Influence of azide and imidazole on the properties of Mn- and Cd-based networks: conductivity and nonlinear phenomena

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Table S1. Selected bond lengths (Å) and angles (°).

	Bond	(Å)	Bond	(Å)	Angle	(°)	Angle	(°)
Cd-1	Cd1—N1	2.417(4)	N8—C1	1.322(7)	N1—Cd1—N4	90.2(2)	N1—Cd1—N7	169.0(2)
	Cd1—N4	2.332(4)	N8—C3	1.342(8)	N1—Cd1—N4^{i}	90.0(2)	N4—Cd1—N1^{ii}	169.3(2)
	Cd1—N4^{i}	2.343 (4)	C2—C3	1.360(8)	N1—Cd1—N1^{ii}	79.1(2)	N4^{i}—Cd1—N1^{iii}	168.8(2)
	Cd1—N1^{ii}	2.471(4)			N1—Cd1—N1^{iii}	79.1(2)	Cd1—N1—Cd1^{iii}	100.9(2)
	Cd1—N1^{iii}	2.419(4)			N4—Cd1—N4^{i}	101.9(2)	Cd1—N1—Cd1^{ii}	100.9(2)
	Cd1—N7	2.242(4)			N4—Cd1—N1^{iii}	80.8(2)	Cd1^{iii}—N1—Cd1^{ii}	95.8(2)
	N1—N2	1.217(5)			N4^{i}—Cd1—N1^{ii}	79.5(2)	Cd1—N4—Cd1^{iv}	101.9(2)
	N2—N3	1.138(6)			N1^{ii}—Cd1—N1^{iii}	95.8(2)	N2—N1—Cd1	116.0(3)
	N4—N5	1.192(6)			N7—Cd1—N4	99.4(2)	N5—N4—Cd1	127.7(3)
	N5—N6	1.148(6)			N7—Cd1—N4^{i}	93.3(2)	N1—N2—N3	178.6(5)
	N7—C1	1.315(6)			N7—Cd1—N1^{ii}	91.2(2)	N4—N5—N6	178.3(5)
	N7—C2	1.368(6)			N7—Cd1—N1^{iii}	97.0(2)		

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) −*x*, −*y*+1, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) *x*+1, *y*, *z*.

	Cd1—N1	2.338(10)	N8—C5	1.35(2)	N1—Cd1—N4	89.1(4)	N1—Cd1—N3^{i}	173.2(4)
	Cd1—N3^{i}	2.441(11)	C5—C6	1.35(2)	N3^{i}—Cd1—N4	84.3(4)	N4—Cd1—N6^{ii}	174.6(5)
	Cd1—N4	2.443(11)	N9—C1	1.27(3)	N6^{ii}—Cd1—N1	94.6(4)	N7—Cd1—N9	176.9(15)
	Cd1—N6^{ii}	2.335(11)	N9—C3	1.34(3)	N6^{ii}—Cd1—N3^{i}	92.1(4)	C4—N7—Cd1	131.1(18)
	Cd1—N7	2.19(4)	N10—C1	1.32(2)	N7—Cd1—N1	89.6(6)	C6—N7—Cd1	130(2)
	Cd1—N9	2.33(4)	N10—C2	1.34(2)	N7—Cd1—N3^{i}	92.1(6)	C1—N9—Cd1	125.3(17)
Cd-2	N1—N2	1.23(3)	C2—C3	1.34(2)	N7—Cd1—N4	89.5(8)	C3—N9—Cd1	126.0(16)
	N2—N3	1.06(3)			N7—Cd1—N6^{ii}	86.6(8)	N2—N1—Cd1	125.6(15)
	N4—N5	1.14(3)			N9—Cd1—N1	90.7(6)	N2—N3—Cd1^{iii}	133.1(18)
	N5—N6	1.17(3)			N9—Cd1—N3^{i}	88.0(6)	N5—N4—Cd1	124.4(14)
	N7—C4	1.34(4)			N9—Cd1—N4	93.6(8)	N5—N6—Cd1^{iv}	133.2(14)
	N7—C6	1.44(3)			N9—Cd1—N6^{ii}	90.3(8)	N1—N2—N3	178(3)
	N8—C4	1.33(2)					N4—N5—N6	174(2)

Symmetry codes: (i) *x*−1/2, *y*−1/2, *z*; (ii) *x*+1/2, *y*+1/2, *z*; (iii) *x*+1/2, *y*+1/2, *z*; (iv) *x*−1/2, *y*+1/2, *z*.

