Supporting Information for:

Open frameworks in the $Na_xMn_y(P_2O_7)_mF_n$ fluoro-pyrophosphates system

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Figure S1.The corresponding EDX spectra for $Na_{5.5}Mn_{1.5}(P_2O_7)_2F_{0.5}$.
Figure S2.The corresponding EDX spectra for $Na_7Mn_{0.75}(P_2O_7)_2F_2$.
Figure S3.The corresponding EDX spectra for $Na_9Mn_3(P_2O_7)_4F$.
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Figure S9. Surrounding coordination environment of the $[Mn_{0.75}(P_2O_7)_2F_2]^{7-}$ group with ORTEP (80% possibility ellipsoids) drawings in $Na_7Mn_{0.75}(P_2O_7)_2F_2$.
Figure S10.View of the structure of $Na_9Mn_3(P_2O_7)_4F$ along the *b* axis(a) with detailed local coordination environment of the (b) $[Mn1/2^{III}O_6]^{9-}$, (c) $[Mn3^{II}O_5]^{7-}$ and (d) PO_4 polyhedra
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Figure S12. χT vs. T curve at 0.1 T after cooling in field.
Figure S13: Representation of the diffusion pathways of Na^+ ions calculated using BVEL and displayed with an energy threshold of 1.6 eV.

Table S1. BVS of $Na_{5.5}Mn_{1.5}(P_2O_7)_2F_{0.5}$, $Na_7Mn_{0.75}(P_2O_7)_2F_2$, $Na_9Mn_3(P_2O_7)_4F$.
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Table S6. Harmonic displacement parameters obtained for the compound $Na_7Mn_{0.75}(P_2O_7)_2F_2$.
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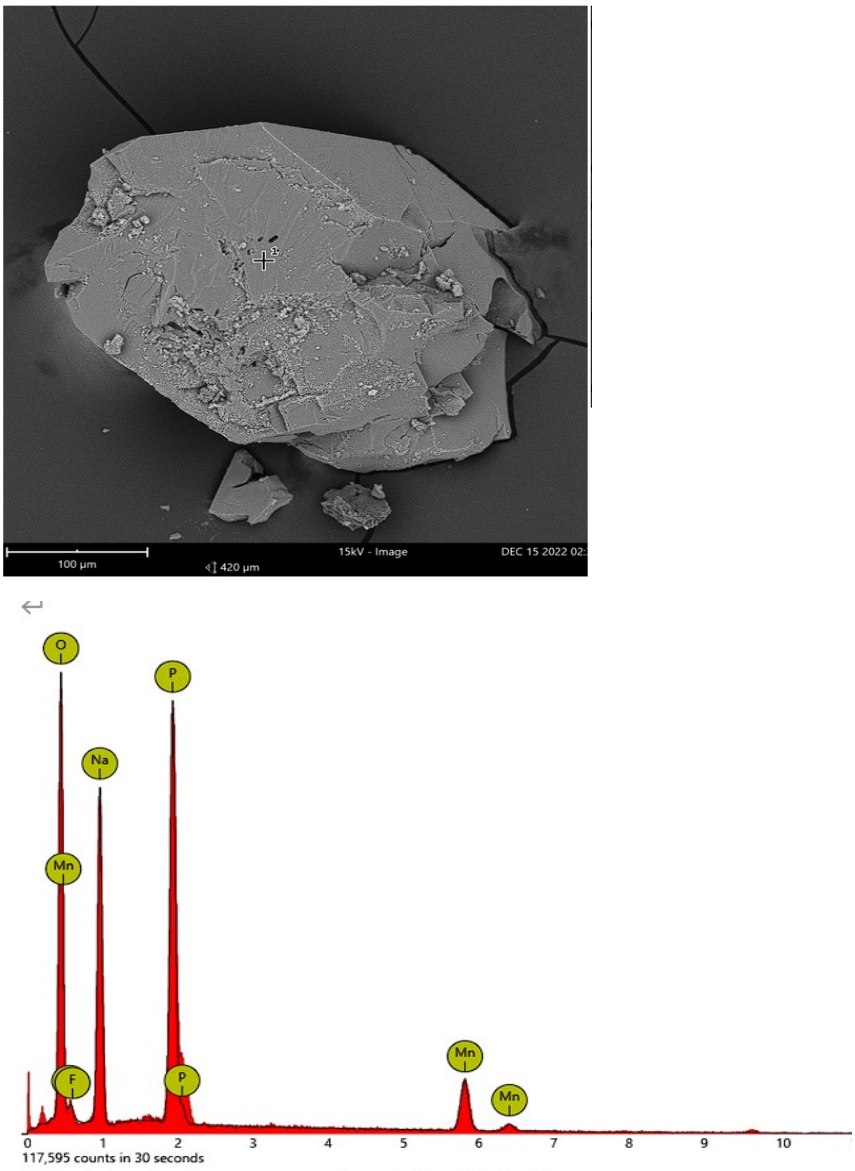
Table S11. Geometrical Parameters Associated with the M- O•••O -M Super-Supperexchange Paths of $Na_9Mn_3(P_2O_7)_4F$.



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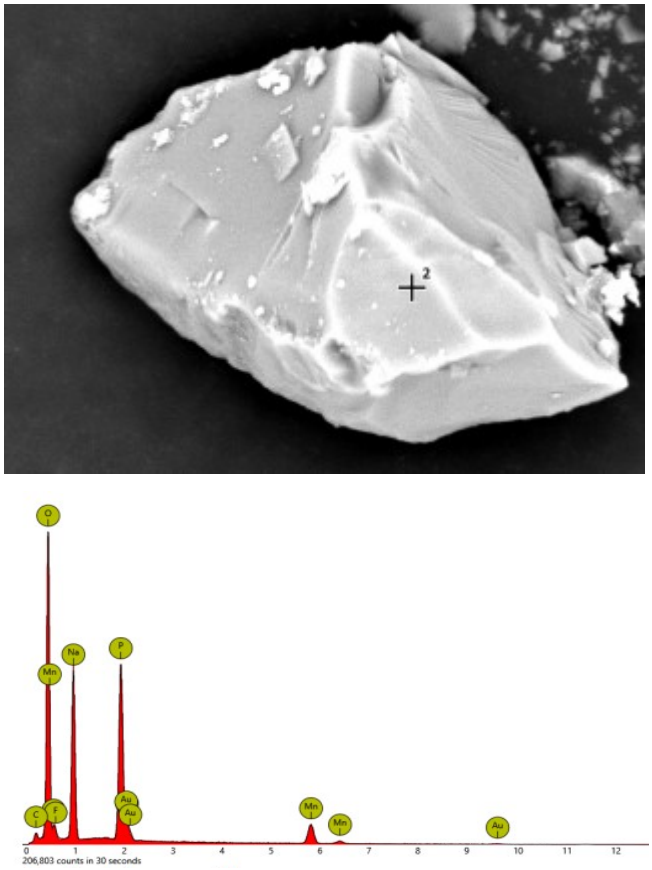
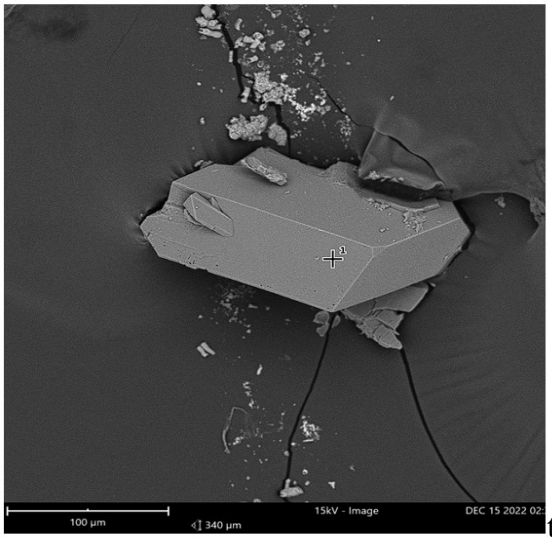


Figure S2.The corresponding EDX spectra for $Na_7Mn_{0.75}(P_2O_7)_2F_2$..



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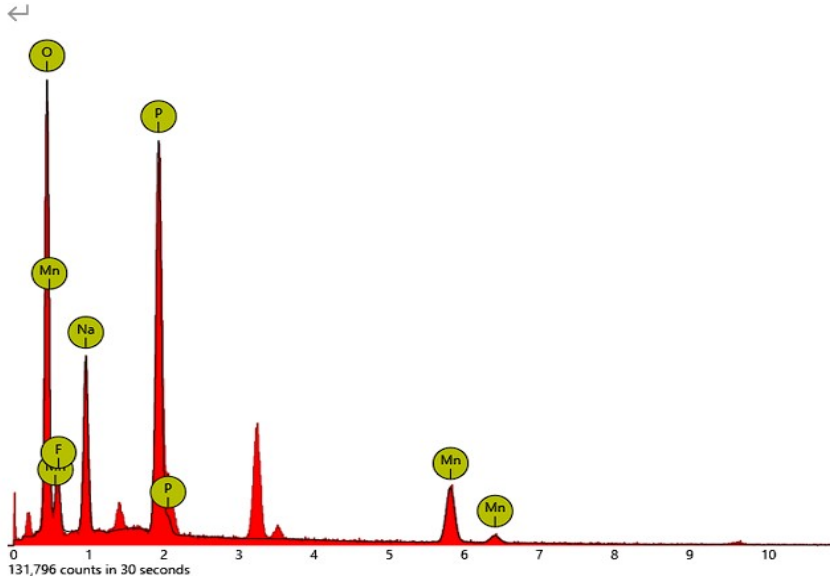

Figure S3.The corresponding EDX spectra for $Na_9Mn_3(P_2O_7)_4F$.

