Electronic Supplementary Material (ESI) for Dalton Transactions.

"Structural, phonon, magnetic and optical properties of novel perovskite-like frameworks of TriBuMe[$M(dca)_3$] (TriBuMe= tributylmethylammonium; dca=dicyanamide; M=Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+})"

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S1. Selected geometric parameters (Å) for TriBuMeMn

Phase I		Phase II	
Mn1—N5^{i}	2.222 (5)	Mn1—N16	2.180 (3)
Mn1—N5^{ii}	2.222 (5)	Mn1—N6^{iv}	2.213 (3)
Mn1—N3^{iii}	2.234 (5)	Mn1—N17	2.221 (3)
Mn1—N3	2.234 (5)	Mn1—N12^{iii}	2.236 (3)
Mn1—N1^{iii}	2.226 (4)	Mn1—N3^{v}	2.244 (3)
Mn1—N1	2.226 (4)	Mn1—N9^{vi}	2.252 (3)
		Mn2—N13	2.192 (3)
		Mn2—N4	2.204 (3)
		Mn2—N1	2.215 (3)
		Mn2—N7	2.240 (3)
		Mn2—N10	2.241 (3)
		Mn2—N19^{vii}	2.246 (3)

Symmetry code(s): (i) *x*-1/2, *y*, -*z*+3/2; (ii) -*x*+3/2, -*y*+1, *z*-1/2; (iii) -*x*+1, -*y*+1, -*z*+1; (iv) *x*+1/2, -*y*+3/2, *z*+1/2; (v) -*x*+1/2, *y*-1/2, -*z*+3/2; (vi) *x*, *y*-1, *z*; (vii) *x*-1/2, -*y*+1/2, *z*-1/2.

Table S2. Room-temperature Raman wavenumbers (in cm^{-1}) of TriBuMeM samples and suggested assignments.[a] Modes corresponding to the dca ligand are denoted by red colour.

Raman Mn	Raman Fe	Raman Co	Raman Ni	Assignment
3045w	3046w	3044w	3045w	$\nu_{as}(CH_3)$
3036w	3034w	3036w	3036w	$\nu_{as}(CH_3)$
2996sh	2995sh	2994sh	2994sh	$\nu_{as}(CH_3)$
2972s	2974s	2974s	2976m	$\nu_{as}(CH_2)$
2940s	2940s	2942s	2943s	$\nu_{as}(CH_2)$
2923sh	2925sh	2923sh	2922sh	$\nu_{as}(CH_2)$
2879m	2881m	2881m	2882m	$\nu_{s}(CH_3)$
2871sh	2870sh	2873sh	2872sh	$\nu_{s}(CH_3)$
2280sh	2279sh	2281sh	2284sh	$\nu_{s}(C\equiv N)$
2244vs	2247vs	2252vs	2259vs	$\nu_{s}(C\equiv N)$
2239sh	2242s	2247sh	2254sh	$\nu_{s}(C\equiv N)$
2180m	2179m	2180m	2180m	$\nu_{as}(C\equiv N)$
2169sh, 2160m	2165m	2169m	2176m	$\nu_{as}(C\equiv N)$
2141vw	2151sh	2151sh	2160sh	$\nu_{as}(C\equiv N)$
1478sh	1478sh	1475sh	1477sh	$\delta_{as}(CH_3)$
1458m	1457w	1457w	1458m	$\delta_{s}(CH_3)$
1449m	1447w	1450w	1447w	$\delta_{s}(CH_3)$
1391vw	1389vw	1392vw	1394vw	$\omega(CH_2)$
1346vw	1347vw	1347vw	1346vw	$\nu_{as}(N\text{-}C)$
1324w	1318w	1319w	1322w	$\omega(CH_2)$
1310sh	1312sh	1312w	1312sh	$\omega(CH_2)$
1278vw	1280vw		1280vw	$\omega(CH_2)$

1239vw			1239vw	$\omega(CH_2)$
1193vw	1193vw		1196vw	$\tau(CH_2)$
1175vw	1177vw	1175vw	1176vw	$\tau(CH_2)$
1154vw	1155vw		1153vw	δ(skeletal)
1131vw	1131vw	1131vw	1132vw	δ(skeletal)
1109w	1107w	1107w	1110w	δ(skeletal)
1085vw	1080vw	1081sh	1081vw	overtone
1067sh			1070sh	δ(C-C-C)
1057w	1057w	1057w	1057w	δ(C-C-C)
1028vw,b	1023vw	1023vw	1026vw,b	δ(C-N-C) + δ(C-C-C)
970vw	969vw	964vw	968vw	δ(C-N-C) + δ(C-C-C)
961vw	960vw	959sh	960vw	δ(C-N-C) + δ(C-C-C)
927m	924m	924m	926m	ν_s(N-C)
910sh	910sh		913sh	ν_s(N-C)
888vw	890vw	885vw	890vw	ν(C-C)
879vw	876vw		879vw	δ(C-N-C)
797vw	796vw	798vw	796vw	ν(C-N-C)
767vw	771vw	777vw	711vw	$\rho(CH_2)$
739vw	740vw	742vw	740vw	$\nu(NC_4) + \rho(CH_2)$
657m	653m	652m	653m	δ_s(N-C-N)
576vw	576vw	576vw	577vw	γ_s(N-C-N)
541vw	541w, 536sh	541vw, 536sh	540w, 536sh	δ_{as}(N-C-N)
508vw	508vw	519sh, 509vw	516vw, 508vw	γ_{as}(N-C-N)
477vw	476vw	476vw	477vw	$\delta(NC_4)$

423vw	424vw	424vw	424vw	$\delta(NC_4)$
353vw	350vw	352vw	351vw	δ(skeletal)
337vw	336vw	334vw	338vw	δ(skeletal)
231sh	242sh	247m	268m	T'(dca) + T'(M^{2+})
221m	231m	238sh	255sh	T'(dca) + T'(M^{2+})
174s	187s	198s	220s	T'(dca) + L(dca) + T'(M^{2+})
	141vw	145vw	156sh	T'(dca) + L(dca)
108w	115w	120w	127w	T'(dca) + L(dca)
70m	74m	77m	84m	T'(dca) + L(dca)
46m	51m	54m	57m	$L(MN_6)$
19vw	20vw	23vw	24vw	$L(MN_6)$

[a]Key: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; b, broad; ν, δ, γ, ω, τ, ρ, T' and L denotes stretching, in-plane bending, out-of-plane bending, wagging, twisting, rocking, translational and librational, respectively.

Table S3. Room-temperature IR wavenumebrs (in cm^{-1}) of powdered TriBuMeM samples and suggested assignments.[a] Modes corresponding to the dca ligand are denoted by red colour.

IR Mn	IR Fe	IR Co	IR Ni	Assignment
3075w	3076w	3079w	3083w	$\nu_{as}(CH_3)$
3038vw	3043vw	3044sh	3044vw	$\nu_{as}(CH_3)$
2997sh	2995sh	2995sh	2993sh	$\nu_{as}(CH_3)$
2967m	2967m	2968m	2968m	$\nu_{as}(CH_2)$
2940m	2940m	2942m	2945m	$\nu_{as}(CH_2)$
2904vw	2903vw	2903sh	2908sh	$\nu_{s}(CH_2)$
2878m	2878m	2879m	2880m	$\nu_{s}(CH_3)$
2305m	2308m	2311s	2312s	$\nu_{s}(C\equiv N)$
2284s	2285s	2286s	2290s	$\nu_{s}(C\equiv N)$
2238s	2242s	2246s	2253s	$\nu_{s}(C\equiv N)$
2198sh	2199sh	2205sh	2209sh	$\nu_{as}(C\equiv N)$
2175vs	2177vs	2182vs	2190vs	$\nu_{as}(C\equiv N)$
2140sh	2142sh	2150sh	2156sh	$\nu_{as}(C\equiv N)$
1480m	1481m	1481m	1481m	$\delta_{as}(CH_3)$
1474m	1474m	1473m	1473m	$\delta_{as}(CH_3)$
1464sh	1465sh	1462sh	1463sh	$\delta_{s}(CH_3)$
1456sh	1457sh	1457sh	1457sh	$\delta_{s}(CH_3)$
1432w	1432w	1432w	1432w	$\omega(CH_2)$
1424w	1424vw	1424vw	1423w	$\omega(CH_2)$
1372m	1377m	1379s	1381s	$\nu_{as}(N\text{-}C)$
1357m	1355m	1358s	1360s	$\nu_{as}(N\text{-}C)$
1343m	1343m	1345s	1348s	$\nu_{as}(N\text{-}C)$