	Mn1—N1	2.222(2)	N6—C4	1.312(3)	N1—Mn1—N1^{i}	99.49(13)	N1—Mn1—N10	169.46(8)
	Mn1—N3	2.239(2)	N6—C5	1.370(4)	N1—Mn1—N3	93.56(9)	N3—Mn1—N3^{i}	179.1(2)
	Mn1—N10	2.257(2)	N7—C4	1.336(4)	N1—Mn1—N3^{i}	87.05(9)	N6—Mn2—N5^{ii}	171.28(8)
	Mn2—N5^{ii}	2.290(2)	N7—C6	1.355(5)	N1^{i}—Mn1—N10	89.26(9)	N8—Mn2—N8^{iv}	179.4(2)
	Mn2—N6	2.220(2)	C2—C3	1.353(4)	N3—Mn1—N10^{i}	86.55(10)	C1—N1—Mn1	127.6(2)
	Mn2—N8	2.196(2)	C5—C6	1.346(4)	N3—Mn1—N10	92.73(9)	C2—N1—Mn1	127.7(2)
	N3—N4	1.160(3)			N10—Mn1—N10^{i}	82.70(13)	N4—N3—Mn1	154.6(2)
Mn-1	N4—N5	1.175(3)			N5^{ii}—Mn2—N5^{iii}	79.37(11)	N4—N5—Mn2^{v}	133.2(2)
	N8—N9	1.150(3)			N6—Mn2—N5^{iii}	92.12(8)	C4—N6—Mn2	126.8(2)
	N9—N10	1.167(3)			N6—Mn2—N6^{iv}	96.44(12)	C5—N6—Mn2	127.6(2)
	N1—C1	1.318(3)			N8—Mn2—N5^{ii}	90.98(9)	N9—N8—Mn2	166.3(2)
	N1—C2	1.372(3)			N8—Mn2—N5^{iii}	88.58(10)	N9—N10—Mn1	131.7(2)
	N2—C1	1.340(4)			N8—Mn2—N6^{iv}	89.68(10)	N3—N4—N5	178.0(3)
	N2—C3	1.349(5)			N8—Mn2—N6	90.70(9)	N8—N9—N10	177.8(3)

Symmetry codes: (i) *x*−1/2, *y*−1/2, *z*; (ii) *x*+1/2, *y*+1/2, *z*; (iii) *x*+1/2, *y*+1/2, *z*; (iv) *x*−1/2, *y*+1/2, *z*.

	Mn1—N1	2.262(6)	N8—C5	1.36(2)	N1—Mn1—N4	90.1(2)	N1—Mn1—N3^{i}	176.8(3)
	Mn1—N3^{i}	2.247(7)	C5—C6	1.35(2)	N3^{i}—Mn1—N4	88.0(3)	N4—Mn1—N6^{ii}	176.8(4)
	Mn1—N4	2.259(7)	N9—C1	1.32(3)	N6^{ii}—Mn1—N1	91.3(3)	N7—Mn1—N9	178.6(4)
	Mn1—N6^{ii}	2.255(8)	N9—C3	1.38(3)	N6^{ii}—Mn1—N3^{i}	92.0(3)	C4—N7—Mn1	125.6(8)
Mn-2	Mn1—N7	2.23(2)	N10—C1	1.338(8)	N7—Mn1—N1	90.6(3)	C6—N7—Mn1	128.9(8)
	Mn1—N9	2.21(2)	N10—C2	1.35(2)	N7—Mn1—N3^{i}	92.0(3)	C1—N9—Mn1	127.2(6)
	N1—N2	1.17(2)	C2—C3	1.35(2)	N7—Mn1—N4	89.4(3)	C3—N9—Mn1	128.4(6)
	N2—N3	1.17(2)			N7—Mn1—N6^{ii}	87.8(3)	N2—N1—Mn1	135.6(7)
	N4—N5	1.18(2)			N9—Mn1—N1	90.7(6)	N2—N3—Mn1^{iii}	136.7(7)

	N5—N6	1.16(2)			N9—Mn1—N3^{i}	87.6(3)	N5—N4—Mn1	135.9(7)
	N7—C4	1.33(2)			N9—Mn1—N4	92.0(3)	N5—N6—Mn1^{iv}	136.5(7)
	N7—C6	1.37(2)			N9—Mn1—N6^{ii}	90.9(3)	N1—N2—N3	179.5(11)
	N8—C4	1.341(9)					N4—N5—N6	179.1(11)
Symmetry codes: (i) *x*−1/2, *y*−1/2, *z*; (ii) *x*+1/2, *y*+1/2, *z*; (iii) *x*+1/2, *y*+1/2, *z*; (iv) *x*−1/2, *y*+1/2, *z*.								
Mn-2 HT	Mn1—N1	2.224(3)	C1—C2	1.321(5)	N3—Mn1—N3^{i}	90.016(3)	N3—Mn1—N3^{iii}	178.11(2)
	Mn1—N3	2.259(3)	C2—H2	0.85(5)	N3—Mn1—N3^{ii}	90.015(3)	N1—Mn1—N1^{i}	180.0
	N3—N4	1.169(3)			N3—Mn1—N1	90.95(9)	C1—N1—Mn1	127.6(2)
	N1—C1	1.346(5)			N3—Mn1—N1^{i}	89.05(9)	N4—N3—Mn1	137.8(2)
	C1—H1	0.94(4)					N3—N4—N3^{iv}	179.9(7)
Symmetry codes: (i) *y*, −x+1, −*z*+1; (ii) −*y*+1, *x*, −*z*+1; (iii) −*x*+1, −*y*+1, *z*; (iv) −*x*+1, −*y*+2, *z*.								

Table S2. Hydrogen bond parameters.

