Electronic Supplementary Information

Cross-linking of cyanide magnetic coordination polymers by rational insertion of formate, cyanide or azide

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Table S1. Crystal structure solution and refinement parameters for **Mn_2Nb** and the cross-linked networks **Mn_2NbL**.

	Mn_2Nb	**$Mn_2NbHCOO$**	**Mn_2NbCN**	**Mn_2NbN_3**
Formula	$C_8H_{16}Mn_2N_8NbO_8$	$C_9H_{15}Mn_2N_9NbO_7$	$C_9H_{13}Mn_2N_{11}NbO_3$	$C_8H_{14}Mn_2N_{12}NbO_5$
Temperature, *K*	293(2)	293(2)	120(2)	170(2)
Diffractometer	Nonius Kappa CCD	Nonius Kappa CCD	Agilent SuperNova	Bruker D8 Quest Eco Photon50 CMOS
λ [Å]	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)
Molecular weight, g/mol	554.87	563.88	525.88	560.87
Crystallographic system	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	*I*4/*m*	*I*4*cm*	*I*4/*mcm*	*I*4/*m*
Unit cell	a = 12.091(5) Å c = 13.387(5) Å	a = 12.07320(10) Å c = 13.4352(3) Å	a = 11.83052(9) Å c = 13.53251(18) Å	a = 12.0837(3) Å c = 13.3147(3) Å
Volume *V*, Å^3	1957.1(14)	1958.34(5)	1894.03(4)	1944.16(11)
Z	1	4	2	16
Density ρ_{calc}, g/cm^3	1.897	1.862	1.799	1.828
F (000)	1116	1056	984	1036
θ, deg	2.27-34.97	3.37-28.29	3.010-28.589	27.632-3.060
Abs. coeff. μ, mm^{-1}	1.899	1.862	1.940	1.886
Data/restrains/parameters	2241/5/68	1265/1/80	668/30/54	1190/0/71
R* [$F_o > 4\sigma(F_o)$]	R_1 = 0.032 (2060) wR_2 = 0.0821 (2241)	R_1 = 0.0295 (1157) wR_2 = 0.0792 (1265)	R_1 = 0.0199 (610) wR_2 = 0.0561 (668)	R_1 = 0.0365 (1134) wR_2 = 0.0844(1190)
GOF on F^2	1.139	1.047	1.176	1.120
max/min/resid. density, e·Å^{-3}	2.436/-0.985/0.109	1.192/-0.68/0.091	0.496/-0.481/0.079	1.790/-1.867/0.116
Reflections collected	12293	13487	12366	9472
Unique reflection	2241	1265	668	1190
R_{int}	0.0256	0.059	0.0331	0.0240
Completness, %	99.9	99.3	98.5	99.8

Table S2. Crystal structure solution and refinement parameters for **Mn_2Mo** and the cross-linked networks **Mn_2MoL**.

	Mn_2Mo*	**$Mn_2MoHCOO$**	**Mn_2MoCN**	**Mn_2MoN_3**
Formula	$C_8H_{16}Mn_2MoN_8O_8$	$C_9H_{15}Mn_2MoN_9O_7$	$C_9H_{13}Mn_2MoN_{11}O_3$	$C_8H_{14}Mn_2MoN_{12}O_5$
Temperature, *K*	298	293(2)	120(2)	120(2)
Diffractometer		Bruker D8 Quest Eco Photon50 CMOS	Bruker D8 Quest Eco Photon50 CMOS	Bruker D8 Quest Eco Photon50 CMOS
λ [Å]		0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)
Molecular weight, g/mol	558.08	567.09	529.09	564.09
Crystallographic system	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	*I*4/*m*	*I*4*cm*	*I*4/*mcm*	*I*4/*m*
Unit cell	a = 11.894(5) Å c = 13.236(3) Å	a = 11.8998(4) Å c = 13.2632(5) Å	a = 11.6902(4) Å c = 13.3582(6) Å	a = 11.9694(3) Å c = 13.1021(4) Å
Volume *V*, Å^3	1872.46	1878.14(14)	1825.54(15)	1877.09
Z	4	4	4	4
Density ρ_{calc}, g/cm^3	1.98	1.956	1.878	1.989
Abs. coeff. μ, mm^{-1}	19.7	2.034	2.072	2.032
F (000)		1064	989	1104
θ, deg		3.912-27.627	3.050-27.520	3.404-28.252
Data/restrains/parameters	1183//67	1150/1/81	592/18/46	1220/11/93
R* [$F_o > 4\sigma(F_o)$]	R_1 = 0.0809 (856) wR_2 = 0.062 (1183)	R_1 = 0.0229 (1071) wR_2 = 0.0510 (1150)	R_1 = 0.0265 (541) wR_2 = 0.0583 (592)	R_1 = 0.0208 (1085) wR_2 = 0.0476 (1220)
GOF on F^2		1.081	1.109	1.033
max/min/resid. density, [e·Å^{-3}]		0.358/-0.402/0.069	0.467/-0.644/0.099	0.641/-0.430/0.076
Reflections collected	1935	6713	9757	7342
Unique reflections	1183	1150	592	1220
R_{int}		0.0336	0.0452	0.0310
Completness, %		99.2	99.8	99.1

