Supporting Information

Synthesis and magnetic properties of two fluorophosphates $K_2Mn(PO_3F)F_3$ and $Na_2Mn(HPO_4)F_3$ with a $S = 2$ uniform spin chain structure

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Fig. S1. The powder XRD patterns of $K_2Mn(PO_3F)F_3$ and $Na_2Mn(HPO_4)F_3$.

Fig. S2. The energy-dispersive spectrometry (EDS) elemental analyses of $K_2Mn(PO_3F)F_3$ and $Na_2Mn(HPO_4)F_3$.

Fig. S3. Heat capacity data at 2-120 K for $K_2Mn(PO_3F)F_3$ and $Na_2Mn(HPO_4)F_3$。The inset shows an enlarged view of low temperature.

Fig. S4. dM/dH vs H curves for $K_2Mn(PO_3F)F_3$ and $Na_2Mn(HPO_4)F_3$。

Fig. S5. Heat capacity data of K_2Mn $(PO_3F)F_3$ and $Na_2Mn(HPO_4)F_3$ with lattice and magnetic contributions .

Fig. S6. Magnetic heat capacity and corresponding magnetic entropy for $K_2Mn(PO_3F)F_3$ and $Na_2Mn(HPO_4)F_3$.

Table S1. The valence bond calculations for $K_2Mn(PO_3F)F_3$.

Table S2. The valence bond calculations for $Na_2Mn(HPO_4)F_3$.

