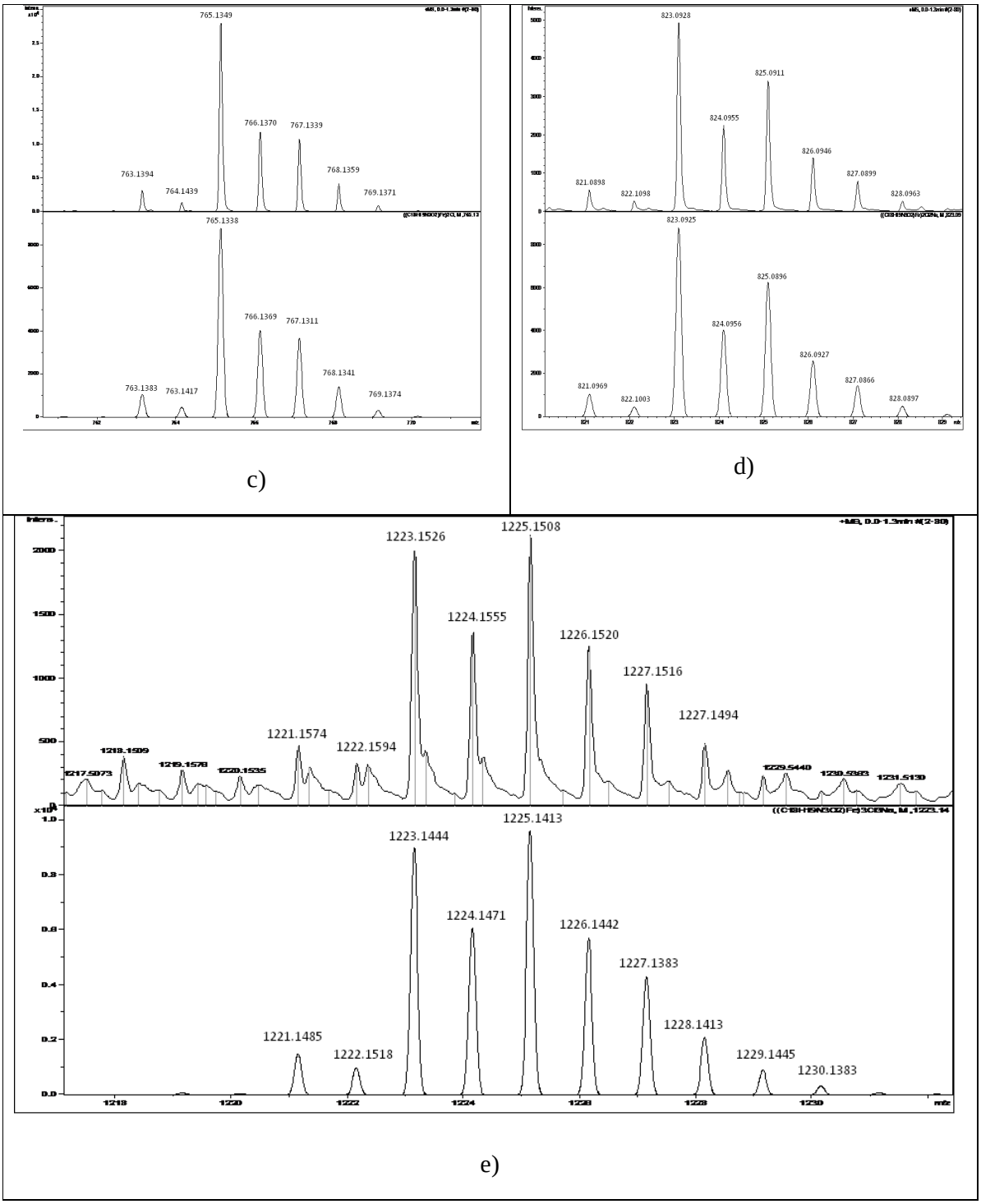


S3. IR spectra of **2c** (blue) and **3c** (red)