* J. M. Herrera, P. Franz, R. Podgajny, M. Pilkington, M. Biner, S. Decurtins, H. Stoeckli-Evans, A. Neels, R. Grade, Y. Dromzee, M. Julve, B. Sieklucka, K. Hashimoto, S. Ohkoshi, M. Verdaguer, *C. R. Chimie,* 2008, **11**, 1192

Table S3. The SHAPE parameters for the coordination spheres of Mn^{II}, Nb^{IV} and Mo^{IV} in **Mn_2Nb**, **Mn_2Mo** and the cross-linked compounds **Mn_2NbL** and **Mn_2MoL**.

	S_{OC-6} (O_h) for Mn^{II}	S_{SAPR-8} (D_{4d}) for Nb^{IV}
Mn_2Nb	0.217	0.131
$Mn_2NbHCOO$	0.184	0.095
Mn_2NbCN	0.201	0.127
Mn_2NbN_3	0.122	0.085
	S_{OC-6} (O_h) for Mn^{II}	S_{SAPR-8} (D_{4d}) for Mo^{IV}
Mn_2Mo	0.388	0.304
$Mn_2MoHCOO$	0.154	0.230
Mn_2MoCN	0.170	0.174
Mn_2MoN_3	0.145	0.222

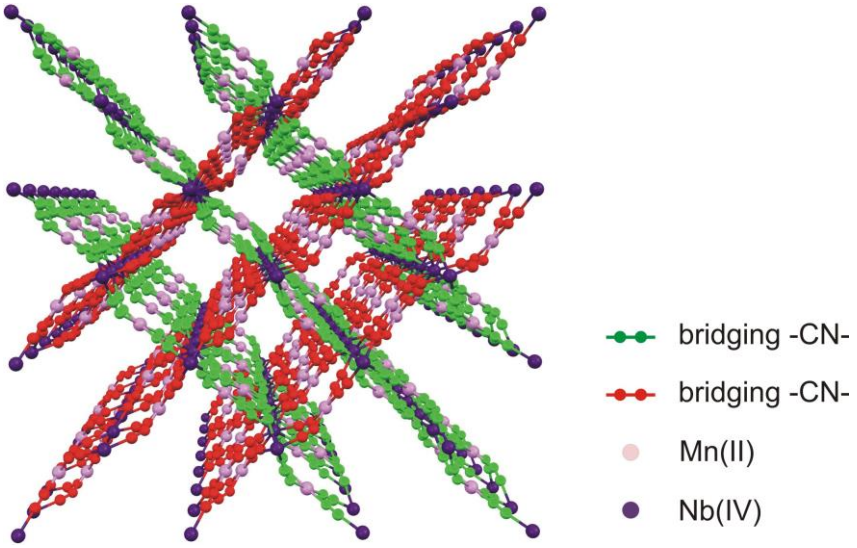

Figure S1. The topology of the 3-D cyanide-skeleton of **Mn_2Nb**. Reproduced with permission from *Chem. Mater.* 2011, **23**, 21-31.

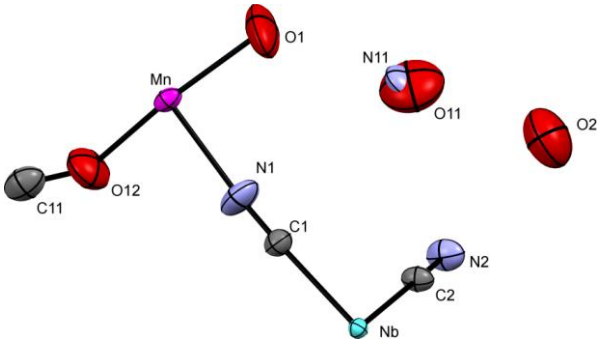

Figure S2. The asymmetric unit of **$Mn_2NbHCOO$** with atom labeling scheme.

