Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

$PbFe(PO_4)F_2$ with a 1/6th Bond Depleted Triangular Lattice

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Experimental Section

Caution. Hydrofluoric acid is toxic and corrosive! It must be handled with extreme caution and the appropriate protective gear.[1-3]

Synthesis. Lead (II, III) teroxide (Pb_3O_4, 97%, Wako), iron (II) oxide (FeO, 99.5%, Wako), phosphoric acid (85% H_3PO_4 by weight, Wako), and aqueous hydrofluoric acid (46.0~48.0% HF by weight, Wako) were used as received. Black single crystals of $PbFePO_4F_2$ were synthesized by adding 0.2 g (0.88 mmol) of Pb_3O_4, 0.1 g (1.39 mmol) of FeO, 0.4 mL (7.67 mmol) of H_3PO_4, 0.8 mL (~22.08 mmol) of 48% aqueous HF to a Teflon [fluoro(ethylenepropylene), FEP] pouch made as described previously;[4-7] All reagents were sealed with a sealer in Teflon pouches, and placed into a 125 mL Parr autoclave with a backfill of 45 mL pure water. The autoclave was quickly heated to 200 °C, held at this temperature for 24 hours and cooled to ambient temperature for 30 hours. The single-crystals of $PbFePO_4F_2$ were recovered in air after vacuum filtration.

Crystallographic Determination. The powder X-ray diffraction pattern (PXRD) was collected on the Bruker D8 ADVANCE using Cu *K*a radiation (λ = 1.54184 Å) at a 0.1° step size and 1-second dwell time. Single crystal X-Ray diffraction experiments for determining crystal structures of $PbFePO_4F_2$ were conducted at room temperature (296 K) on a Rigaku R-AXIS RAPID image plate diffractometer with Mo *K*α radiation (λ = 0.71073 Å). The crystal-to-detector distance was 127 mm and data integrations were made using Rigaku RAPID-AUTO.[8] Multiscan absorption corrections were applied with Rigaku RAPID-AUTO. The structures were determined by direct methods, completed by Fourier difference syntheses with SIR97,[9] and refined using SHELXL-2014.[10] No additional

symmetry elements were found using the program PLATON.[11] Crystallographic data are reported in Table 1.

Thermo-gravimetric Analysis (TG-DTA). The thermogravimetric measurement for $PbFePO_4F_2$ was performed in air from ambient temperature to 900 °C on a Rigaku Thermo plus TG8121 using a Pt pan with a heating rate of 1 °C/min. The sample was held at this temperature for two hours and then cooled to room temperature at a rate of 5 °C/min.

Magnetic Characterization. A Quantum Design MPMS-XL superconducting quantum interference device (SQUID) magnetometer was used to collect DC magnetic susceptibility for $PbFePO_4F_2$ between 2 K and 350 K, and magnetization curves at 2 K and 300 K between 0 and 7 T. The magnetic susceptibility was approximate by $\chi = M/H$ with subtraction of the sample container background and diamagnetic correction derived from Pascal's constants.[12]

Table 1 Crystal data for $PbFePO_4F_2$.

Compound formula	$PbFePO_4F_2$
Formula weight ($g \cdot mol^{-1}$)	396.02
Temperature (K)	296(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	5.257(2)
b (Å)	12.404(5)
c (Å)	7.098(3)
β (°)	102.765(9)
V (Å^3)	451.4(3)
Z	4
Maximum θ (°)	27.5
λ (Mo/Cu $K\alpha$) (Å)	0.71073
$\rho_{calc.}$ ($g \cdot cm^{-3}$)	5.827
R_{int}	0.031
R_1	0.037
wR_2	0.070
Goodness-of-fit	1.01

Table 2 Selected bond lengths, angles and BVS calculations for $PbFePO_4F_2$.