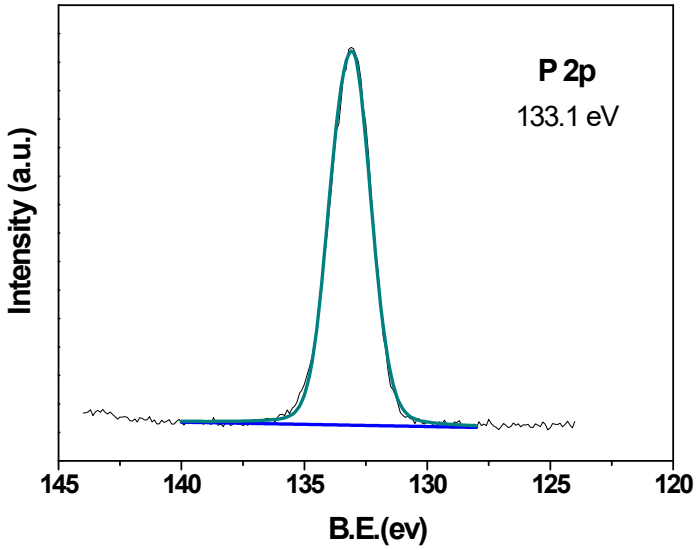

Figure S4. XPS spectra of P 2p region for $Na_9Mn_3(P_2O_7)_4F$.

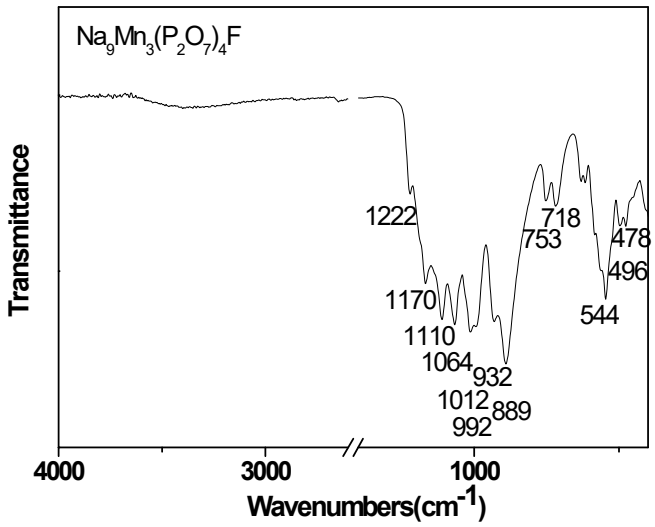

Figure S5. Infrared spectra of $Na_9Mn_3(P_2O_7)_4F$.

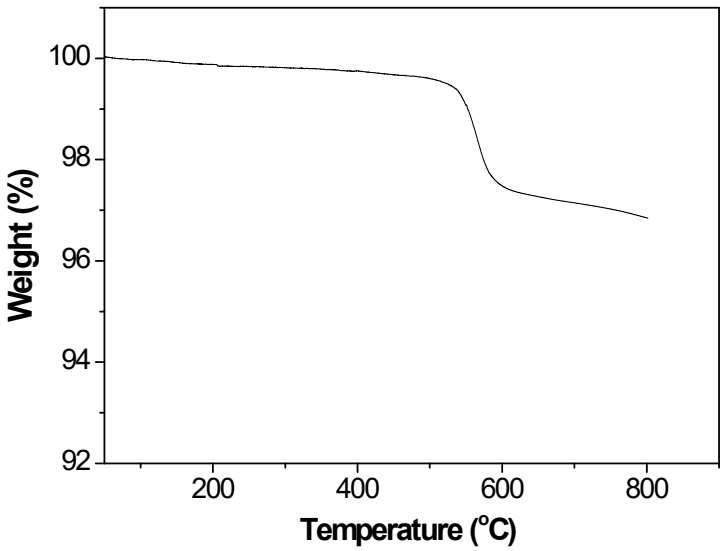

Figure S6. TGA diagram for $Na_9Mn_3(P_2O_7)_4F$.

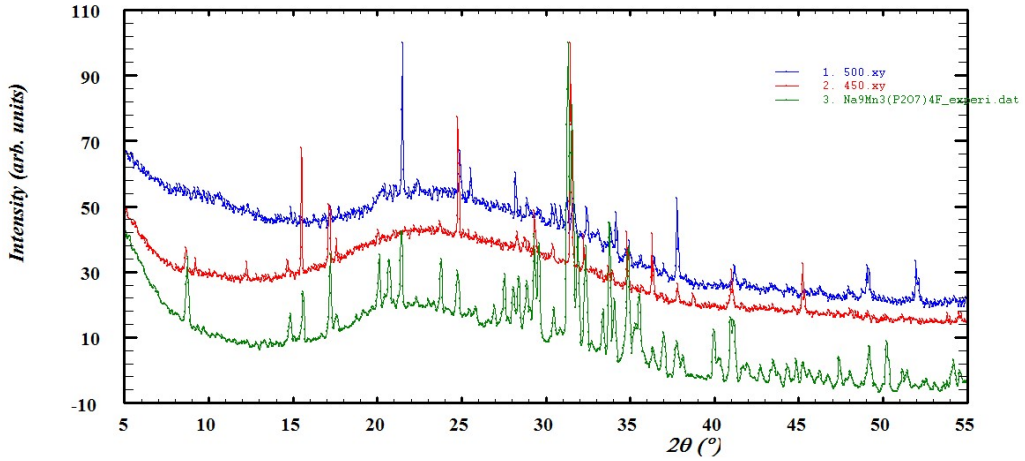

Figure S7. PXRD patterns annealing at 500^{O}C (blue) and 450^{O}C (red) in Argon, compared with experimental PXRD patterns (green)for $Na_9Mn_3(P_2O_7)_4F$.

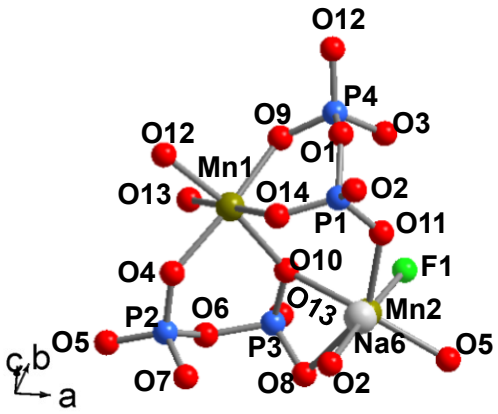

Figure S8.Surrounding coordination environment (dotted-line linkage) of the $[Na_{0.5}Mn_{1.5}(P_2O_7)_2F_{0.5}]^{5-}$ group in $Na_{5.5}Mn_{1.5}(P_2O_7)_2F_{0.5}$.

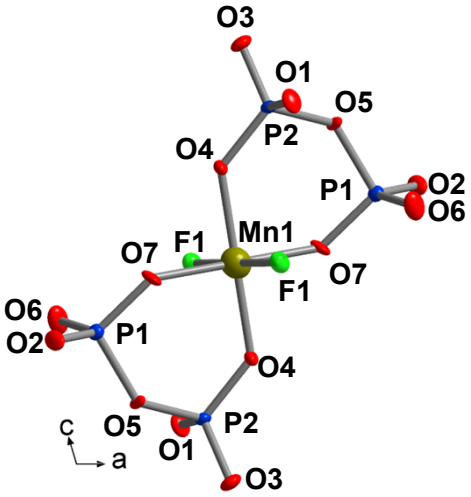

Figure S9. Surrounding coordination environment of the $[Mn_{0.75}(P_2O_7)_2F_2]^{7-}$ group with ORTEP (80% possibility ellipsoids) drawings in $Na_7Mn_{0.75}(P_2O_7)_2F_2$.