	D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
Cd-1	N8—H8···N6^{v}	0.86	2.19	2.999(7)	158
	C3—H3···N6^{vi}	0.93	2.69	3.568(7)	158
Symmetry codes: (v) *x*, *y*+1, *z*; (vi) -*x*, -*y*+1, -*z*.					
Cd-2	N8—H8···N4^{v}	0.86	2.10	2.944(18)	166
	N10—H10···N1^{vi}	0.86	2.13	2.981(16)	172
	C2—H2···N3^{vii}	0.93	2.52	3.42(2)	163
	C5—H5···N6^{viii}	0.93	2.57	3.48(2)	166
Symmetry codes: (v) *x*–1/2, –*y*+1/2, *z*–1/2; (vi) *x*, –*y*+1, *z*+1/2; (vii) *x*+1/2, –*y*+1/2, *z*+1/2; (viii) *x*, –*y*+1, *z*–1/2.					
Mn-1	N2—H2···N5^{vi}	0.86	2.34	3.152(3)	158
	N7—H7···N10^{vii}	0.86	2.18	3.013(4)	162
Symmetry codes: (vi) *x*–1/2, *y*+1/2, *z*+1/2; (vii) *x*+1/2, *y*+1/2, *z*–1/2.					
Mn-2	N8—H8···N4^{v}	0.86	2.17	3.009(9)	167
	N10—H10···N1^{vi}	0.86	2.17	3.019(9)	168
	C2—H2···N3^{vii}	0.93	2.54	3.437(10)	161
	C5—H5···N6^{viii}	0.93	2.52	3.420(12)	163
Symmetry codes: (v) *x*–1/2, –*y*+1/2, *z*–1/2; (vi) *x*, –*y*+1, *z*+1/2; (vii) *x*+1/2, –*y*+1/2, *z*+1/2; (viii) *x*, –*y*+1, *z*–1/2.					
Mn-2 HT	N2—H2···N3^{ix}	0.85	2.41(5)	3.220(5)	158(4)
	C2—H2···N3^{ix}	0.85	2.41(5)	3.220(5)	158(4)
Symmetry codes: (ix) *x*–1/2, –*y*+3/2, –*z*+1/2.					

Table S3. The Raman and IR modes (in cm^{-1}) of Cd-1, Cd-2 and Mn-2 observed at RT and their proposed assignment.

IR	Raman	IR	Raman	IR	Raman	Assignment
Cd-1	**Cd-1**	**Cd-2**	**Cd-2**	**Mn-2**	**Mn-2**	
3556sh				3448vw		$\nu_{as}(\nu_3)N_3^- + \nu_s(\nu_1)N_3^-$

	3307vw	3427vw		3412w		$\nu_{as}(\nu_3)N_3^- + \nu_s(\nu_1)N_3^-$
3349w		3397vw				νNH, $\nu_{as}(\nu_3)N_3^-$ + $\nu_s(\nu_1)N_3^-$
3308m		3378vw		3370vw		νNH
3235m		3325vw				νNH
3161m	3161m			3169m		νNH
	3148w					νNH
3139m	3138m	3141m	3146m	3146m	3151w	νCH
3128m	3128w	3127m	3128w	3130m	3131w	νCH
3057w	3060vw	3059w	3060vw	3058w	3059vw	overtone
2945w		2945w	2947vw	2945w	2946vw	overtone
2838w		2838w	2841vw	2838w	2850vw	overtone
2791vw		2791vw		2787vw		combination
2704vw		2705vw		2699vw		combination
2596vw		2593vw		2589vw		combination
	2106vw			2114sh		$\nu_{as}(\nu_3)N_3^-$
2088sh	2089w			2078vs	2072vw	$\nu_{as}(\nu_3)N_3^-$
2059vs		2056vs	2052vw	2062sh		$\nu_{as}(\nu_3)N_3^-$
2035vs		2045sh				$\nu_{as}(\nu_3)N_3^-$
		2016s		2006m		$\nu_{as}(\nu_3)N_3^-$
1694vw		1718vw		1713vw		γNH
1679vw		1644vw		1672vw		γNH
1605vw		1618vw		1637vw		γNH
1535m	1535w	1536m	1536w	1534m	1535w	νRing
1504w	1506vw	1501w	1503vw	1502w	1502w	νRing
1488w	1487vw	1489w	1489vw	1488m	1488w	νRing
1433w	1434w	1431w	1436w	1432sh	1435sh	δNH, νRing
	1427sh	1425w	1426w	1423w	1425w	δNH, νRing
1384w		1384vw				combination
	1355m	1353vw	1354vs	1357w	1358vs	$\nu_s(\nu_1)N_3^-$
1330m	1338vs	1328m	1328m	1325m	1326w	$\nu_s(\nu_1)N_3^-$
	1291vw		1291vw			δCH
	1272vw				1276vw	δCH
1261w	1257m	1260m	1258m	1258m	1255m	δCH
	1224vw	1243vw	1243vw	1239w	1238vw	δCH
	1178w		1177m		1175m	δCH, δRing
1172w	1171m	1169w	1134w	1164w		δCH, δRing
1136w	1134m	1138w		1135w	1132w	δCH, δRing
1128w						δCH, δRing
1108w	1105w					δCH, δRing
1098w	1099w	1099w	1100w	1097w	1098w	δCH, δRing
1067m	1068w	1069s	108w	1066s	1066vw	δRing
939w	940w	941w	940w	940w	938vw	γCH
921w	921w	915vw	917w	916w	917vw	γCH
		883vw	886vw	879vw	882vw	γCH, γNH