Bond	**Bond Length (Å)**	**s_{ij}**	**Angle**	**Degree (°)**
		$PbFePO_4F_2$		
Fe(1)–F(1)	2 × 1.941(5)	2 × 0.480	F(1)–Fe(1)–F(1)	180
Fe(1)–F(2)	2 × 1.933(5)	2 × 0.491	F(2)–Fe(1)–F(2)	180
Fe(1)–O(1)	2 × 1.985(5)	2 × 0.542	O(1)–Fe(1)–O(1)	180
		$\Sigma s_{ij} = 3.03$	Fe(1)–F(1)–Fe(2)	127.7
Fe(2)–F(1)	2 × 2.012(5)	2 × 0.397	F(1)–Fe(2)–F(1)	180

Fe(2)–O(3)	2 × 1.978(5)	2 × 0.554	O(3)–Fe(2)–O(3)	180
Fe(2)–O(4)	2 × 2.074(5)	2 × 0.427	O(4)–Fe(2)–O(4)	180
		$\Sigma s_{ij} = 2.76$	O(1)–P–O(2)	108.7
P–O(1)	1.536(6)	1.202	O(1)–P–O(3)	112.9
P–O(2)	1.533(6)	1.213	O(1)–P–O(4)	109.5
P–O(3)	1.518(6)	1.261	O(2)–P–O(3)	108.2
P–O(4)	1.552(6)	1.152	O(2)–P–O(4)	108.4
		$\Sigma s_{ij} = 4.83$	O(3)–P–O(4)	109.0

Figure S1 Experimental PXRD pattern and simulated pattern for compound $PbFePO_4F_2$ and PXRD pattern for product after TGA at 900 ℃.

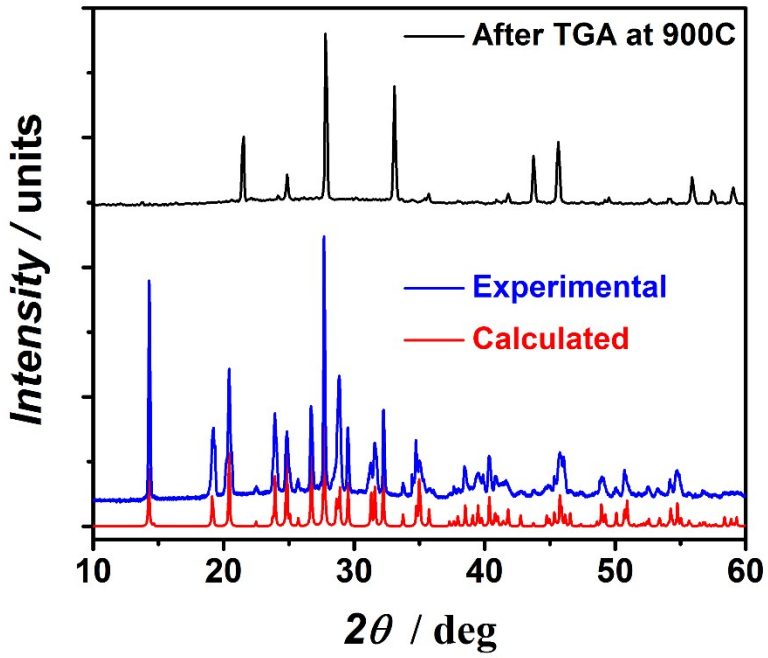


Figure S2 Coordination for Pb in $PbFePO_4F_2$.

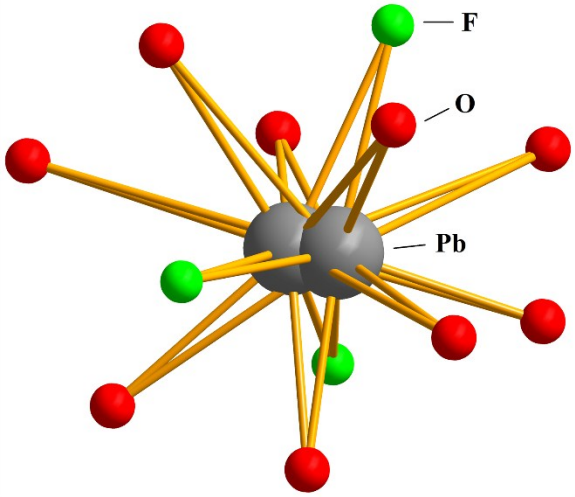


Figure S3 TGA curve of $PbFePO_4F_2$.

