Electronic Supporting Information

The transformation of a zero-dimensional cluster into a one-dimensional chain structure achieving a dramatically enhanced birefringence in tin(II)-based oxalates

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Table S1. Crystal data and structure refinement for $K_2Sn(C_2O_4)_2 \cdot H_2O$ and $K_2Sn_2(C_2O_4)_2F_2 \cdot H_2O$.

Formula	$K_2Sn(C_2O_4)_2 \cdot H_2O$	$K_2Sn_2(C_2O_4)_2F_2 \cdot H_2O$
Formula weight	390.95	547.669
Crystal system	triclinic	monoclinic
Space group	*P*-1	$P2_1/c$
a(Å)	6.43740(10)	10.2509(2)
b(Å)	6.61500(10)	9.3149(2)
c(Å)	11.8275(2)	12.4438(3)
α/°	95.605(2)	90
β/°	93.355(2)	94.397(2)
γ/°	101.985(2)	90
V(Å^3)	488.712(14)	1184.71(5)
Z	2	4
ρ(calcd)(g/cm$^{3)}$	2.657	3.071
Temperature(K)	299.55(10)	302.59(10)
F(000)	372.0	1013.5
μ/mm^{-1}	3.499	4.985
R_1, wR_2 (I>=2σ (I))	0.0284/0.0718	0.0188/ 0.0476
GOF on F^2	1.157	0.995

$R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and calculated Bond Valence Sum for $K_2Sn(C_2O_4)_2 \cdot H_2O$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U_{eq}(Å^2)	BVS
Sn1	7457.9(3)	1589.8(3)	2292.2(2)	22.87(9)	2.04
K1	2551.3(10)	600.5(10)	4162.1(5)	28.85(16)	1.21
K2	174.2(12)	7292.9(15)	1148.3(6)	39.52(19)	0.92
O1	6839(3)	2467(3)	4218.4(17)	24.4(4)	2.09
O2	6848(3)	2482(4)	488.8(17)	27.3(5)	1.99
O3	8293(4)	4904(3)	2640.9(17)	29.0(5)	2.22
O4	4146(3)	1827(4)	2105.4(17)	28.8(5)	2.12
O5	8892(4)	7699(3)	3909.8(19)	30.2(5)	1.96
O6	7475(4)	5216(4)	5549.6(18)	31.9(5)	1.70
O7	4224(3)	2782(4)	9245.2(17)	29.2(5)	1.68
O8	3584(4)	7406(4)	2779(2)	38.9(6)	1.92
O9	1551(4)	2476(6)	969(2)	63.7(11)	1.75
C1	4940(4)	2554(4)	202(2)	20.6(5)	
C2	7451(4)	4388(4)	4564(2)	20.2(5)	
C3	8285(4)	5816(5)	3652(2)	21.7(6)	
C4	3394(5)	2283(5)	1164(2)	26.9(6)	

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and calculated Bond Valence Sum for $K_2Sn_2(C_2O_4)_2F_2 \cdot H_2O$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	$U_{eq}(Å^2)$	BVS
Sn1	1354.7(2)	8088.9(2)	4987.9(2)	21.00(5)	1.97
Sn2	5200.6(2)	6513.8(2)	8906.6(2)	19.90(5)	1.95
K1	6562.8(5)	9641.7(6)	890.8(4)	27.68(11)	1.14
K2	9788.0(6)	5020.2(8)	3152.5(6)	42.50(16)	0.88
F1	5590.0(14)	8667.1(14)	8959.5(11)	24.8(3)	1.01
F2	1221.2(13)	5932.9(15)	4846.9(12)	28.3(3)	1.16
O1	7230.4(16)	6211(2)	8230.0(14)	28.0(4)	1.90
O2	4920.0(15)	6951.4(19)	7088.1(13)	25.1(3)	2.04
O3	2934.5(16)	7708.8(19)	8288.0(13)	24.6(3)	1.89
O4	3602.9(16)	7284(2)	5603.2(13)	29.7(4)	1.80
O5	7075.9(16)	6830.8(19)	336.6(14)	26.2(4)	1.85
O6	1566.6(15)	7779(2)	6810.9(13)	25.7(3)	1.97
O7	9365.2(18)	6722(2)	8406.7(16)	35.7(4)	1.89
O8	9216.8(17)	7241(2)	533.6(16)	38.3(5)	1.81
O9	7275.8(18)	5487(2)	2461.7(16)	35.2(4)	2.40
C1	3832(2)	7246(2)	6601.4(18)	19.7(4)	
C2	8270(2)	6590(2)	8763.7(19)	21.9(4)	
C3	8187(2)	6913(2)	9983.6(19)	21.2(4)	
C4	2678(2)	7604(2)	7302.1(17)	19.1(4)	