	856vw	873vw		871vw		γNH, δRing
837w	839vw	841sh	835vw	840w	837vw	γNH, δRing
		818w		804w		γNH
780w		780m		776m		γNH
757w	756vw	757sh				γNH
732m						γNH
649s	653vw	654s	655vw	657s	658vw	$\delta(\nu_2)N_3^-$
637w				640m		$\delta(\nu_2)N_3^-$
618w	619vw	623m	623vw	619m	620vw	$\delta(\nu_2)N_3^-$
612s		613m		610m		$\delta(\nu_2)N_3^-$
	265vw		263w	259vw		T'(Mn)
	224sh	231sh	231m	234m		LN_3^- T'(Mn)
	214m	215m	210m		213m	LN_3^- LIm
	179sh				184sh	T'(Mn)
					180m	T'(Mn)
	173m		168s	172m	172m	$T'N_3^-$ LIm
	139s	155m	152m	164sh	148w	$T'N_3^-$
	116m		124m	132w	120m	$T'N_3^-$ T'Im T'Cd
			109m			T'Cd

Key: s-very strong, s-strong, m-medium, w-weak, vw-very weak; ν_s–symmetric stretching, ν_{as}-asymmetric stretching, ν_s–symmetric stretching, ν_{as}–asymmetric stretching, δ_{as}-asymmetric bending, δ_s, δ-symmetric bending (scissoring), γ – out-of-plane bending, ρ-rocking, ω-wagging, τ-twisting (torsion), T–translation, L–libration.

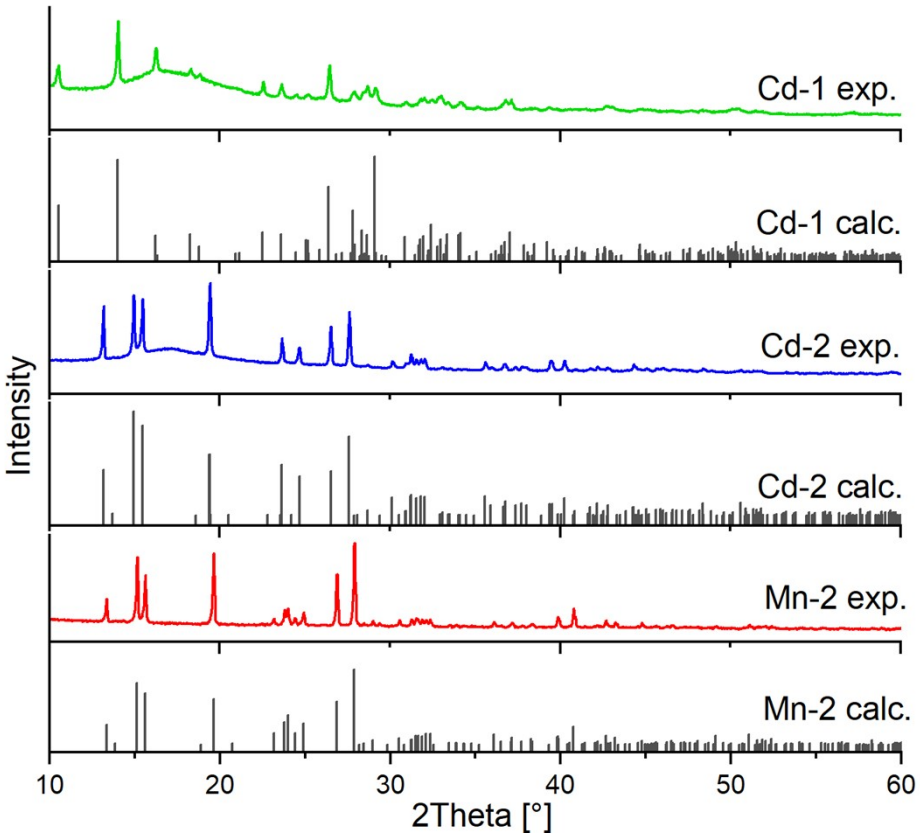

Fig. S1. PXRD patterns of Cd-1, Mn-1 and Mn-2.

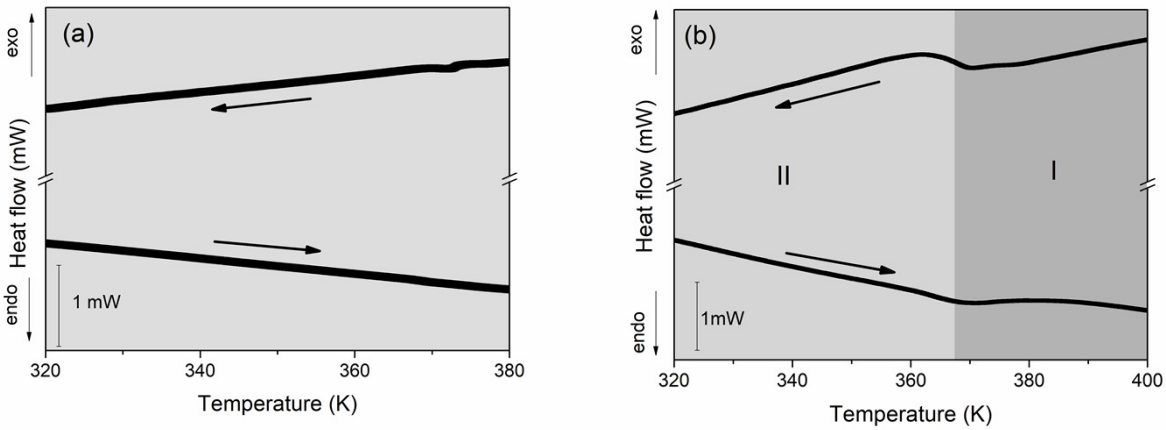

Fig. S2. DSC traces of (a) Cd-2 and (b) Mn-2 measured in a heating and cooling run.

