Table S1. Data collection, cell, and refinement parameters for DMMnD, DMMn, DMNiD and DMNi at 298 K.

Compound	**DMMnD**	**DMMn**	**DMNiD**	**DMNi**
	$[(CH_3)_2ND_2][Mn(HCOO)_3]$	$[(CH_3)_2NH_2][Mn(HCOO)_3]$	$[(CH_3)_2ND_2][Ni(HCOO)_3]$	$[(CH_3)_2NH_2][Ni(HCOO)_3]$
Crystal data				
Chemical formula	$C_5H_9D_2NO_6Mn$	$C_5H_{11}NO_6Mn$	$C_5H_9D_2NO_6Ni$	$C_5H_{11}NO_6Ni$
M_r	*238.1*	*235.75*	*241.87*	*239.86*
Crystal system, space group	Trigonal, *R*-3*c*	Trigonal, R-3c	Trigonal, *R*-3*c*	Trigonal, *R*-3*c*
Temperature (K)	298	298	298	298
$a=b$, c (Å)	8.3315(6), 22.886(3)	8.3170(6), 22.851(3)	8.1211(6), 21.997(3)	8.147(1), 22.067(5)
γ (°), Z	120, 8	120, 8	120, 8	120, 8
V (Å^3)	1375.8(2)	1368.9(2)	1256.4(2)	1268.5(4)
Crystal description	pink rectangular prism (0.18 x 0.18 x 0.16 mm)	pink rectangular prism (0.19 x 0.17 x 0.13 mm),	green rectangular prism (0.20 x 0.18 x 0.16 mm)	green rectangular prism (0.20 x 0.15 x 0.12 mm)
Data collection and refinement				
Θ range (°)	3.44<θ<25.68	3.44<θ<25.64	4.71<θ<25.68	4.69<θ<25.66
No. of measured and unique ref.	4021, 273	4425, 290	4288, 271	4187, 272
R_{int}	0.043	0.031	0.035	0.020
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.061, 1.07	0.020, 0.054, 1.03	0.017, 0.046, 1.03	0.014, 0.040, 1.14
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.17, -0.29	0.18, -0.28	0.18, -0.19	0.18, -0.16

Table S2. The correlation diagram showing the correspondence between the optical modes in the $R\bar{3}c$ and *Cc* structures of $[(CH_3)_2NH_2][M(HCOO)_3]$, where X=H or D, M=Mn or Ni (the data for the *Cc* structure are given in parentheses). For the *Cc* structure, the model of full ordering of DMA^+ cations proposed for $[(CH_3)_2NH_2][Mn(HCOO)_3]$ was used.[10]

ion	vibration	Free ion symmetry	Site symmetry	Factor group symmetry
HCOO-		**C_{2v}**	**C_2 (C_1)**	**D_{3d} (C_s)**
	ν_1, ν_2 or ν_3	A_1	A (A)	$A_{1g}+E_g+A_{1u}+E_u$ (3A'+3A")
	ν_4, ν_5 or ν_6	B_1	B (A)	$A_{2g}+E_g+A_{2u}+E_u$ (3A'+3A")
	T'	$A_1 + B_1 + B_2$	A+2B (3A)	$A_{1g}+2A_{2g}+3E_g+A_{1u}+2A_{2u}+3E_u$ (9A'+9A")
	L	$A_2 + B_1 + B_2$	A+2B (3A)	$A_{1g}+2A_{2g}+3E_g+A_{1u}+2A_{2u}+3E_u$ (9A'+9A")
DMA^+		**C_{2v}**	**C_2 (C_1)**	**D_{3d} (C_s)**
	$\nu_s(NH_2)$	A_1	A (A)	(A'+A")
	$\nu_{as}(NH_2)$	B_2	B (A)	(A'+A")
	$\delta(NH_2)$	A_1	A (A)	(A'+A")
	$\rho(NH_2)$	B_2	B (A)	(A'+A")
	$\omega(NH_2)$	B_1	B (A)	(A'+A")
	$\tau(NH_2)$	A_2	A (A)	(A'+A")
	$\nu_s(CNC)$	A_1	A (A)	(A'+A")
	$\nu_{as}(CNC)$	B_1	B (A)	(A'+A")
	$\delta(CNC)$	A_1	A (A)	(A'+A")
	$\nu_s(CH_3)$	A_1+B_1	A+B (2A)	$A_{1g}+A_{2g}+A_{1u}+A_{2u}$ (2A'+2A")
	$\nu_{as}(CH_3)$	$A_1+B_1+ B_2+A_2$	2A+2B (4A)	$2E_g+2E_u$ (4A'+4A")
	$\delta_s(CH_3)$	A_1+B_1	A+B (2A)	$A_{1g}+A_{2g}+A_{1u}+A_{2u}$ (2A'+2A")
	$\delta_{as}(CH_3)$	$A_1+B_1+ B_2+A_2$	2A+2B (4A)	$2E_g+2E_u$ (4A'+4A")
	$\rho(CH_3)$	$A_1+B_1+ B_2+A_2$	2A+2B (4A)	$2E_g+2E_u$ (4A'+4A")

	$\tau(CH_3)$	A_2+B_2	A+B (2A)	$A_{1g}+A_{2g}+A_{1u}+A_{2u}$ (2A'+2A")
	T'	$A_1 + B_1 + B_2$	A+2B (3A)	(3A'+3A")
	L	$A_2 + B_1 + B_2$	A+2B (3A)	(3A'+3A")
M^{2+}			**S_6 (C_1)**	**D_{3d} (C_s)**
			A_u (A)	$A_{1u}+A_{2u}$ (A"+A')
			E_u (2A)	$2E_u$ (2A"+2A')

Table S3. IR and Raman frequencies (in cm^{-1}) of DMMn and DMNi and suggested assignments.[a]

DMMn				DMNi		Assignment
Raman 295 K	Raman 5 K	IR 295 K	IR 5 K	IR 295 K	IR 5 K	
	3116w	3106sh	3122w	3110sh	3127w	overtone
		3069w	3062w	3061w	3066w	$\nu(NH_2)$
3046m	3041m		3041w	3034w	3054w	$\nu_{as}(CH_3)$
3036m	3031m, 3027m					$\nu_{as}(CH_3)$
		3029m	3030w, 3018m	3024m	3005m, 2995m	$\nu(NH_2)$
			3000m			
2972s	2970s	2974w	2972w		2977w	$\nu_{s(}CH_3)$
2942w	2944w	2940w	2947m	2946m	2952w	$\nu_{s(}CH_3)$
	2908vw, 2896vw		2906w			$\nu_4(HCOO^-) + \nu_5(HCOO^-)$
2870sh		2865sh		2868w		$\nu_4(HCOO^-) + \nu_2(HCOO^-)$
2854s	2873m	2853m	2873w	2849w	2882sh, 2877w	$\nu_1(HCOO^-)$
2827m	2841s, 2831w	2828m	2852sh, 2842m	2832w	2861vw, 2848w	$\nu_1(HCOO^-)$
	2821vw		2823w		2827vw	$2\delta_{as}(CH_3)$
	2798w, 2786w	2799m	2801s, 2789sh	2798m	2807s, 2789sh	$\nu(NH_2)$
2718w	2719w, 2706vw	2717w	2721w, 2707w			$2\nu_2(HCOO^-)$
			2689w			
		2499w	2569w, 2557vw	2502w	2571w, 2558w	$\rho(NH_2)+\delta(NH_2)$ and
			2533sh, 2522w		2538w, 2524w	$\rho(NH_2)+\delta(CH_3)$
			2509w, 2454vw		2515w, 2508w	
			2479v, 2471vw			combinations of $\rho(CH_3)$, $\delta(CH_3)$ and $\nu_{as}(CNC)$
			2464vw, 2454w			
1625vw	1641vw	1632m	1645m	1634m	1645m	$\delta(NH_2)$