Table S4. Selected bond lengths [Å] and angles [°] for $K_2Sn(C_2O_4)_2 \cdot H_2O$.

Sn1-O1	2.373(2)	K2-O7^{ix}	2.832(2)
Sn1-O2	2.301(2)	K2-O8	2.820(3)
Sn1-O3	2.138(2)	K2-O9^{ix}	2.711(3)
Sn1-O4	2.170(2)	K2-O9^{iii}	3.389(4)
K1-O1^{iii}	2.774(2)	O1-C2	1.268(3)
K1-O1^{vi}	2.991(2)	O2-C1	1.267(3)
K1-O4^{iii}	2.822(2)	O3-C3	1.286(4)
K1-O5^{iv}	2.740(2)	O4-C4	1.276(4)
K1-O5	2.693(2)	O5-C3	1.228(4)
K1-O6^{iv}	2.759(3)	O6-C2	1.236(3)
K1-O8	2.760(2)	O7-C1	1.232(3)
K2-O2^{viii}	2.796(2)	O9-C4	1.230(4)
K2-O3	2.661(2)	C1-C4	1.554(4)
K2-O5	3.414(2)	C2-C3	1.550(4)
O2-Sn1-O1	141.47(7)	Sn1-O3-K2	121.82(9)
O3-Sn1-O1	72.32(7)	Sn1-O4-K1^{i}	103.3(2)
O3-Sn1-O2	80.34(8)	C4-O4-Sn1	119.24(19)
O5-K1-O1^{iv}	161.48(7)	C4-O4-K1^{i}	136.97(19)
O5^{iii}-K1-O1^{vi}	79.23(6)	O7-C1-O2	126.1(3)
O5^{iii}-K1-O4^{iv}	139.22(7)	O7-C1-C4	118.5(3)
O2^{viii}-K2-O5	151.69(6)	O1-C2-C3	117.4(3)
O3-K2-O5	40.47(6)	O6-C2-O1	126.7(3)
C2-O1-Sn1	113.94(17)	O5-C3-O3	123.7(3)
Sn1-O2-K2^{viii}	123.81(8)	O5-C3-C2	120.3(3)
O9-C4-O4	124.7(3)	O4-C4-C1	119.0(3)

Symmetry codes:

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

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

Table S5. Selected bond lengths [Å] and angles [°] for $K_2Sn_2(C_2O_4)_2F_2 \cdot H_2O$.

