Supporting Information for:

Open-framework ammonium transition metal fluorophosphates with a Kagomé lattice network: synthesis, structure and magnetic properties

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Table S4. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of $(NH_4)Co_3(PO_3F)_2(PO_2F_2)F_2$.

Table S5**.** Harmonic displacement parameters obtained for the compound $(NH_4)Co_3(PO_3F)_2(PO_2F_2)F_2$.

Table S6.Bond lengths **(**Å) and Band angles (degrees) of $(NH_4)Co_3(PO_3F)_2(PO_2F_2)F_2$.

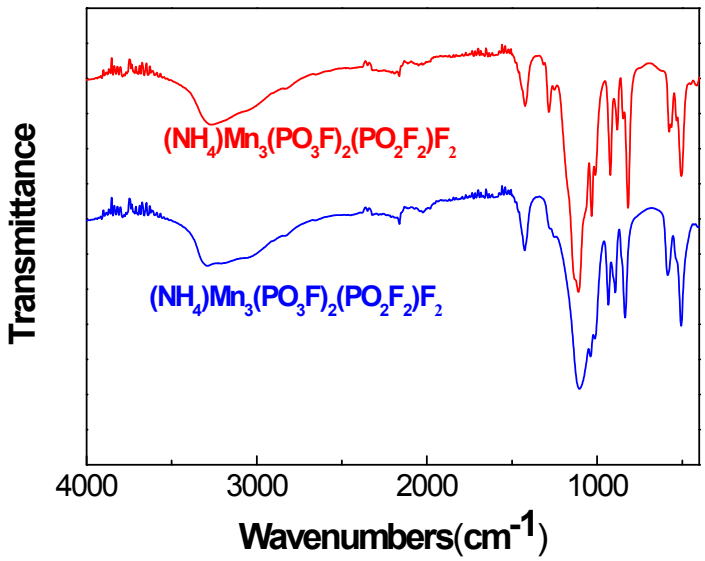
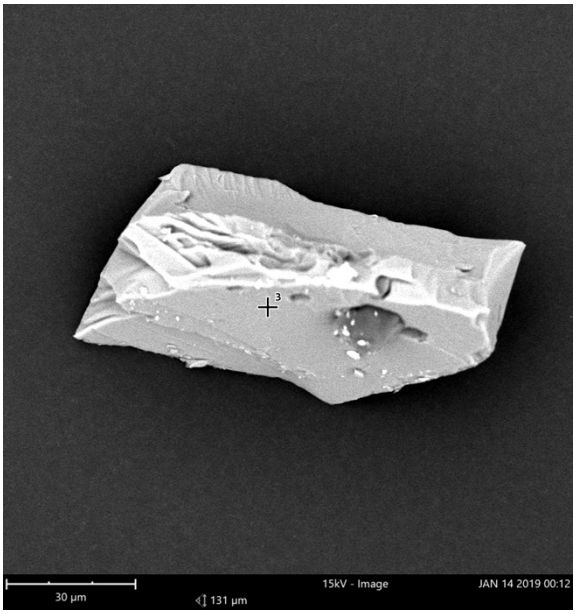


Figure S1. Infrared spectra of $(NH_4)M_3(PO_3F)_2(PO_2F_2)F_2$ (M= Co, and Mn).