1578vw	1595vw, 1575vw	1594vs	1597vs, 1571w	1587vs	1599sh, 1590s 1580sh, 1567sh	$\nu_4(HCOO^-)$
1472sh	1485sh, 1475w	1472w	1486vw, 1480w 1476w	1475w	1482w, 1479w	$\delta_{as}(CH_3)$
1459w	1457m	1459w	1459w	1460w	1461w	$\delta_{as}(CH_3)$
1444sh	1442w, 1430w	1441w	1443w, 1429vw	1443w	1445w, 1431vw	$\delta_{as}(CH_3)$
	1425w		1425w		1423w	$\omega(NH_2)$
	1416w		1417w		1418vw	$\tau(NH_2)$ and $\delta_s(CH_3)$
	1379sh, 1376m		1378s			$\nu_5(HCOO^-)$
1368s	1369s	1371s	1369s	1369s	1372s, 1370sh	$\nu_5(HCOO^-)$
1364s	1363m	1364m	1363m	1353m	1355m	$\nu_2(HCOO^-)$
1352m	1357w, 1350m 1347m	1352s	1353s, 1349sh	1345s	1346s, 1340w 1337s	$\nu_2(HCOO^-)$
	1267vw	1255vw	1267vw	1257vw	1269vw	$\rho(CH_3)$
	1091w	1092vw	1092vw	1093vw	1094vw	$\rho(CH_3)$
1071w	1080w					$\nu_6(HCOO^-)$
1064sh	1073w					$\nu_6(HCOO^-)$
	1051w					$\rho(CH_3)$
1026w	1030w	1025w	1030w	1029w	1034w	$\nu_{as}(CNC)$
	930w	904w,b	930w	910w,b	935w	$\rho(NH_2)$
893m	897m	893w	897w	900w	905w	$\nu_s(CNC)$
794sh	799w	795s	800s	814s	817s	$\nu_3(HCOO^-)$
789m	792m	792sh	795s	810sh	812s	$\nu_3(HCOO^-)$
406w	406w					$\delta(CNC)$
	326w		337w, 324vw		333s	$\tau(CH_3)$
		289s	302s	333s	362s, 345s	$T'(M^{2+})$

				283s	299s, 288s	T'(M^{2+})
226w	256w, 239vw	240w	258w, 243m	262m	269s, 256w	T'(M^{2+}) and T'($HCOO^-$)
	223vw, 217vw		240m, 230w			
			227w, 218w			
	210w	212sh	209w	238s	249s, 240s	T'(M^{2+}) and T'($HCOO^-$)
					221w	
		197s	203w, 198w	187m	206s, 195w	T'($HCOO^-$)
181s	192w, 185m		186w, 178vw		188vw	L($HCOO^-$)
	178s, 164m		163sh			
148w	157w, 147m	145m	157m, 144m	170m	176s, 157vw	L(DMA)
	139vw, 131w		133w, 127vw		152vw, 135w	L(DMA)
119m	122m, 114m					L($HCOO^-$)
	105m					
					121w, 114m	T'(DMA)
			98w	101m	103s	T'(DMA)

[a]Key: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder

Table S4. IR and Raman frequencies (in cm^{-1}) of DMMnD and DMNiD and suggested assignments.[a]

DMMnD				DMNiD		Assignment
Raman 295 K	Raman 5 K	IR 295 K	IR 5 K	IR 295 K	IR 5 K	
3046m	3041m		3041w		3055w	$\nu_{as}(CH_3)$
3036m	3031m, 3027m	3035vw	3031w, 3028w	3041w	3038w, 3034w	$\nu_{as}(CH_3)$
		3001w	3003w, 2994w	3001w	3012w, 3000w	$\delta_{as}(CH_3) + \nu_4(HCOO^-)$
2972s	2969s	2973vw	2970w	2980vw	2977w	$\nu_s(CH_3)$
	2940w	2932w	2936w, 2920w	2946m	2951w	$\nu_s(CH_3)$
				2920w	2933w, 2920w	$\nu_4(HCOO^-) + \nu_5(HCOO^-)$
2863sh		2863sh		2868w		$\nu_4(HCOO^-) + \nu_2(HCOO^-)$
2852s	2868m, 2863w	2852m	2868m	2850w	2876m, 2858m	$\nu_1(HCOO^-)$
2827m	2840s, 2831vw	2830m	2842m		2848w	$\nu_1(HCOO^-)$
	2822w				2827vw	$2\delta_{as}(CH_3)$
	2779vw		2804w, 2784w	2784m	2787m, 2777m	combinations of $\delta(CH_3)$
			2772sh			
2715w	2728vw, 2720w	2720w	2721w, 2708w	2700w	2730vw, 2719vw	$2\nu_2(HCOO^-)$
	2707w, 2688w		2691w		2704w, 2697w	
	2482vw	2466vw		2468vw	2486vw	combinations of $\rho(CH_3)$, $\delta(CH_3)$ and $\nu_{as}(CNC)$
		2439vw	2446vw	2444sh	2449vw	
	2423vw	2415vw	2418vw	2420vw	2432vw	
2270w	2271w	2271m	2272w, 2244sh	2271m	2278w, 2268sh	$\nu(ND_2)$
			2223m		2253sh, 2230m	
2215w	2219w, 2211w	2208w	2219w, 2212m	2213w	2224w, 2217m	$\nu(ND_2)$
			2195w		2204m	

					2183w	$\nu(ND_2)$
2139	2136m, 2130m	2149w	2152sh, 2136m	2149m	2152w, 2140m	$\nu(ND_2)$
			2132m		2134m, 2128m	
		2126sh	2122w	2127w	2117w	$\nu(ND_2)$
2087vw	2097w	2087w	2096m	2088sh	2100m	$\nu(ND_2)$
	2056vw	2048vw	2057m	2055vw	2065w	$\nu_2(HCOO^-) + \nu_3(HCOO^-)$
		2029vw	2040w			$\nu_2(HCOO^-) + \nu_3(HCOO^-)$
	1964vw, 1912vw 1876vw	1977vw	2012vw, 1994w	2000vw	2022vw, 2007vw	$\rho(NH_2)+\delta(NH_2)$ and
		1942vw	1989w, 1964w	1947vw	1992vw, 1968w	$\rho(NH_2)+\delta(CH_3)$
		1889w	1950vw, 912w, 1875w	1890vw	1955vw, 1914w 1874w	
1578vw	1591vw, 1580vw	1596vs	1593vs, 1587sh	1587vs	1596sh, 1590s	$\nu_4(HCOO^-)$
	1568vw		1567w		1579sh, 1563w	
	1473w	1468w	1473w	1472w	1486w, 1477w	$\delta_{as}(CH_3)$
1456w	1464w, 1456w	1459w	1461sh, 1458w	1459w	1466w, 1459w	$\delta_{as}(CH_3)$
1442vw	1445w, 1438w	1440w	1445vw, 1437w	1441w	1440w, 1436sh	$\delta_{as}(CH_3)$
1421vw	1430vw, 1418w			1421vw	1427vw, 1421vw	$\delta_s(CH_3)$
	1379sh, 1376m		1377s			$\nu_5(HCOO^-)$
1368s	1370s	1370s	1369s	1369s	1372s	$\nu_5(HCOO^-)$
1364s	1363m	1364m	1363m	1354m	1354m	$\nu_2(HCOO^-)$
1352m	1357w, 1350m	1352s	1353s, 1349sh	1345s	1345s, 1337s	$\nu_2(HCOO^-)$
	1347m					
1233w	1236w	1233w	1242w	1234w	1244w, 1237vw	$\rho(CH_3)$
1210w	1209w	1209w	1210w	1208w	1220vw, 1211w	$\delta(ND_2)$
1184w	1188w	1184w	1190w	1186w	1191w	$\delta(ND_2)$
1177w		1179sh		1177sh	1187vw	$\rho(CH_3)$
1071w	1080w	1072vw	1073vw	1071vw	1075w	$\nu_6(HCOO^-)$