1314sh	1316sh	1320sh	1321sh	$\omega(CH_2)$
1283vw	1284vw	1283vw	1283vw	$\omega(CH_2)$
1270vw	1270vw	1270vw	1271vw	$\omega(CH_2)$
1251vw	1250vw	1250vw	1252vw	$\omega(CH_2)$
1239vw	1239vw	1239vw	1238vw	$\omega(CH_2)$
1193w	1193w	1193w	1193w	$\tau(CH_2)$
1175w	1174w	1174w	1175w	$\tau(CH_2)$
1153w	1153w	1153w	1154w	δ(skeletal)
1129w	1129w	1129w	1130w	δ(skeletal)
1109sh, 1103w	1109sh, 1103w	1110sh, 1104w	1109sh, 1104w	δ(skeletal)
1065sh	1068sh	1067sh	1068sh	δ(C-C-C)
1057w	1057w, 1051sh	1057w, 1050sh	1058w	δ(C-C-C)
1027w, 1018sh	1029w, 1017sh	1028w, 1018sh	1030w, 1019sh	δ(C-C-C)
997vw	999vw	997vw	998vw	δ(C-N-C) + δ(C-C-C)
972w	972vw	972vw	972vw	δ(C-N-C) + δ(C-C-C)
959vw	960vw	959vw	959vw	δ(C-N-C) + δ(C-C-C)
934sh	934sh	934sh	935sh	δ(C-N-C)
924w	923w	923sh	925sh	ν_s(N-C)
	918sh	917m	916m	ν_s(N-C)
897sh, 889w	899sh, 889w	897sh, 889m	896sh, 890w	ν(C-C)
877sh	878sh	878sh	878sh	δ(C-N-C)
797vw,b	793vw,b	795vw	795vw	ν(C-N-C)
736w	735w	735m	735w	$\nu(NC_4) + \rho(CH_2)$
656w	653w	649m	652w	δ_s(N-C-N)

574vw		576vw	576vw	γ_s(N-C-N)
542sh		540sh	538sh	δ_{as}(N-C-N)
515m, 508sh	511m	505s	516sh, 504m	γ_{as}(N-C-N)
214m	225m	244m	267m	T'(dca) + T'(M^{2+})
194m	212m	228m	244m	T'(dca) + T'(M^{2+})
155w	177w			T'(dca) + L(dca) + T'(M^{2+})

[a]Key: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; b, broad; ν, δ, γ, ω, τ, ρ, T' and L denotes stretching, in-plane bending, out-of-plane bending, wagging, twisting, rocking, translational and librational, respectively.

Table S4. The CIE chromaticity of TBuMeMn at different temperatures and positions of emission maxima λ_{max} (nm).

Temperature (K)	CIE chromaticity		Position λ_{max} (nm)
	x	y	
80	0.46	0.45	615
150	0.45	0.44	615
175	0.44	0.44	610
200	0.43	0.44	610
225	0.43	0.44	610
250	0.43	0.44	610
275	0.47	0.45	626
300	0.47	0.45	626
325	0.47	0.45	626
350	0.47	0.45	626

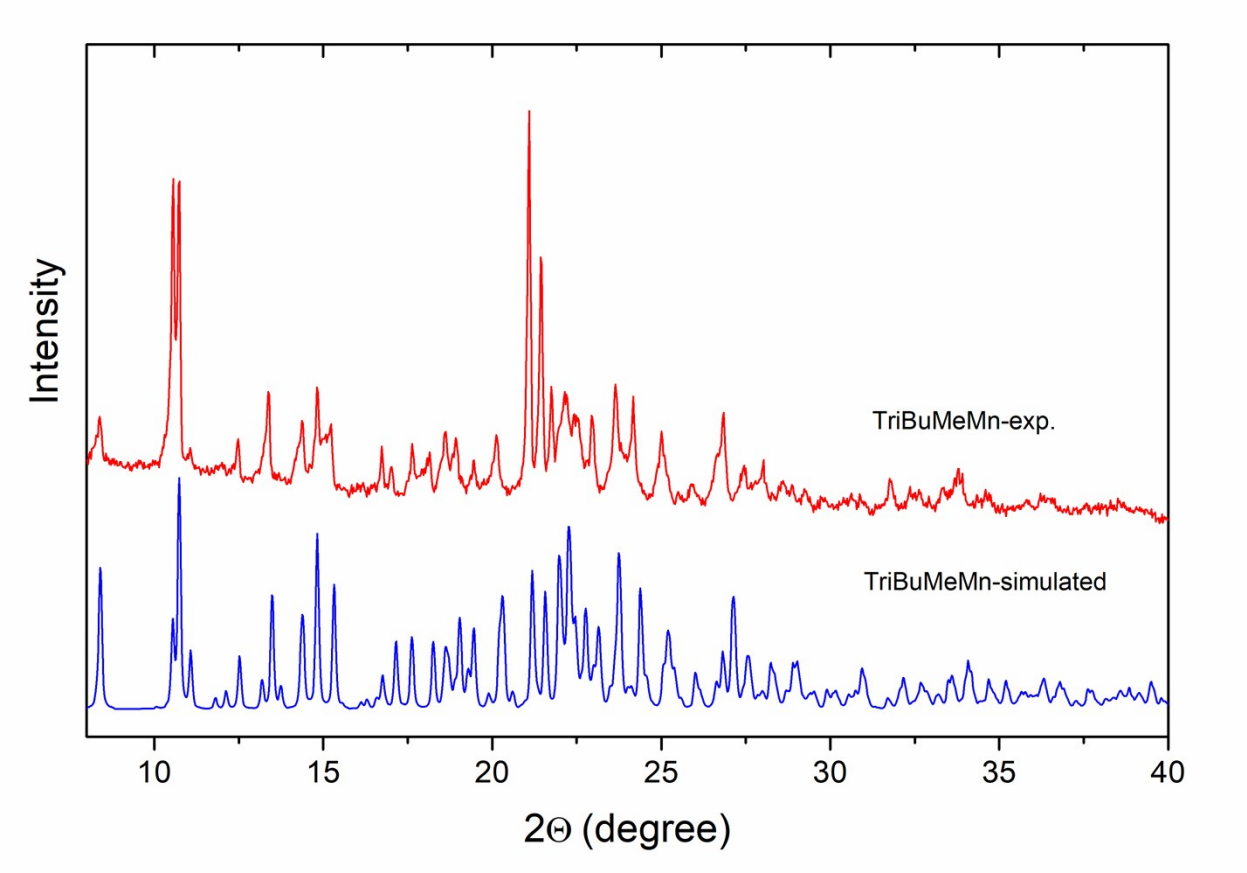

Figure S1. Room-temperature powder XRD pattern for the as-prepared TriBuMeMn sample together with the calculated one based on the single crystal structure.

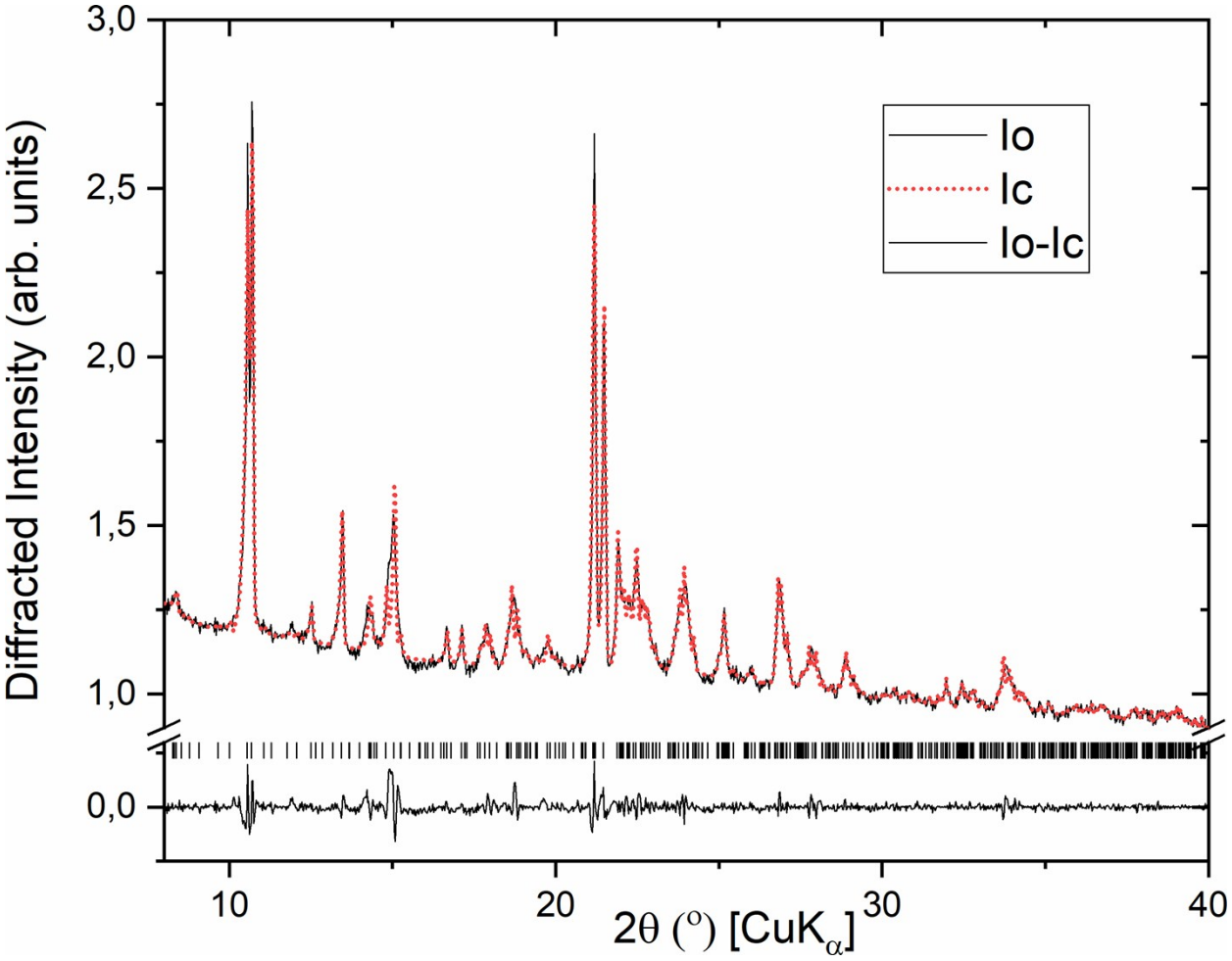

Figure S2. The results of the Le Bail refinement of the unit cell and profile parameters for TriBuMeFe. The red line stands for the calculated intensity; the difference plot is drawn in the bottom. Black sticks show positions of the Bragg peaks; a=19.537(2)Å, b=13.165(2)Å, c=20.233(2)Å, β=115.3(1)°, V=4705(1)Å^3; Rp=1.35, wRp= 2.08.

