Electronic Supplementary Material (ESI) for Dalton Transactions.

$K_4(PO_2F_2)_2(S_2O_7)$: First Fluorooxophosphorsulfate with Mixed-Anion $[S_2O_7]^{2-}$ and $[PO_2F_2]^-$ Groups

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Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and BVS for $K_4(PO_2F_2)_2(S_2O_7)$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	S.O.F	x	y	z	U(eq)	BVS
K(1)	1	2981(1)	3362(1)	1872(1)	37(1)	1.06
K(2)	1	4129(1)	6289(1)	411(1)	35(1)	1.14
S(1)	1	1413(1)	3021(1)	2943(1)	28(1)	5.99
P(1)	1	4465(1)	1827(2)	695(1)	26(1)	5.27
O(1)	1	4221(3)	2689(4)	-76(2)	38(1)	2.10
O(2)	1	4597(3)	2865(4)	1386(2)	39(1)	2.04
O(3)	1	2283(3)	4597(4)	3248(2)	43(1)	1.78
O(4)	1	1241(3)	2069(4)	2214(2)	42(1)	2.09
O(5)	1	1806(3)	1963(4)	3715(2)	44(1)	2.13
O(6)	1	0	3998(5)	2500	28(1)	2.10
F(1)	1	3439(3)	367(4)	351(2)	60(1)	1.18
F(2)	1	5721(3)	659(4)	1173(2)	62(1)	1.09

Table S2.Selected bond distances (Å) and angles (deg) for $K_4(PO_2F_2)_2(S_2O_7)$

K(1)-O(2)$^{\#1}$	2.756(5)	S(1)-O(5)	1.445(3)
K(1)-O(1)$^{\#2}$	2.809(5)	S(1)-O(3)	1.478(3)
K(1)-O(2)	2.812(5)	S(1)-O(6)	1.623(3)
K(1)-O(3)$^{\#3}$	2.852(5)	P(1)-O(1)	1.440(3)
K(1)-F(2)$^{\#4}$	2.893(5)	P(1)-O(2)	1.442(3)
K(1)-O(4)	2.895(5)	P(1)-F(1)	1.516(3)
K(1)-O(5)$^{\#5}$	3.016(5)	P(1)-F(2)	1.535(3)
K(1)-O(4)$^{\#5}$	3.098(5)	O(4)-S(1)-O(5)	115.8(2)
K(1)-O(3)	3.405(4)	O(4)-S(1)-O(3)	112.5(2)
K(2)-O(5)$^{\#5}$	2.664(4)	O(5)-S(1)-O(3)	111.4(2)
K(2)-O(1)$^{\#6}$	2.712(4)	O(4)-S(1)-O(6)	107.66(17)
K(2)-O(4)$^{\#7}$	2.742(5)	O(5)-S(1)-O(6)	108.63(16)
K(2)-O(1)	2.896(5)	O(3)-S(1)-O(6)	99.3(2)
K(2)-F(1)$^{\#2}$	2.929(5)	O(1)-P(1)-O(2)	120.1(2)
K(2)-O(5)$^{\#8}$	2.953(5)	O(1)-P(1)-F(1)	109.43(19)
K(2)-O(2)	3.005(5)	O(2)-P(1)-F(1)	110.05(19)
K(2)-F(1)$^{\#9}$	3.185(5)	O(1)-P(1)-F(2)	108.40(19)
K(2)-O(3)$^{\#8}$	3.225(5)	O(2)-P(1)-F(2)	108.3(2)
S(1)-O(4)	1.445(3)	F(1)-P(1)-F(2)	98.2(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2	#2 -x+1/2,-y+1/2,-z	#3 -x+1/2,y-1/2,-z+1/2
#4 x-1/2,y+1/2,z	#5 -x+1/2,y+1/2,-z+1/2	#6 -x+1,-y+1,-z
#7 x+1/2,y+1/2,z	#8 x,-y+1,z-1/2	#9 x,y+1,z

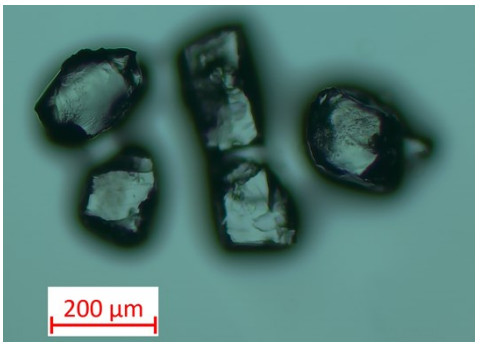

Figure S1 Photograph of crystals of KSPOF.

