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## Supporting information for compounds 1-4

Compou	nd <b>1</b>					
Nb1	Nb2	Nb3	Nb4			V1
5.03	5.19	4.94	5.19			4.16
Compou	nd <b>2</b>			·	·	
Nb1	Nb2					V1
5.05	5.01					3.98
Compou	nd <b>3</b>					
Nb1	Nb2	Nb3	Nb4	Nb5	Nb6	V1
5.02	5.12	5.01	5.15	4.87	4.89	4.12
Compou	nd <b>4</b>					
Nb1	Nb2					
4.55	4.56					

Table s1. Calculation results of niobium and vanadium in compounds 1-4

Nb<sub>i</sub>=EXP((-(B<sub>i</sub>-1.911))/0.37); V<sub>i</sub>=EXP((-(B<sub>i</sub>-1.784))/0.37).



Fig. s1 disordered results of Cu(2) and Cu(3) complexes in compound 1.



Fig. s2 disordered results of Cu(1) and Cu(2) complexes in compound 2.



Fig. s3 IR spectra of compounds 1-3.





Fig. s5 EPR spectra of compounds 1-3.



Fig.S6 simulated, experimental and XRD patterns after three runs of repeated experiments of compound 3



Fig. s7 IR spectra of compound **3** and the crystal after three cycles.