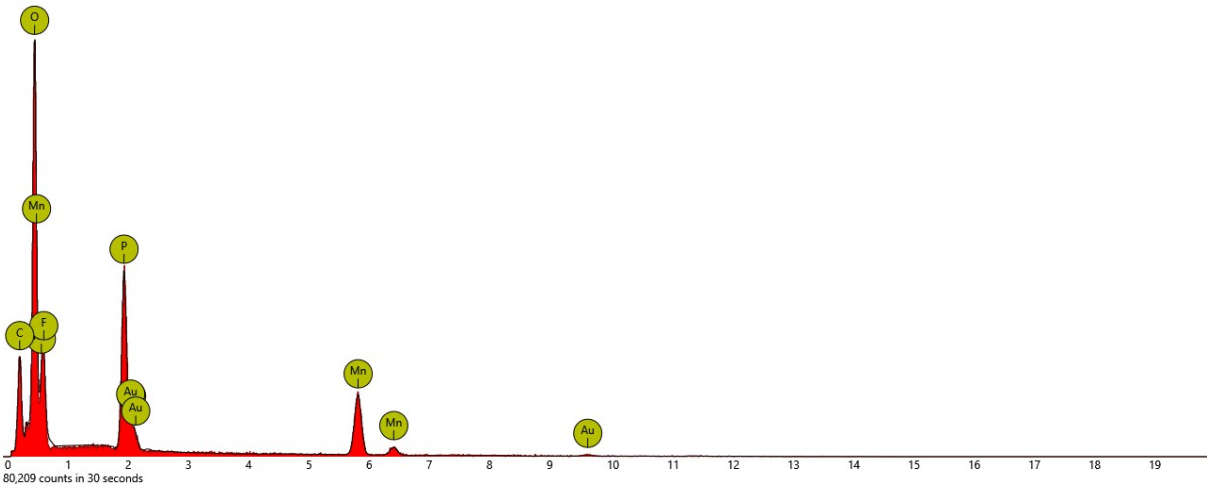
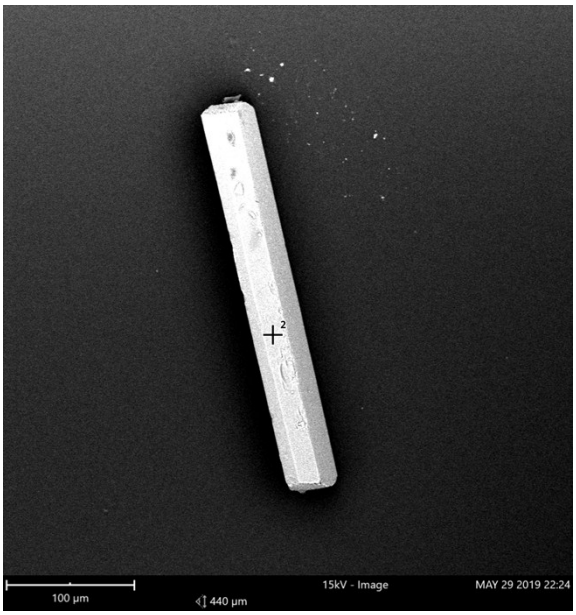


Figure S2.The corresponding EDX spectra for $(NH_4)Mn_3(PO_3F)_2(PO_2F_2)F_2$.