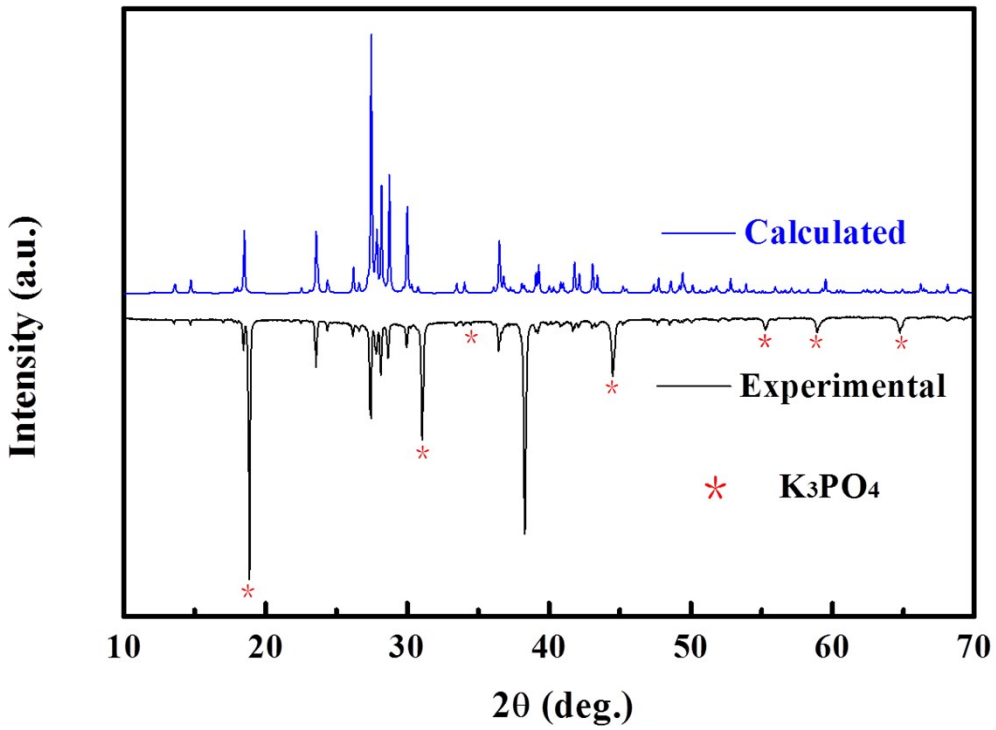

Figure S2 Powder X-ray diffraction patterns of KSPOF in comparison to the calculated one from the single crystal data.

Table S3 The BVS and GII values in $K_4(PO_2F_2)_2(S_2O_7)$

Compounds	BVS K^+	GII
$K_4(PO_2F_2)(S_2O_7)$	1.06-1.14	0.138

Birefringence Measurements.

The birefringences of KSPOF were characterized by using the polarizing microscope equipped (ZEISS Axio Scope A1) with Berek compensator. The wavelength of the light source was 546 nm. Before the scanning, the small and transparent KSPOF lamellar crystals were chosen to measure, in order to improve the accuracy of the birefringences. The formula for calculating the birefringence is listed below,

$R = | N_e - N_o | \times T = \Delta n \times T$ Eq. (1)

Here, R represents the optical path difference, Δn means the birefringence, and T denotes the thickness of the crystal.