1064sh	1072w					$\nu_6(HCOO^-)$
1027w	1030w	1025w	1031m	1029w	1034m	$\nu_{as}(CNC)$
950w	961w	949w	961w	948w	960w	$\omega(ND_2)$
	921vw		921vw		920w	$\tau\ (ND_2)$
891vw	896w	891vw	896vw	897w	903w	$\rho(CH_3)$
880m	886m	880vw	885vw	885w	891w	$\nu_s(CNC)$
					831m	$\nu_3(HCOO^-)$
	805w	799s	806s	817s	822s	$\nu_3(HCOO^-)$
	796m		798s	811sh	816m	$\nu_3(HCOO^-)$
793m	792m	793sh	791s		809s	$\nu_3(HCOO^-)$
		767w	776w	772w	785m	?
	733w	715w	732m	718w	736m	$\rho(ND_2)$
402w	402w					$\delta(CNC)$
	306w		333w		319m	$\tau(CH_3)$
		289s	302s	332s	361s, 344s	$T'(M^{2+})$
					337sh	
				283s	298s, 288s	$T'(M^{2+})$
226w	257w, 240vw	240w	258w, 243m	262m	269s, 256w	$T'(M^{2+})$ and $T'(HCOO^-)$
	223vw, 217vw		240m, 230w			
			226w, 218w			
	210w	212sh	209w, 207w	240s	249s, 241s	$T'(M^{2+})$ and $T'(HCOO^-)$
					220m	
		197s	203w, 197w	193m	206s, 195w	$T'(HCOO^-)$
181s	192w, 185m		186w, 182sh			$L(HCOO^-)$
	178s, 164m		177w, 164sh			
148w	156w, 145m	145m	159m, 155w	170sh	176s, 157vw	L(DMA)

		143m			
	139vw, 131w	131w, 126vw		152vw, 135w	L(DMA)
119m	122m, 114m				L($HCOO^-$)
	105m				
				120w, 113m	T’(DMA)
		97w	101m	103s	T’(DMA)

[a]Key: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder

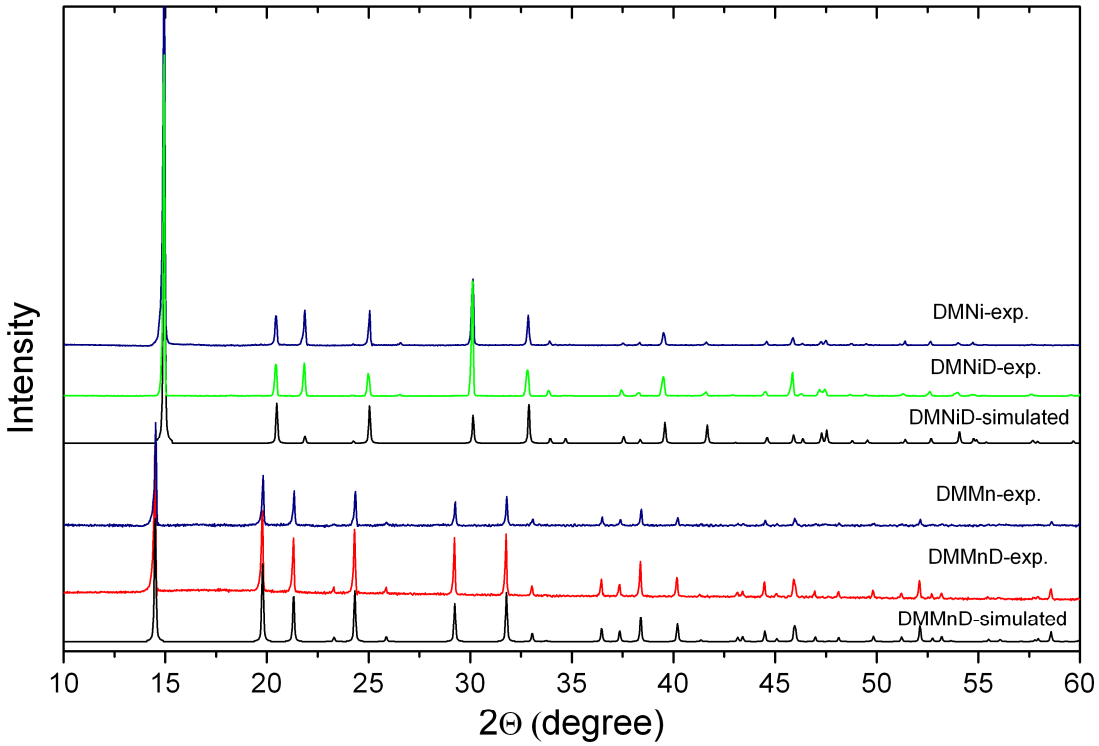

Figure S1. Powder XRD patterns for the as-prepared bulk samples of DMMn, DMMnD, DMNi and DMNiD, with the calculated ones for DMMnD and DMNiD based on the single crystal structures at 295 K.