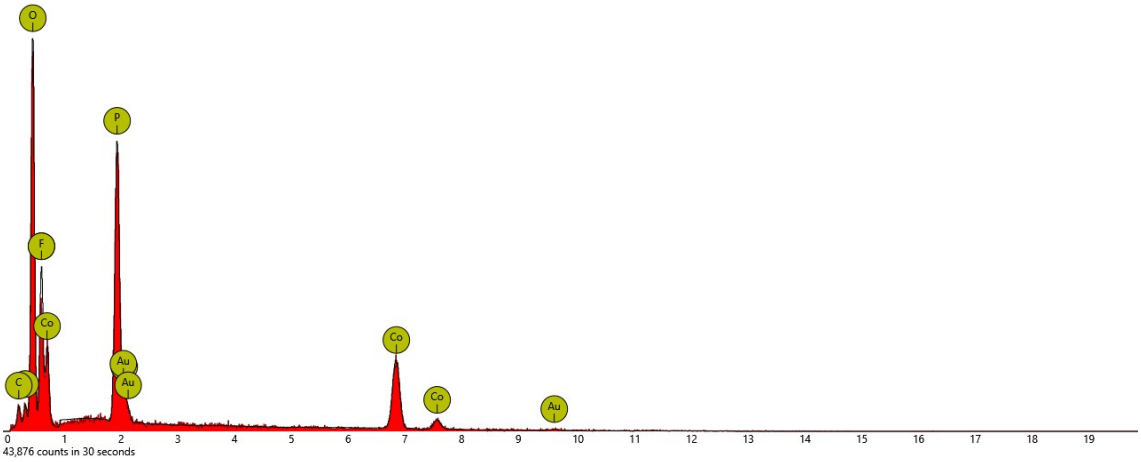


Figure S3**.**The corresponding EDX spectra for $(NH_4)Co_3(PO_3F)_2(PO_2F_2)F_2$.

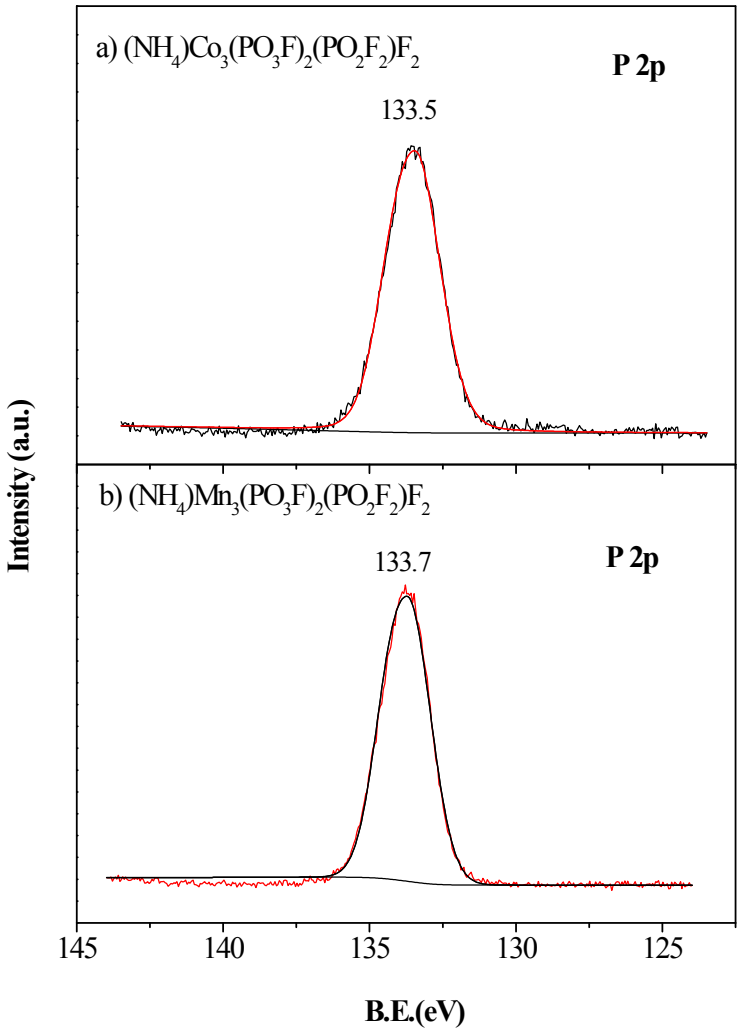


Figure S4. XPS spectra of P 2p region for $(NH_4)M_3(PO_3F)_2(PO_2F_2)F_2$ (M=Co, Mn).