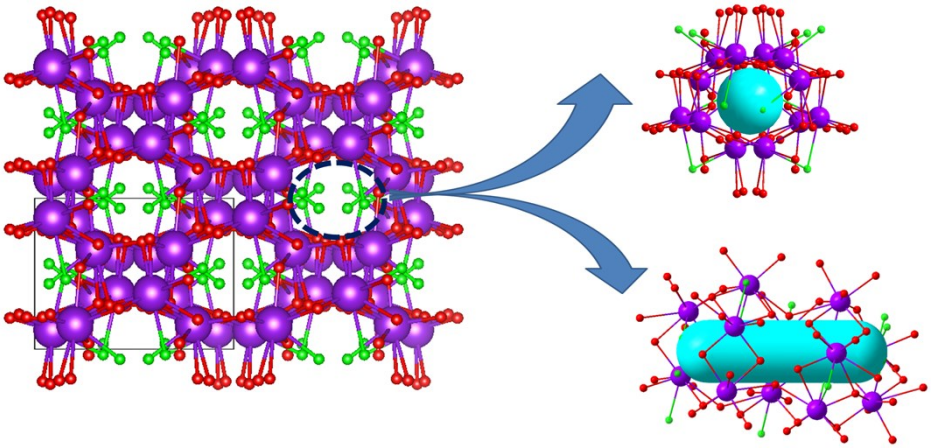

Figure S3 Two types of the [KOF] polyhedra connect with each other via corner-sharing or edge-sharing to form a three-dimension (3D) framework and eight-membered ring (8-MRs) channel.

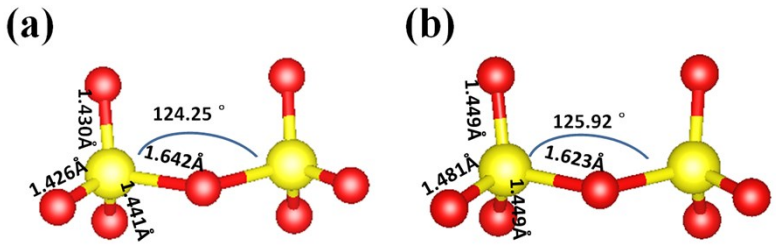

Figure S4 The dimer $[S_2O_7]^{2-}$ unit in (a) $K_2S_2O_7$ and (b) KSPOF

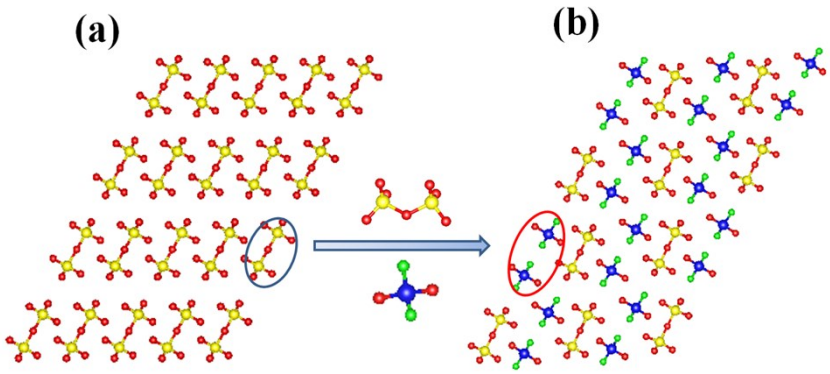

Figure S5 Anion arrangement manners (a) the isolated $[S_2O_7]^{2-}$ dimers and (b) the isolated $[S_2O_7]^{2-}$ and isolated $[PO_2F_2]^-$ anion groups.

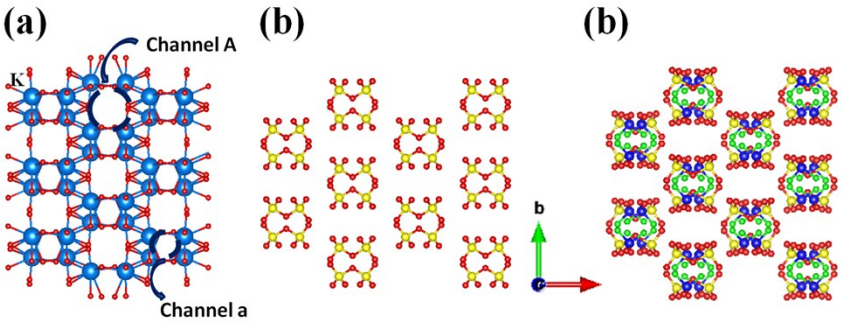

Figure S6 (a) The 3D framwork of K-O in $K_2S_2O_7$ and (b) different clusters in $K_2S_2O_7$ and KSPOF.