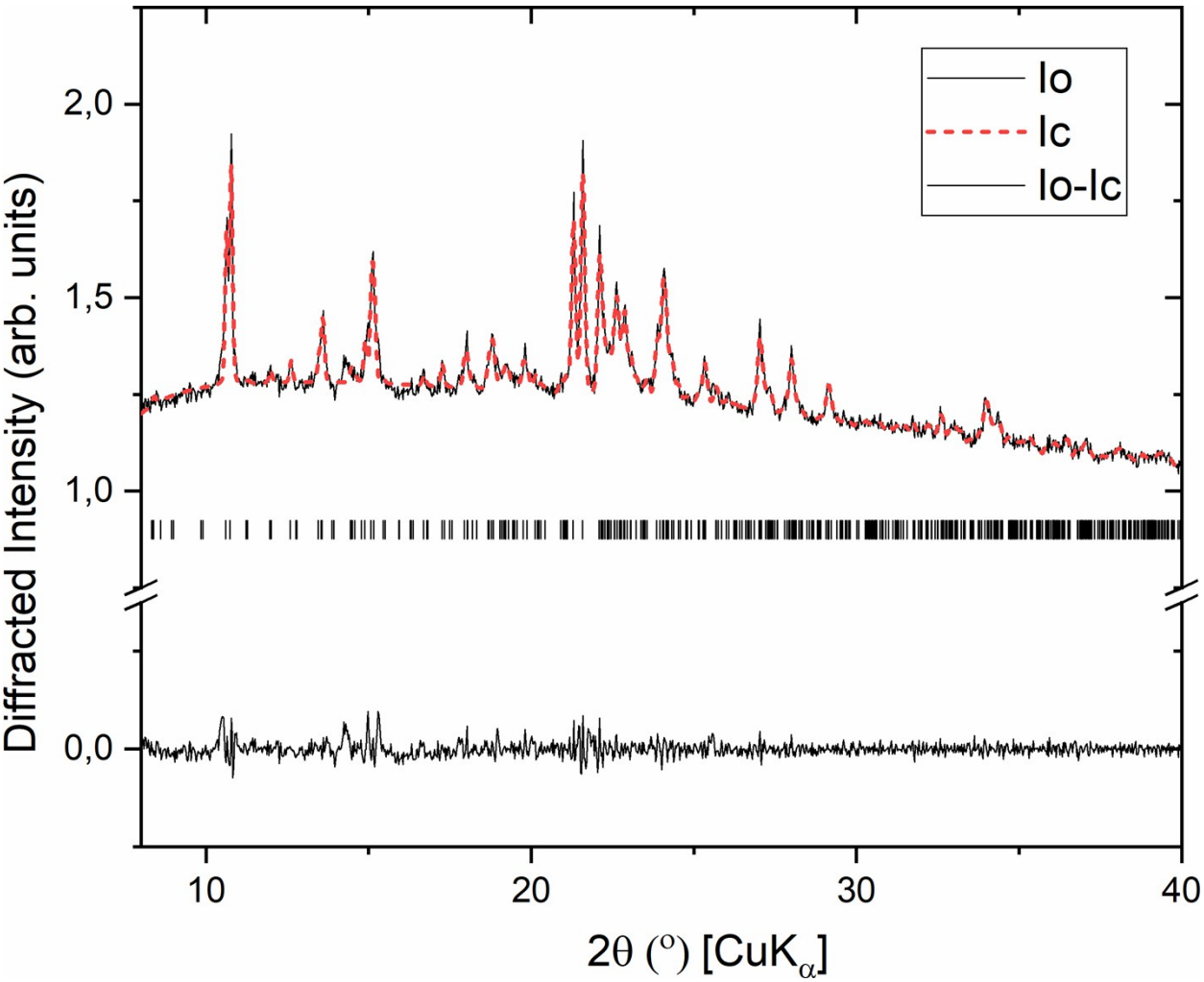

Figure S3. The results of the Le Bail refinement for TriBuMeCo. The red line stands for the calculated intensity; the difference plot is drawn in the bottom. Black sticks show positions of the Bragg peaks; a=19.706(2)Å, b=13.029(2)Å, c=19.845(2)Å, β=115.0(1)°, V=4617.8(6)Å^3; Rp=1.05, wRp= 1.55.

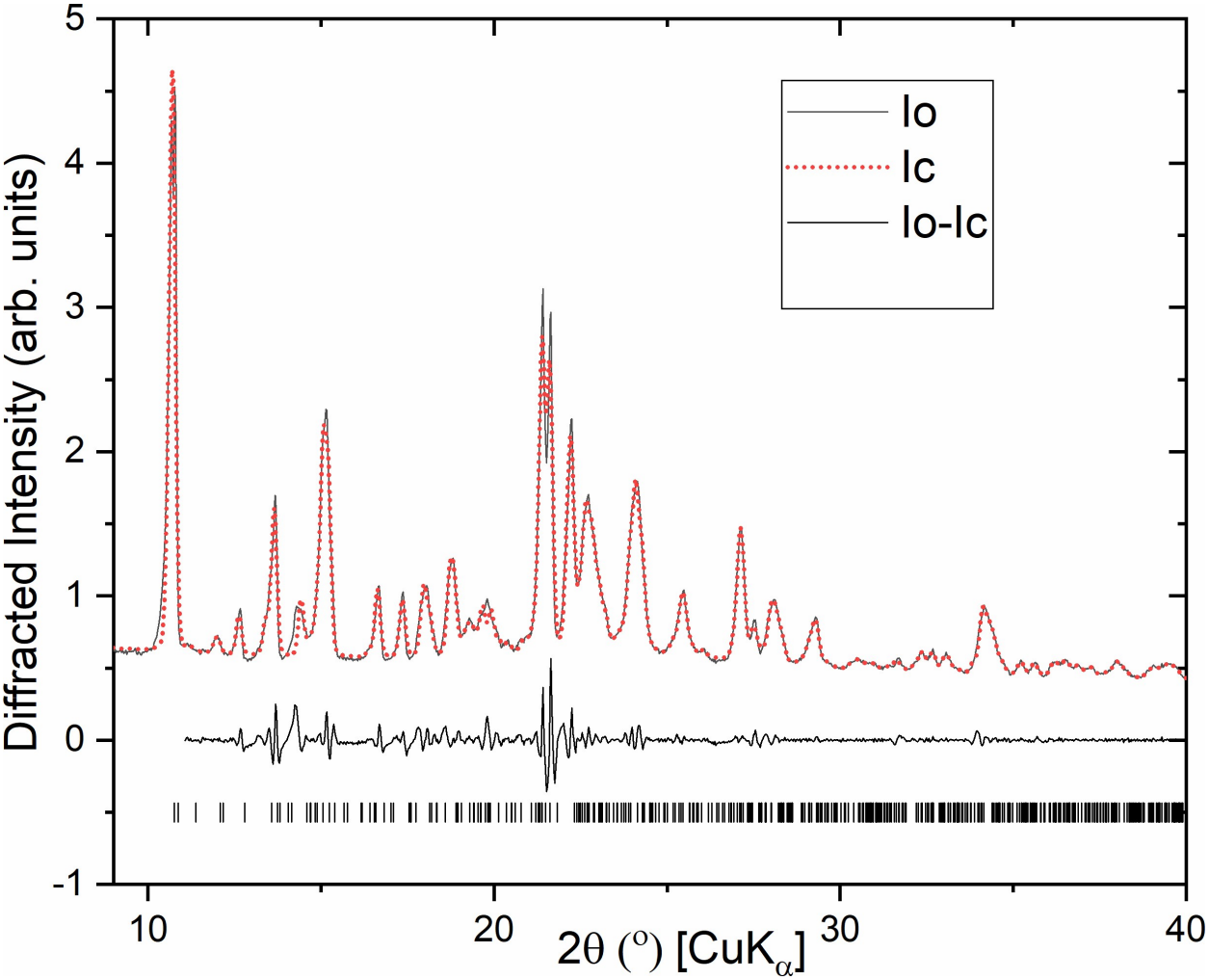

Figure S4. The results of the Le Bail refinement for TBuMeANi_dca. The red line stands for the calculated intensity; the difference plot is drawn in the bottom. Black sticks show positions of the Bragg peaks; a=19.41(2)Å, b=12.81(2)Å, c=19.64(2)Å, β=114.7(1)°, V=4737(30)Å^3; Rp=3.63, wRp= 6.45. I_o of the most intense peak is disrupted by the texture, thus the I_o-I_c is not presented for the picture clarity.