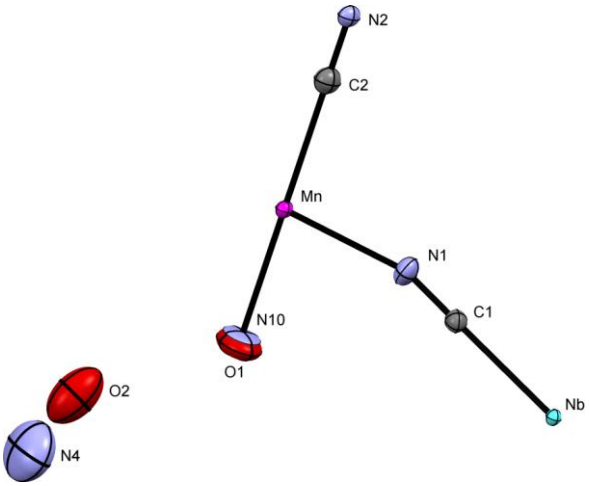

Figure S3. The asymmetric unit of **Mn_2NbCN** with atom labeling scheme.

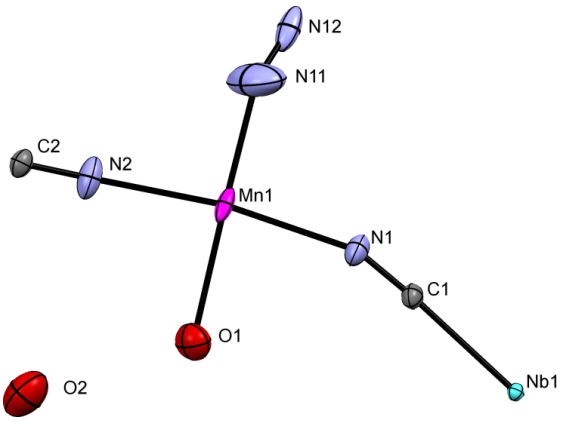

Figure S4. The asymmetric unit of **Mn_2NbN_3** with atom labeling scheme.

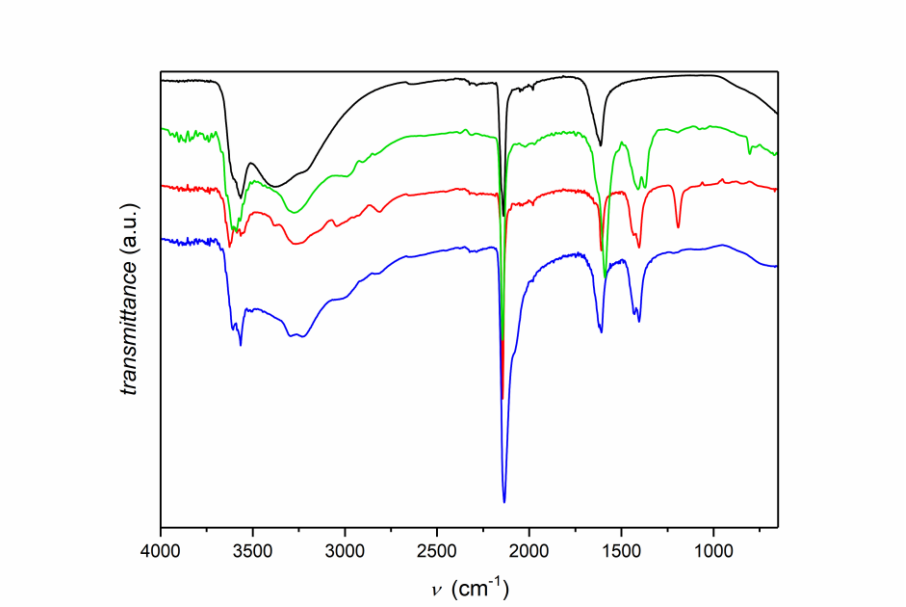

Figure S5. IR spectra of **Mn_2Nb** (black), **$Mn_2NbHCOO$** (green), **Mn_2NbCN** (red) and **Mn_2NbN_3** (blue).