Table S4 Anhydrous and disorder-free compounds

No.	Structural formula	Space group	S-O units	P-O/F units	ICSD ode/Ref.
1	$KSb_2(SO_4)_2(PO_4)$	$P\bar{1}$	SO_4	PO_4	430367
2	$RbSb_2(SO_4)_2(PO_4)$	$P\bar{1}$	SO_4	PO_4	430368
3	$Na_2La[PO_4][S_2O_3]$	$P2_1/c$	S_2O_3	PO_4	154708
4	**$K_4(PO_2F_2)_2(S_2O_7)$**	***C*2/*c***	**S_2O_7**	**PO_2F_2**	**This work**

Table S5 Anhydrous and disorder compounds

No.	Structural formula	Space group	S-O units	P-O/F units	ICSD Code/Ref.
1	$NaFe_2(PO_4)(SO_4)_2$	$R\bar{3}cH$	SO_4	PO_4	264480
2	$Pb_4(PO_4)_2(SO_4)$	$I\bar{4}3d$	SO_4	PO_4	79126
3	$Zr_2(PO_4)_2(SO_4)$	*Pbcn*	SO_4	PO_4	202395
4	$Ca_{9.84}((SiO_4)_{2.4}(PO_4)_{1.2}(SO_4)_{2.4})Cl_{1.6}$	$P6_3/m$	SO_4	PO_4	237973
5	$Ca_{10}(PO_4)_{4.67}(SO_4)_{0.66}(SiO_4)_{0.66}Cl_2$	$P6_3/m$	SO_4	PO_4	237975

Table S6 Hydrous and disorder-free compounds

No.	Structural formula	Space group	S-O units	P-O/F units	ICSD Code/Ref.
1	$Na(HSO_4)(H_3PO_4)$	$P2_1$	SO_4	PO_4	411163
2	$Pb_2Cu(PO_4)(SO_4)(OH)$	$P2_1/m$	SO_4	PO_4	76613
3	$PbFe_3(SO_4)(PO_4)(OH)_6$	$R3mH$	SO_4	PO_4	68352
4	$Rb_2(HSO_4)(H_2PO_4)$	$P2_1/c$	SO_4	PO_4	410918
5	$Rb_4(HSO_4)_3(H_2PO_4)$	$P2_12_12$	SO_4	PO_4	410919
6	$Cs_3(HSO_4)_2(H_2PO_4)$	$C2/c$	SO_4	PO_4	429151
7	$Cs_6H(HSO_4)_3(H_2PO_4)_4$	$I\bar{4}3d$	SO_4	PO_4	256209
8	$Al_2(PO_4)(SO_4)(OH)\cdot(H_2O)_9$	$P2_1/n$	SO_4	PO_4	181637
9	$Al_3(PO_4)(SO_4)_2(OH)_2(H_2O)_{10}\cdot(H_2O)_4$	$P\bar{1}$	SO_4	PO_4	189132