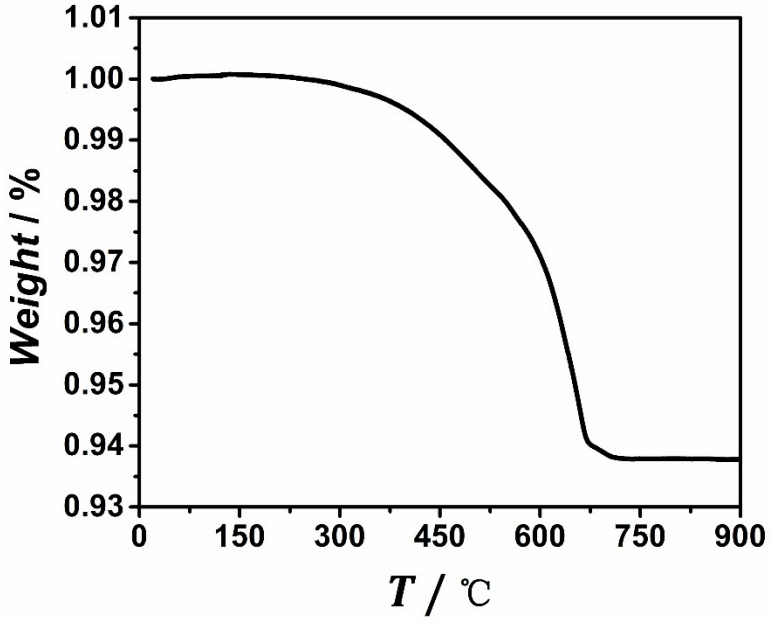
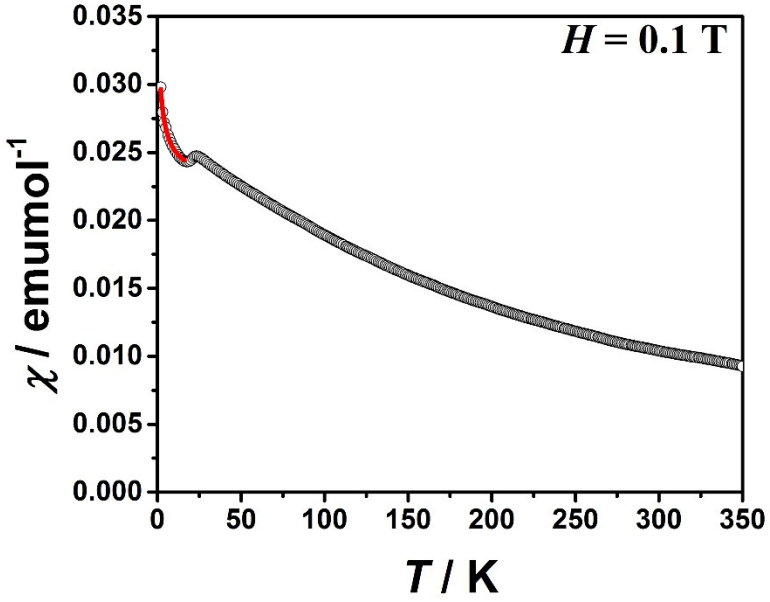
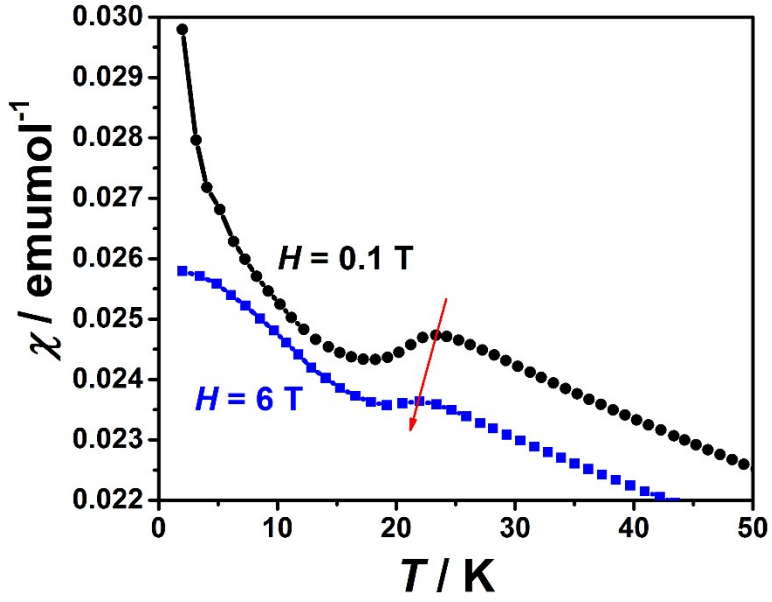