Sn1-F2	2.0197(14)	K2-O6^{ii}	2.9560(19)
Sn1-O4	2.4877(17)	K2-O6^{vii}	3.2834(18)
Sn1-O6	2.2806(17)	K2-O9	2.687(2)
Sn2-F1	2.0451(13)	O1-C2	1.262(3)
Sn2-O1	2.3209(17)	O2-K1^{vii}	2.7645(17)
Sn2-O2	2.2957(17)	O2-C1	1.258(3)
Sn2-O5	2.5347(18)	O3-C4	1.239(3)
K1-F1	2.6883(15)	O4-C1	1.247(3)
K1-F1^{iv}	2.7293(15)	O5-C3	1.254(3)
K1-F2^{v}	2.7874(15)	O6-C4	1.262(3)
K1-O1^{vi}	3.0441(18)	O7-K2^{ix}	3.085(2)
K1-O2^{vi}	2.7644(17)	O7-K2^{viii}	2.722(2)
K1-O3^{iv}	2.7055(18)	O7-C2	1.245(3)
K1-O4^{v}	3.082(2)	O8-K2^{v}	3.187(2)
K1-O5	2.7683(19)	O8-C3	1.251(3)
K2-F2	2.6177(16)	C1-C4	1.558(3)
K2-F2^{ii}	2.9071(16)	C2-C3	1.556(3)
F2-Sn1-O4	77.42(6)	O7^{iii}-K2-O8^{i}	142.02(6)
O6-Sn1-O4	68.92(5)	Sn2-F1-K1^{iv}	114.29(6)
O8^{iii}-Sn1-O4	136.87(6)	K1-F1-K1^{iv}	89.46(4)
F1-Sn2-O1	87.28(6)	Sn1-F2-K2^{ii}	104.80(6)
O1-Sn2-O5	67.42(6)	K1^{i}-F2-K2^{ii}	120.19(5)
O2-Sn2-O5	134.61(6)	K2-F2-K1^{i}	90.91(5)
F1-K1-F1^{iv}	90.54(4)	C2-O1-K1^{vii}	134.04(14)
F1^{iv}-K1-F2^{v}	117.19(5)	Sn2-O2-K1^{vii}	113.61(6)
F1-K1-O1^{vi}	143.85(5)	C1-O4-Sn1	114.50(14)
F1^{iv}-K1-O2^{vi}	75.17(5)	C3-O5-K1	102.97(14)
F1^{iv}-K1-O5	137.14(5)	K2^{ii}-O6-K2^{vi}	105.25(5)
O3^{iv}-K1-F1^{iv}	65.12(5)	Sn1^{ix}-O8-K2^{v}	89.18(6)
O3^{iv}-K1-O5	157.30(5)	C3-O8-Sn1^{ix}	124.96(15)
O3^{iv}-K1-C3	138.47(6)	O2-C1-C4	117.40(19)
F2^{ii}-K2-O6^{ii}	61.25(4)	O4-C1-O2	125.3(2)
F2^{ii}-K7-O3	70.88(5)	O7-C2-O1	126.0(2)
O7^{viii}-K2-F2^{ii}	125.61(6)	O5-C3-C2	116.7(2)

Symmetry codes:

(i) 1-*x*, -1/2+*y*, 3/2-*z*; (ii) -*x*, 1-*y*, 1-*z*; (iii) -1+*x*, 3/2-*y*, -1/2+*z*; (iv) 1-*x*, 2-*y*, 2-*z*; (v) 1-*x*, 1/2+*y*, 3/2-*z*; (vi) +*x*, 3/2-*y*, 1/2+*z*; (vii) +*x*, 3/2-*y*, -1/2+*z*; (viii) 1-*x*, 1-*y*, 1-*z*; (ix) 1+*x*, 3/2-*y*, 1/2+*z*.

Table S6. The dihedral angles (γ) between the two CO_2 in one $C_2O_4^{2-}$ group, polarizability anisotropy and HOMO-LUMO gap of Sn^{2+}-polyhedra in $K_2Sn(C_2O_4)_2{\cdot}H_2O$ and $K_2Sn_2(C_2O_4)_2F_2{\cdot}H_2O$.

formula	groups	γ	polarizability anisotropy	HOMO-LUMO gap (eV)
$K_2Sn(C_2O_4)_2{\cdot}H_2O$ (hkl:010)	$C_2O_4^{2-}$(I)	1.512	22.30	5.68
	$C_2O_4^{2-}$(II)	6.736	22.20	5.72
	Sn^{2+}(I)	——	35.14	1.85
$K_2Sn_2(C_2O_4)_2F_2{\cdot}H_2O$ (hkl:010)	$C_2O_4^{2-}$(III)	6.571	22.60	5.63
	$C_2O_4^{2-}$(IV)	2.482	22.40	5.67
	Sn^{2+}(II)	——	106.50	1.50
	Sn^{2+}(III)	——		

Table S7. The calculation of the contribution of Sn^{2+} cations and $C_2O_4^{2-}$ anions to birefringence in a unit cell in $K_2Sn(C_2O_4)_2{\cdot}H_2O$ and $K_2Sn_2(C_2O_4)_2F_2{\cdot}H_2O$.