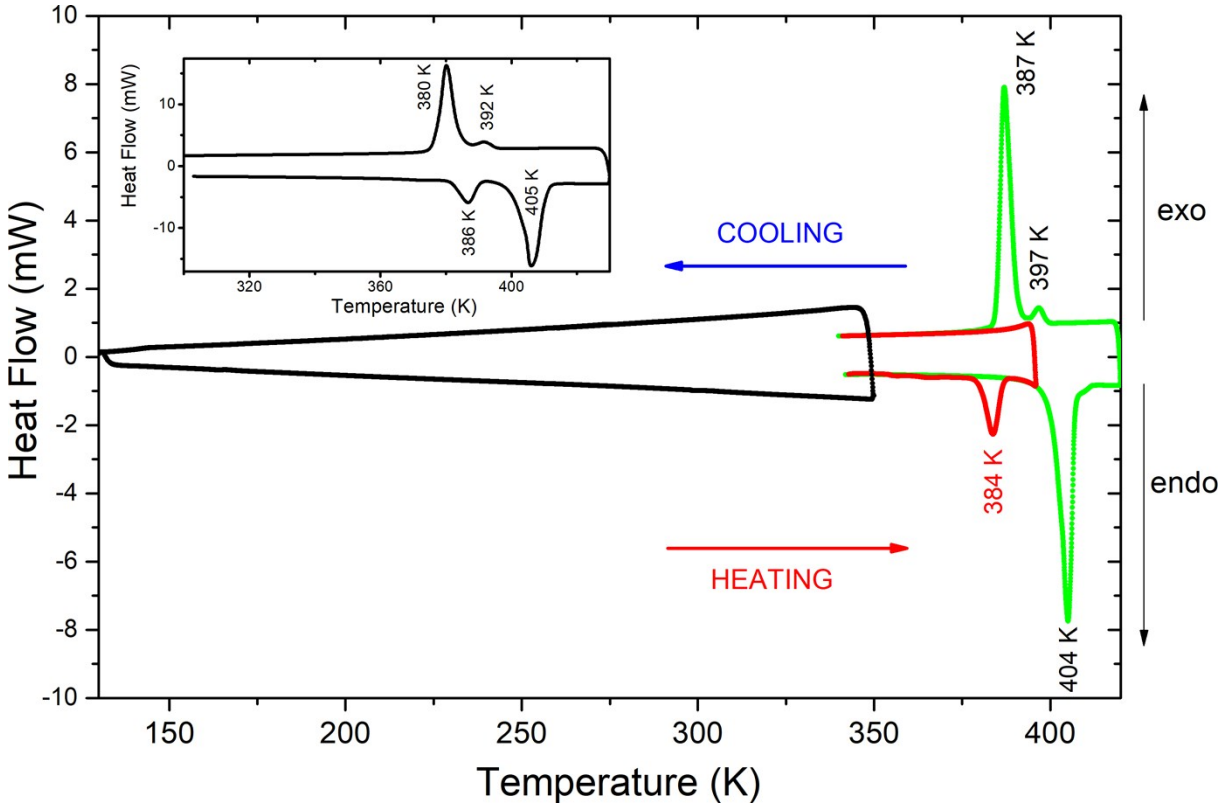

Figure S5. DSC traces for TriBuMeMn: heating up to 396 K and cooling to 340 K (1st run, red line) followed by heating to 420 K and cooling to 340 K (green, 2nd run). Inset shows DSC trace of new sample heated to 430 K and cooled down to RT.

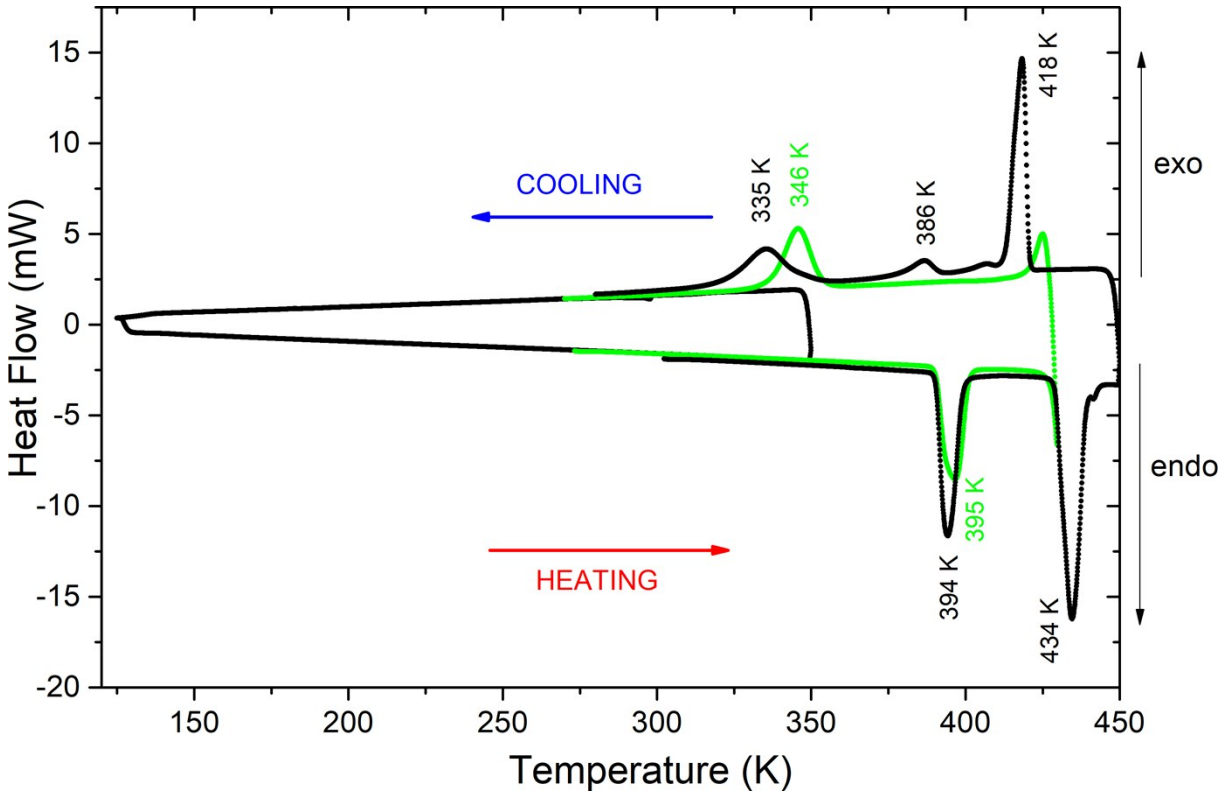

Figure S6. DSC traces for TriBuMeNi in the range 270-430 K (green) and 130-450 K (black).

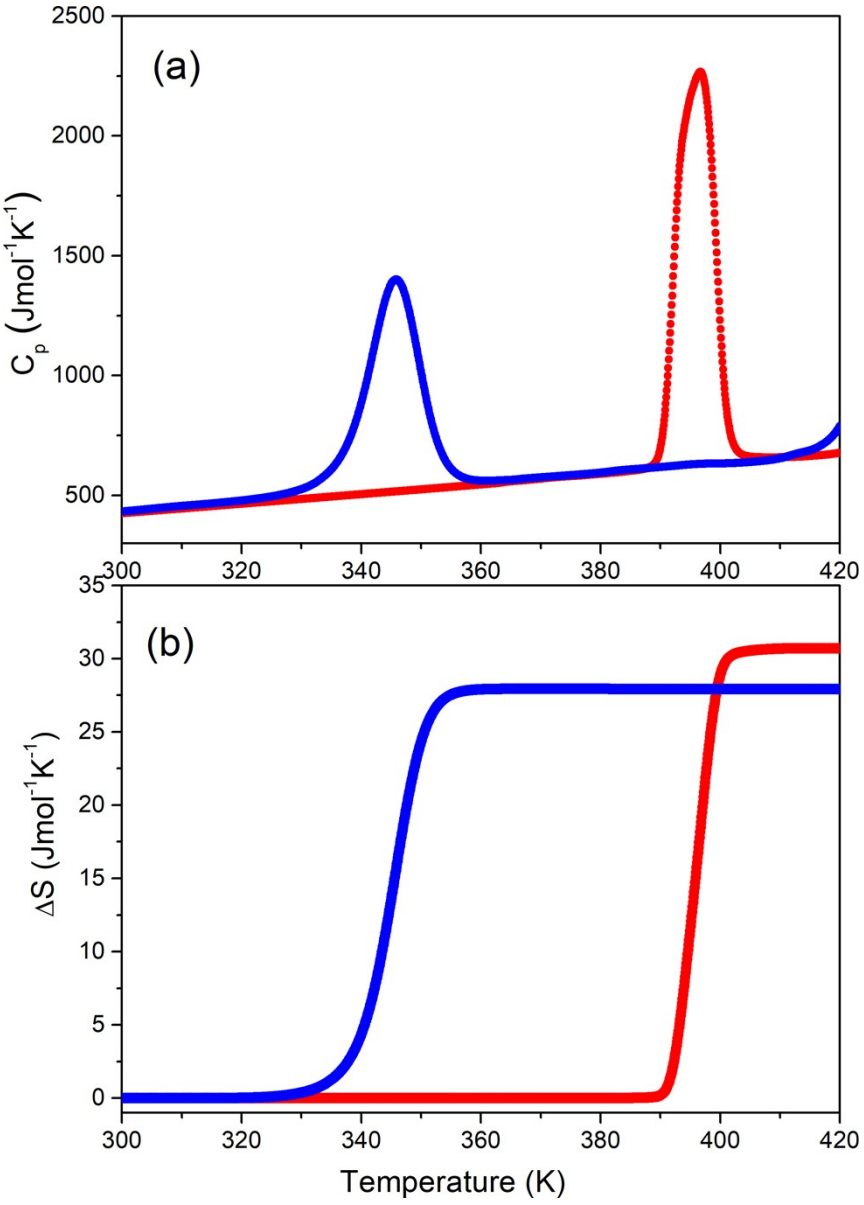

Figure S7. Temperature dependence of (a) C_p and (b) ΔS related to the phase transitions in TriBuMeNi in heating (red) and cooling (blue) run.