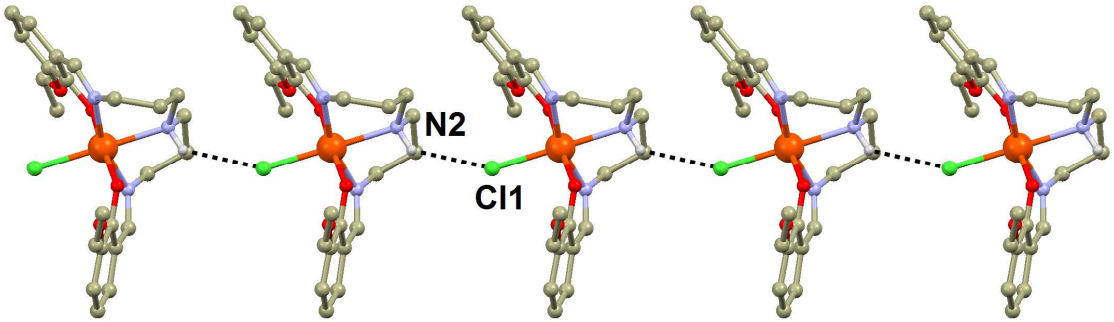


S4. High resolution ESI ToF MS spectra (upper part) and simulation (lower part) for **2a** complex.
a) $[Fe(1a_{-2H})]^+$ ($C_{18}H_{19}FeN_3O_2$) m/z = 365.08 (calc. *m/z* = 365.09);
b) $[Fe(1a_{-2H})Cl]Na^+$ ($C_{18}H_{19}ClFeN_3O_2Na$) m/z = 423.04 (calc. *m/z* = 423.04);
c) $[Fe_2(1a_{-2H})_2Cl]^+$ ($C_{36}H_{38}ClFe_2N_6O_4$) m/z = 823.10 (calc. *m/z* = 823.09);
d) $[Fe_2(1a_{-2H})_2Cl_2]Na^+$ ($C_{36}H_{38}Cl_2Fe_2N_6O_4Na$) m/z = 823.10 (calc. *m/z* = 823.09);
e) $[Fe_3(1a_{-2H})_3Cl_3]Na^+$ ($C_{54}H_{57}Cl_3Fe_3N_9O_6Na$) m/z =1225.15 (calc. *m/z* = 1225.14).