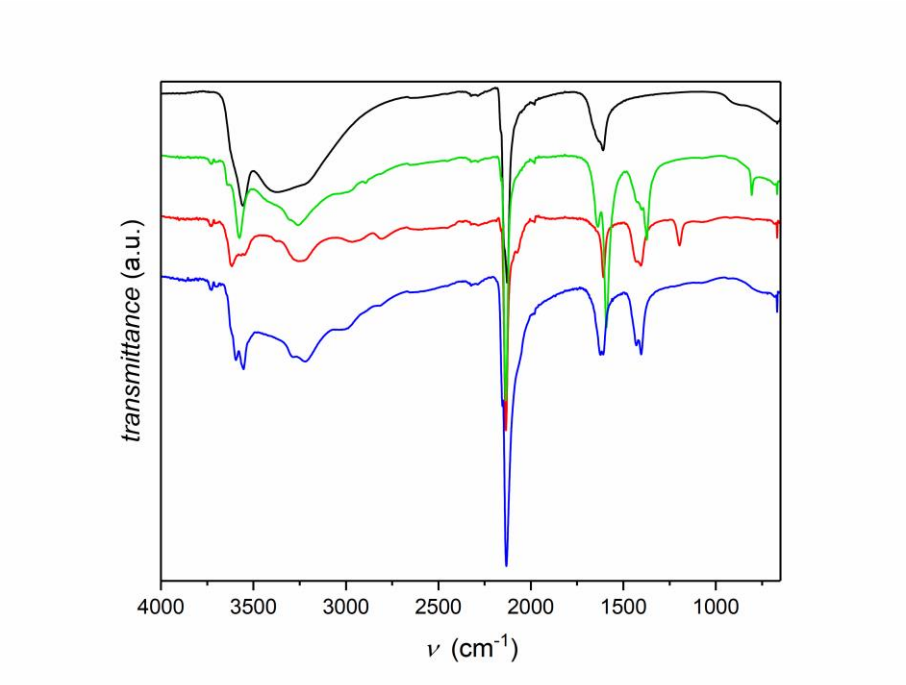

Figure S6. IR spectra of **Mn_2Mo** (black), **$Mn_2MoHCOO$** (green), **Mn_2MoCN** (red) and **Mn_2MoN_3** (blue).