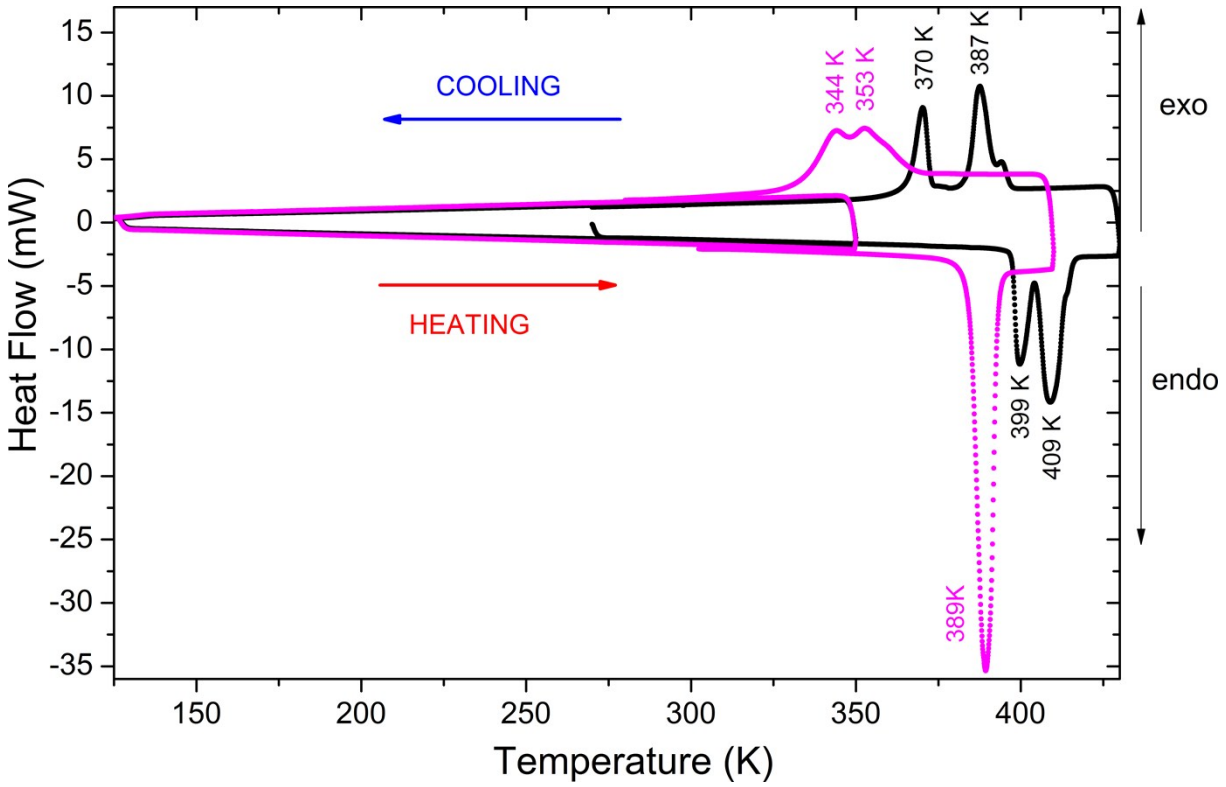

Figure S8. DSC traces for TriBuMeFe (black) and TriBuMeCo (magenta).

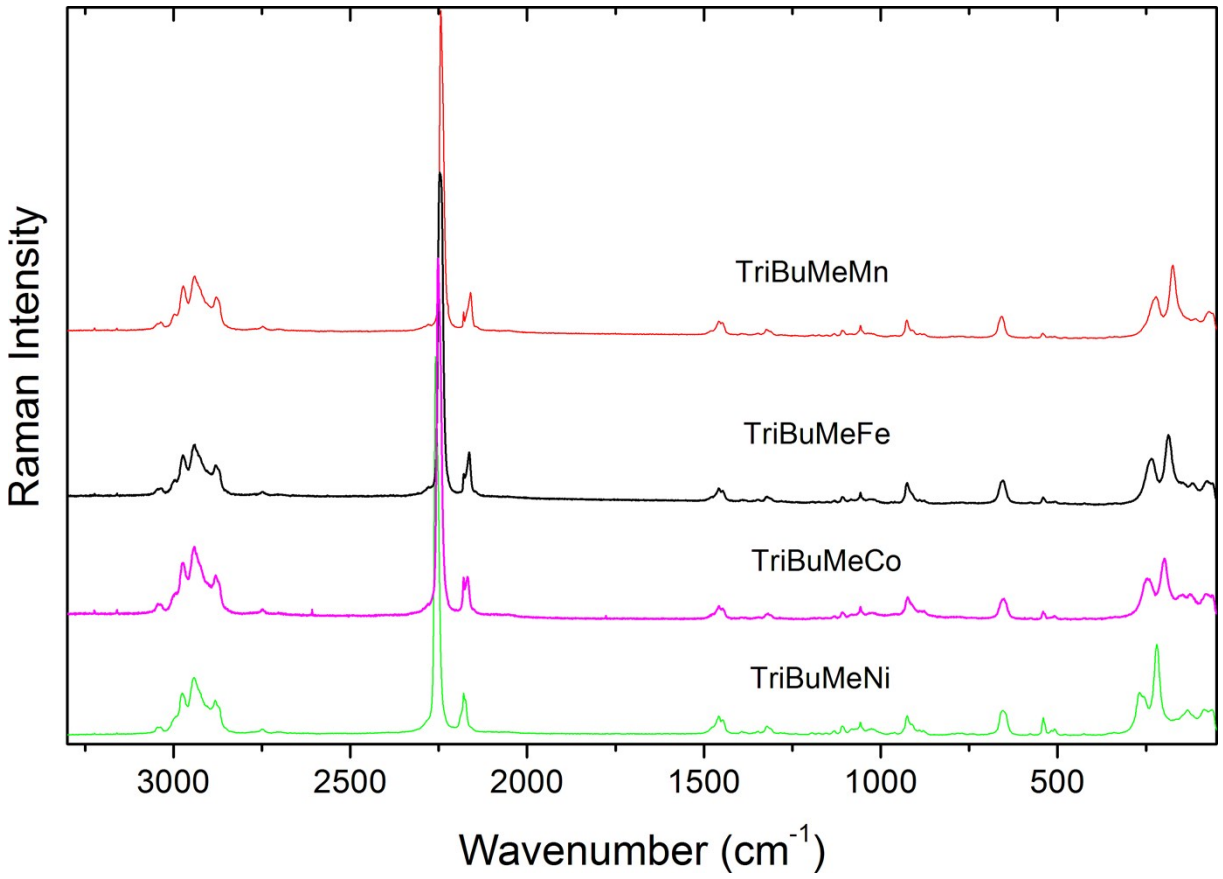

Figure S9. Raman spectra of TriBuMeM samples at room temperature.