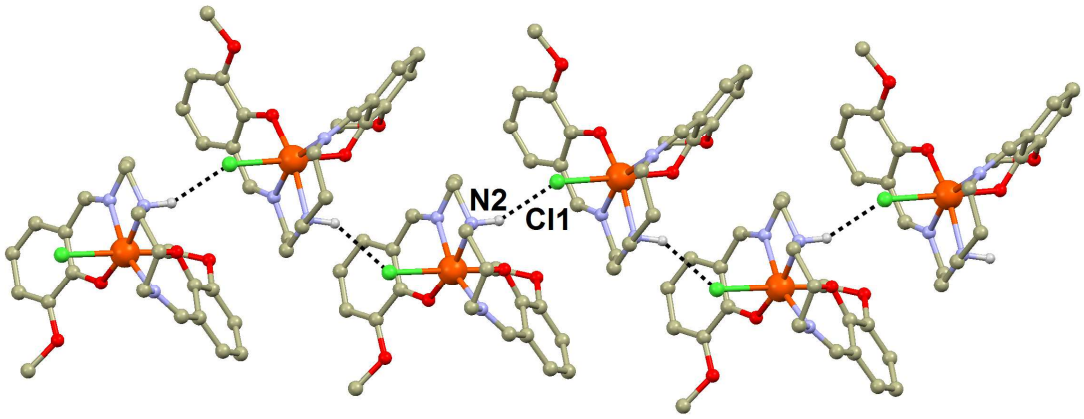




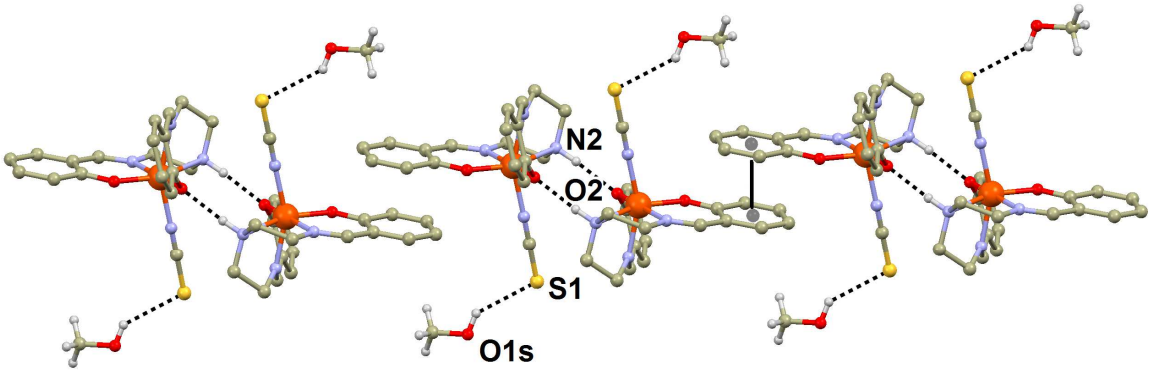
S5. A perspective view on the quasi 1D chain through NH…Cl hydrogen bonding (dashed black line) in **2b** (hydrogen atoms, except those involved in hydrogen bonding, are omitted for clarity). Parameters of hydrogen bond: *d*(N2…Cl1) = 3.4334 (11), <(N2-H1N2-Cl1) = 134.89(2)° deg, symmetry operation: x-1,+y,+z



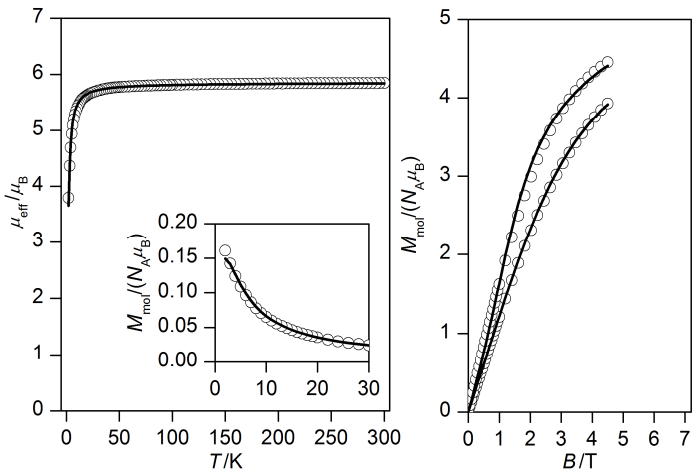
S6 A perspective view on the quasi 1D chain through NH…Cl hydrogen bonding (dashed black line) in **2c** (hydrogen atoms, except those involved in hydrogen bonding, are omitted for clarity). Parameters of hydrogen bond: *d*(N2…Cl1) = 3.2501 (12), <(N2-H1N2-Cl1) = 141.97(3) deg, symmetry operation: x,-y+1/2,+z+1/2