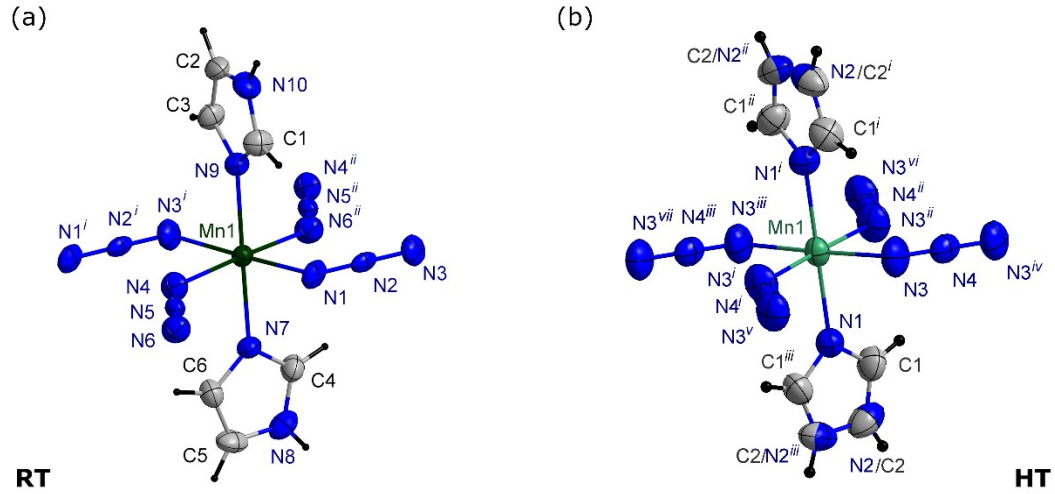

Fig. S3. The comparison of the asymmetric unit of **Mn-2** with the part that complete octahedral coordination of the Mn ion presented with atom numbering scheme for (a) RT (symmetry codes: (i) *x*−1/2, *y*−1/2, *z*; (ii) *x*+1/2, *y*+1/2, *z*) and (b) HT phase (symmetry codes: (i) *y*, −x+1, −*z*+1; (ii) −*y*+1, *x*, −*z*+1; (iii) −*x*+1, −*y*+1, *z*; (iv) −*x*+1, −*y*+2, *z*; (v) −*y*+2, *y*, −*z*+1; (vi) *y*−1, −*x*+1, −*z*+1; (vii) *x*, *y*−1, *z*). All non-hydrogen atoms are shown in ellipsoid representation at 50% probability level.

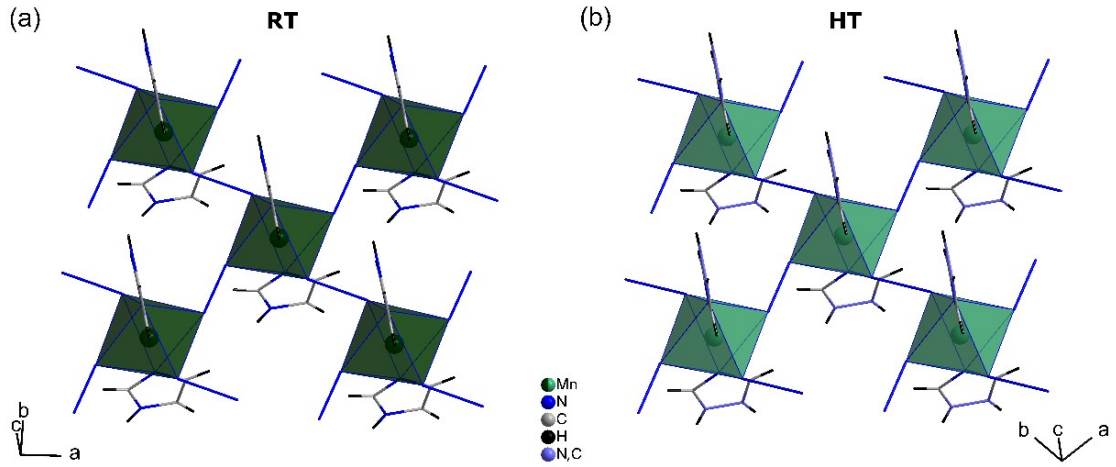

Fig. S4. The view at single *ab*-planes of **Mn-2** structures showing azides anions linking Mn octahedra in two different phases: (a) RT and (b) HT phase.