Table S7 Hydrous and disorder compounds

No.	Structural formula	Space group	S-O units	P-O/F units	ICSD Code/Ref.
1	$K_4(HSO_4)_3(H_2PO_4)$	$P\bar{1}$	SO_4	PO_4	411162
2	$K_2(HSO_4)(H_2PO_4)$	$P2_1/c$	SO_4	PO_4	411161
3	$Cs_4(HSO_4)_3(H_2PO_4)$	$I41/amdZ$	SO_4	PO_4	257883
4	$Al_2F(PO_4)(SO_4)\cdot 9H_2O$	$P2/a$	SO_4	PO_4	241342
5	$CaAl_3(PO_4)(SO_4)(OH)_6$	$R\bar{3}mH$	SO_4	PO_4	40087
6	$SrAl_3(PO_4)(SO_4)(OH)_6$	$R\bar{3}mH$	SO_4	PO_4	34345
7	$(Cs_3(HSO_4)_2(H_2PO_4))_{1.3333}$	$I41/amdZ$	SO_4	PO_4	257881
8	$(Cs_3(HSO_4)_2(H_2PO_4))_{0.3333}$	$Pm\bar{3}m$	SO_4	PO_4	257882
9	$(Cs_4(HSO_4)_3(H_2PO_4))_{0.25}$	$Pm\bar{3}m$	SO_4	PO_4	257884
10	$Cs_3(HSO_4)_2(H_{1.5}(S_{0.5}P_{0.5})O_4)$	$C2/c$	SO_4	PO_4	280111
11	$Cs_2(HSO_4)(H_2PO_4)$	$P2_1/n$	SO_4	PO_4	280146
12	$Cs_5(HSO_4)_3(H_2PO_4)_2$	$C2/c$	SO_4	PO_4	51100
13	$Li_6Na_{18}((SO_4)(UO_2)_{20}(O_2)_{27}(HPO_4)_6(H_2PO_4)_6)\cdot(H_2O)_{42}$	$P2_1/n$	SO_4	PO_4	243540
14	$LiNa_{18}((SO_4)(UO_2)_{20}(O_2)_{27}(HPO_4)_6)\cdot(H_2O)_{40}$	$P2/c$	SO_4	PO_4	243539
15	$Rb(HSO_4)_{0.43}(H_2PO_4)_{0.57}$	$P2_1/n$	SO_4	PO_4	410917
16	$Na_2Co(SO_4)_{1.8}(PO_3F)_{0.2}\cdot(H_2O)_2$	$P\bar{1}$	SO_4	PO_3F	253311
17	$Na_2Co(SO_4)_{1.9}(PO_3F)_{0.1}\cdot(H_2O)_2$	$P\bar{1}$	SO_4	PO_3F	253309
18	$Na_2Co(SO_4)_{1.75}(PO_3F)_{0.25}\cdot(H_2O)_2$	$P\bar{1}$	SO_4	PO_3F	253312
19	$Na_2Co(SO_4)_{1.85}(PO_3F)_{0.15}\cdot(H_2O)_2$	$P\bar{1}$	SO_4	PO_3F	253310
20	$Na_2Cu(SO_4)_{1.7}(PO_3F)_{0.3}\cdot(H_2O)_2$	$P\bar{1}$	SO_4	PO_3F	253315
21	$Na_2Cu(SO_4)_{1.8}(PO_3F)_{0.2}\cdot(H_2O)_2$	$P\bar{1}$	SO_4	PO_3F	253314
22	$Na_2Cu(SO_4)_{1.9}(PO_3F)_{0.1}\cdot(H_2O)_2$	$P\bar{1}$	SO_4	PO_3F	253313
23	$Na_2Fe(SO_4)_{1.95}(PO_3F)_{0.05}\cdot(H_2O)_2$	$P2_1/c$	SO_4	PO_3F	253308
24	$Ce_2(PO_4)_2(HPO_4)_{0.4}(SO_4)_{0.6}\cdot(H_2O)_5$	$I2/a$	SO_4	PO_4	108907
25	$Na_{12}((Mo_2O_4)_4(O_3PCH_2PO_3)_4(SO_3)_2)\cdot(H_2O)_{39}$	$P\bar{1}$	SO_3	PO_3	240359
26	$(NH_4)_{12}((Mo_2O_4)_4(O_3PCH_2PO_3)_4(SO_3)_2)\cdot(H_2O)_{26}$	$P\bar{1}$	SO_3	PO_3	240356
27	$Na_2(NH_4)_{11}((Mo_2O_4)_4(O_3PCH_2PO_3)_4(SO_3)_2)\cdot(H_2O)_{13}$	$P\bar{1}$	SO_3	PO_3	240361