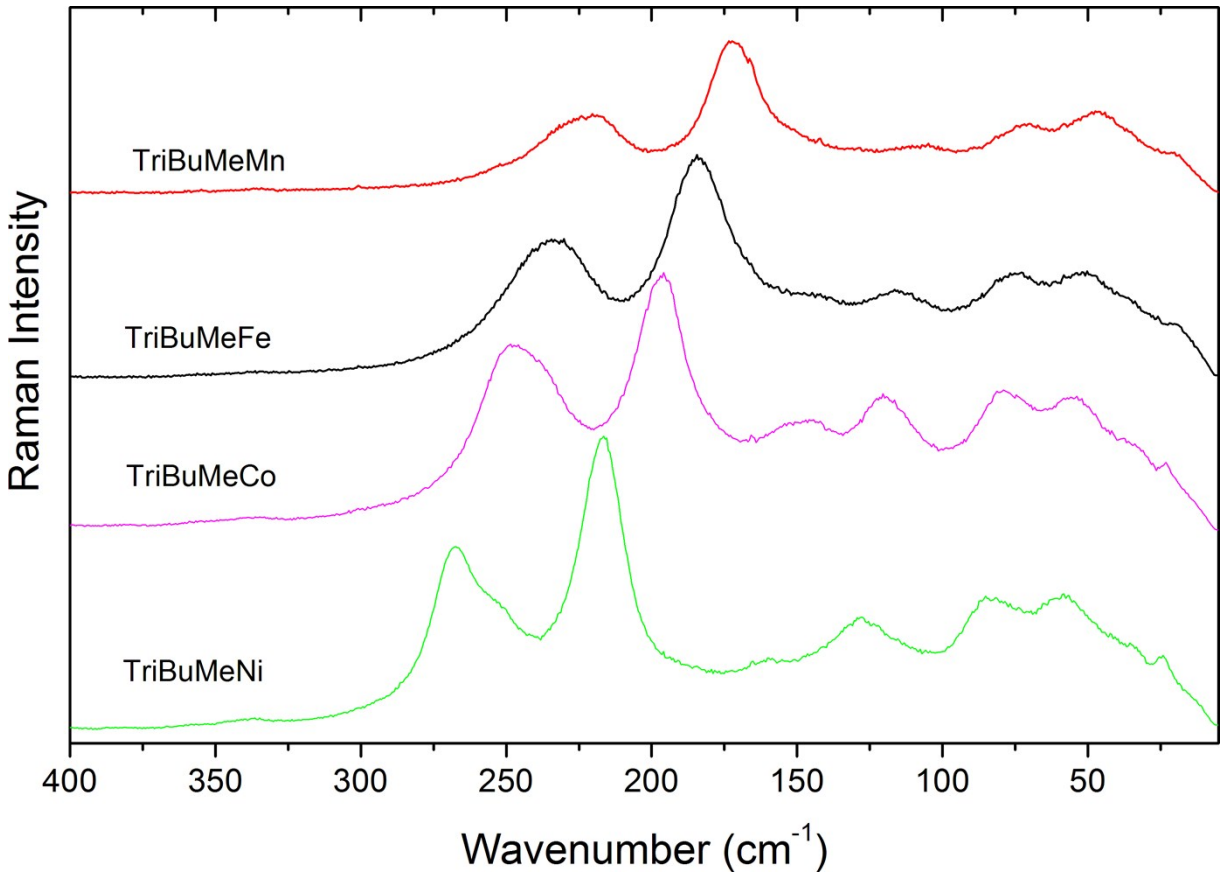

Figure S10. Raman spectra of TriBuMeM samples measured with use of eclipse filter to show low-wavenumber region down to 5 cm^{-1}.

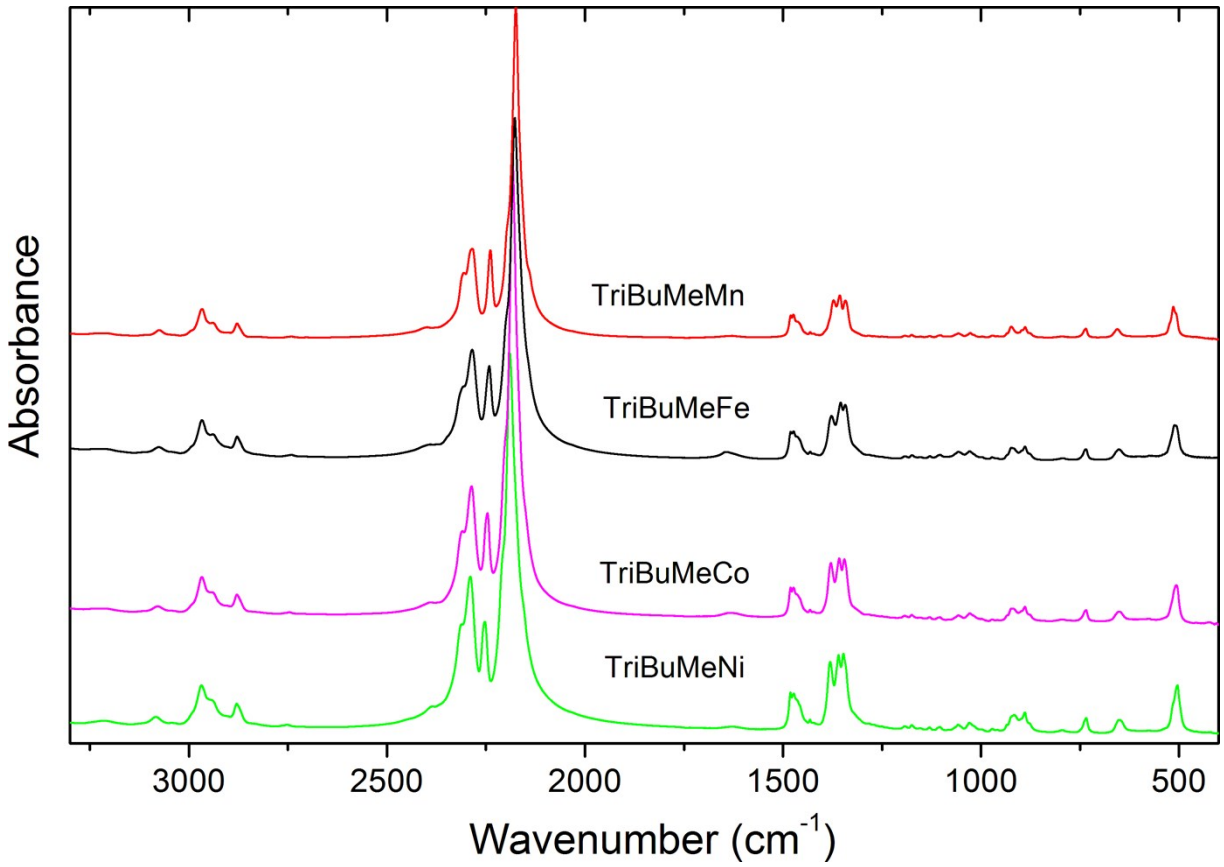

Figure S11. Mid-IR spectra of TriBuMeM samples at room temperature.

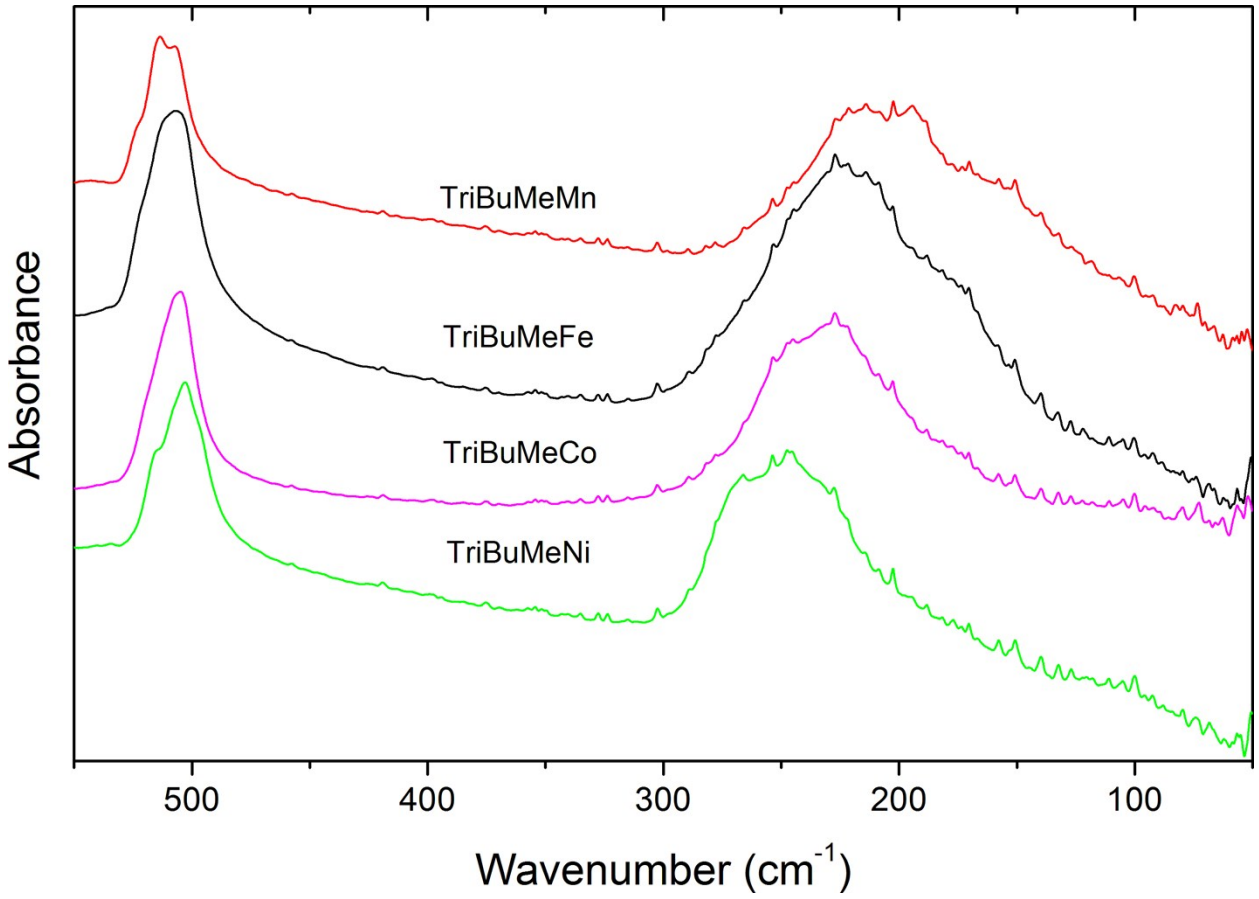

Figure S12. Far-IR spectra of TriBuMeM samples at room temperature.