Figure S4 (a) Curie Weiss fitting for impurity amount of Curie tail; (b) magnetic susceptibility χ(T) at 0.1 T(black circle) and 6 T (blue square) for $PbFePO_4F_2$.

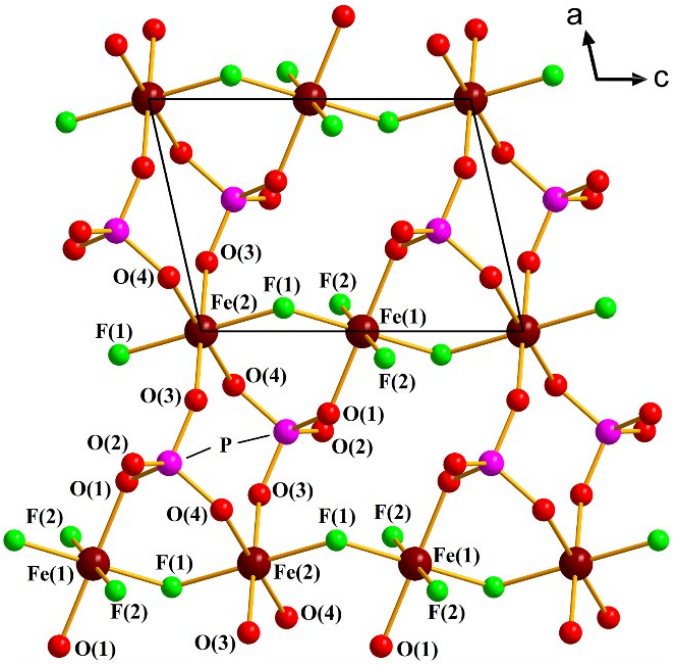


(a)

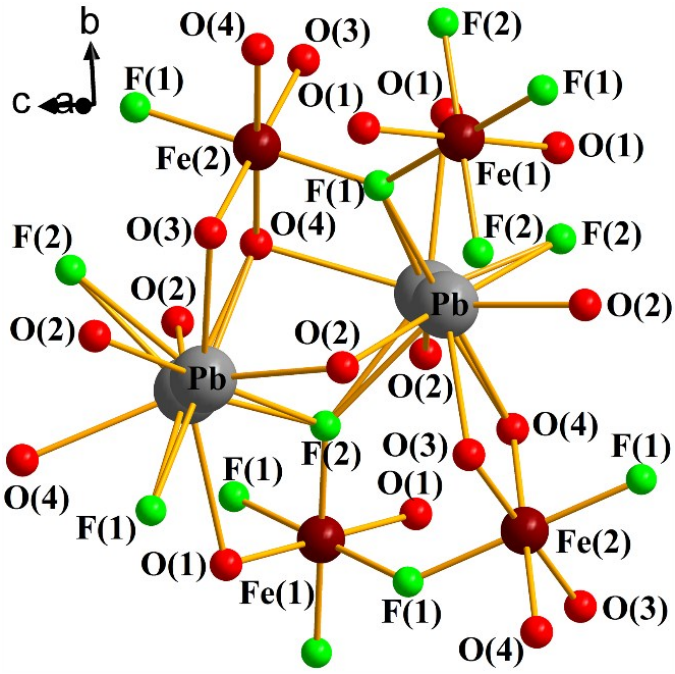


(b)

Figure S5 Crystal structure for $PbFePO_4F_2$ for reviewing (a) interchain interactions pathways; (b) interlayer interactions pathways.



(a)



(b)

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