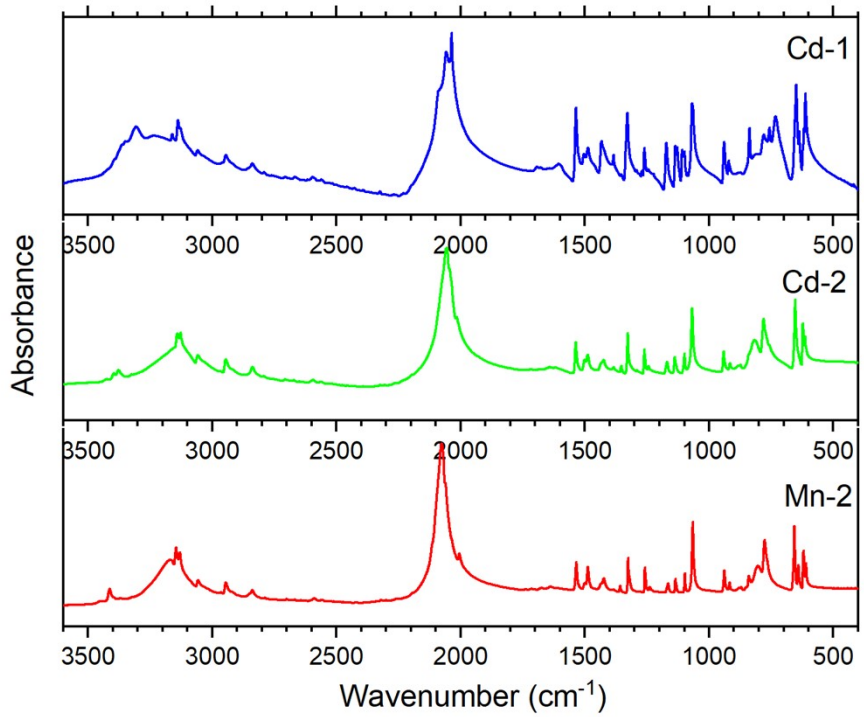

Fig. S5. The IR spectra of metal-imidazole azides.

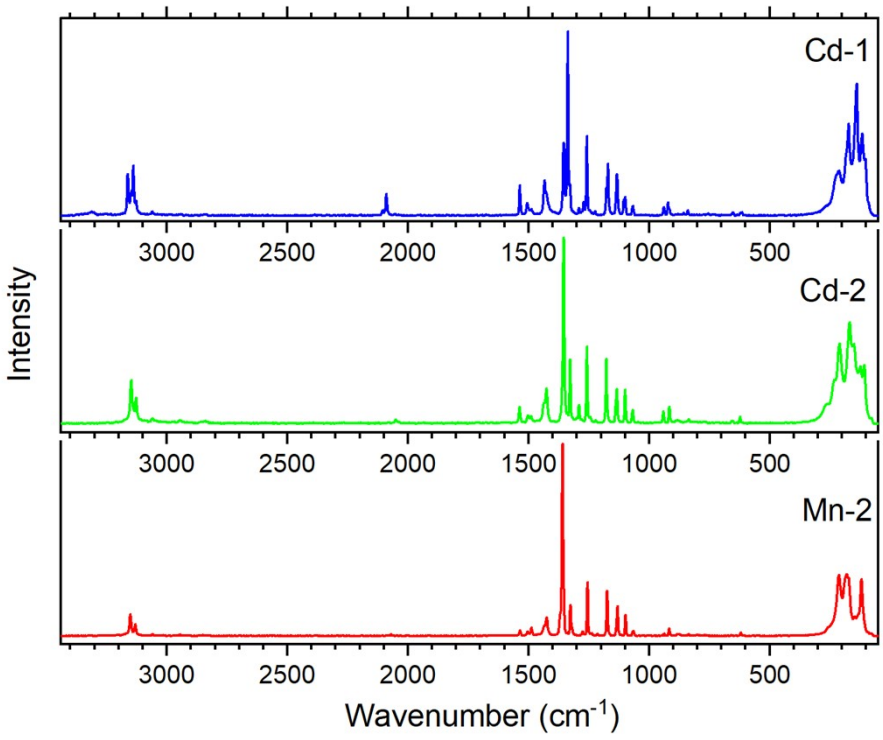

Fig. S6. The Raman spectra of metal-imidazole azides.

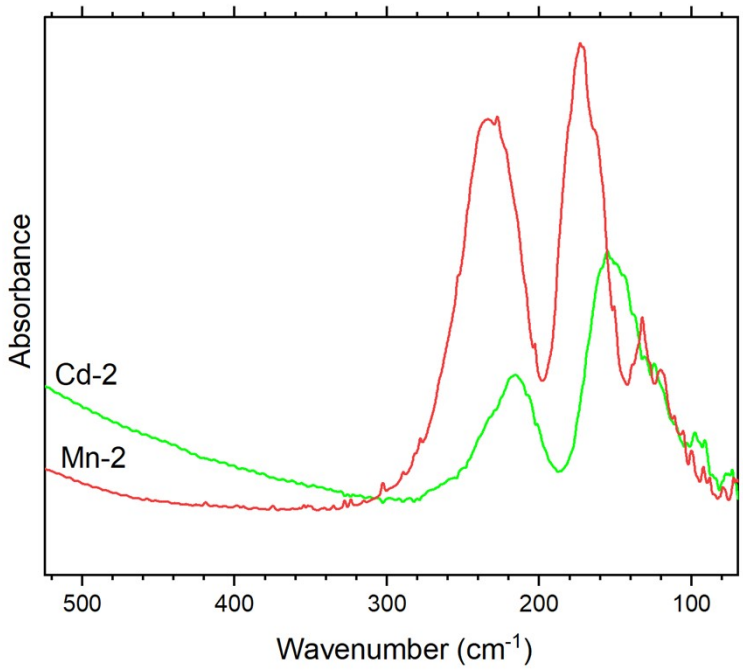

Fig. S7. The far- IR spectra of metal-imidazole azides.