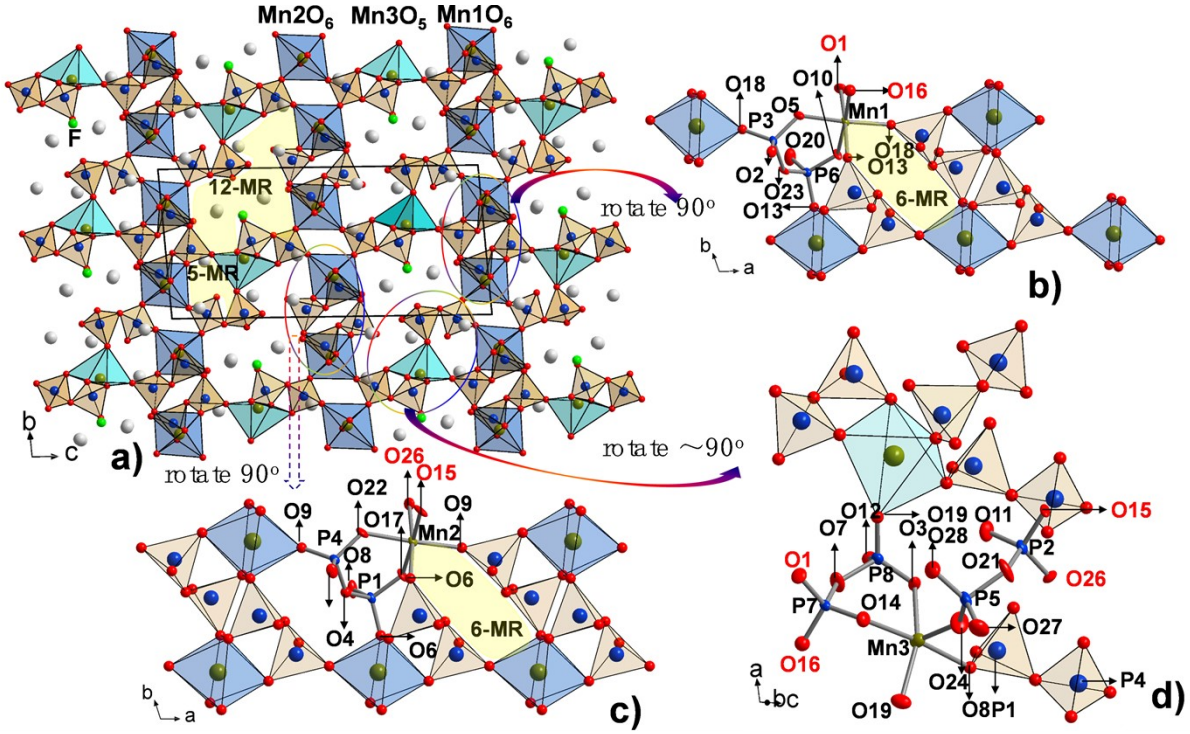

Figure S10.View of the structure of $Na_9Mn_3(P_2O_7)_4F$ along the *b* axis(a) with detailed local coordination environment of the (b) $[Mn1/2^{III}O_6]^{9-}$, (c) $[Mn3^{II}O_5]^{7-}$ and (d) PO_4 polyhedra

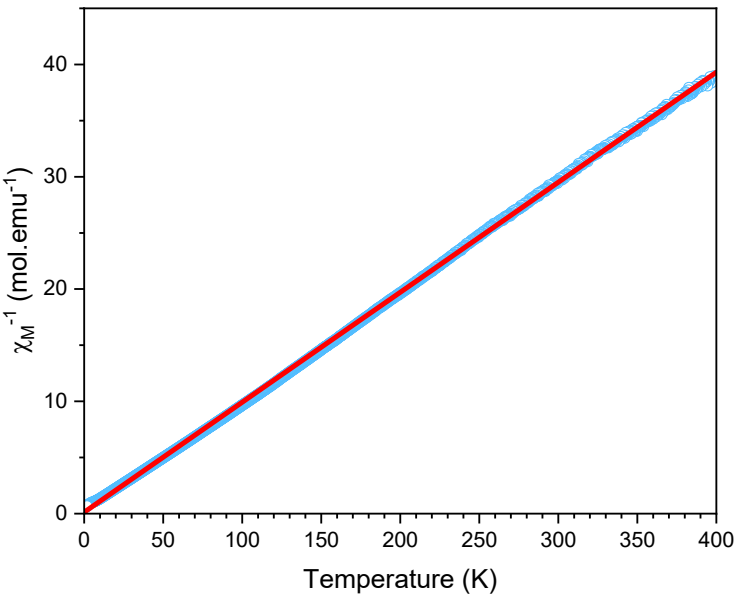

Figure S11. Inverse magnetic susceptibility $1/\chi$ of $Na_9Mn_3(P_2O_7)_4F$ as a function of temperature. The red solid lines denote the fits to the Curie-Weiss law.

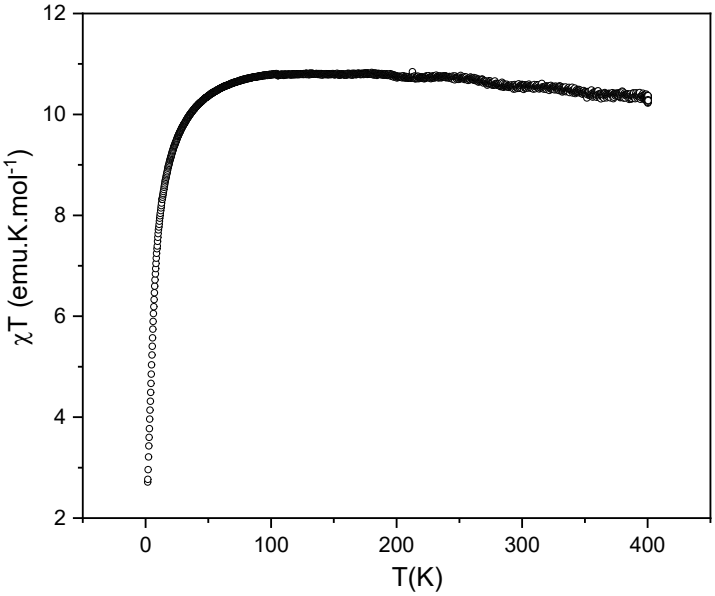

Figure S12. χT vs. T curve at 0.1 T after cooling in field.

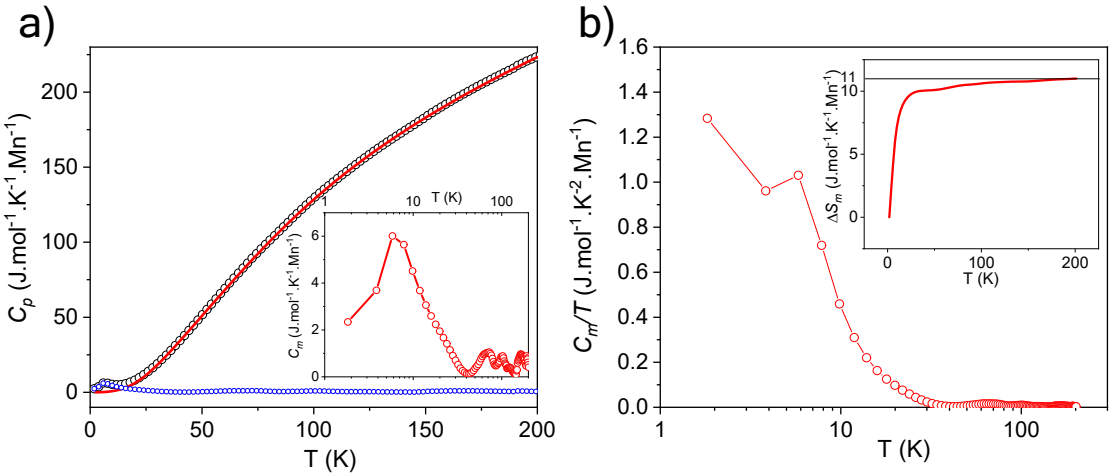

Figure S13. (a) Temperature dependence of total specific heat $C_p(T)$ with magnetic specific heat $C_m(T)$ (blue circles) and lattice contribution $C_{lat}(T)$ (red solid line). The inset shows $C_m(T)$ vs temperature. (b) Temperature dependence of $C_m(T)$/T and calculated magnetic entropy ΔS_m (inset).

To evaluate the magnetic specific heat C_m, the lattice heat capacity was estimated as a combination of one Debye model and two Einstein models:[1]

$$C_{lattice} = C_{Debye} + C_{Einstein}^{\ i} = c_o\left[9R\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^2e^x}{(e^x-1)^2}dx\right] + 3R\sum_{i=1}^{2}c_i\left[\left(\frac{\theta_E^i}{T}\right)^2\frac{e^{\theta_E^i/T}}{\left(e^{\theta_E^i/T}-1\right)^2}\right].$$

where R is the universal gas constant; and θ_D and θ_E^i are the Debye characteristic temperature and Einstein characteristic temperature, respectively; and c_o and c_i are the oscillator strengths for the Debye term and Einstein term, respectively. For fittings, the sum of the weighting factors for the total number of atoms per Mn formula unit ($c_o+c_1+c_2=49/3$) is fixed. The fitting parameters yield θ_D=1402(10) K, θ_E^1=473(5) K, θ_E^2=207(6) K, c_o=7.2(3), c_1=6.1(2), and c_2= 3.1(2) in the high-temperature range between 35 K and 200 K. As shown in Figure S13a, the calculated lattice specific heat C_{latt} reproduces the high-T behaviour of the total heat capacity C_p well.

The magnetic specific heat C_m was subtracted C_{latt} from C_p, as displayed in the inset of Figure S13a. $C_m(T)$ clearly increases with decreasing temperature below 30 K and shows a broad peak at T_N=5.0 K. By integrating $C_m/T(T)$ against temperature (Figure S13b), the magnetic entropy change ΔS_m is estimated, as shown in the inset of Figure S13b. The saturation of the magnetic entropy is calculated to be 11.0 J·mol^{-1}·K^{-1}, which is lower than the theoretical expected value [2×Rln(2S_1+1)+ Rln(2S_2+1)]/3=13.88 J·mol^{-1}·K^{-1} for S_1=2, S_2=5/2. Above 30

K, ΔS_m is nearly temperature independent. However, below 30 K, approximately 76% of ΔS_m is released, accompanied by long-range ordering at T_N.