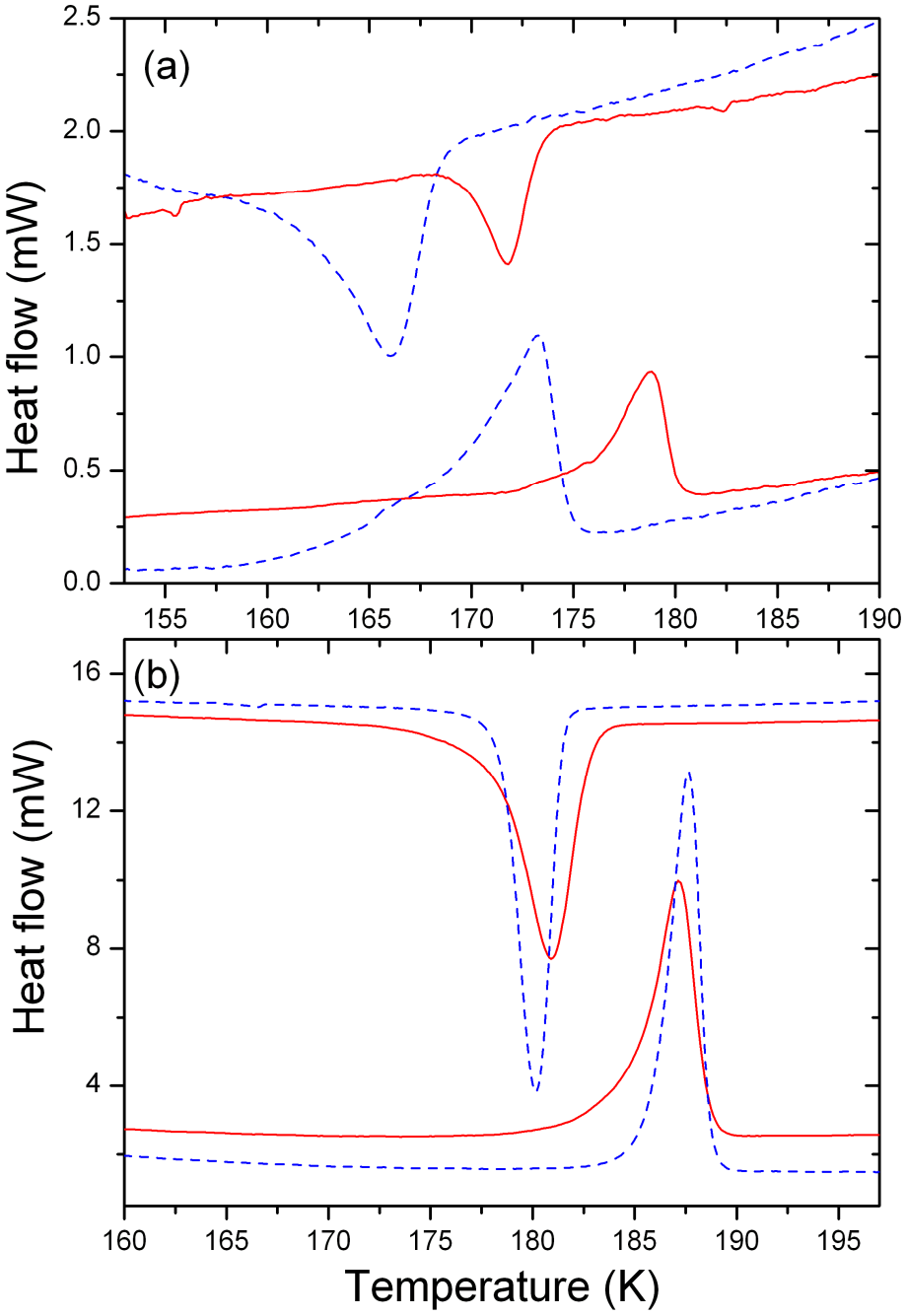

Figure S2. DSC traces for (a) DMNi (solid, red lines) and DMNiD (dash, blue lines) as well as (b) DMMn (solid, red lines) and DMMnD (dash, blue lines) in heating and cooling modes.

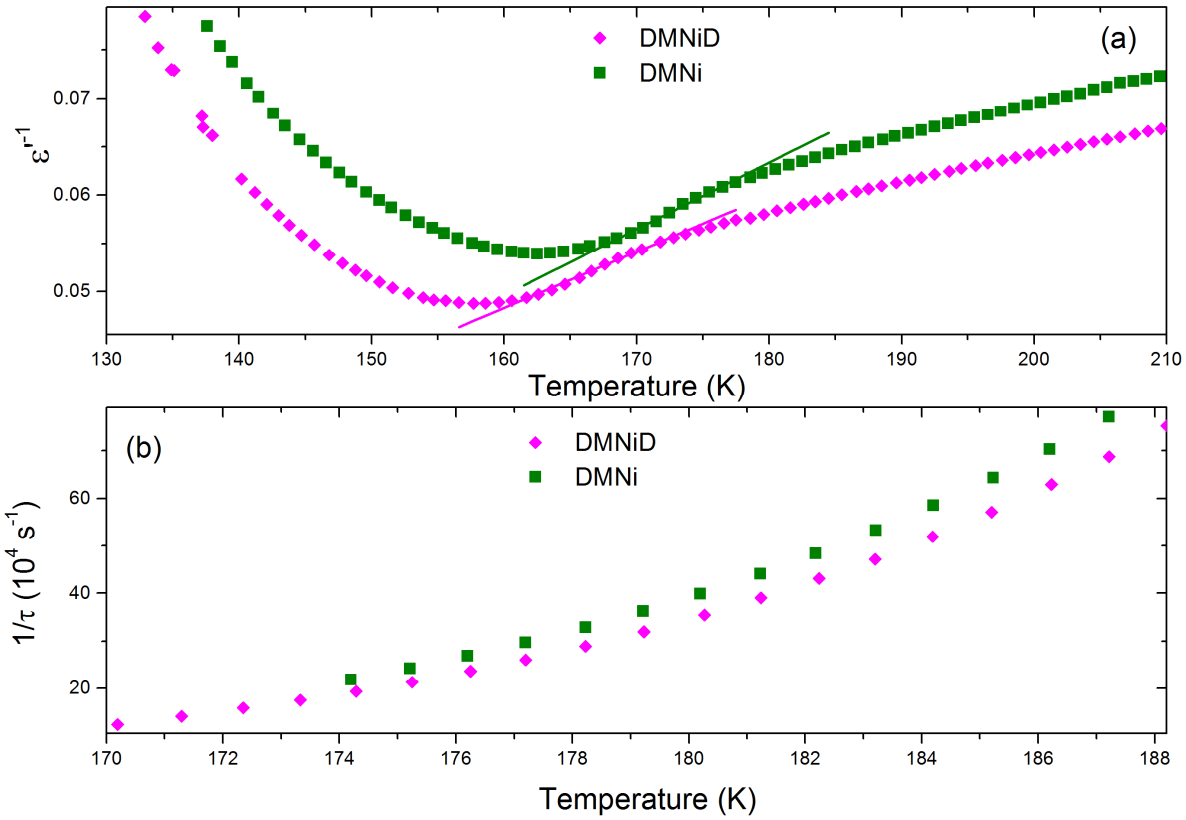

Figure S3. (a) The reciprocal dielectric permittivity at 1.2 Hz *vs* T plot and the Curie-Weiss fitting. (b) Temperature dependence of the reciprocal relaxation time in the paraelectric phases of DMNi and DMNiD.