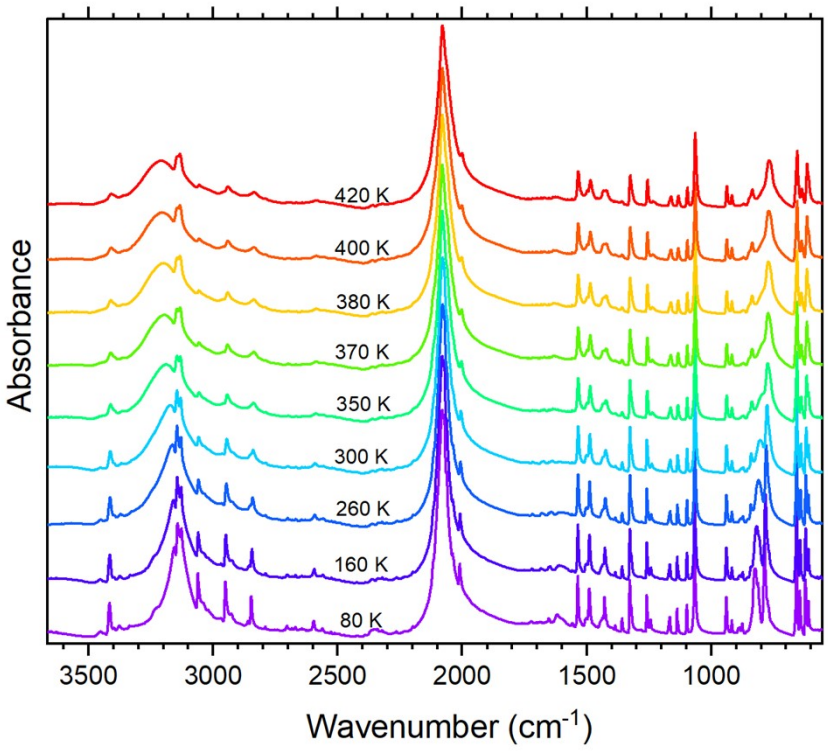

Fig. S8. The IR spectra of Mn-2.

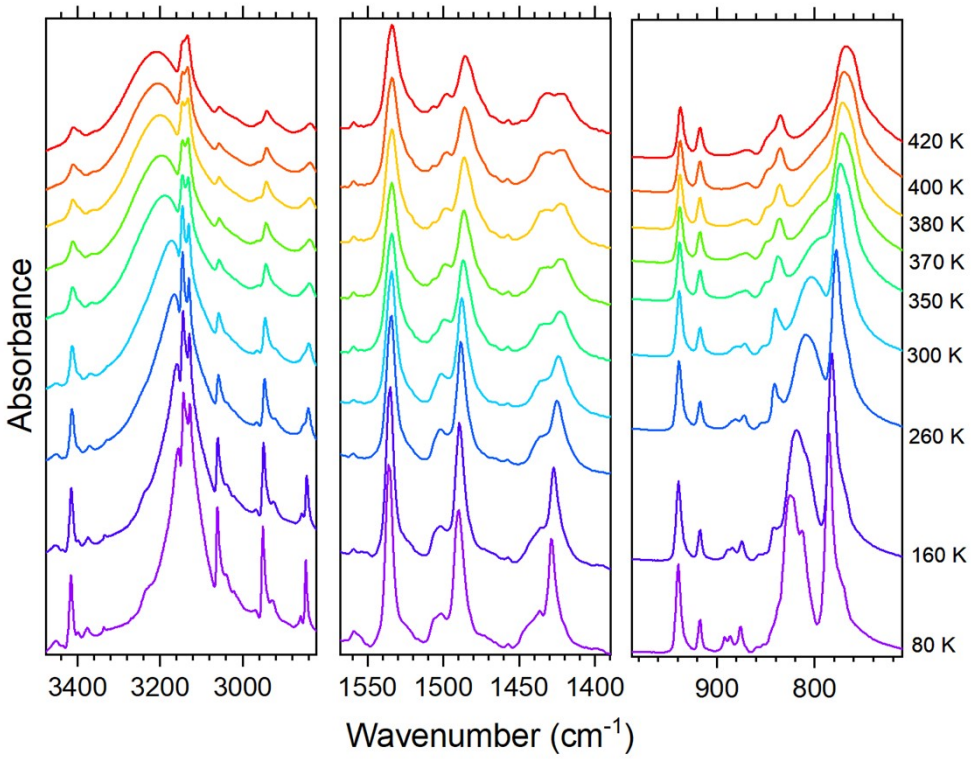

Fig. S9. The details of IR spectra of Mn-2.