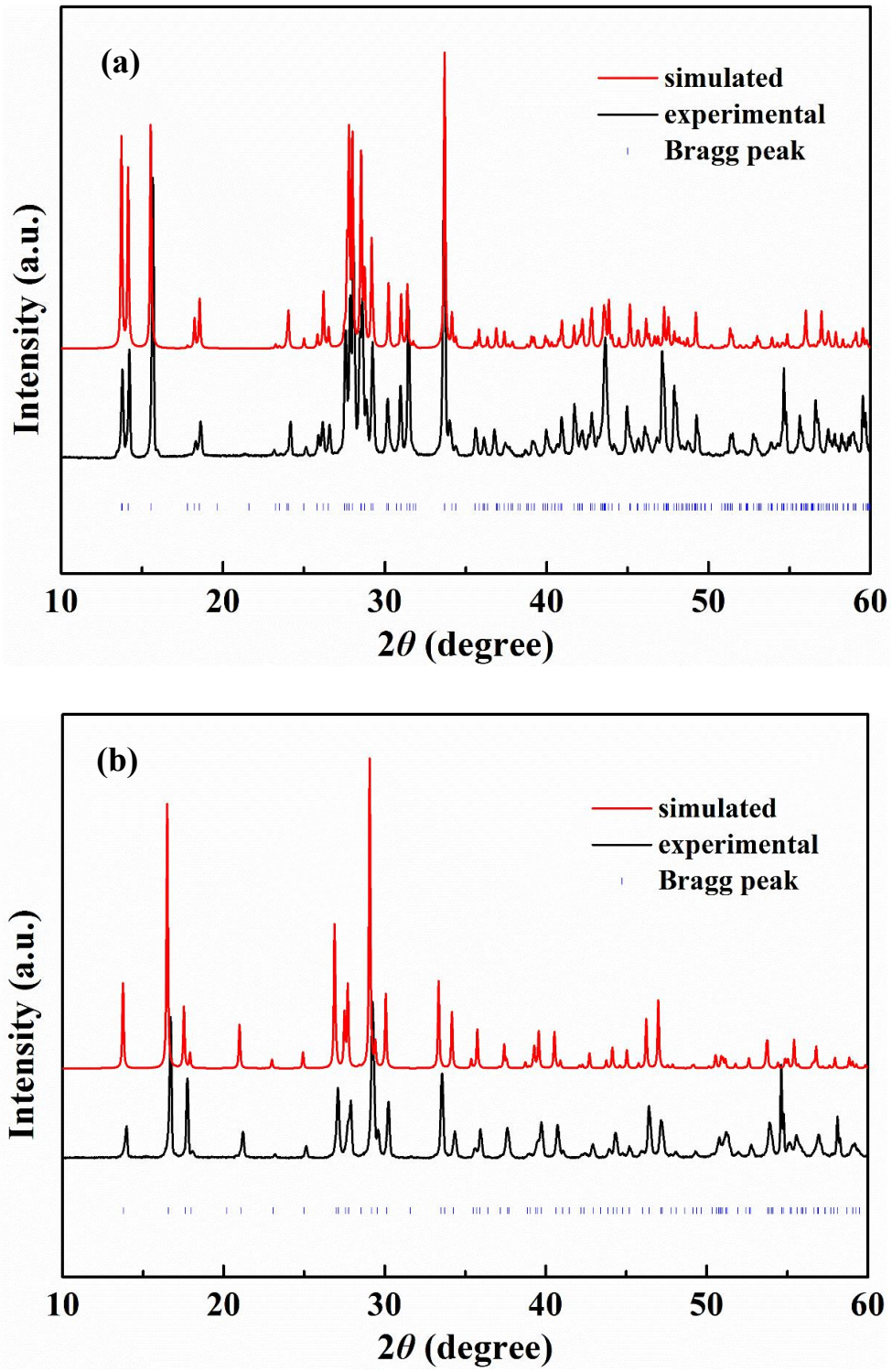

Fig. S1. The powder XRD patterns of $K_2Mn(PO_3F)F_3$ (a) and $Na_2Mn(HPO_4)F_3$ (b).

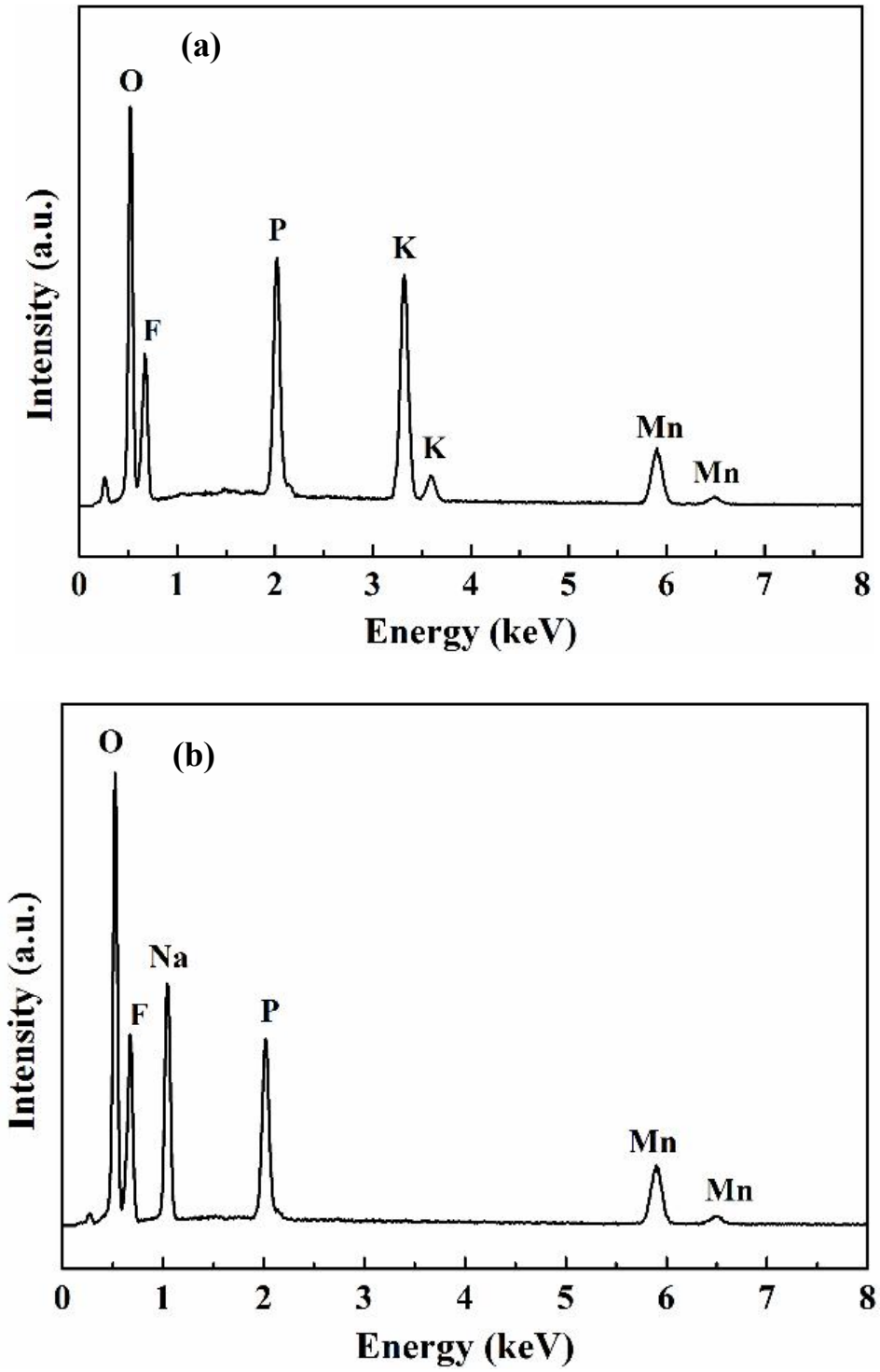

Fig. S2. The energy-dispersive spectrometry (EDS) elemental analyses of $K_2Mn(PO_3F)F_3$ (a) and $Na_2Mn(HPO_4)F_3$ (b).