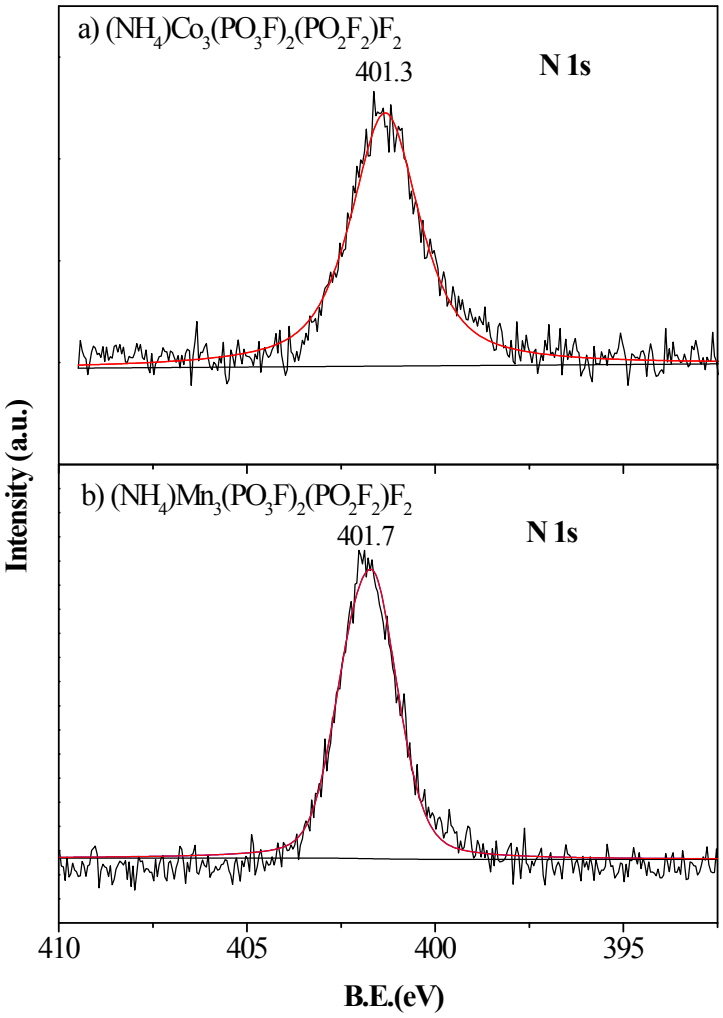


Figure S5. N 1s core level for $(NH_4)M_3(PO_3F)_2(PO_2F_2)F_2$ (M=Co, Mn).

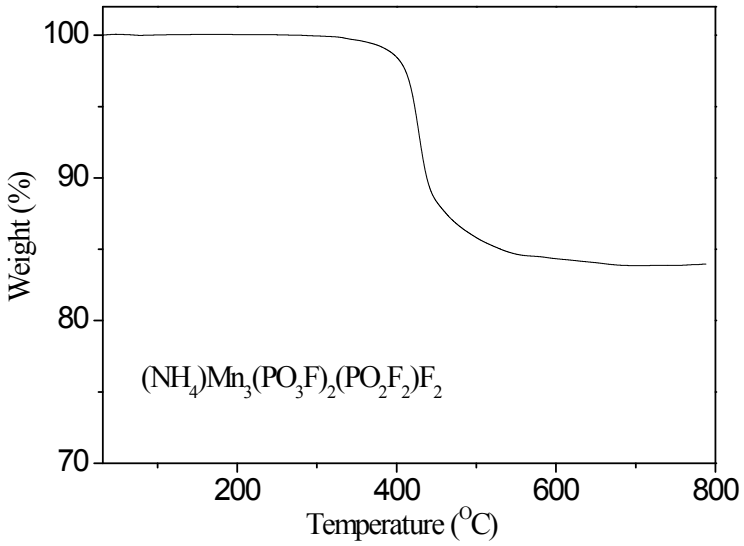


Figure S6. TGA diagram for $(NH_4)Mn_3(PO_3F)_2(PO_2F_2)F_2$.

