Supplementary Information for the Article: 3D Oxalate-Based Coordination Polymers: Relationship between Structure, Magnetism and Color, studied by High-Field ESR Spectroscopy

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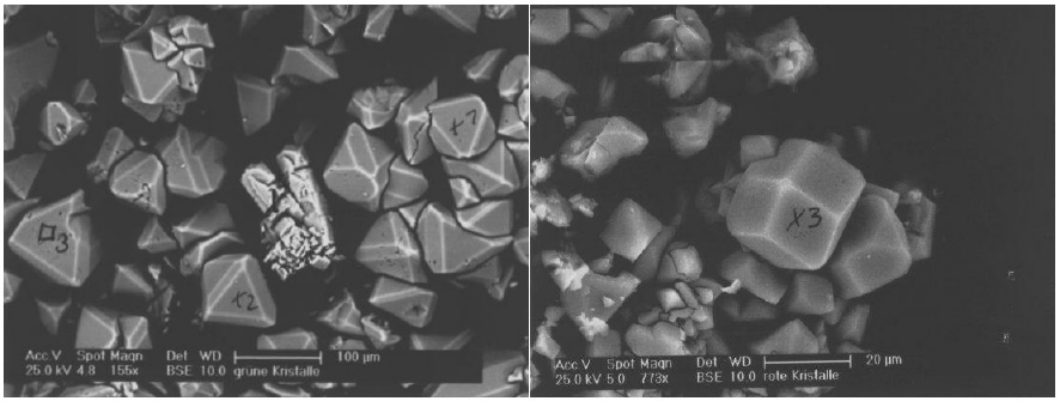

Suppl. Figure 1: SEM pictures of CuMn2-Green (left) and CuMn2-Red (right) single crystals. CuMn2-Red crystals have approximately 5 times smaller dimensions comparing to the CuMn2-Green crystals.

X-band ESR spectroscopy

X-band results on CuMn2-Green sample, performed on single crystal, as well as on powder, were presented in Ref. 11. Representative X-band ESR spectra

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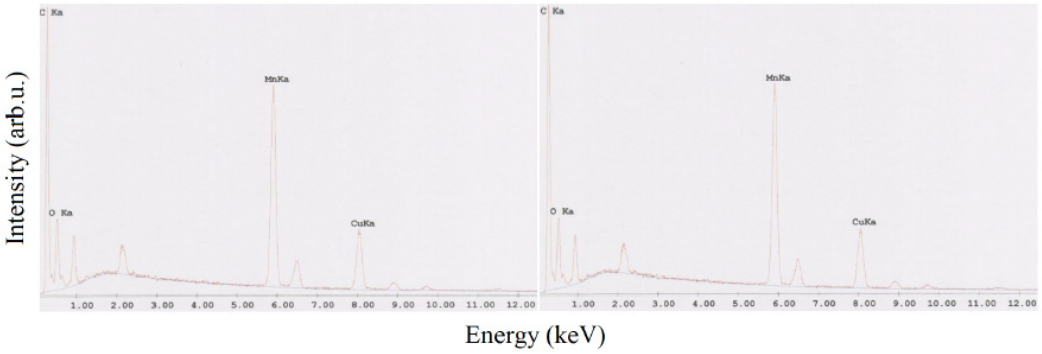
Suppl. Table 1: Crystallographic data and structure refinement for compound $\{[Cu(bpy)_3][Mn_2(C_2O_4)_3]\cdot H_2O\}_n$ (CuMn2-Red)