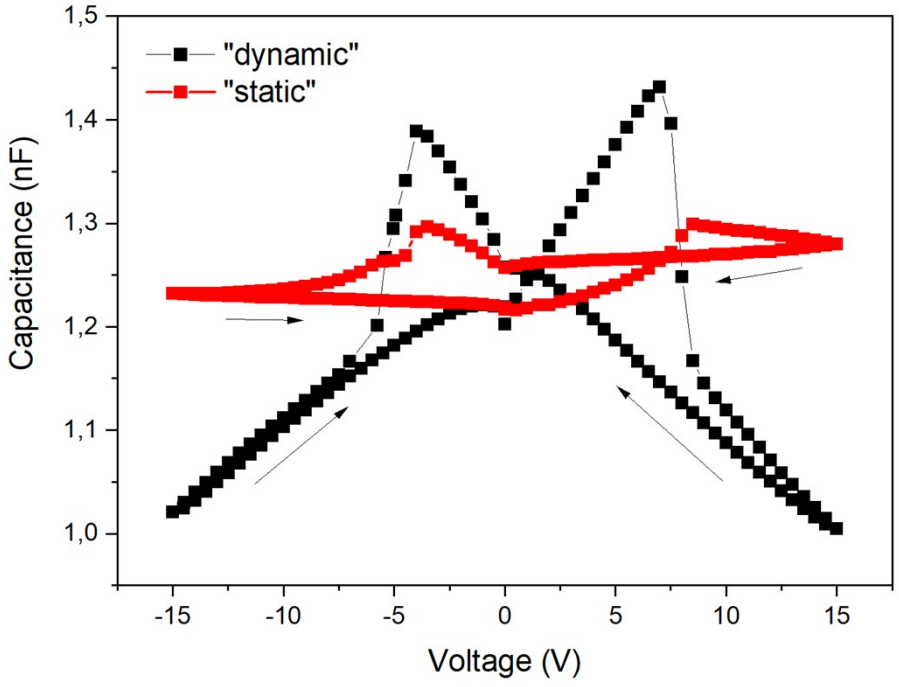

Fig. S10. The C-V characteristics of the PZT thin film.

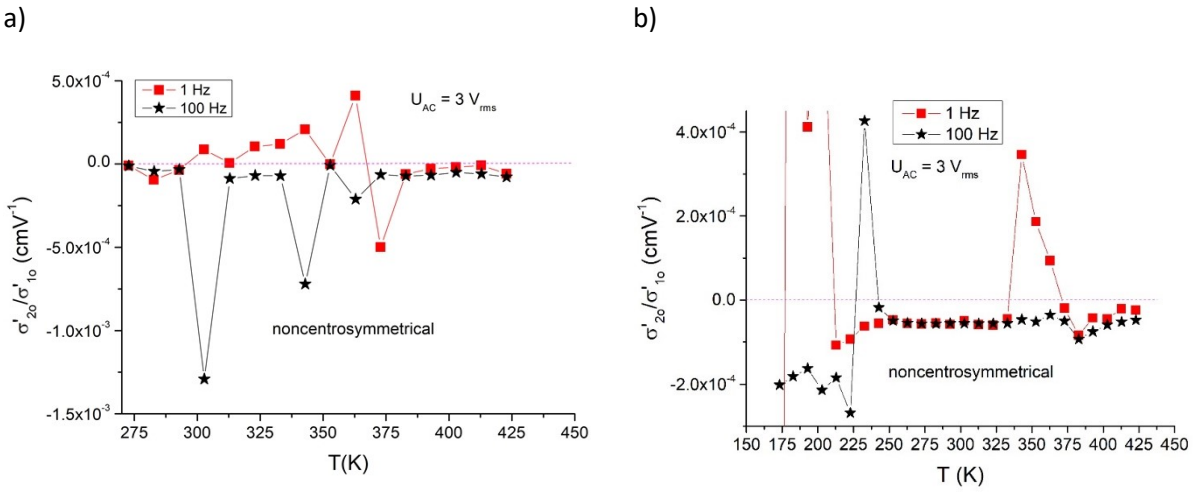

Fig. S11. The ratio of the second-order conductivity coefficient to the linear conductivity versus temperature at frequencies of 1 and 100 Hz for samples: (a) Mn-2 and (b) Cd-2.

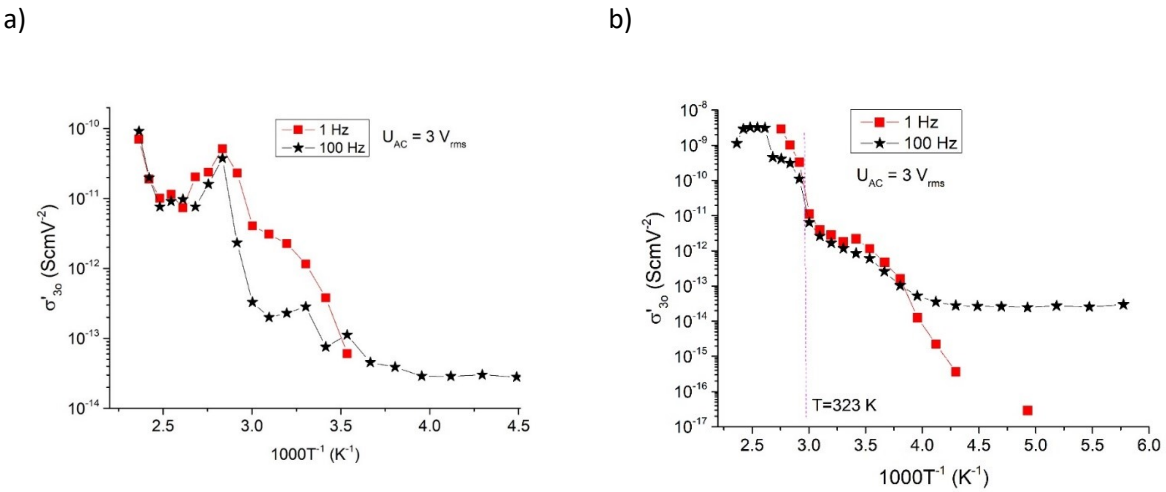

Fig. S12. The third-order conductivity coefficient versus temperature measured at frequencies of 1 and 100 Hz for samples: (a) Mn-2 and b) Cd-2.