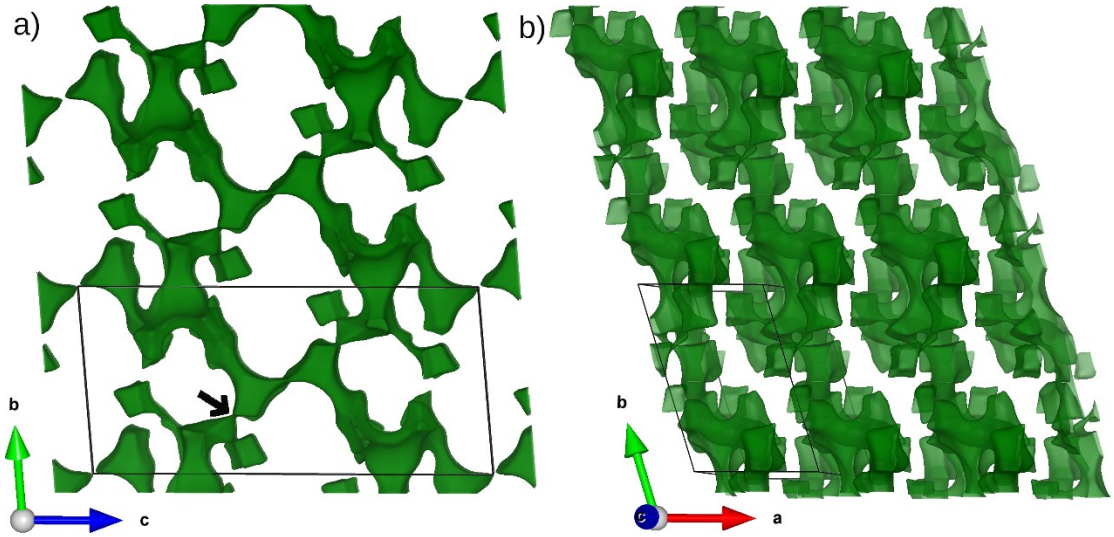

Figure S14: Representation of the diffusion pathways of Na^+ ions calculated using BVEL and displayed with an energy threshold of 1.6 eV. All atoms have been omitted to emphasize a) the continuous diffusion pathway along the *b* diection, with the tighter jump indicated by a black arrow and b) the absence of continuous path along the *a* axis.

Table S1. BVS of $Na_{5.5}Mn_{1.5}(P_2O_7)_2F_{0.5}$, $Na_7Mn_{0.75}(P_2O_7)_2F_2$, $Na_9Mn_3(P_2O_7)_4F$.

$Na_{5.5}Mn_{1.5}(P_2O_7)_2F_{0.5}$				$Na_7Mn_{0.75}(P_2O_7)_2F_2$				$Na_9Mn_3(P_2O_7)_4F$			
Atom	**V_{Na^*}**	**V_{Mn^*}**	**V_{P^*}**	**Atom**	**V_{Na^*}**	**V_{Mn^*}**	**V_{P^*}**	**Atom**	**V_{Na^*}**	**V_{Mn^*}**	**V_{P^*}**
Na(1)	1.05(1)			Na(1)	1.14(1)			Na(1)	0.88(1)		
Na(2)	1.17(1)			Na(2)	1.04(1)			Na(2)	1.04(1)		
Na(3)	1.18(1)			Na(3)	1.01(1)			Na(3)	1.16(1)		
Na(4)	0.95(1)			Na(4)	1.16(1)			Na(4)	0.74(1)		
Na(5)	0.83(1)			Mn(1)		4.06(2)		Na(5)	1.15(1)		
Mn(1)		2.06(1)		P(1)			4.95(3)	Na(6)	1.17(1)		
Na(6)	1.46(1)			P(2)			4.97(3)	Na(7)	1.27(1)		
Mn(2)		1.28(1)						Na(8)	0.77(1)		
P(1)			4.98(4)					Na(9)	1.10(1)		
P(2)			4.94(4)					Mn(1)		2.93(1)	
P(3)			4.98(4)					Mn(2)		2.97(1)	
P(4)			4.96(4)					Mn(3)		1.67(1)	
								P(1)			5.02(3)
								P(2)			5.02(3)
								P(3)			4.97(3)
								P(4)			5.01(3)

						P(5)		5.00(3)
						P(6)		5.01(3)
						P(7)		5.04(3)
						P(8)		5.01(3)
Atom	**V_{F^*}**	**V_{O^*}**	**Atom**	**V_{F^*}**	**V_{O^*}**	**Atom**	**V_{F^*}**	**V_{O^*}**
F(1)	-0.78(1)		F(1)	-1.20(1)		F(1)	-0.81(1)	
O(1)		-2.07(2)	O(1)		-2.14(2)	O(1)		-1.97(2)
O(2)		-2.04(2)	O(2)		-1.98(2)	O(2)		-2.10(2)
O(3)		-2.10(2)	O(3)		-2.11(2)	O(3)		-1.97(2)
O(4)		-1.97(3)	O(4)		-1.97(1)	O(4)		-2.14(2)
O(5)		-1.92(2)	O(5)		-1.99(2)	O(5)		-1.94(1)
O(6)		-2.21(2)	O(6)		-1.92(2)	O(6)		-2.03(2)
O(7)		-1.93(2)	O(7)		-1.97(2)	O(7)		-2.21(2)
O(8)		-1.86(2)				O(8)		-1.94(2)
O(9)		-2.01(2)				O(9)		-2.00(2)
O(10)		-2.00(2)				O(10)		-2.16(1)
O(11)		-2.05(2)				O(11)		-1.98(2)
O(12)		-2.02(2)				O(12)		-2.13(2)
O(13)		-1.97(2)				O(13)		-1.98(2)
O(14)		-1.85(2)				O(14)		-1.91(2)
						O(15)		-2.10(1)
						O(16)		-2.04(1)
						O(17)		-2.15(1)
						O(18)		-1.97(2)
						O(19)		-1.87(1)
						O(20)		-1.90(2)
						O(21)		-2.13(2)
						O(22)		-1.97(1)
						O(23)		-2.15(2)
						O(24)		-1.89(2)
						O(25)		-2.11(2)
						O(26)		-1.99(2)
						O(27)		-1.96(2)
						O(28)		-1.91(2)

* (R, b) parameters being for Na^{+}-O (1.803, 0.37), Na^{+}-F (1.677, 0.37), Mn^{2+}-O (1.765, 0.37), Mn^{2+}-F (1.698, 0.37), Mn^{3+}-O (1.732, 0.37), Mn^{3+}-F (1.66, 0.37),Mn^{4+}-O (1.753, 0.37), Mn^{4+}-F (1.71, 0.37),P^{5+}-O (1.617, 0.37)

Table S2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of $Na_{5.5}Mn_{1.5}(P_2O_7)_2F_{0.5}$.

	x	y	z

	Wyck.				Uiso*/Ueq	Occ.(<1)
Na1	2i	1.6277(3)	0.1186(3)	0.3664(3)	0.0183(12)	1
Na2	2i	1.3774(3)	0.5504(3)	0.2219(3)	0.0163(6)	1
Na3	2i	1.2572(3)	0.5849(3)	0.5864(3)	0.0192(12)	1
Na4	2i	1.2103(3)	0.9258(3)	-0.0404(3)	0.0218(12)	1
Na5	2i	1.1276(3)	1.1913(3)	0.2647(3)	0.0233(13)	1
Mn1	2i	0.97176(11)	0.65017(12)	0.17490(11)	0.0102(4)	1
Na6	2i	0.4925(16)	0.8463(15)	0.2942(15)	0.0342(7)	0.5
Mn2	2i	0.4830(7)	0.8221(6)	0.3058(6)	0.0342(7)	0.5
P1	2i	0.6062(2)	0.7911(2)	-0.0241(2)	0.0123(7)	1
P2	2i	1.0449(2)	0.8842(2)	0.3310(2)	0.0119(7)	1
P3	2i	0.8031(2)	0.6918(2)	0.49501(19)	0.0108(7)	1
P4	2i	0.7664(2)	0.4397(2)	0.0870(2)	0.0123(7)	1
O1	2i	0.6776(5)	0.6192(5)	-0.0417(5)	0.0138(19)	1
O2	2i	0.5198(6)	0.9072(5)	-0.1785(5)	0.023(2)	1
O3	2i	1.6361(5)	0.3860(5)	0.2047(5)	0.019(2)	1
O4	2i	1.0585(6)	0.8301(6)	0.2002(5)	0.024(2)	1
O5	2i	1.2193(5)	0.8675(5)	0.3918(5)	0.0198(11)	1
O6	2i	0.9755(5)	0.7501(5)	0.4801(5)	0.0130(19)	1
O7	2i	0.9151(5)	1.0452(5)	0.2946(5)	0.023(2)	1
O8	2i	0.6513(5)	0.8242(5)	0.5093(5)	0.0193(11)	1
O9	2i	0.9156(5)	0.4504(5)	0.1645(5)	0.0138(19)	1
O10	2i	0.7844(5)	0.6697(5)	0.3483(5)	0.015(2)	1
O11	2i	1.4809(5)	0.7679(5)	0.1060(5)	0.017(2)	1
O12	2i	1.1754(5)	0.6568(5)	0.0118(5)	0.017(2)	1
O13	2i	1.1620(5)	0.4635(5)	0.3629(5)	0.018(2)	1
O14	2i	0.7676(5)	0.8273(5)	0.0037(5)	0.0147(10)	1
F1	2i	1.4814(11)	0.5576(10)	0.4514(11)	0.039(6)	0.5