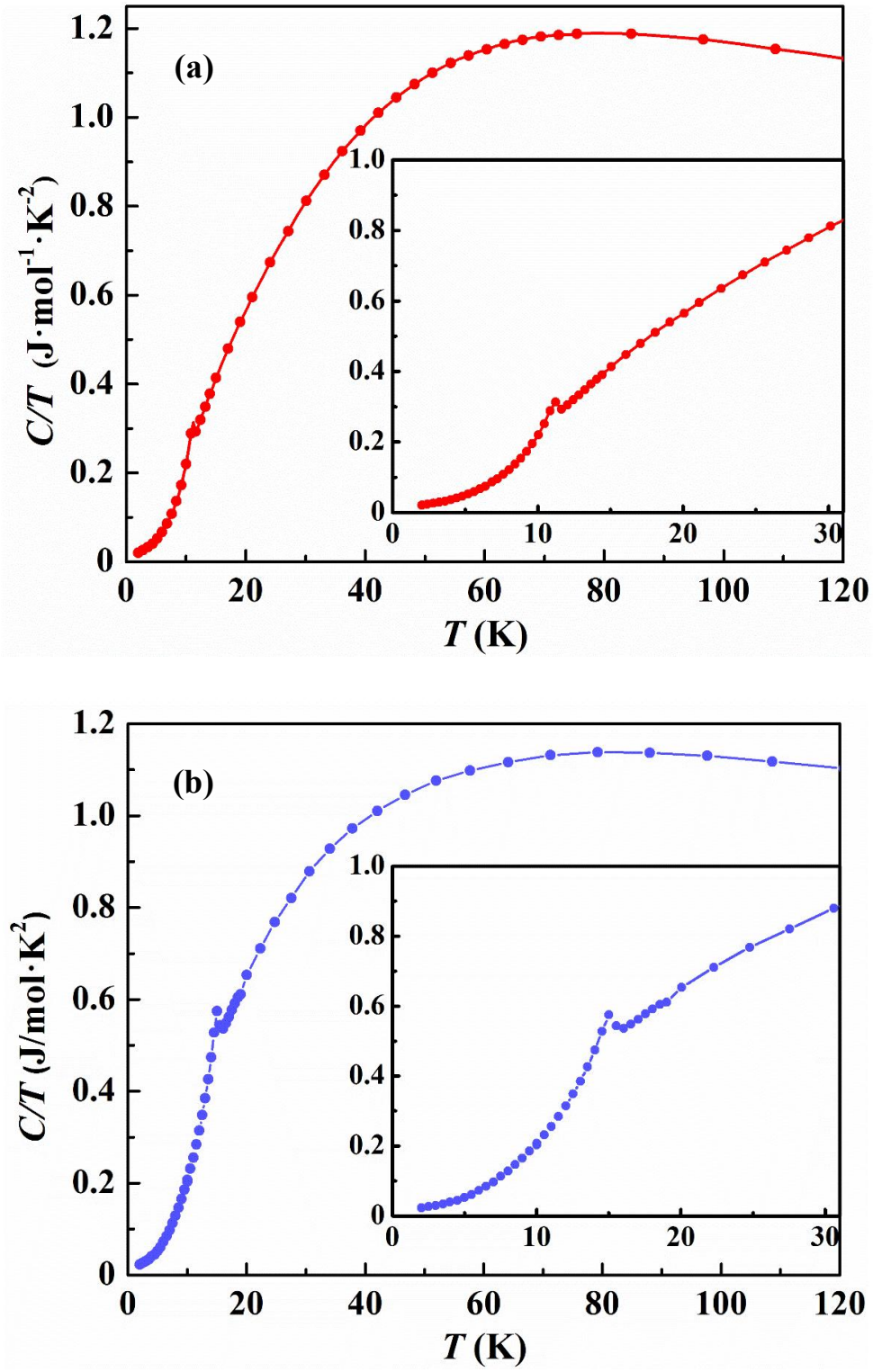

Fig. S3. The heat capacity at 2-120 K for $K_2Mn(PO_3F)F_3$ (a) and $Na_2Mn(HPO_4)F_3$ (b). The inset shows an enlarged view of low temperature.