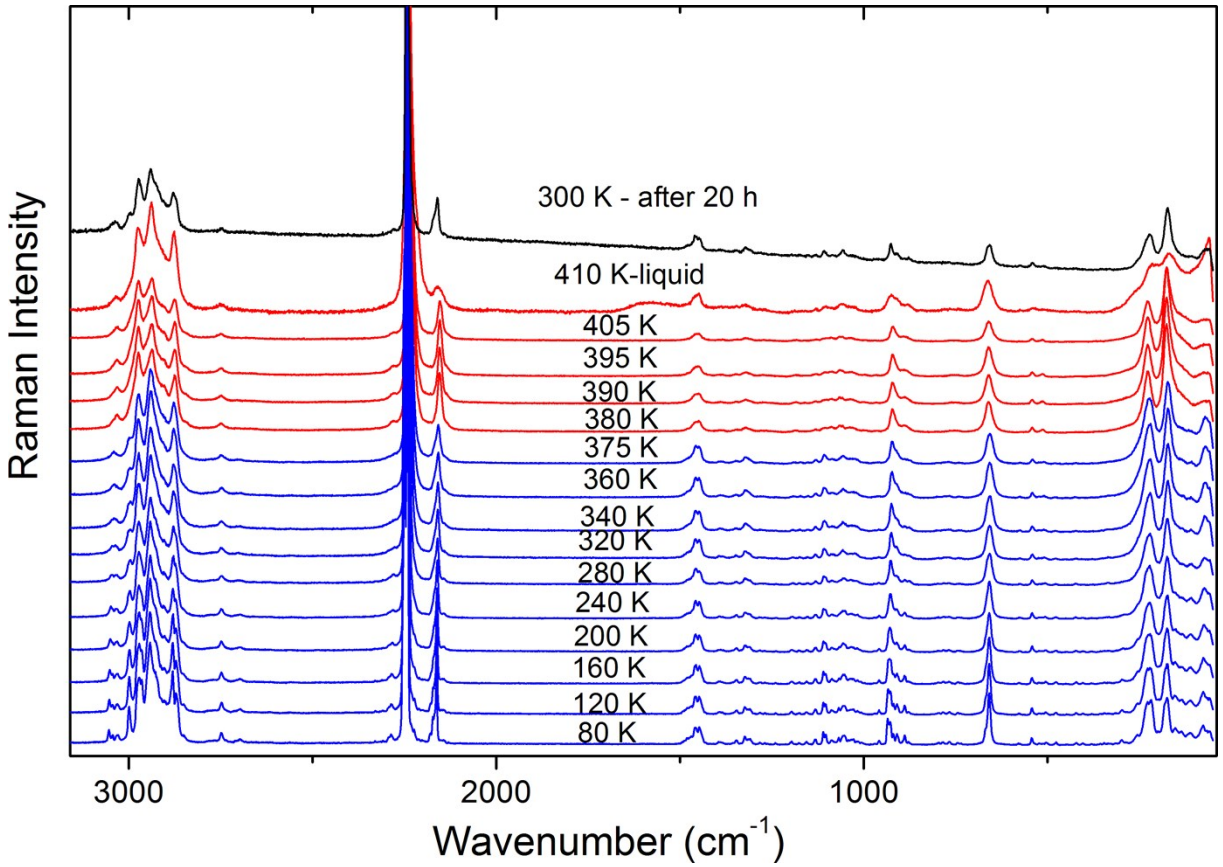

Figure S13. Temperature-dependent Raman spectra of TriBuMn in the whole wavenumber range.

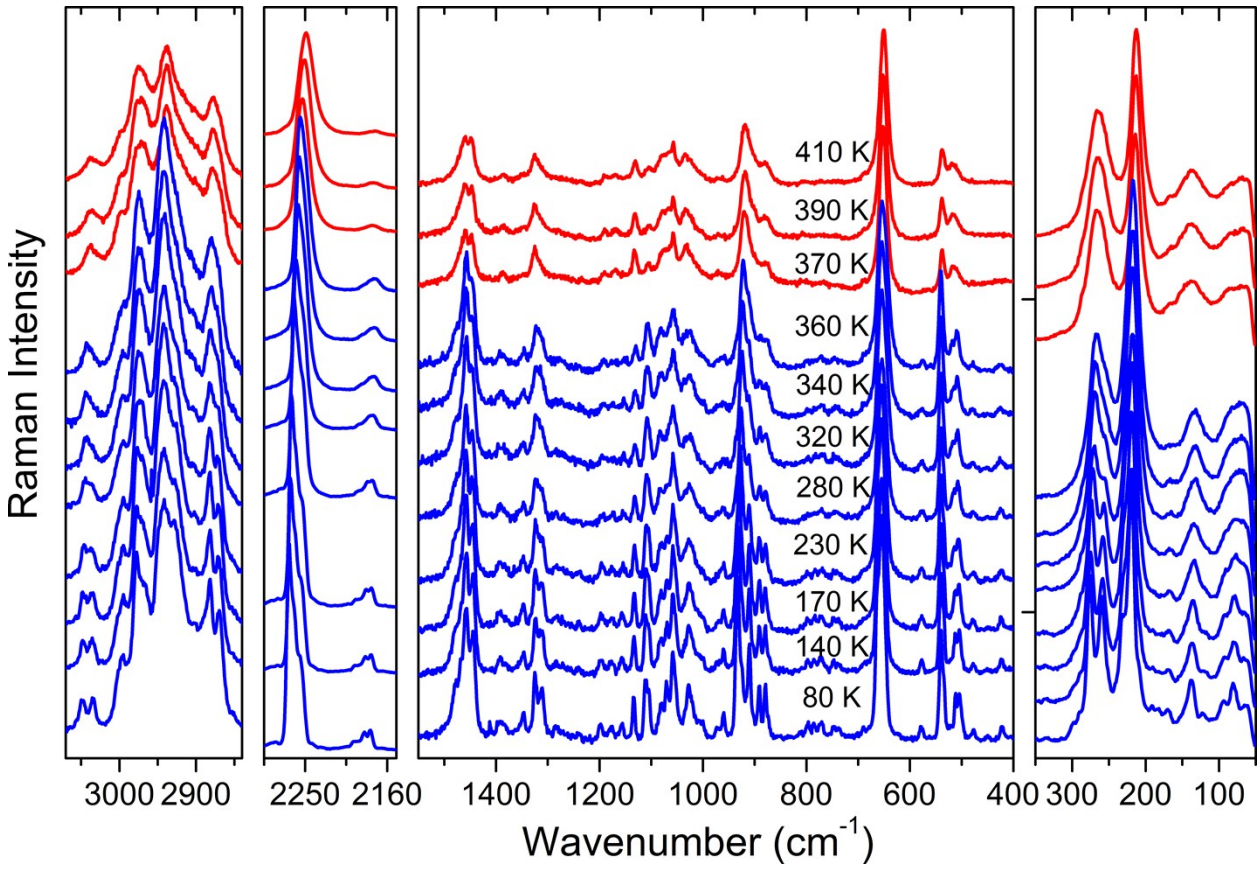

Figure S14. Details of the temperature-dependent Raman spectra of TriBuMeNi.