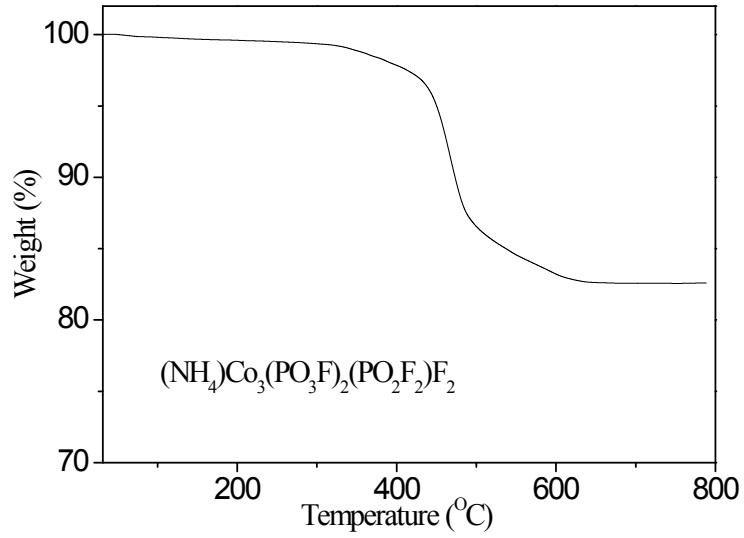


Figure S7. TGA diagram for $(NH_4)Co_3(PO_3F)_2(PO_2F_2)F_2$.

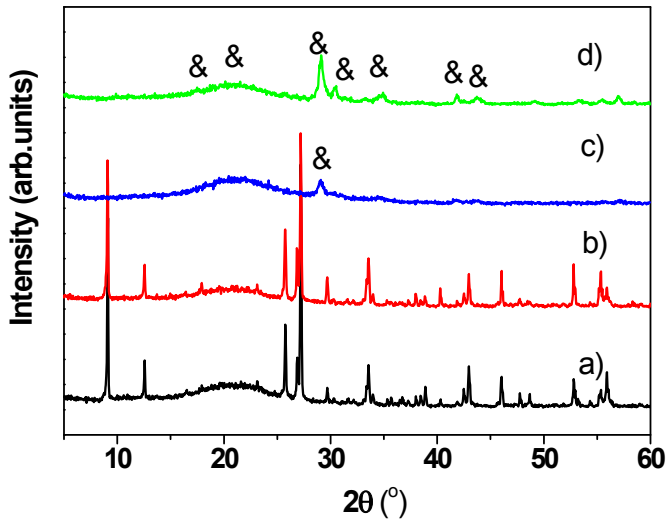


Figure S8. PXRD patterns of $(NH_4)Mn_3(PO_3F)_2(PO_2F_2)F_2$ at the elevated temperature for 10h, a) 200^{O}C, b) 300^{O}C, c) 400^{O}C, b) 500^{O}C. The markers refer to:$^{\&}$= $Mn_2P_2O_7$.

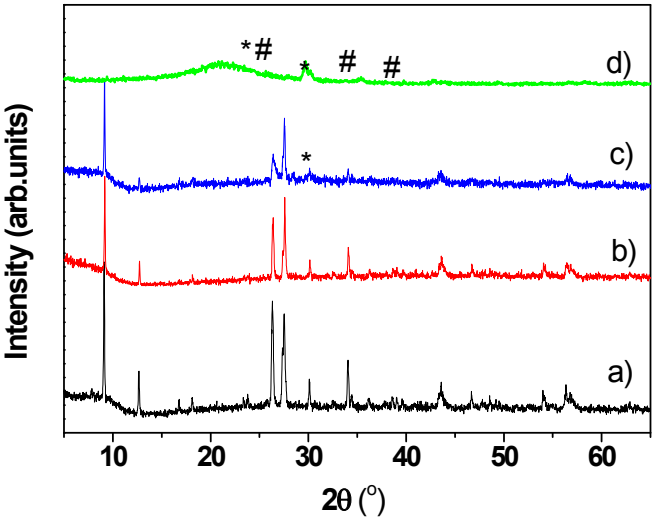


Figure S9. PXRD patterns of $(NH_4)Co_3(PO_3F)_2(PO_2F_2)F_2$ at the elevated temperature for 10h, a) 200^{O}C, b) 300^{O}C, c) 400^{O}C, b) 500^{O}C. The markers refer to:*= $Co_2P_4O_{12}$, # =CoF_3.