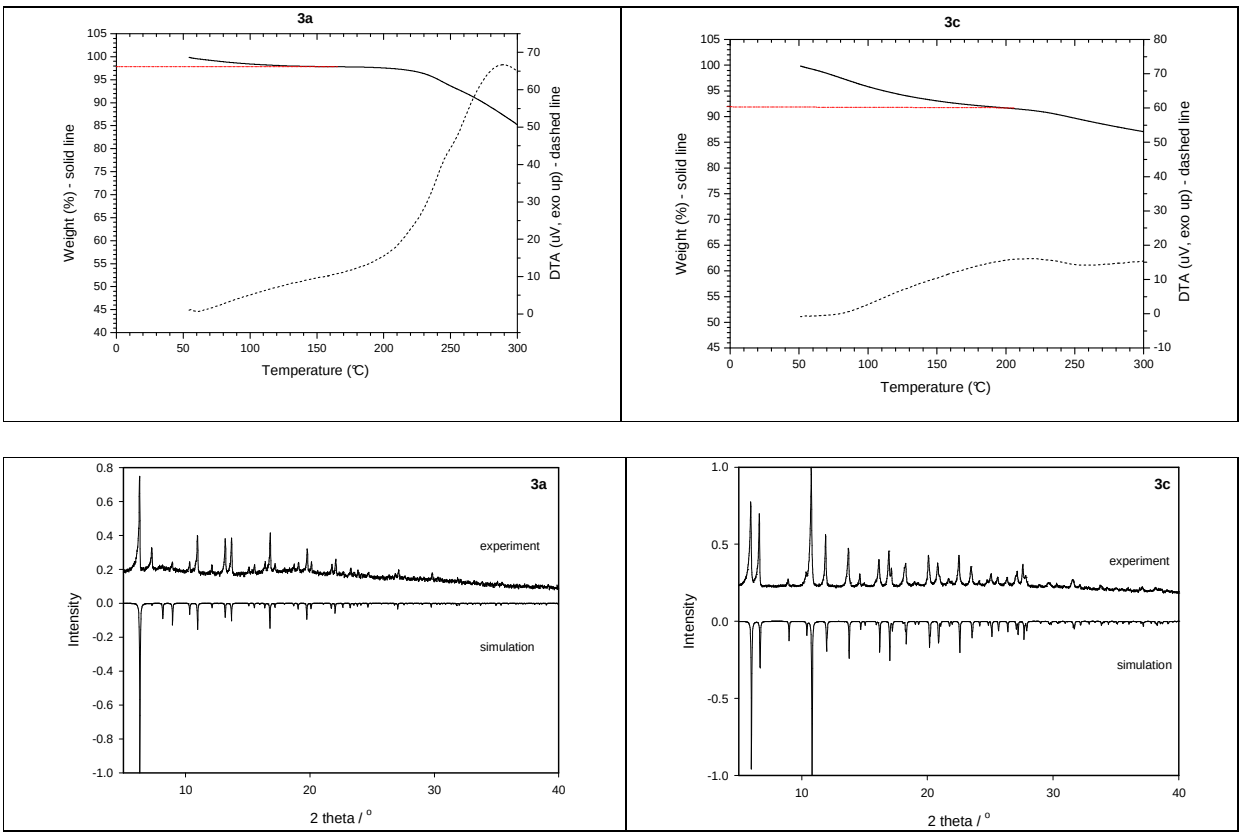
S7 A perspective view on the quasi 1D chain through NH…Cl hydrogen bonding (dashed black line) and π–π stacking interaction (centroid-centroid distance is highlighted with the black line) in **2d** (hydrogen atoms, except those on the methanol molecule and involved in hydrogen bonding, are omitted for clarity). Parameters of hydrogen bond: *d*(N2…O2) = 2.8820 (2), <(N2-H1N2-Cl1) = 167.02(2) deg, symmetry operation: -x+2,-y+1,-z+1; *d*(S1…O1s) = 3.2722 (2), <(O1S-H1S1-S1) = 137.72(1) deg, symmetry operation: x,+y+1,+z