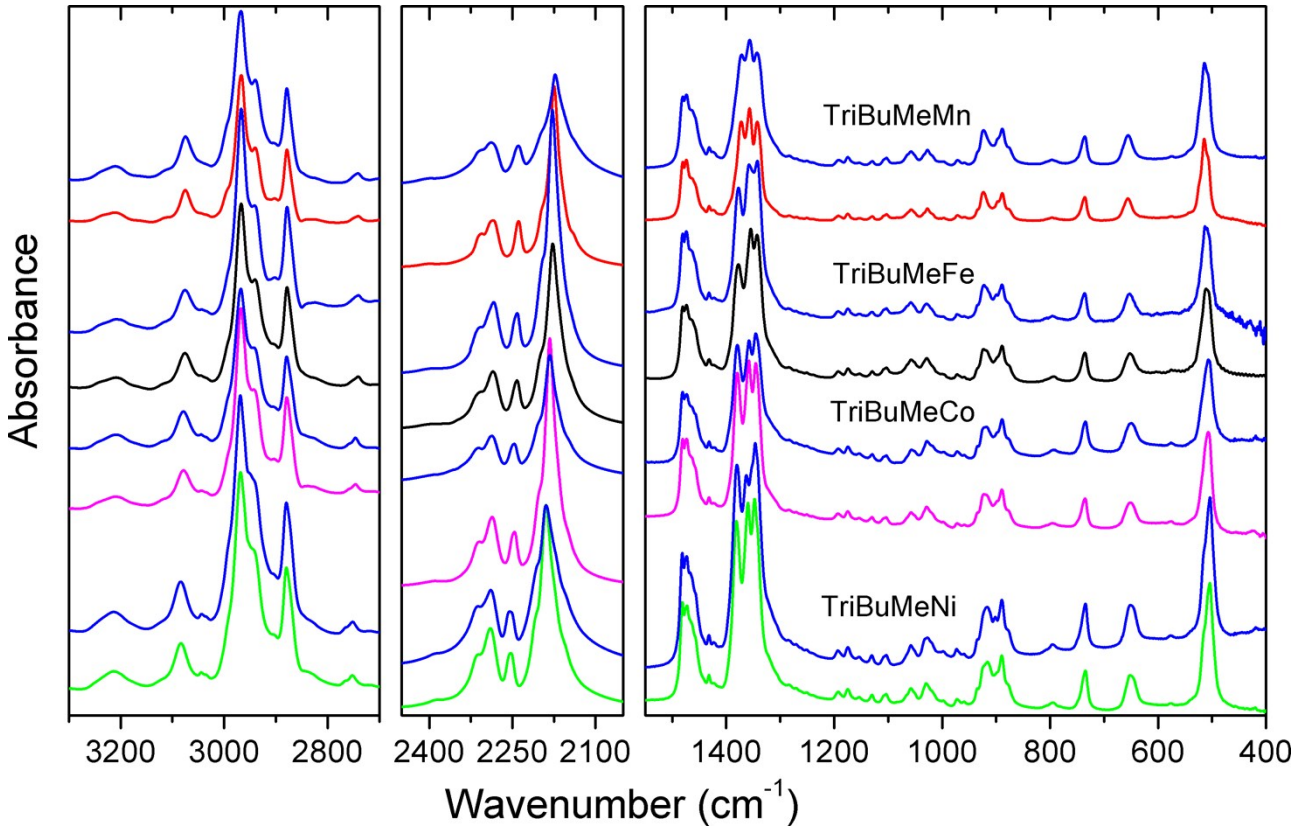

Figure S15. IR spectra of original TriBuMeM samples measured at RT (red, black, magnenta, green lines) and RT spectra of TriBuMeM (M=Mn, Co, Fe) samples after DSC experiment with heating up to 430 K and TriBuMeNi after DSC experiment with heating up to 450 K (blue lines).

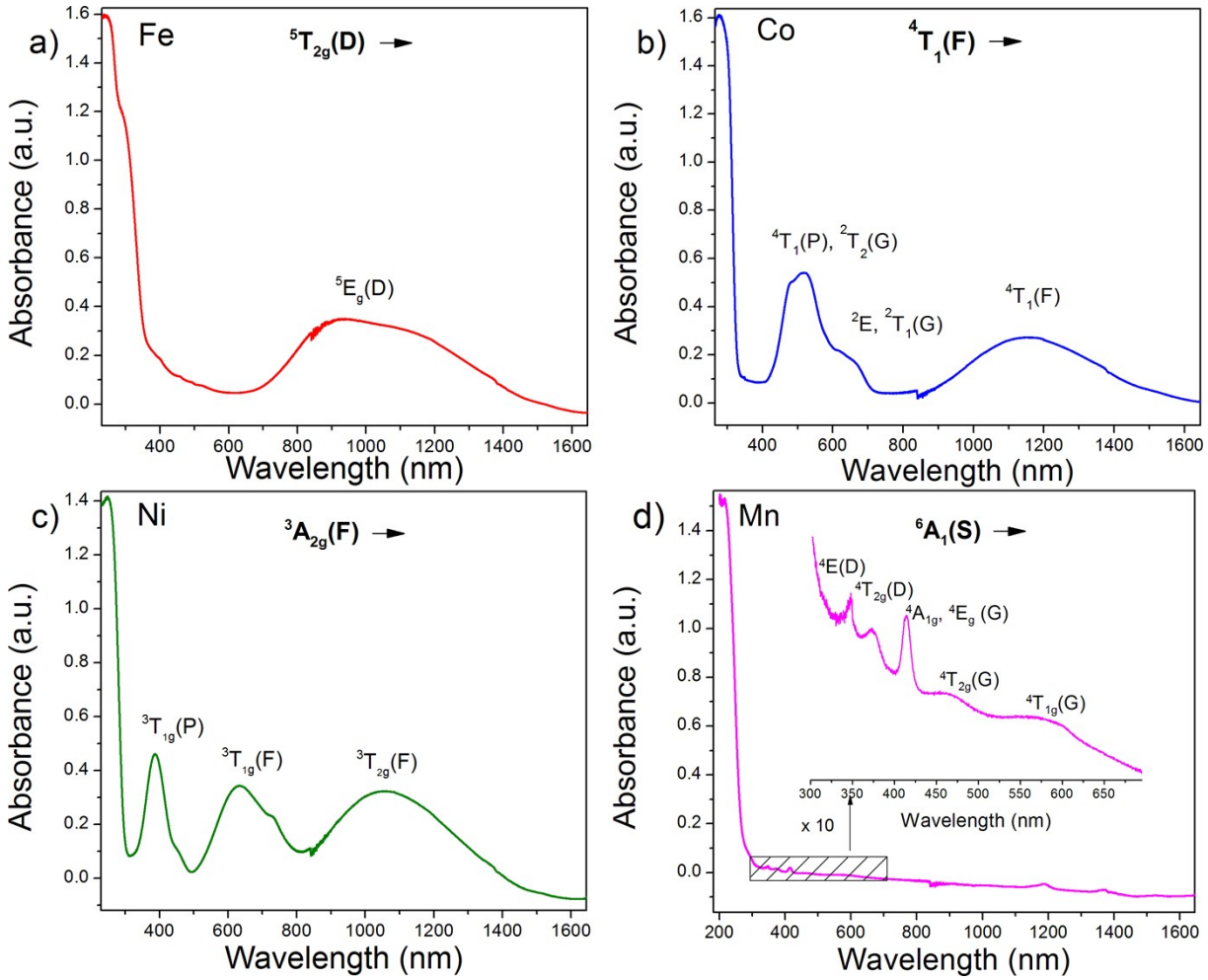

Figure S16. Absorption spectra of a) TriBuMeFe b) TriBuMeCo c) TriBuMeNi and d) TriBuMeMn recorded at 300 K.

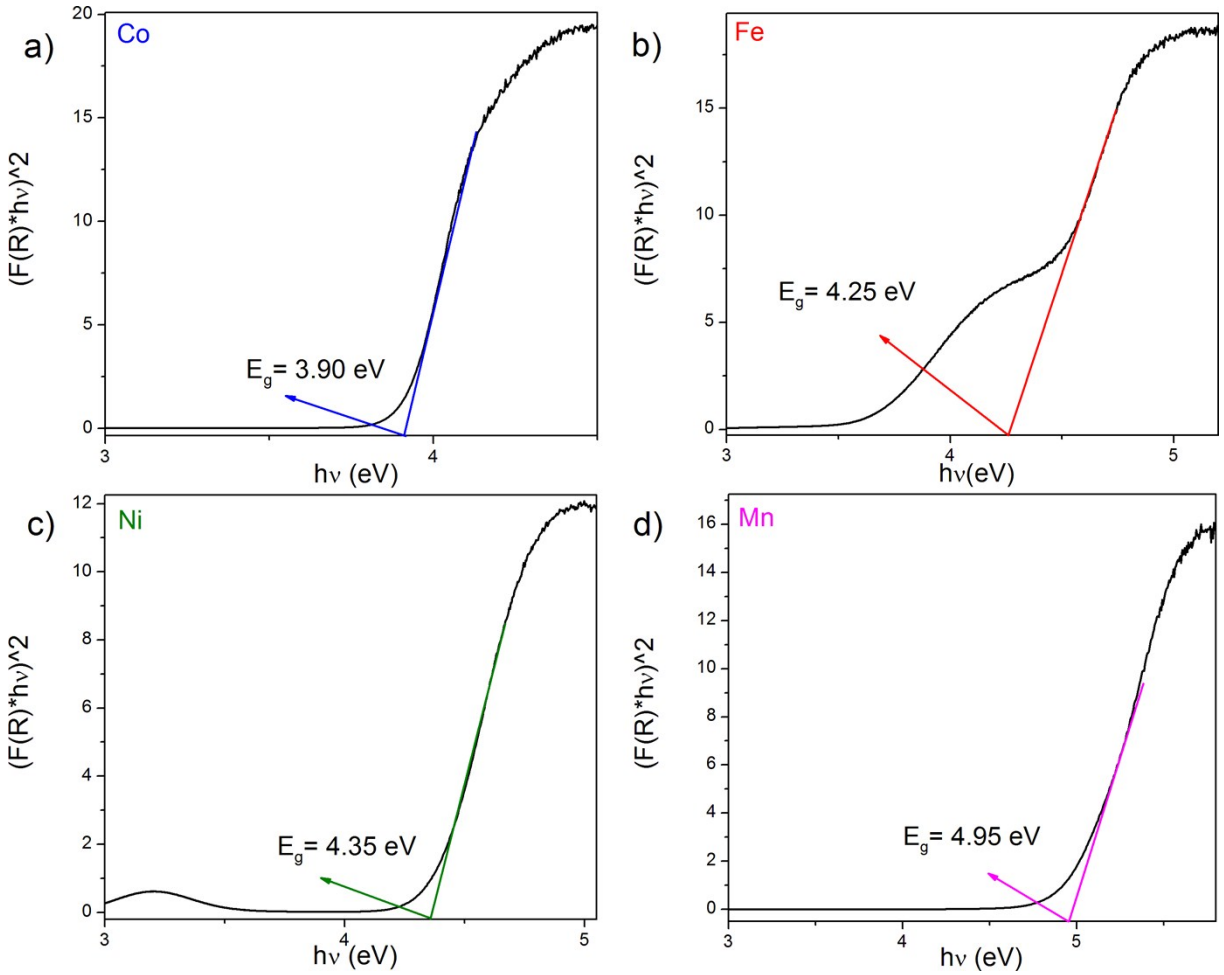

Figure S17. The energy band gap of TriBuMeM, (M= Fe, Co, Ni, Mn) determined using Kubelka – Munk function.