Table S3. Harmonic displacement parameters obtained for the compound $Na_{5.5}Mn_{1.5}(P_2O_7)_2F_{0.5}$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na1	0.0201(14)	0.0185(15)	0.0190(16)	-0.0072(11)	0.0056(12)	-0.0099(13)
Na3	0.0180(14)	0.0206(16)	0.0170(16)	-0.0054(11)	0.0000(12)	-0.0057(13)
Na4	0.0186(14)	0.0207(16)	0.0225(17)	-0.0039(12)	0.0000(12)	-0.0064(13)
Na5	0.0251(15)	0.0200(16)	0.0277(18)	-0.0086(12)	0.0054(13)	-0.0119(14)
Mn1	0.0093(5)	0.0111(5)	0.0115(6)	-0.0042(4)	0.0014(4)	-0.0054(4)
P1	0.0091(8)	0.0147(9)	0.0120(10)	-0.0006(7)	-0.0010(7)	-0.0060(8)
P2	0.0127(8)	0.0132(9)	0.0104(9)	-0.0061(7)	0.0023(7)	-0.0042(8)
P3	0.0111(8)	0.0118(9)	0.0090(9)	-0.0038(7)	0.0011(7)	-0.0035(7)
P4	0.0129(8)	0.0133(9)	0.0126(10)	-0.0045(7)	0.0012(7)	-0.0068(8)

O1	0.014(2)	0.013(2)	0.015(3)	0.0004(18)	-0.0036(19)	-0.008(2)
O2	0.032(3)	0.014(3)	0.015(3)	0.004(2)	-0.013(2)	-0.004(2)
O3	0.017(2)	0.023(3)	0.021(3)	-0.011(2)	0.008(2)	-0.011(2)
O4	0.041(3)	0.028(3)	0.014(3)	-0.025(2)	0.012(2)	-0.011(2)
O5	0.014(2)	0.016(3)	0.009(2)	-0.0088(19)	-0.0004(19)	-0.002(2)
O6	0.017(2)	0.015(3)	0.028(3)	-0.003(2)	0.004(2)	-0.002(2)
O7	0.0201(14)	0.0185(15)	0.0190(16)	-0.0072(11)	0.0056(12)	-0.0099(13)
O8	0.017(3)	0.019(3)	0.025(3)	-0.003(2)	0.010(2)	-0.014(3)
O9	0.014(2)	0.015(3)	0.013(3)	-0.0041(18)	-0.0052(19)	-0.006(2)
O10	0.015(2)	0.023(3)	0.017(3)	-0.0090(19)	0.002(2)	-0.014(2)
O11	0.010(2)	0.030(3)	0.018(3)	-0.008(2)	0.007(2)	-0.016(2)
O12	0.020(2)	0.014(3)	0.018(3)	-0.0054(19)	0.003(2)	-0.008(2)
O13	0.015(2)	0.016(3)	0.015(3)	-0.0090(19)	-0.002(2)	0.004(2)
O14	0.011(2)	0.016(3)	0.017(3)	-0.003(2)	-0.004(2)	-0.005(2)
F1	0.020(5)	0.047(7)	0.056(9)	-0.014(5)	0.020(5)	-0.027(6)

Table S4. Bond lengths **(**Å) and Band angles (degrees) of $Na_{5.5}Mn_{1.5}(P_2O_7)_2F_{0.5}$.

Atom1	Atom2	distances	Band angles	degrees
Na1	O2^vii^	2.372(7)	O4-Mn1-O9	172.67(15)
	O3	2.371(5)	O4-Mn1-O10	87.7(2)
	O5^ii^	2.345(5)	O4-Mn1-O12	82.7(2)
	O7^v^	2.496(5)	O4-Mn1-O13	88.09(18)
	O8^v^	2.469(5)	O4-Mn1-O14	93.89(18)
	O8^vi^	2.469(5)	O9-Mn1-O10	94.51(19)
Na2	O3	2.248(5)	O9-Mn1-O12	94.78(19)
	O11	2.260(6)	O9-Mn1-O13	84.98(18)
	O12	2.381(5)	O9-Mn1-O14	93.21(18)
	O13	2.237(5)	O10-Mn1-O12	170.4(2)
	F1	2.447(12)	O10-Mn1-O13	89.09(15)
Na3	O3^ii^	2.387(7)	O10-Mn1-O14	86.54(15)
	O5	2.487(5)	O12-Mn1-O13	89.29(15)
	O6	2.386(4)	O12-Mn1-O14	95.37(15)
	O9^vi^	2.583(5)	O13-Mn1-O14	175.13(16)
	O10^vi^	2.344(6)	O2^xii^-Mn2-O5^xiii^	96.3(2)
	F1	2.137(9)	O2^xii^-Mn2-O10	105.6(3)
	F1^ii^	2.236(9)	O2^xii^-Mn2-O11^xiii^	98.8(3)
Na4	O4	2.444(5)	O2^xii^-Mn2-F1^xiii^	175.0(4)
	O4^x^	2.671(4)	O5^xiii^-Mn2-O10	149.9(3)
	O7^x^	2.592(6)	O5^xiii^-Mn2-O11^xiii^	108.9(3)
	O11	2.428(4)	O5^xiii^-Mn2-F1^xiii^	81.2(3)
	O12	2.479(6)	O10-Mn2-O11^xiii^	88.1(3)
Na5	O5	2.673(5)	O10-Mn2-F1^xiii^	75.3(3)
	O7	2.436(6)	O11^xiii^-Mn2-F1^xiii^	86.1(4)
	O9^xi^	2.398(4)	O1-P1-O2	103.6(3)

	O14^x^	2.673(6)	O1-P1-O11^xiii^	107.1(3)
Mn1	O4	2.127(6)	O1-P1-O14	104.6(2)
	O9	2.111(6)	O2-P1-O11^xiii^	112.7(2)
	O10	2.161(4)	O2-P1-O14	112.2(3)
	O12	2.150(4)	O11^xiii^-P1-O14	115.4(3)
	O13	2.234(4)	O4-P2-O5	113.2(3)
	O14	2.193(4)	O4-P2-O6	106.3(3)
Na6	O2^xii^	2.100(13)	O4-P2-O7	112.0(3)
	O5^xiii^	2.302(13)	O5-P2-O6	101.8(2)
	O8	2.424(16)	O5-P2-O7	115.0(3)
	O10	2.414(12)	O6-P2-O7	107.4(2)
	O11^xiii^	2.222(18)	O6-P3-O8	107.5(3)
	F1^xiii^	2.535(15)	O6-P3-O10	107.2(3)
Mn2	O2^xii^	2.328(7)	O6-P3-O13^vi^	104.2(2)
	O5^xiii^	2.197(7)	O8-P3-O10	110.8(3)
	O8	2.414(6)	O8-P3-O13^vi^	113.3(2)
	O10	2.167(9)	O10-P3-O13^vi^	113.2(3)
	O11^xiii^	2.306(10)	O1-P4-O3^xiii^	109.3(2)
	F1^xiii^	2.328(7)	O1-P4-O9	107.5(3)
P1	O1	1.630(5)	O1-P4-O12^vii^	101.6(3)
	O2	1.503(4)		
	O11^xiii^	1.509(5)		
	O14	1.517(5)		
P2	O4	1.514(6)		
	O5	1.518(5)		
	O6	1.648(4)		
	O7	1.493(4)		
P3	O6	1.619(5)		
	O8	1.516(5)		
	O10	1.522(6)		
	O13^vi^	1.499(4)		
P4	O1	1.619(4)		
	O3^xiii^	1.499(5)		
	O9	1.522(5)		
	O12^vii^	1.520(6)		

Note: symmetry transformations used to generate equivalent atoms:

(i)-x+3,-y,-z+1；(ii)-x+3,-y+1,-z+1；(iii) -x+3,-y+1,-z；(iv)x,y-1,z；(iv)x,y-1,z；(v) x+1,y-1,z；(vi)-x+2,-y+1,-z+1；(vii)-x+2,-y+1,-z；(viii)x+1,y,z；(ix)-x+2,-y+2,-z+1；(x)-x+2,-y+2,-z；(xi)x,y+1,z；(xii) -x+1,-y+2,-z；(xiii)x-1,y,z；

Table S5. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of $Na_7Mn_{0.75}(P_2O_7)_2F_2$.