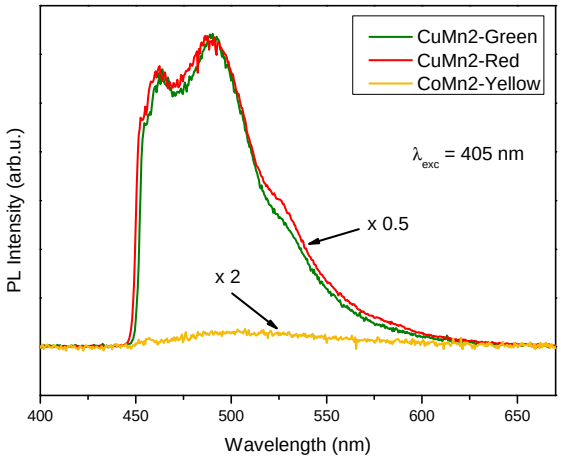
Compound	CuMn2-Red
Empirical formula	$C_{36}H_{24}CuMn_2N_6O_{13}$
Formula wt/g mol^{-1}	922.04
Crystal size/mm^{-3}	0.08 x 0.05 x 0.04
Crystal system	Cubic
Space group	$P4_132$
a/Å	15.6547(2)
Z	4
V/Å^3	3836.49(15)
ρ_c/g cm^{-3}	1.596
μ/mm^{-1}	6.559
Θrange/°	2.82 – 76.04
T/K	293(2)
Diffractometer type	Xcalibur Nova
Range of h, k, l	$-18 < h < 11$,
	$-18 < k < 19$,
	$-19 < l < 10$
Reflections collected	6839
Independent reflections	1334
Observed reflections ($I \leq 2\sigma$)	1058
Absorption correction	Multi-scan
R_{int}	0.0296
$R(F)$	0.0346
$R_w(F^2)$	0.0869
Goodness of fit	0.947
H atom treatment	Constrained
No. of parameters	90
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /eÅ^{-3}	0.336; -0.177
Flack parameter	0.004(5)



Suppl. Figure 2: EDX spectra of a CuMn2-Green (left) and CuMn2-Red (right) single crystals.

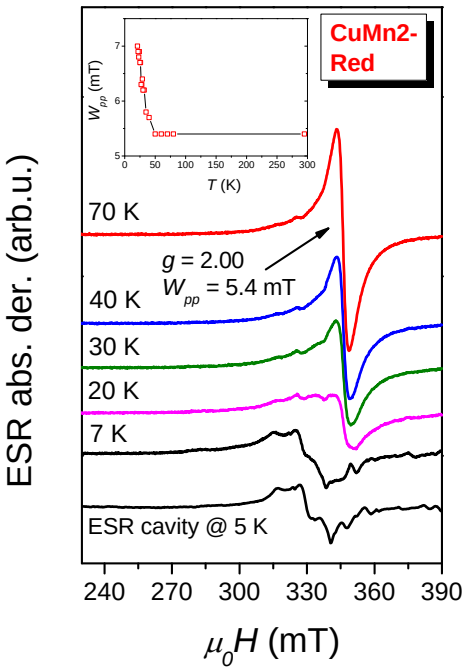
Suppl. Table 2: Manganese vs. copper atomic ratio obtained by EDX analysis.

	CuMn2-Green				CuMn2-Red			
Mn	4.39	4.34	5.39	5.38	5.19	3.26	4.83	7.79
Cu	2.16	2.11	2.64	2.74	2.67	1.64	2.43	3.95
Mn:Cu ratio	2.03	2.06	2.04	1.96	1.94	1.99	1.99	1.97
Average Mn:Cu ratio	2.02±0.04				1.97±0.02			

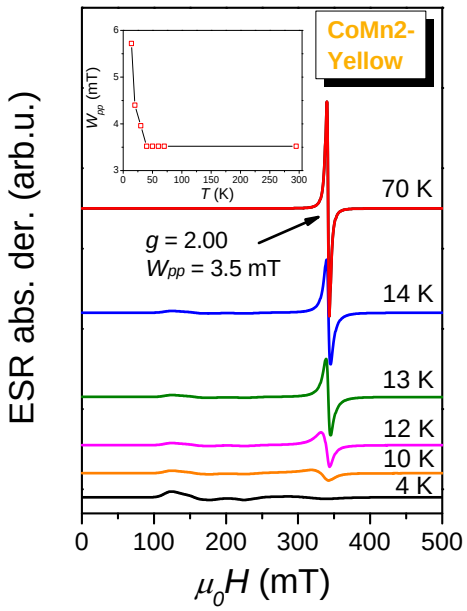


Suppl. Figure 3: The photoluminescence spectra of CuMn2-Green, CuMn2-Red and CoMn2-Yellow recorded at room temperature under laser radiation (λ_{exc} = 405 nm). Intensity of CuMn2-Red and CoMn2-Yellow are shown multiplied by 0.5 and 2, respectively.