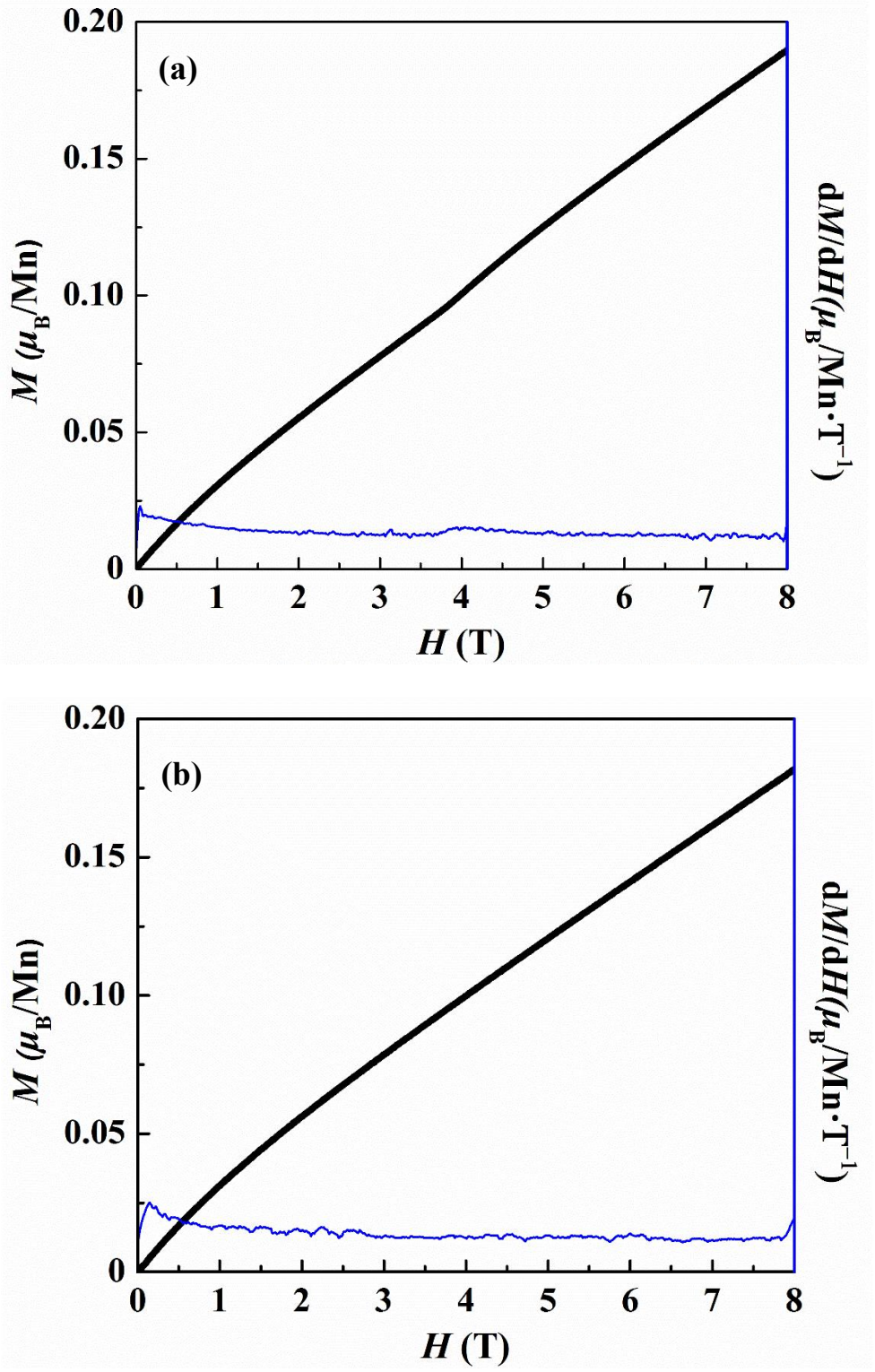

Fig. S4. dM/dH vs H curves for $K_2Mn(PO_3F)F_3$ (a) and $Na_2Mn(HPO_4)F_3$ (b).