Table S1: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of $(NH_4)Mn_3(PO_3F)_2(PO_2F_2)F_2$.

	Wyck.	x	y	z	Uiso*/Ueq	Occ.(<1)
Mn1	4c	0.25	0.25	0	0.0124(2)	1
Mn2	8f	0.34124(3)	0.47185(7)	-0.29419(7)	0.01265(16)	1
P1	4e	0.5	0.62673(17)	-0.25	0.0152(4)	1

P2	8f	0.32642(4)	0.14076(12)	0.42129(12)	0.0109(3)	1
F1	8f	0.33837(10)	0.3727(3)	-0.0461(2)	0.0172(7)	1
F2	8f	0.38564(11)	0.0197(3)	0.3944(3)	0.0279(8)	1
F3	8f	0.53075(13)	0.7591(3)	-0.0985(3)	0.0410(10)	1
O1	8f	0.44436(12)	0.5248(4)	-0.2049(3)	0.0251(9)	1
O2	8f	0.35596(13)	0.2337(3)	0.5900(3)	0.0190(8)	1
O3	8f	0.31024(12)	0.2599(3)	0.2630(3)	0.0167(8)	1
O4	8f	0.23172(12)	0.5192(3)	0.0735(3)	0.0177(8)	1
N1	4e	0	0.3480(6)	0.25	0.0308(18)	1
H1	8f	0.0126	0.4204	0.3372	0.033993	1
H2	8f	0.0311	0.2764	0.2321	0.033993	1

Table S2. harmonic displacement parameters obtained for the compound $(NH_4)Mn_3(PO_3F)_2(PO_2F_2)F_2$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn1	0.0134(4)	0.0117(4)	0.0114(4)	-0.0024(3)	0.0015(3)	-0.0014(3)
Mn2	0.0120(3)	0.0128(3)	0.0128(3)	0.0008(2)	0.0020(2)	0.0002(2)
P1	0.0129(6)	0.0138(6)	0.0182(7)	0	0.0024(5)	0
P2	0.0097(4)	0.0106(4)	0.0113(5)	-0.0003(3)	0.0001(3)	0.0007(4)
F1	0.0187(11)	0.0218(11)	0.0121(11)	-0.0052(9)	0.0054(9)	-0.0001(9)
F2	0.0217(12)	0.0281(13)	0.0340(14)	0.0085(10)	0.0070(10)	-0.0032(11)
F3	0.0521(17)	0.0331(15)	0.0359(15)	0.0009(13)	0.0067(13)	-0.0101(12)
O1	0.0120(13)	0.0337(16)	0.0284(16)	-0.0038(12)	0.0022(11)	0.0071(13)
O2	0.0248(14)	0.0155(13)	0.0136(13)	0.0019(11)	-0.0018(11)	-0.0025(10)
O3	0.0223(14)	0.0151(12)	0.0105(13)	-0.0039(11)	-0.0007(10)	0.0048(10)
O4	0.0151(13)	0.0128(12)	0.0234(14)	0.0037(10)	0.0010(11)	-0.0053(11)
N1	0.031(3)	0.028(3)	0.034(3)	0	0.011(2)	0

Table S3. Bond lengths **(**Å) and Band angles (degrees) of $(NH_4)Mn_3(PO_3F)_2(PO_2F_2)F_2$.