	Wyck.	x	y	z	Uiso*/Ueq	Occ.(<1)
Na1	8f	1.08159(15)	0.3317(4)	0.01714(19)	0.0113(8)	1
Na2	4e	1	-0.3636(7)	0.25	0.0181(13)	1
Na3	8f	1.12455(16)	-0.1586(5)	0.1400(2)	0.0133(9)	1
Na4	8f	1.27914(16)	0.2714(5)	0.11931(19)	0.0152(9)	1
Mn1	4d	0.75	0.25	0	0.0213(7)	0.75
P1	8f	0.93321(9)	0.1286(3)	0.10086(11)	0.0048(5)	1
P2	8f	0.84004(9)	0.3146(3)	0.22726(11)	0.0041(5)	1
O1	8f	0.8682(3)	-0.4359(7)	0.2361(3)	0.0087(13)	1
O2	8f	0.9832(3)	-0.0884(7)	0.1130(3)	0.0089(13)	1
O3	8f	1.1700(3)	0.2164(8)	0.1800(3)	0.0098(14)	1
O4	8f	0.7647(2)	0.2739(7)	0.1390(3)	0.0070(13)	1
O5	8f	0.9094(3)	0.1552(7)	0.2031(3)	0.0073(13)	1
O6	8f	0.9727(3)	0.3491(8)	0.0831(4)	0.0123(15)	1
O7	8f	0.8515(3)	0.0884(7)	0.0222(3)	0.0088(13)	1
F1	8f	1.1999(2)	0.4741(6)	-0.0008(3)	0.0093(11)	1

Table S6. Harmonic displacement parameters obtained for the compound $Na_7Mn_{0.75}(P_2O_7)_2F_2$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na1	0.0091(13)	0.0132(13)	0.0115(14)	-0.0007(9)	0.0024(10)	-0.0004(10)
Na2	0.0069(18)	0.026(2)	0.022(2)	0	0.0053(16)	0
Na3	0.0126(14)	0.0148(13)	0.0132(14)	0.0011(10)	0.0045(11)	0.0046(10)
Na4	0.0145(14)	0.0227(15)	0.0091(14)	0.0086(11)	0.0048(11)	0.0068(11)
Mn1	0.0198(11)	0.0216(11)	0.0218(12)	-0.0009(9)	0.0046(9)	0.0005(9)
P1	0.0044(7)	0.0057(7)	0.0044(8)	0.0008(5)	0.0016(6)	-0.0001(5)
P2	0.0045(7)	0.0053(7)	0.0028(8)	0.0000(5)	0.0014(6)	0.0004(5)
O1	0.007(2)	0.005(2)	0.013(2)	-0.0026(15)	0.0012(17)	-0.0022(16)
O2	0.008(2)	0.009(2)	0.009(2)	0.0051(16)	0.0018(18)	-0.0020(17)
O3	0.011(2)	0.015(2)	0.006(2)	-0.0005(17)	0.0053(18)	-0.0003(17)
O4	0.004(2)	0.011(2)	0.005(2)	0.0000(16)	0.0006(17)	-0.0011(16)
O5	0.006(2)	0.013(2)	0.004(2)	0.0054(16)	0.0027(17)	0.0015(16)
O6	0.009(2)	0.010(2)	0.018(2)	-0.0024(16)	0.0032(19)	0.0049(18)
O7	0.006(2)	0.012(2)	0.005(2)	0.0023(16)	-0.0025(16)	-0.0020(16)
F1	0.0080(17)	0.0094(17)	0.0099(19)	-0.0015(14)	0.0016(14)	0.0017(14)

Table S7. Bond lengths (Å) and Band angles (degrees) of $Na_7Mn_{0.75}(P_2O_7)_2F_2$.

Atom1	Atom2	distances	Band angles	degrees
Na1	O2^i^	2.332(5)	O4-Mn1-O4^xii^	180.0(5)
	O3	2.468(5)	O4-Mn1-O7	90.96(18)

	O6	2.325(6)	O4-Mn1-O7^xii^	89.04(18)
	O6^ii^	2.349(5)	O4-Mn1-F1^vii^	89.65(17)
	O7^i^	2.805(5)	O4-Mn1-F1^ii^	90.35(17)
	F1	2.282(5)	O4^xii^-Mn1-O7	89.04(18)
Na2	O1	2.268(5)	O4^xii^-Mn1-O7^xii^	90.96(18)
	O1^vi^	2.268(5)	O4^xii^-Mn1-F1^vii^	90.35(17)
	O2	2.457(5)	O4^xii^-Mn1-F1^ii^	89.65(17)
	O2^vi^	2.457(5)	O7-Mn1-O7^xii^	180.0(5)
	O6^ix^	2.812(5)	O7-Mn1-F1^vii^	89.30(17)
	O6^x^	2.812(5)	O7-Mn1-F1^ii^	90.70(17)
Na3	O1^vi^	2.348(5)	O7^xii^-Mn1-F1^vii^	90.70(17)
	O2	2.397(5)	O7^xii^-Mn1-F1^ii^	89.30(17)
	O3	2.314(5)	F1^vii^-Mn1-F1^ii^	180.0(5)
	O4^xi^	2.456(5)	O2-P1-O5	105.1(2)
	O7^i^	2.477(6)	O2-P1-O6	116.8(3)
Na4	O1^v^	2.255(5)	O2-P1-O7	109.6(2)
	O3	2.304(6)	O5-P1-O6	108.2(3)
	O7^v^	2.784(6)	O5-P1-O7	104.2(2)
	F1	2.192(4)	O6-P1-O7	111.9(2)
	F1^iv^	2.299(5)	O1^iii^-P2-O3^vi^	113.9(3)
Mn1	O4	1.915(4)	O1^iii^-P2-O4	112.9(2)
	O4^xii^	1.915(4)	O1^iii^-P2-O5	108.5(3)
	O7	1.930(4)	O3^vi^-P2-O4	112.0(3)
	O7^xii^	1.930(4)	O3^vi^-P2-O5	104.4(2)
	F1^vii^	1.808(4)	O4-P2-O5	104.3(2)
	F1^ii^	1.808(4)		
P1	O2	1.501(5)		
	O5	1.618(5)		
	O6	1.497(5)		
	O7	1.548(4)		
P2	O1^iii^	1.512(4)		
	O3^vi^	1.483(5)		
	O4	1.545(4)		
	O5	1.621(5)		

Note: symmetry transformations used to generate equivalent atoms:
(i)-x+2,-y,-z; (ii)-x+2,-y+1,-z; (iii) x,y+1,z; (iv)-x+5/2,-y+1/2,-z; (v)x+1/2,y+1/2,z; (vi)-x+2,y,-z+1/2; (vii)x-1/2,y-1/2,z; (viii)-x+5/2,y-1/2,-z+1/2; (ix)x,y-1,z; (x)-x+2,y-1,-z+1/2; (xi)x+1/2,y-1/2,z; (xii)-x+3/2,-y+1/2,-z;(xiii)x,-y,z+1/2; (xiv)-x+5/2,y+1/2,-z+1/2; (xv)x-1/2,y+1/2,z; (xvi)-x+2,y+1,-z+1/2;

Table S8. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of $Na_9Mn_3(P_2O_7)_4F$.

Wyck.	x	y	z	Uiso*/Ueq	Occ.(<1)

Na1	2i	0.9031(5)	0.1462(3)	0.25826(12)	0.0290(11)	1
Na2	2i	0.0158(4)	0.7965(3)	0.32383(12)	0.0195(9)	1
Na3	2i	0.5314(4)	0.8024(3)	0.31971(11)	0.0180(9)	1
Na4	2i	-0.4107(4)	0.0702(3)	0.08875(13)	0.0279(10)	1
Na5	2i	0.5899(3)	0.8843(2)	0.61610(11)	0.0141(8)	1
Na6	2i	0.0846(4)	0.3822(2)	0.11858(11)	0.0155(9)	1
Na7	2i	0.9502(4)	0.7082(2)	0.16989(11)	0.0154(9)	1
Na8	2i	0.9036(4)	0.4145(3)	0.40965(13)	0.0266(10)	1
Na9	2i	0.4719(4)	0.7206(3)	0.17296(12)	0.0195(9)	1
Mn1	2i	0.76123(14)	0.72906(9)	0.48452(4)	0.0075(3)	1
Mn2	2i	0.73743(14)	0.77291(9)	1.01128(4)	0.0082(3)	1
Mn3	2i	0.39848(15)	0.60519(10)	0.75809(5)	0.0159(3)	1
P1	2i	0.3671(2)	0.53746(16)	0.91996(8)	0.0081(5)	1
P2	2i	0.0550(3)	0.02778(16)	0.11003(8)	0.0102(5)	1
P3	2i	1.2837(2)	0.80417(16)	0.46904(8)	0.0075(5)	1
P4	2i	-0.2147(2)	0.30198(16)	-0.02686(8)	0.0079(5)	1
P5	2i	0.6405(3)	0.96910(17)	0.77297(8)	0.0123(5)	1
P6	2i	1.1341(2)	0.95135(16)	0.57852(8)	0.0079(5)	1
P7	2i	0.5606(2)	0.52898(16)	0.61161(8)	0.0076(5)	1
P8	2i	0.1683(3)	0.51085(16)	0.26981(8)	0.0107(5)	1
O1	2i	0.7146(6)	0.5801(4)	0.55795(19)	0.0127(14)	1
O2	2i	1.3208(6)	0.8537(4)	0.40104(18)	0.0103(14)	1
O3	2i	0.2934(6)	0.4416(4)	0.22311(19)	0.0145(15)	1
O4	2i	0.2197(6)	0.5610(4)	0.97920(18)	0.0101(9)	1
O5	2i	1.0542(6)	0.6945(4)	0.47589(19)	0.0121(14)	1
O6	2i	0.3509(6)	0.3810(4)	0.91726(19)	0.0115(14)	1
O7	2i	0.3098(6)	0.5499(4)	0.34147(19)	0.0169(15)	1
O8	2i	0.2669(6)	0.5741(4)	0.85704(19)	0.0153(15)	1
O9	2i	-0.0315(6)	0.2530(4)	0.00641(19)	0.0124(14)	1
O10	2i	0.8895(6)	0.8755(4)	0.55265(18)	0.0086(13)	1
O11	2i	-0.0203(6)	0.1413(4)	0.14566(19)	0.0166(15)	1
O12	2i	0.1714(6)	0.6565(4)	0.25127(18)	0.0103(13)	1
O13	2i	0.8308(6)	0.8914(4)	0.40666(18)	0.0113(14)	1
O14	2i	0.4981(6)	0.6407(4)	0.65347(19)	0.0145(15)	1
O15	2i	0.8477(6)	0.9005(4)	1.08790(18)	0.0121(14)	1
O16	2i	0.6564(6)	0.5894(4)	0.41271(19)	0.0135(9)	1
O17	2i	0.6064(6)	0.6329(4)	0.93883(18)	0.0108(14)	1
O18	2i	0.4642(6)	0.7493(4)	0.50052(18)	0.0099(14)	1
O19	2i	-0.0600(6)	0.4132(4)	0.28310(19)	0.0177(15)	1
O20	2i	1.2106(6)	0.8796(4)	0.63383(20)	0.0195(16)	1
O21	2i	0.8130(7)	1.0424(4)	0.83885(19)	0.0200(16)	1
O22	2i	0.4402(6)	0.8097(4)	1.02030(19)	0.0124(14)	1
O23	2i	1.2840(6)	0.9397(4)	0.51758(18)	0.0075(13)	1
O24	2i	0.5104(7)	0.8224(4)	0.7901(2)	0.0226(16)	1
O25	2i	-0.1757(6)	0.3499(4)	-0.09476(18)	0.0114(14)	1