formula	groups	n	ρ	α/β	Cosα/ Cosβ	$\rho\times$Cosα/ $\rho\times$Cosβ	Contribution percentage (%)
$K_2Sn(C_2O_4)_2{\cdot}H_2O$ (hkl:010)	$C_2O_4^{2-}$(I)	2	0.0041	82.579	0.1637	0.0007	61.04
	$C_2O_4^{2-}$(II)	2	0.0041	9.817	0.9854	0.0040	
	Sn^{2+}(I)	2	0.0041	42.345	0.7391	0.0030	38.96
$K_2Sn_2(C_2O_4)_2F_2{\cdot}H_2O$ (hkl:010)	$C_2O_4^{2-}$(III)	4	0.0034	13.454	0.9726	0.0033	49.62
	$C_2O_4^{2-}$(IV)	4	0.0034	15.859	0.9619	0.0033	
	Sn^{2+}(II)	4	0.0034	6.085	0.9944	0.0034	50.38
	Sn^{2+}(III)	4	0.0034	11.266	0.9807	0.0033	

n: the number of Sn^{2+} cations or $C_2O_4^{2-}$ in a unit cell. ρ: the density of Sn^{2+} cations or $C_2O_4^{2-}$ in a unit cell. α: The angle between the of direction the lone pair electron of Sn^{2+} and *YZ* plane. β: the dihedral angle between $C_2O_4^{2-}$ plane and *YZ* plane

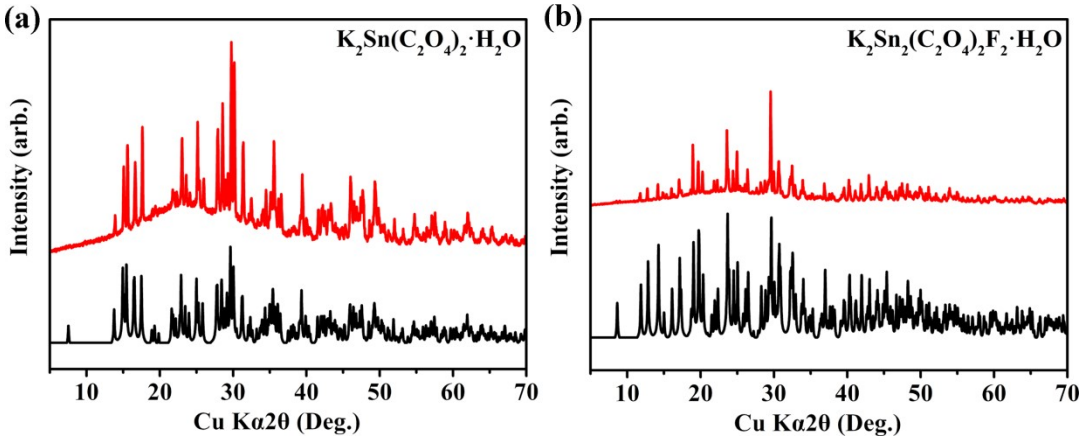

Fig. S1 Powder XRD patterns of (a) $K_2Sn(C_2O_4)_2{\cdot}H_2O$ and (b) $K_2Sn_2(C_2O_4)_2F_2{\cdot}H_2O$. The red curves are patterns of samples, the black are the simulated ones.

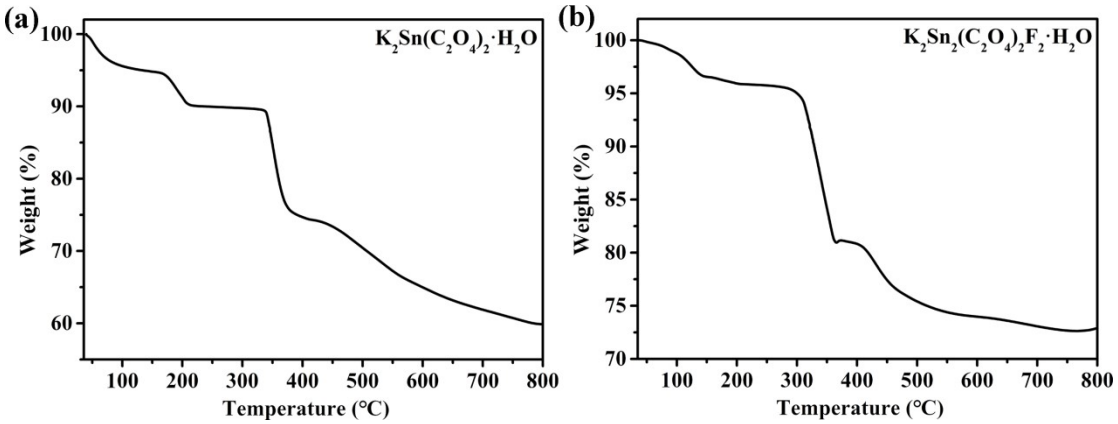

Fig. S2 The TG curves of (a) $K_2Sn(C_2O_4)_2·H_2O$ and (b) $K_2Sn_2(C_2O_4)_2F_2·H_2O$.