Atom1	Atom2	d	Band angles	degrees
Mn1	2×F1	2.130(2)	F1-Mn1-F1	180.0(5)
	2×O3	2.136(2)	2×F1-Mn1-O3	99.62(8)
	2×O4	2.191(2)	2×F1-Mn1-O3	80.38(8)
Mn2	F1	2.099(2)	2×F1-Mn1-O4	99.60(9)
	F1	2.291(2)	2×F1-Mn1-O4	80.40(9)
	O1	2.086(2)	O3-Mn1-O3	180.0(5)
	O2	2.085(3)	2×O3-Mn1-O4	78.91(9)
	O3	2.220(2)	2×O3-Mn1-O4	101.09(9)
	O4	2.224(2)	O4-Mn1-O4	180.0(5)
P1	2×F3	1.572(2)	F1-Mn2-F1	169.51(8)

	2×O1	1.482(3)	F1-Mn2-O1	90.21(9)
P2	F2	1.570(3)	F1-Mn2-O2	97.23(9)
	O2	1.496(2)	F1-Mn2-O3	94.33(9)
	O3	1.510(2)	F1-Mn2-O4	101.54(9)
	O4	1.510(3)	F1-Mn2-O1	90.48(9)
Mn1	Mn2	3.024(1)	F1-Mn2-O2	93.15(9)
	Mn2	3.691(1)	F1-Mn2-O3	75.18(8)
			F1-Mn2-O4	76.28(8)
			O1-Mn2-O2	94.55(10)
			O1-Mn2-O3	93.65(10)
			O1-Mn2-O4	165.05(10)
			O2-Mn2-O3	165.79(9)
			O2-Mn2-O4	93.11(9)
			O3-Mn2-O4	76.44(8)
			F3-P1-F3	99.97(14)
			2×F3-P1-O1	110.37(14)
			2×F3-P1-O1	109.13(13)
			O1-P1-O1	116.59(17)
			F2-P2-O2	103.72(13)
			F2-P2-O3	105.69(14)
			F2-P2-O4	105.69(13)
			O2-P2-O3	113.82(14)
			O2-P2-O4	114.95(15)
			O3-P2-O4	111.81(13)
			Mn1-F1-Mn2	121.56(8)
			Mn1-F1-Mn2	86.22(8)
			Mn2-F1-Mn2	127.53(10)
			Mn1-O3-Mn2	87.90(8)
			Mn1-O4-Mn2	86.47(8)
			Mn1-Mn2-Mn2	141.99(18)
			Mn2-Mn1-Mn2	108.95(14)
			Mn2-Mn2-Mn1	108.95(14)

Table S4: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of $(NH_4)Co_3(PO_3F)_2(PO_2F_2)F_2$.

	Wyck.	x	y	z	Uiso*/Ueq	Occ.(<1)
Co1	4c	0.25	0.25	0	0.0107(3)	1
Co2	8f	0.33979(4)	0.51991(10)	0.19292(10)	0.0119(3)	1
P1	4e	0.5	0.3819(3)	0.25	0.0120(6)	1
P2	8f	0.17406(7)	0.63773(18)	0.08005(18)	0.0093(4)	1
F1	8f	0.16366(16)	0.1282(4)	0.0565(4)	0.0144(10)	1

F2	8f	0.1148(2)	0.5134(5)	0.1070(6)	0.0292(14)	1
F3	8f	0.4714(3)	0.2496(6)	0.0935(7)	0.0458(18)	1
O1	8f	0.4421(2)	0.4887(6)	0.2885(7)	0.0251(15)	1
O2	8f	0.1460(2)	0.7338(5)	-0.0948(6)	0.0188(13)	1
O3	8f	0.3105(2)	0.2612(5)	0.2578(6)	0.0166(13)	1
O4	8f	0.2340(2)	0.5165(5)	0.0724(6)	0.0164(13)	1
N1	4e	0.5	0.1352(10)	-0.25	0.021(2)	1
H1	8f	0.4633	0.1987	-0.2829	0.037995	1
H2	8f	0.4997	0.0662	-0.3454	0.037995	1