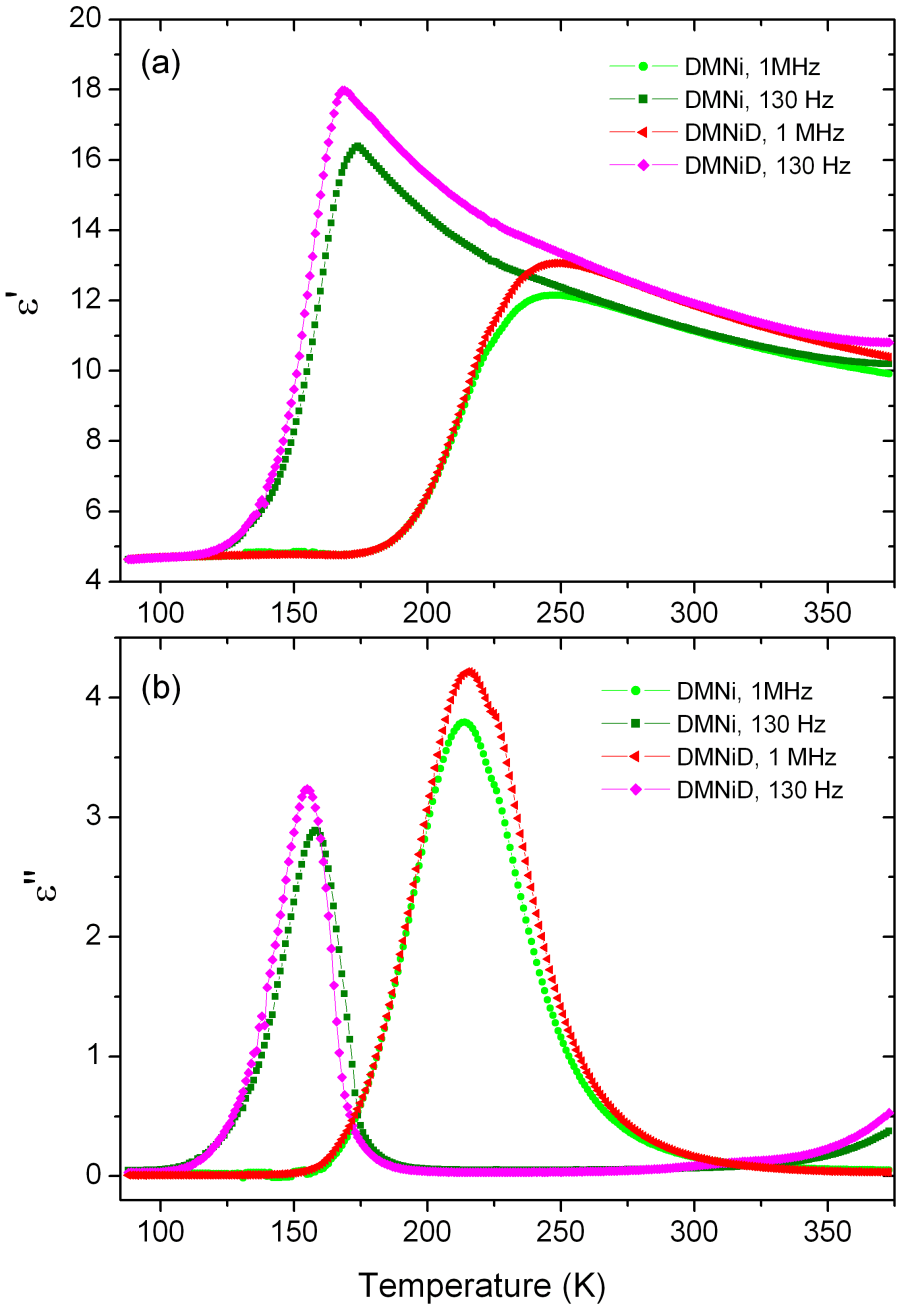

Figure S4. (a) The real part and (b) the imaginary part of the complex dielectric constant of DMNi and DMNiD measured at 1MHz and 0.13 KHz showing the difference between the both samples.

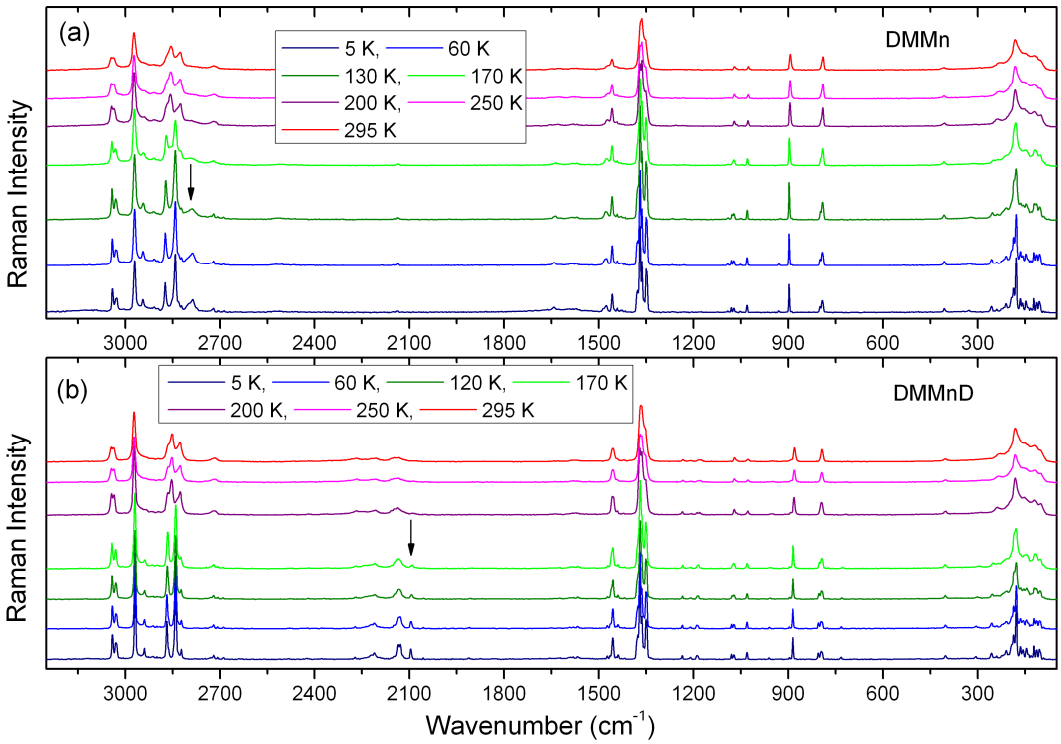

Figure S5. Raman spectra of (a) DMMn and (b) DMMnD recorded at various temperatures corresponding to the whole spectral range 80-3500 cm^{-1}. Arrows indicate the bands that exhibit pronounced increase in intensity upon cooling.

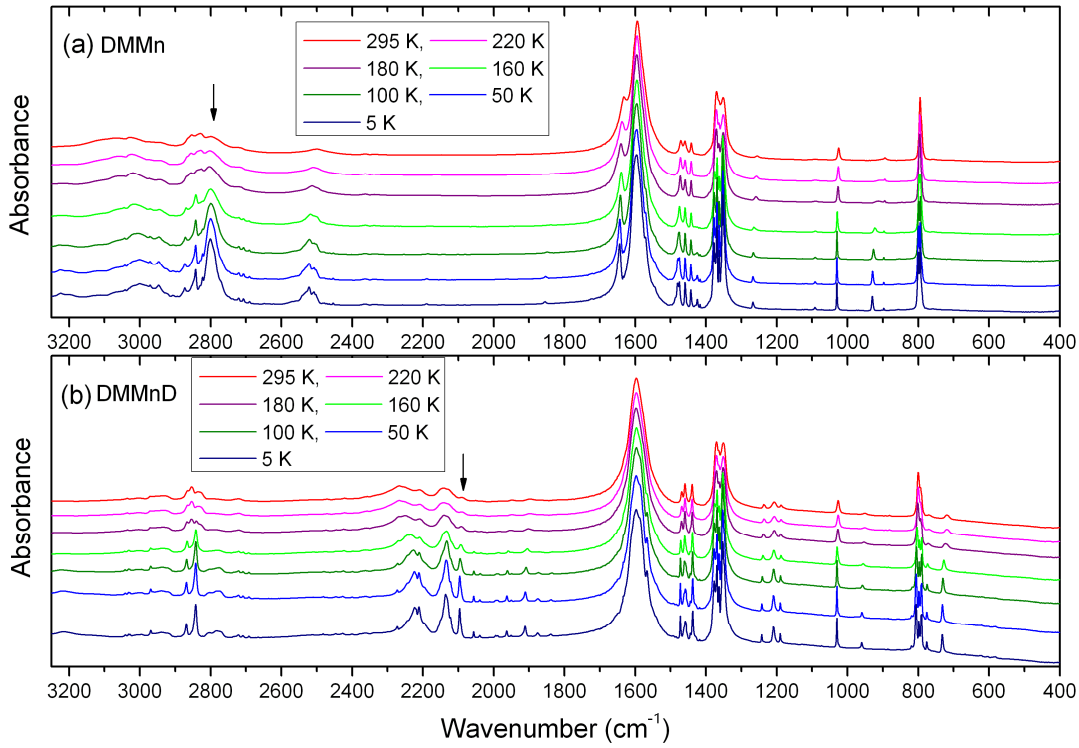

Figure S6. IR spectra of (a) DMMn and (b) DMMnD recorded at various temperatures corresponding to the spectral range 400-3250 cm^{-1}. Arrows indicate the bands that exhibits pronounced increase in intensity upon cooling.