O26	2i	0.2094(6)	0.0704(4)	0.05508(19)	0.0118(14)	1
O27	2i	0.4916(6)	1.0623(4)	0.7691(2)	0.0230(16)	1
O28	2i	0.7937(6)	0.9739(4)	0.7172(2)	0.0204(16)	1
F1	2i	0.7141(5)	0.6858(4)	0.25136(17)	0.0338(16)	1

Table S9. Harmonic displacement parameters obtained for the compound $Na_9Mn_3(P_2O_7)_4F$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na1	0.0436(18)	0.0339(17)	0.0146(15)	0.0182(14)	0.0085(13)	0.0046(13)
Na2	0.0153(14)	0.0282(15)	0.0151(14)	0.0097(11)	-0.0047(11)	-0.0098(11)
Na3	0.0136(13)	0.0280(15)	0.0123(13)	0.0066(11)	0.0030(11)	-0.0020(11)
Na4	0.0123(14)	0.0429(17)	0.0321(17)	0.0099(12)	0.0045(12)	0.0196(14)
Na5	0.0111(13)	0.0166(13)	0.0144(13)	0.0047(10)	0.0005(10)	-0.0030(10)
Na6	0.0145(13)	0.0189(13)	0.0130(13)	0.0060(11)	0.0000(11)	-0.0033(11)
Na7	0.0152(13)	0.0230(14)	0.0085(13)	0.0068(11)	-0.0007(10)	0.0006(11)
Na8	0.0149(14)	0.0439(18)	0.0274(16)	0.0142(12)	0.0052(12)	0.0209(14)
Na9	0.0143(13)	0.0313(15)	0.0136(14)	0.0101(11)	-0.0035(11)	-0.0066(12)
Mn1	0.0055(5)	0.0084(5)	0.0075(5)	0.0005(4)	0.0002(4)	-0.0007(4)
Mn2	0.0067(5)	0.0080(5)	0.0086(5)	0.0005(4)	-0.0004(4)	-0.0004(4)
Mn3	0.0133(5)	0.0231(6)	0.0123(5)	0.0067(4)	0.0019(4)	0.0018(4)
P1	0.0058(8)	0.0111(8)	0.0064(8)	0.0010(6)	0.0001(6)	-0.0006(6)
P2	0.0125(9)	0.0075(8)	0.0082(8)	0.0001(7)	-0.0011(7)	-0.0007(6)
P3	0.0053(8)	0.0086(8)	0.0076(8)	0.0010(6)	0.0001(6)	-0.0012(6)
P4	0.0075(8)	0.0083(8)	0.0064(8)	0.0005(6)	0.0005(7)	-0.0001(6)
P5	0.0157(9)	0.0115(8)	0.0073(8)	0.0011(7)	-0.0022(7)	0.0004(6)
P6	0.0076(8)	0.0082(8)	0.0072(8)	0.0016(6)	0.0012(6)	-0.0007(6)
P7	0.0074(8)	0.0085(8)	0.0057(8)	0.0003(6)	-0.0001(6)	0.0017(6)
P8	0.0091(8)	0.0133(8)	0.0091(8)	0.0033(7)	-0.0018(7)	-0.0008(7)
O1	0.015(2)	0.011(2)	0.011(2)	0.0012(18)	0.0051(18)	0.0058(18)
O2	0.012(2)	0.014(2)	0.005(2)	0.0054(18)	-0.0009(17)	0.0002(17)
O3	0.012(2)	0.022(2)	0.012(2)	0.0108(18)	-0.0015(18)	-0.0048(19)
O5	0.010(2)	0.008(2)	0.017(2)	0.0002(17)	0.0033(18)	-0.0025(18)
O6	0.013(2)	0.006(2)	0.013(2)	0.0002(17)	-0.0026(18)	-0.0043(17)
O7	0.024(2)	0.020(2)	0.011(2)	0.0138(20)	-0.0075(19)	0.0002(19)
O8	0.009(2)	0.029(3)	0.009(2)	0.0067(19)	-0.0005(18)	0.0027(19)
O9	0.010(2)	0.015(2)	0.012(2)	0.0043(18)	-0.0035(18)	0.0040(18)
O10	0.006(2)	0.012(2)	0.005(2)	0.0000(17)	-0.0001(16)	-0.0052(17)
O11	0.027(3)	0.009(2)	0.015(2)	0.0059(19)	0.003(2)	0.0000(18)
O12	0.012(2)	0.011(2)	0.010(2)	0.0054(17)	0.0012(17)	0.0049(17)
O13	0.010(2)	0.011(2)	0.012(2)	0.0024(17)	0.0002(17)	-0.0040(17)
O14	0.015(2)	0.012(2)	0.015(2)	0.0021(18)	0.0019(19)	-0.0027(18)
O15	0.010(2)	0.012(2)	0.008(2)	-0.0060(17)	0.0030(17)	-0.0034(17)

O17	0.006(2)	0.014(2)	0.009(2)	-0.0015(17)	-0.0013(17)	-0.0037(18)
O18	0.008(2)	0.014(2)	0.009(2)	0.0055(17)	-0.0003(17)	0.0024(17)
O19	0.013(2)	0.018(2)	0.020(2)	0.0010(18)	-0.0009(19)	0.0074(19)
O20	0.016(2)	0.031(3)	0.014(2)	0.011(2)	0.0012(19)	0.005(2)
O21	0.031(3)	0.012(2)	0.014(2)	0.004(2)	-0.013(2)	-0.0032(19)
O22	0.009(2)	0.009(2)	0.015(2)	-0.0031(17)	-0.0006(18)	-0.0011(18)
O23	0.008(2)	0.007(2)	0.005(2)	-0.0022(16)	0.0045(16)	-0.0035(16)
O24	0.029(3)	0.011(2)	0.022(3)	-0.0048(19)	0.008(2)	0.0029(19)
O25	0.011(2)	0.018(2)	0.004(2)	0.0031(18)	0.0003(17)	0.0035(17)
O26	0.010(2)	0.014(2)	0.011(2)	0.0039(18)	0.0059(18)	0.0023(18)
O27	0.018(2)	0.025(3)	0.027(3)	0.009(2)	-0.006(2)	-0.001(2)
O28	0.019(2)	0.026(3)	0.012(2)	0.001(2)	0.0044(19)	0.0011(19)
F1	0.014(2)	0.072(3)	0.017(2)	0.019(2)	-0.0008(16)	-0.006(2)

Table S10. Bond lengths **(**Å) and Band angles (degrees) of $Na_9Mn_3(P_2O_7)_4F$.