Table S5. harmonic displacement parameters obtained for the compound $(NH_4)Co_3(PO_3F)_2(PO_2F_2)F_2$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co1	0.0125(6)	0.0105(6)	0.0086(5)	-0.0009(4)	0.0015(4)	-0.0008(4)
Co2	0.0128(4)	0.0114(4)	0.0114(4)	0.0006(3)	0.0026(3)	0.0007(3)
P1	0.0098(10)	0.0130(10)	0.0119(9)	0	-0.0008(8)	0
P2	0.0097(7)	0.0087(7)	0.0091(7)	-0.0003(5)	0.0012(5)	-0.0011(5)
F1	0.0175(18)	0.0156(18)	0.0115(16)	-0.0043(12)	0.0060(14)	0.0002(12)
F2	0.025(2)	0.030(2)	0.034(2)	-0.0067(16)	0.0103(18)	-0.0005(17)
F3	0.056(3)	0.041(3)	0.036(3)	0.005(2)	0.001(2)	-0.017(2)
O1	0.012(2)	0.030(2)	0.032(3)	0.0003(18)	0.0017(19)	-0.010(2)
O2	0.027(2)	0.015(2)	0.012(2)	-0.0011(17)	-0.0002(17)	0.0021(16)
O3	0.023(2)	0.012(2)	0.013(2)	-0.0060(16)	-0.0004(17)	0.0022(15)
O4	0.016(2)	0.015(2)	0.018(2)	0.0024(16)	0.0017(17)	-0.0070(16)
N1	0.016(4)	0.024(4)	0.024(4)	0	0.005(3)	0

Table S6. Bond lengths **(**Å) and Band angles (degrees) of $(NH_4)Co_3(PO_3F)_2(PO_2F_2)F_2$.

Atom1	Atom2	d	Band angles	degrees
Co1	2×F1	2.076(3)	F1-Co1-F1	180.0(5)
	2×O3	2.058(4)	2×F1-Co1-O3	99.42(15)
	2×O4	2.112(4)	2×F1-Co1-O3	80.58(15)
Co2	F1	2.077(3)	2×F1-Co1-O4	100.46(16)
	F1	2.178(3)	2×F1-Co1-O4	79.54(16)
	O1	2.026(4)	O3-Co1-O3	180.0(5)
	O2	2.031(4)	2×O3-Co1-O4	78.85(16)
	O3	2.113(4)	2×O3-Co1-O4	101.15(16)
	O4	2.110(4)	O4-Co1-O4	180.0(5)
P1	2×F3	1.554(5)	F1-Co2-F1	171.54(14)
	2×O1	1.486(5)	F1-Co2-O1	87.24(18)
P2	F2	1.554(5)	F1-Co2-O2	90.84(16)

	O2	1.502(4)	F1-Co2-O3	94.57(15)
	O3	1.513(4)	F1-Co2-O4	99.72(16)
	O4	1.513(5)	F1-Co2-O1	95.06(18)
Co1	Co2	2.878(1)	F1-Co2-O2	97.23(16)
	Co2	3.662(1)	F1-Co2-O3	77.09(15)
			F1-Co2-O4	77.34(15)
			O1-Co2-O2	91.42(19)
			O1-Co2-O3	96.91(18)
			O1-Co2-O4	171.44(19)
			O2-Co2-O3	170.27(16)
			O2-Co2-O4	93.43(17)
			O3-Co2-O4	77.70(16)
			F3-P1-F3	100.8(3)
			2×F3-P1-O1	108.7(3)
			2×F3-P1-O1	111.4(3)
			O1-P1-O1	114.9(3)
			F2-P2-O2	104.8(2)
			F2-P2-O3	106.6(3)
			F2-P2-O4	106.0(2)
			O2-P2-O3	113.1(2)
			O2-P2-O4	113.5(3)
			O3-P2-O4	112.1(2)
			Co1-F1-Co2	123.70(14)
			Co1-F1-Co2	85.11(13)
			Co2-F1-Co2	126.26(16)
			Co1-O3-Co2	87.24(16)
			Co1-O4-Co2	85.95(16)
			Co1-Co2-Co2	140.95(20)
			Co2-Co1-Co2	108.32(20)
			Co2-Co2-Co1	108. 32(20)