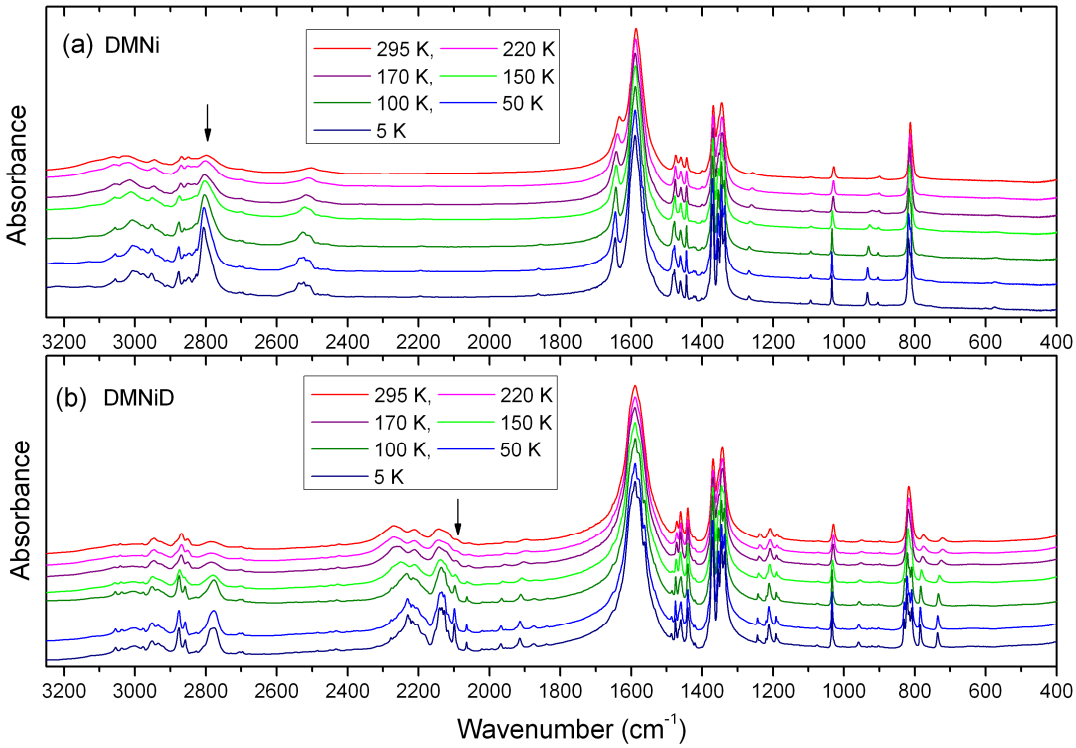

Figure S7. IR spectra of (a) DMNi and (b) DMNiD recorded at various temperatures corresponding to the spectral range 400-3250 cm^{-1}. Arrow indicates the band that exhibits pronounced increase in intensity upon cooling.

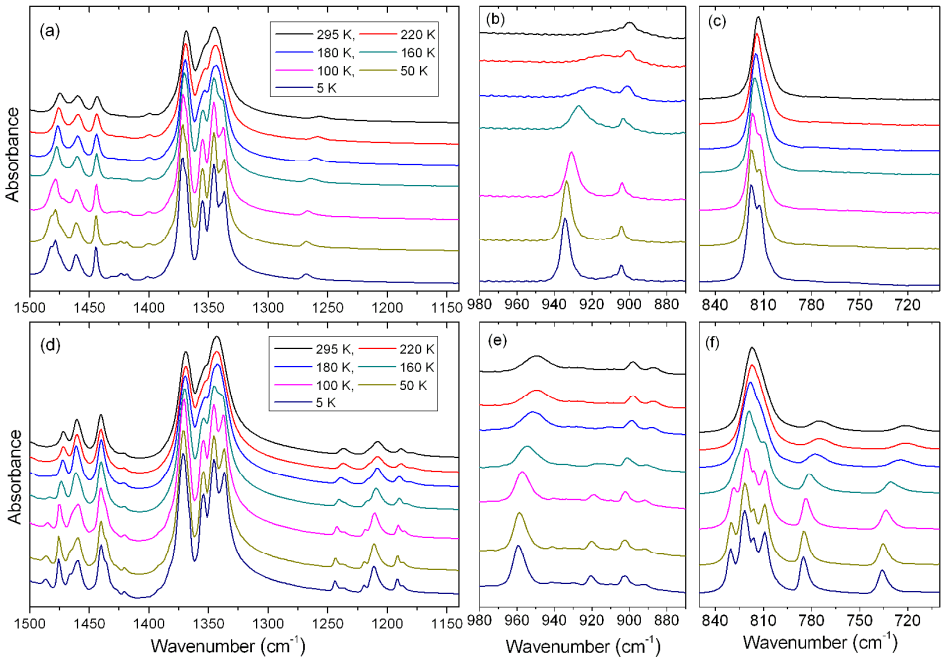

Figure S8. Detail of the IR spectra results corresponding to the spectral ranges 1140-1500, 870-980 and 700-850 cm^{-1} for DMNi ((a), (b) and (c)) and DMNiD ((d), (e) and (f)).

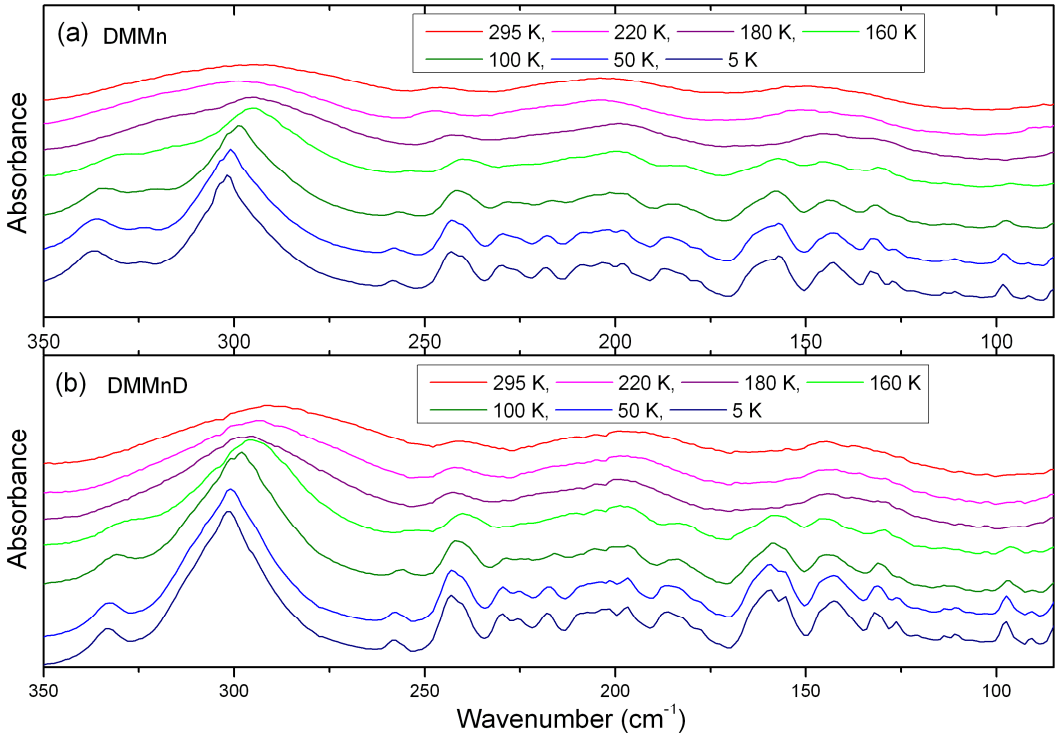

Figure S9. IR spectra of (a) DMMn and (b) DMMnD recorded at various temperatures corresponding to the spectral range 85-350 cm^{-1}.