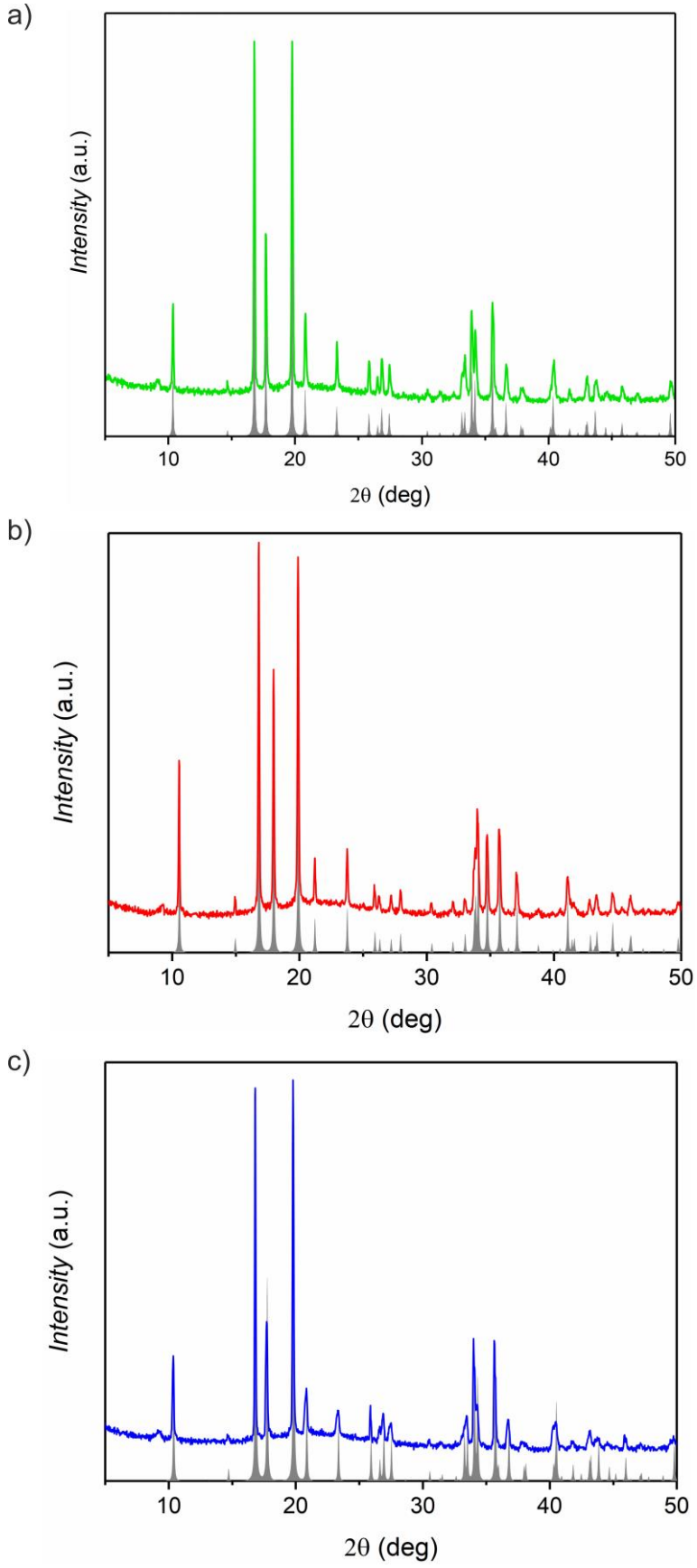

Figure S7. Experimental (colored lines) and simulated (gray lines) from RT single crystal XRD structure models PXRD patterns of **Mn_2NbHCOO** (a), **MnNbCN** (b) and **$MnNbN_3$** (c).