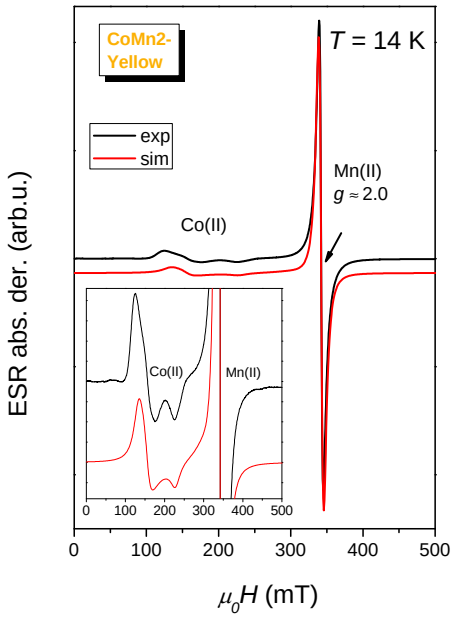
of CuMn2-Red and CoMn2-Yellow polycrystals are presented in Suppl. Figs. 4 and 5, respectively. At higher temperature $T > 70$ K, one Lorentzian line at $g = 2.00$ due to Mn(II) ions with $S = 5/2$ was detected. Hyperfine lines, due to nuclear spin $I = 5/2$, were not observed. In the temperature range 50–297 K manganese linewidth stays approximately constant, as could be seen in the inset in Suppl. Figs. 4 and 5. With decreasing temperature below 50 K, the width of the ESR line increases followed by the decrease of the peak-to-peak intensity and around $T_N \approx 12$ K, for CoMn2-Yellow, this line disappears. This effect showed that oxalate-bridged Mn(II) ions are AFM coupled at low temperatures, in agreement with magnetization measurements.[10] This temperature was not precisely determined for CuMn2-Red, due to the very small amount of the CuMn2-Red sample ($m \approx 0.1$ mg) and parasitic signal from the ESR cavity. ESR spectra of CoMn2-Yellow at low temperatures show additional lines in the field range 100–250 mT that could be assigned to Co(II) ions.



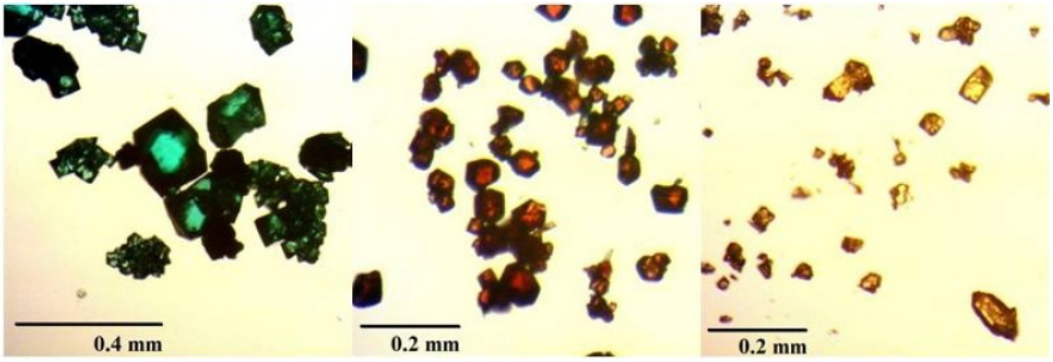
Suppl. Figure 4: X-band ESR spectra of CuMn2-Red polycrystals for different selected temperatures. Intensities of the lines are presented in real ratios. Due to the very small amount of the CuMn2-Red sample, the spectra at low temperatures (T = 7 K) are covered by the spectrum of the ESR cavity (the spectrum of ESR cavity at T = 5 K is also presented). Inset: temperature dependence of the peak-to-peak linewidth (W_{pp}) above 20 K.



Suppl. Figure 5: X-band ESR spectra of CoMn2-Yellow polycrystals for different selected temperatures. Intensities of the lines are presented in real ratios. Phase transition into the AFM state occurs at $T_N \approx 12$ K. Inset: temperature dependence of the peak-to-peak linewidth (W_{pp}) above T_N.



Suppl. Figure 6: Experimental and simulated X-band ESR spectrum of CoMn2-Yellow, at $T = 14$ K. Inset: Enlarged Co(II) lines.



Suppl. Figure 7: From the left to the right: polycrystals of CuMn2-Green, CuMn2-Red and CoMn2-Yellow compounds.