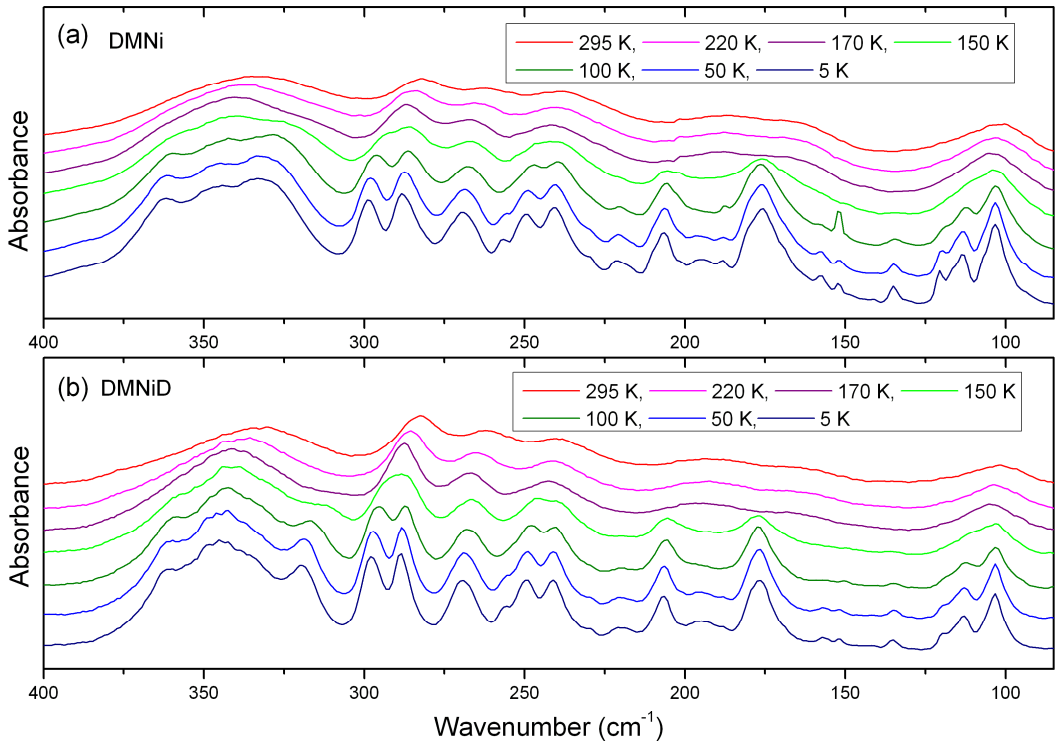

Figure S10. IR spectra of (a) DMNi and (b) DMNiD recorded at various temperatures corresponding to the spectral range 85-400 cm^{-1}.

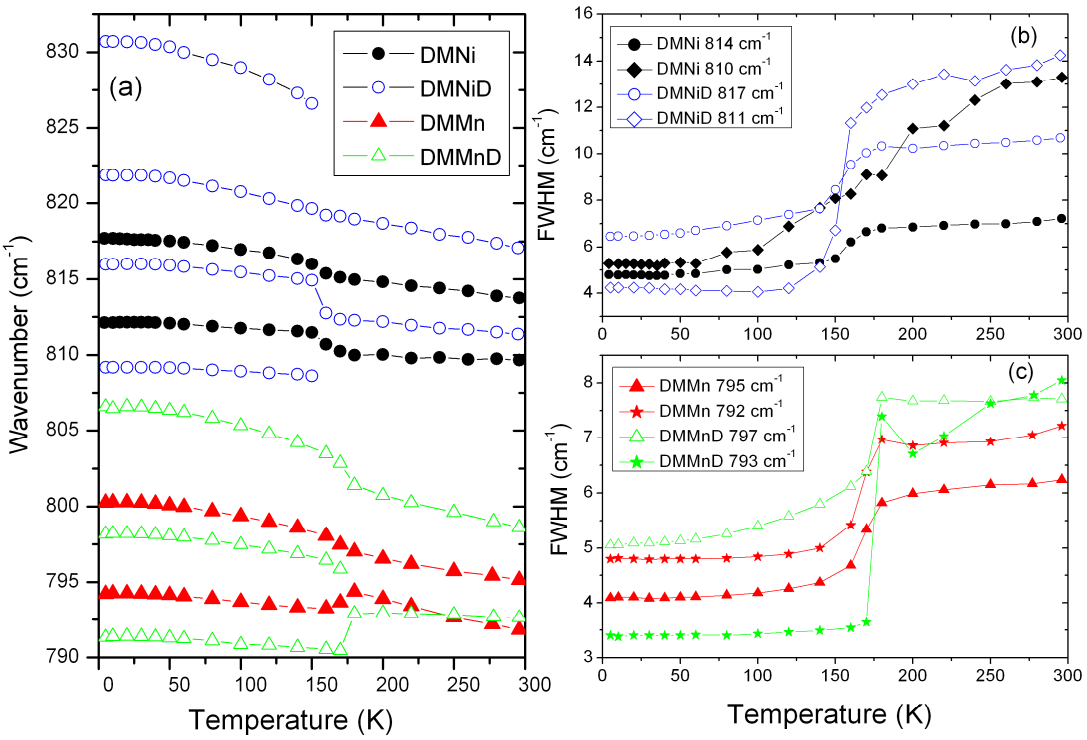

Figure S11. (a) Temperature evolution of $\nu_3(HCOO^-)$ mode IR frequencies and (b and c) FWHM of the respective modes of all studied samples. Solid lines are to guide the eye.