S8. Magnetic data analysis for **2a** as a dimer

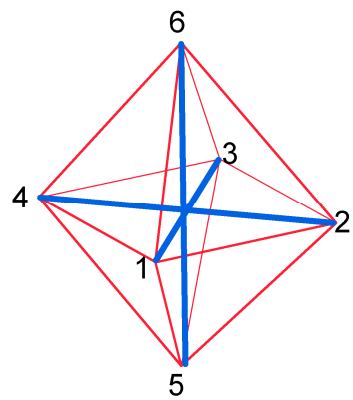


S9. TG/DTA analysis and X-ray powder diffraction of **3a** and **3c**

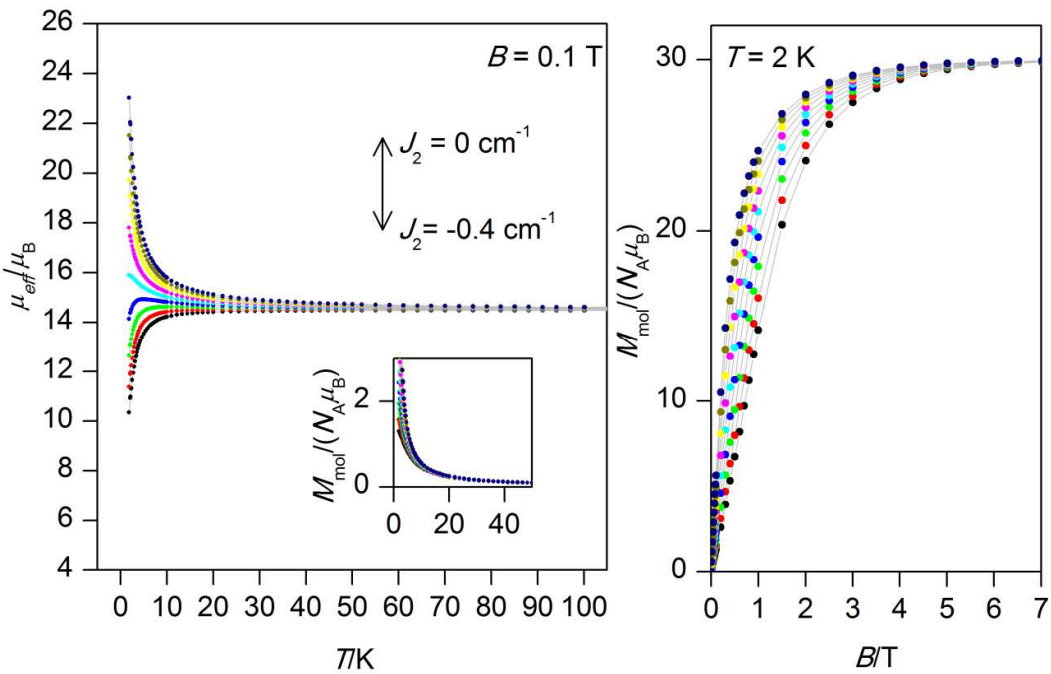


Comment: The results of TG/DTA analysis revealed 2 and 8 % loss of mass for **3a** and **3c** respectively, which are in good agreement with expected solvent liberation at elevated temperature for monohydrate **3a** (0.8%) and decahydrate **3c** (5.6%). The comparison of experimental and simulated X-ray powder difractogram proves the phase purity of both **3a** and **3c** samples submitted for further magnetic investigation. Both results together with elemental analysis rule out significant presence of impurities in the samples as well as possible existence of various polymorphic forms with different number of solvent molecules.

S10. Modeling of competition of ferromagnetic and antiferromagnetic interaction among Fe(III) centers. Spin Hamiltonian in equation 4 (main article) was changed according to scheme



where blue lines corresponds to AF interactions (J_{AF}) and red lines to F interaction (J_F).
Magnetic functions for (J_F = +0.1 cm-1 and varying J_{AF} from -0.4 to 0.0 cm^{-1} with step 0.05 cm^{-1}:



Comment: The combination of AF and F interaction does not lead to similar behavior observed in **3a** and **3c**. The effective magnetic moment is either increasing or decreasing on lowering the temperature. Moreover, the saturation limit of isothermal magnetization is the same for all the cases.