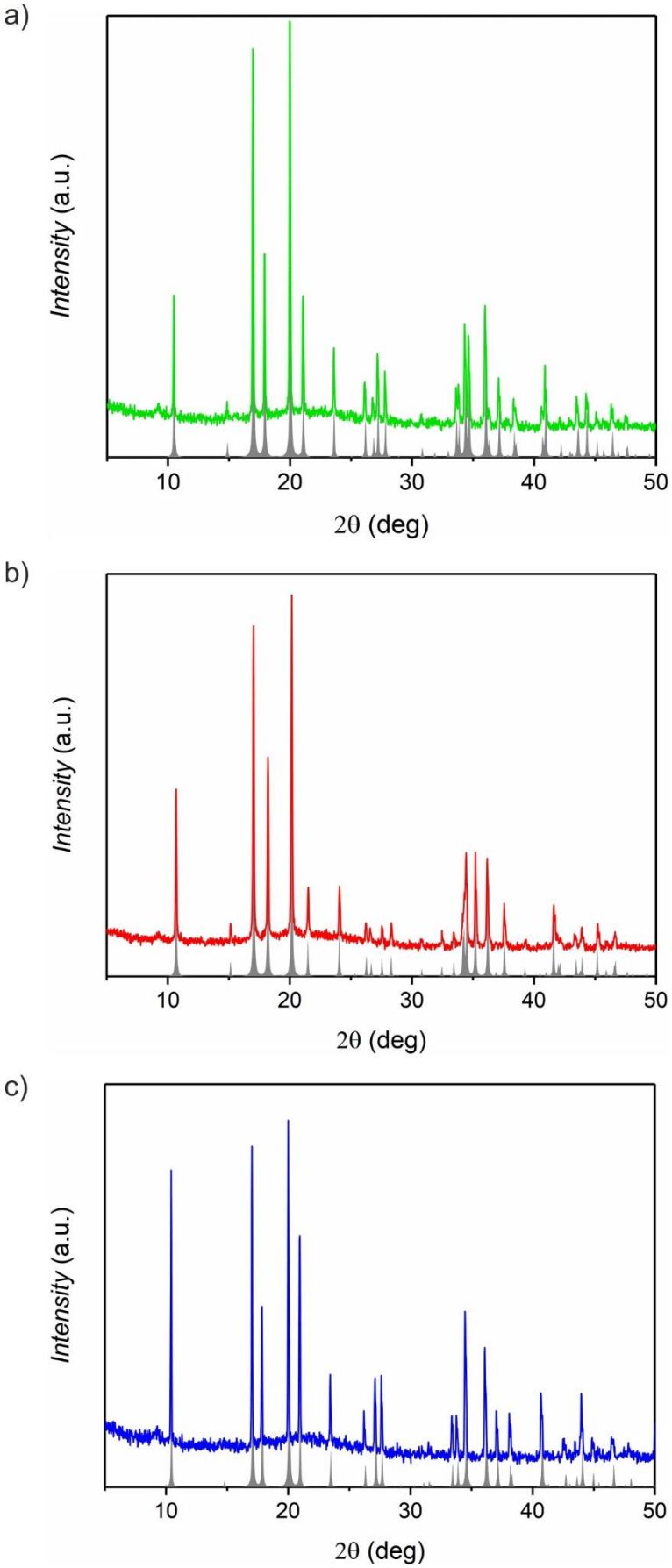

Figure S8. Experimental (colored lines) and simulated (gray lines) from RT single crystal XRD structure models PXRD patterns of **$Mn_2MoHCOO$** (a), **MnMoCN** (b) and **$MnMoN_3$** (c).

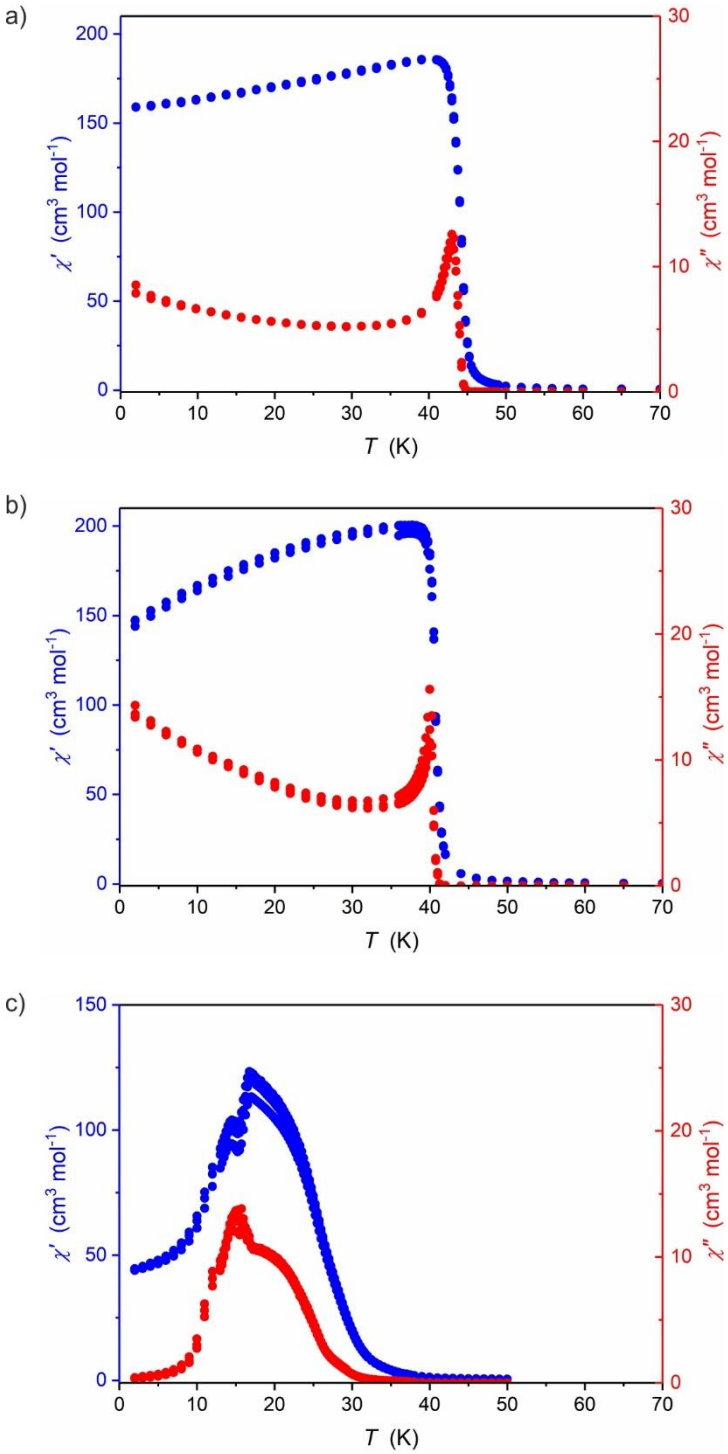

Figure S9. Temperature dependence of the AC magnetic susceptibility for **$Mn_2NbHCOO$** (a), **Mn_2NbCN** (b) and **Mn_2NbN_3** (c) at 7, 70 and 700 Hz and H_{AC} = 0.1 mT.