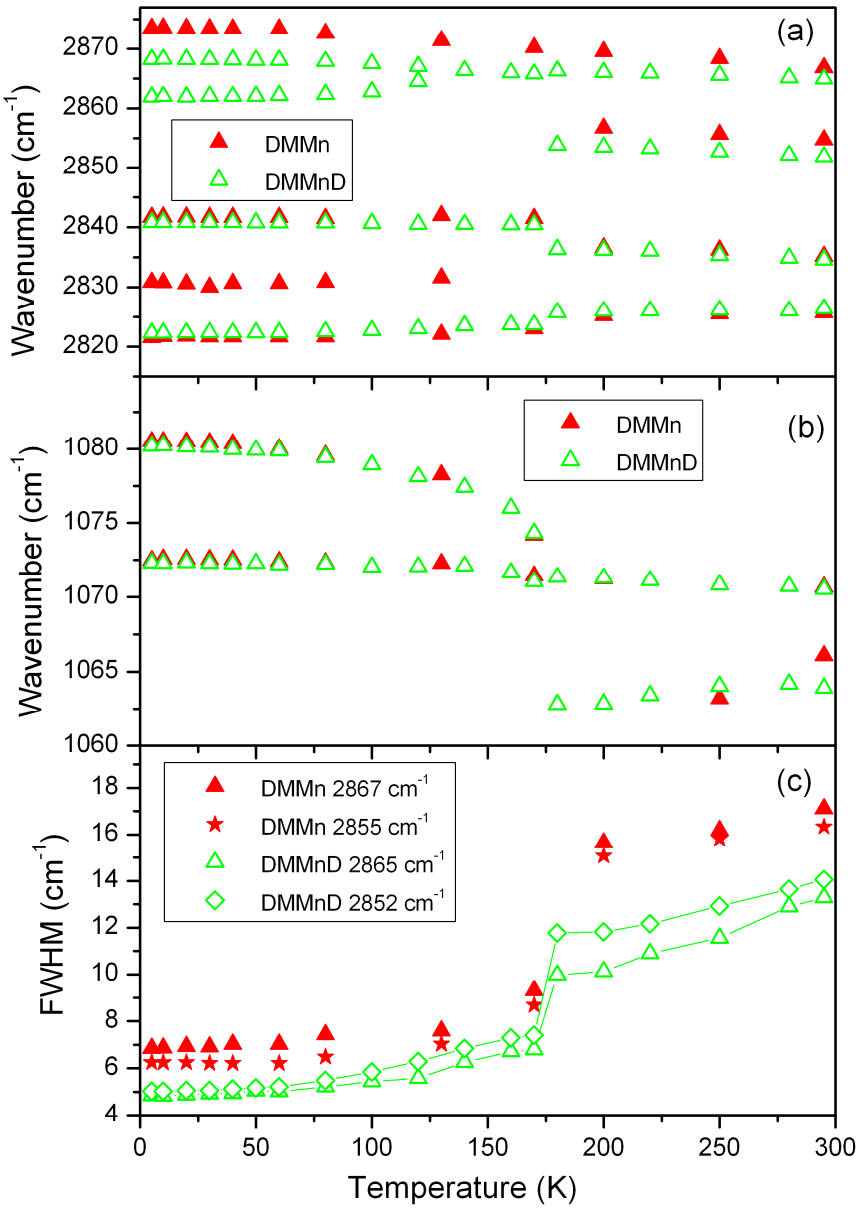

Figure S12. Temperature evolution of (a) $\nu_1(HCOO^-)$ and (b) $\nu_6(HCOO^-)$ mode Raman frequencies of DMMn and DMMnD. (c) Temperature evolution of FWHM of the 2852-2867 cm^{-1} Raman bands of DMMn and DMMnD corresponding to $\nu_1(HCOO^-)$ mode . Solid lines are to guide the eye.

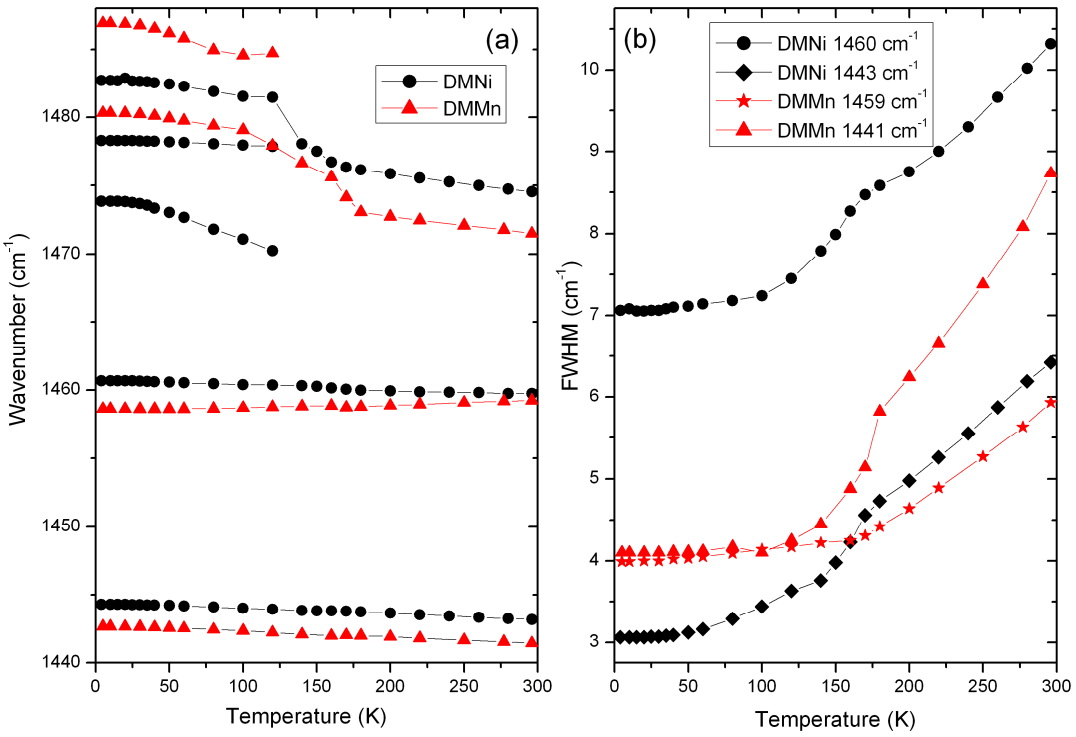

Figure S13. (a) Temperature evolution of $\delta(CH_3)$ mode IR frequencies and (b) FWHM of the respective modes of DMNi and DMMn. Solid lines are to guide the eye.

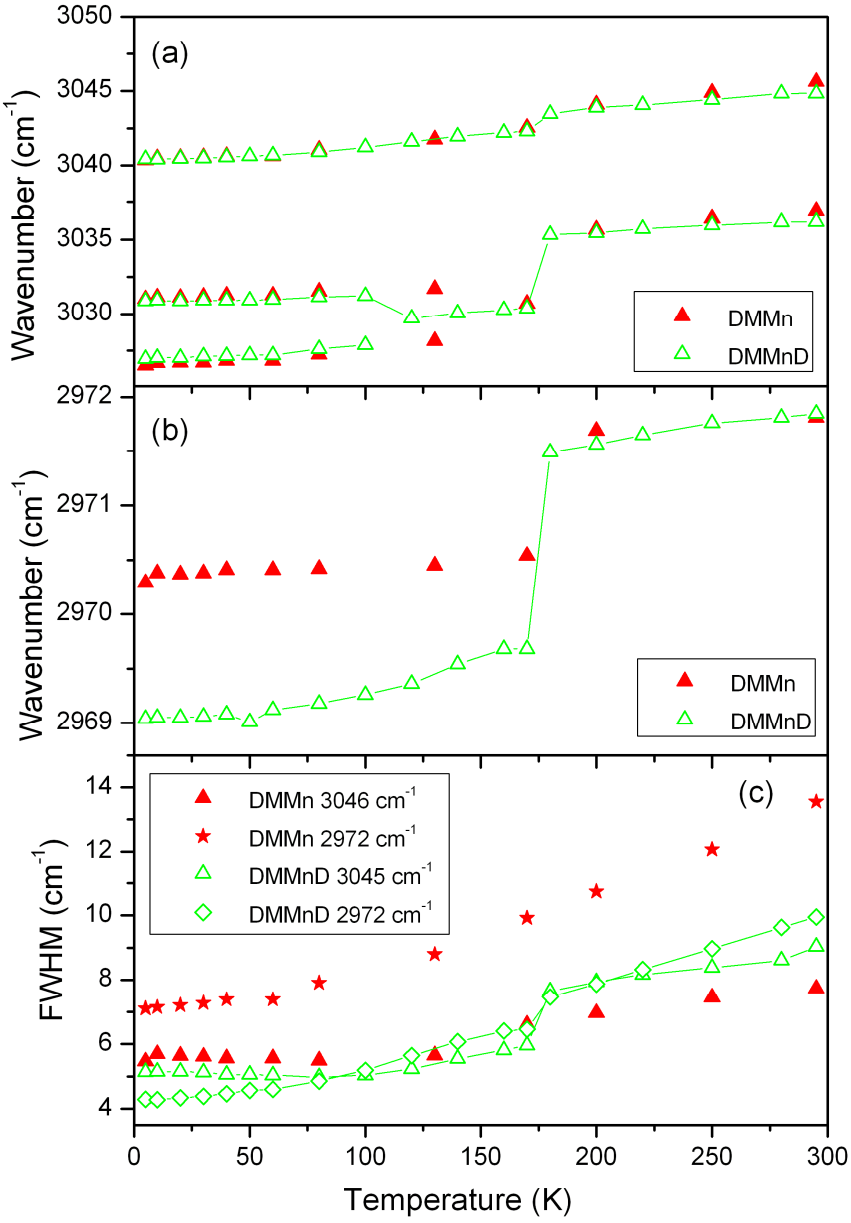

Figure S14. (a and b) Temperature evolution of ν(CH_3) mode Raman frequencies and (b) FWHM of the respective modes of DMMn and DMMnD. Solid lines are to guide the eye.