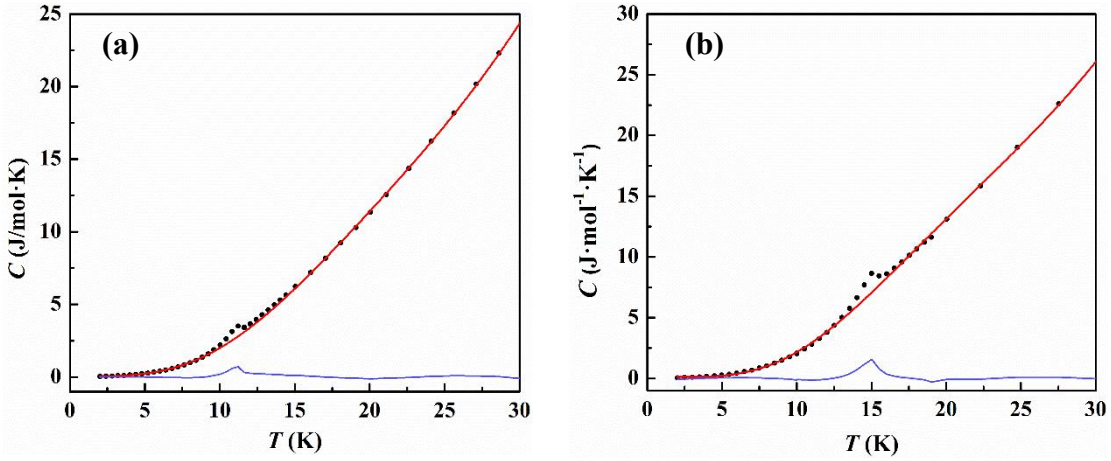

Fig. S5. Heat capacity data of $K_2Mn(PO_3F)F_3$ (a) and $Na_2Mn(HPO_4)F_3$ (b) with lattice and magnetic contributions, where the red line is the lattice contribution (C_L) fitted by the Thirring formula and the blue line is the magnetic one (C_m).

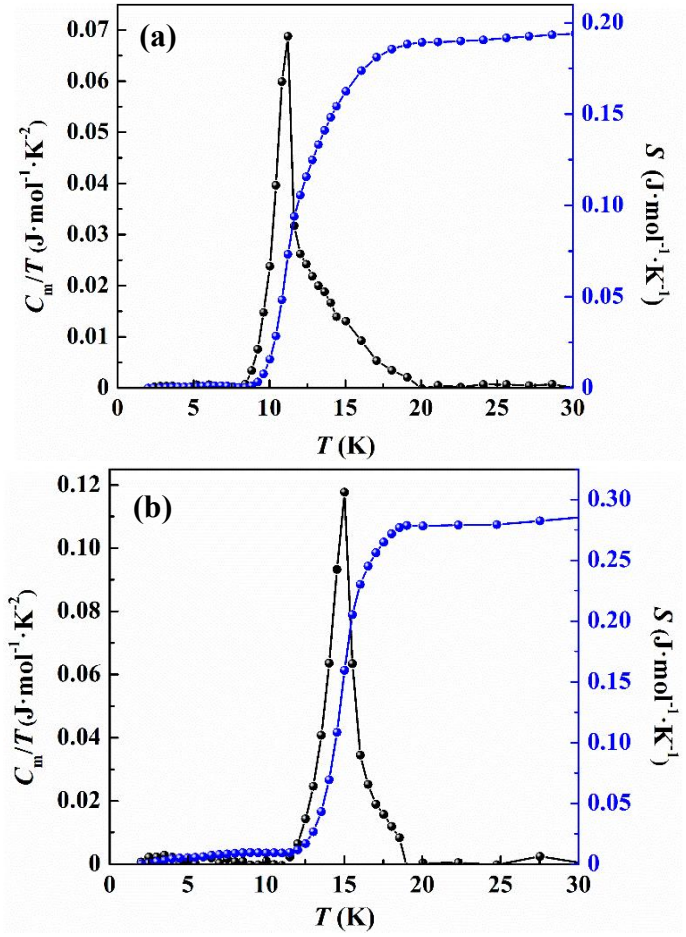

Fig. S6. Magnetic heat capacity and corresponding magnetic entropy for $K_2Mn(PO_3F)F_3$ (a) and $Na_2Mn(HPO_4)F_3$ (b) from 2 to 30 K.

Table S1. The valence bond calculations for K2Mn(PO3F)F3.

Atom	BVS	Valence	Atom	BVS	Valence
Mn1	3.05	+3	F2	0.95	-1
Mn2	3.05	+3	F3	1.05	-1
P1	4.73	+5	F4	1.13	-1
K1	1.12	+1	O1	2.06	-2
K2	1.15	+1	O2	2.02	-2
F1	1.07	-1	O3	1.77	-2

Table S2. The valence bond calculations for $Na_2Mn(HPO_4)F_3$.

Atom	BVS	Valence	Atom	BVS	Valence
Mn	3.16	+3	F2	1.02	-1
P	4.92	+5	O1	2.09	-2
Na1	0.82	+1	O2	2.04	-2
Na2	1.06	+1	O3	2.02	-2
F1	0.96	-1			