Atom1	Atom2	distances	Band angles	degrees
Na1	O11^iii^	2.334(5)	O1-Mn1-O5	84.72(16)
	O19^iii^	2.592(5)	O1-Mn1-O10	88.62(15)
	O20^v^	2.318(5)	O1-Mn1-O13	177.02(14)
	O24^iv^	2.845(5)	O1-Mn1-O16	94.31(15)
	O27^iv^	2.716(4)	O1-Mn1-O18	89.24(16)
	O28^v^	2.574(6)	O5-Mn1-O10	90.26(16)
Na2	O2^vi^	2.321(4)	O5-Mn1-O13	92.56(15)
	O12	2.380(5)	O5-Mn1-O16	85.97(16)
	O13^vi^	2.370(5)	O5-Mn1-O18	173.96(16)
	O28^vii^	2.441(5)	O10-Mn1-O13	90.18(14)
	F1^vi^	2.287(4)	O10-Mn1-O16	174.99(16)
Na3	O2^vi^	2.271(5)	O10-Mn1-O18	89.45(16)
	O7	2.543(4)	O13-Mn1-O16	86.69(15)
	O12	2.572(4)	O13-Mn1-O18	93.47(15)
	O13	2.429(4)	O16-Mn1-O18	94.64(16)
	O27^vii^	2.323(5)	O6^xix^-Mn2-O9^iv^	96.54(16)
	F1	2.291(5)	O6^xix^-Mn2-O15	83.38(15)
Na4	O11	2.538(4)	O6^xix^-Mn2-O17	91.90(15)
	O15^xiii^	2.660(5)	O6^xix^-Mn2-O22	89.24(16)
	O22^xiii^	2.718(4)	O6^xix^-Mn2-O26^iv^	173.21(17)
	O22^viii^	2.584(5)	O9^iv^-Mn2-O15	94.42(16)
	O24^viii^	2.765(5)	O9^iv^-Mn2-O17	88.51(16)
	O26^vi^	2.453(5)	O9^iv^-Mn2-O22	173.97(17)
Na5	O2^ix^	2.529(4)	O9^iv^-Mn2-O26^iv^	90.17(16)
	O10	2.337(4)	O15-Mn2-O17	174.69(15)
	O14	2.475(4)	O15-Mn2-O22	87.94(16)
	O18	2.572(4)	O15-Mn2-O26^iv^	95.07(15)
	O20^vi^	2.411(5)	O17-Mn2-O22	89.57(16)

	O28	2.329(4)	O17-Mn2-O26^iv^	89.33(15)
Na6	O3	2.372(4)	O22-Mn2-O26^iv^	84.09(16)
	O8^viii^	2.436(5)	O3^iv^-Mn3-O8	98.88(15)
	O9	2.486(4)	O3^iv^-Mn3-O14	87.27(15)
	O11	2.378(4)	O3^iv^-Mn3-O19^viii^	160.66(15)
	O17^iv^	2.336(5)	O3^iv^-Mn3-O24	98.06(16)
	O25^xiv^	2.616(4)	O8-Mn3-O14	173.83(16)
Na7	O6^iv^	2.438(4)	O8-Mn3-O19^viii^	89.02(15)
	O8^iv^	2.720(4)	O8-Mn3-O24	85.83(15)
	O12^iii^	2.282(5)	O14-Mn3-O19^viii^	84.98(15)
	O15^xv^	2.789(5)	O14-Mn3-O24	93.81(15)
	O21^ix^	2.490(4)	O19^viii^-Mn3-O24	100.11(16)
	O25^xvii^	2.274(5)	O4-P1-O6	105.2(2)
	F1	2.233(4)	O4-P1-O8	107.6(2)
Na8	O1^v^	2.442(5)	O4-P1-O17	106.8(2)
	O5^v^	2.638(5)	O6-P1-O8	111.6(2)
	O14^iv^	2.663(4)	O6-P1-O17	111.8(2)
	O16	2.646(5)	O8-P1-O17	113.3(2)
	O19^iii^	2.563(5)	O11-P2-O15^xiii^	108.6(2)
Na9	O6^iv^	2.477(5)	O11-P2-O21^iv^	110.9(2)
	O12	2.471(4)	O11-P2-O26	117.5(2)
	O25^xiv^	2.292(4)	O15^xiii^-P2-O21^iv^	101.3(2)
	O27^vii^	2.318(5)	O15^xiii^-P2-O26	112.7(2)
	F1	2.257(4)	O21^iv^-P2-O26	104.6(2)
Mn1	O1	2.118(4)	O2-P3-O5	114.6(2)
	O5	1.982(4)	O2-P3-O18^iii^	116.2(2)
	O10	1.890(3)	O2-P3-O23	106.9(2)
	O13	2.274(4)	O5-P3-O18^iii^	108.5(2)
	O16	1.881(4)	O5-P3-O23	104.7(2)
	O18	1.972(4)	O18^iii^-P3-O23	104.8(2)
Mn2	O6^xix^	2.127(4)	O4^viii^-P4-O9	104.0(2)
	O9^iv^	1.983(4)	O4^viii^-P4-O22^viii^	105.1(2)
	O15	1.892(3)	O4^viii^-P4-O25	106.8(2)
	O17	1.916(3)	O9-P4-O22^viii^	108.8(2)
	O22	2.019(4)	O9-P4-O25	116.1(2)
	O26^iv^	2.069(4)	O22^viii^-P4-O25	114.9(2)
Mn3	O3^iv^	2.144(4)	O21-P5-O24	106.2(2)
	O8	2.191(4)	O21-P5-O27	103.1(2)
	O14	2.238(4)	O21-P5-O28	103.6(2)
	O19^viii^	2.200(4)	O24-P5-O27	110.6(2)
	O24	2.096(4)	O24-P5-O28	115.4(3)
P1	O4	1.586(4)	O27-P5-O28	116.3(3)
	O6	1.516(4)	O10-P6-O13^ix^	110.2(2)
	O8	1.501(4)	O10-P6-O20	112.7(2)
	O17	1.533(3)	O10-P6-O23	106.20(19)

P2	O11	1.495(5)	O13^ix^-P6-O20	115.0(2)
	O15^xiii^	1.541(3)	O13^ix^-P6-O23	105.4(2)
	O21^iv^	1.608(5)	O20-P6-O23	106.5(2)
	O26	1.498(4)	O1-P7-O7^iv^	104.7(2)
P3	O2	1.485(4)	O1-P7-O14	116.4(2)
	O5	1.540(3)	O1-P7-O16^iv^	114.3(2)
	O18^iii^	1.526(4)	O7^iv^-P7-O14	109.1(2)
	O23	1.605(4)	O7^iv^-P7-O16^iv^	103.4(2)
P4	O4^viii^	1.616(4)	O14-P7-O16^iv^	108.0(2)
	O9	1.521(4)	O3-P8-O7	107.9(2)
	O22^viii^	1.530(3)	O3-P8-O12	112.6(2)
	O25	1.479(4)	O3-P8-O19	113.1(2)
P5	O21	1.654(4)	O7-P8-O12	100.9(2)
	O24	1.505(4)	O7-P8-O19	106.1(2)
	O27	1.499(5)	O12-P8-O19	115.0(2)
	O28	1.501(4)		
P6	O10	1.545(3)		
	O13^ix^	1.510(4)		
	O20	1.493(5)		
	O23	1.595(4)		
P7	O1	1.490(4)		
	O7^iv^	1.602(5)		
	O14	1.500(4)		
	O16^iv^	1.544(3)		
P8	O3	1.506(4)		
	O7	1.621(4)		
	O12	1.504(4)		
	O19	1.516(4)		

Note: symmetry transformations used to generate equivalent atoms:

(i)x+1,y-1,z; (ii)x,y-1,z; (iii)x+1,y,z; (iv)-x+1,-y+1,-z+1; (v)-x+2,-y+1,-z+1; (vi)x-1,y,z; (vii)-x+1,-y+2,-z+1; (viii)-x,-y+1,-z+1; (ix)-x+2,-y+2,-z+1; (x) -x-1,-y,-z; (xi)x-2,y-1,z; (xii)x-1,y-1,z; (xiii)x-1,y-1,z-1; (xiv)-x,-y+1,-z; (xv)x,y,z-1; (xvi)x+1,y+1,z; (xvii)-x+1,-y+1,-z; (xviii) x+1,y+1,z+1; (xix)-x+1,-y+1,-z+2; (xx)x-1,y+1,z;

Table S11. Geometrical Parameters Associated with the M- O•••O -M Super Supperexchange Paths of $Na_9Mn_3(P_2O_7)_4F$.

	Mn1-Mn1	Mn1-Mn1	Mn1-Mn3	Mn1-Mn3	Mn1-Mn1×2	Mn2-Mn2	Mn2-Mn2	Mn2-Mn3	Mn2-Mn3	Mn2-Mn2×2	Mn3-Mn3×2
<M -O•••O(°)	151.1(2)	107.9(2)	162.7(2)	112.3(1)	153.9(2)	104.9(2)	140.5(2)	136.8(2)	149.2(2)	151.5(2)	129.2(2)
<O•••O-M(°)	113.6(2)	126.5(2)	106.8(2)	147.2(2)	153.8(2)	130.0(2)	126.4(2)	105.7(2)	116.0(2)	150.2(2)	135.8(2)
M•••M(Å)	5.278(1)	4.826(1)	5.588(1)	6.097(1)	6.281(1)	4.770(1)	5.304(1)	5.391(1)	6.068(1)	6.281(1)	6.281(1)
O•••O(Å)	2.505(5)	2.548(5)	2.462(5)	2.504(6)	2.489(5)	2.530(5)	2.524(5)	2.535(5)	2.495(6)	2.480(5)	2.511(5)
torsion angle(°)	±36.9(5)	±70.3(3)	160.2(7)	-164.0(3)	±166.3(3)	±70.0(3)	±16.6(5)	116.0(3)	-153.4(3)	±167.9(3)	±155.2(2)
Exchange type	J_2	J_3	-	-	J_1	J_3'	J_2'	-		J_1'	-

References:

1 T. Zhu, B. Zhu, O. Mentré, S. Lee, D. Chen, Y. Jin, W. Zhu, A. M. Arevalo-Lopez, C. Minaud and K.-Y. Choi, *Chem. Mater.*, 2023, **35**, 3951-3959.