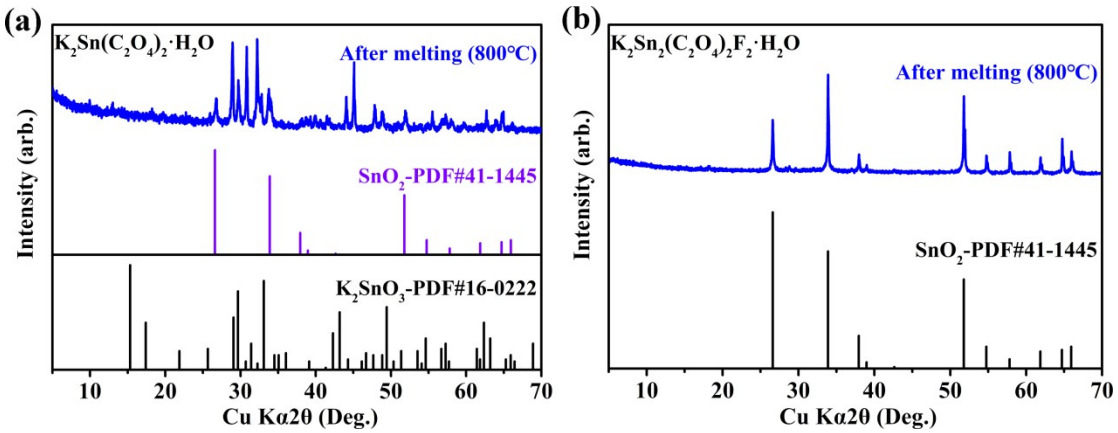

Fig. S3 XRD patterns for compounds (a) $K_2Sn(C_2O_4)_2·H_2O$ and (b) $K_2Sn_2(C_2O_4)_2F_2·H_2O$ after melting.

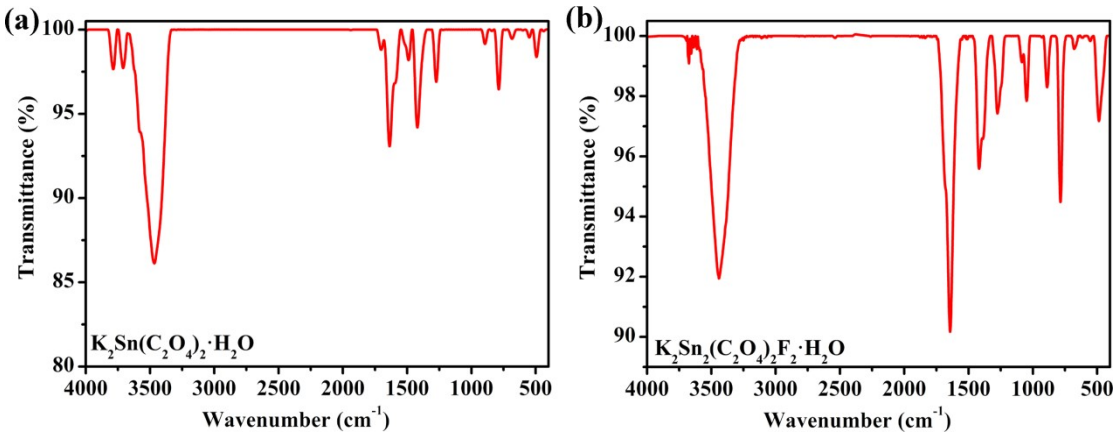

Fig. S4 IR spectra of (a) $K_2Sn(C_2O_4)_2·H_2O$ and (b) $K_2Sn_2(C_2O_4)_2F_2·H_2O$.

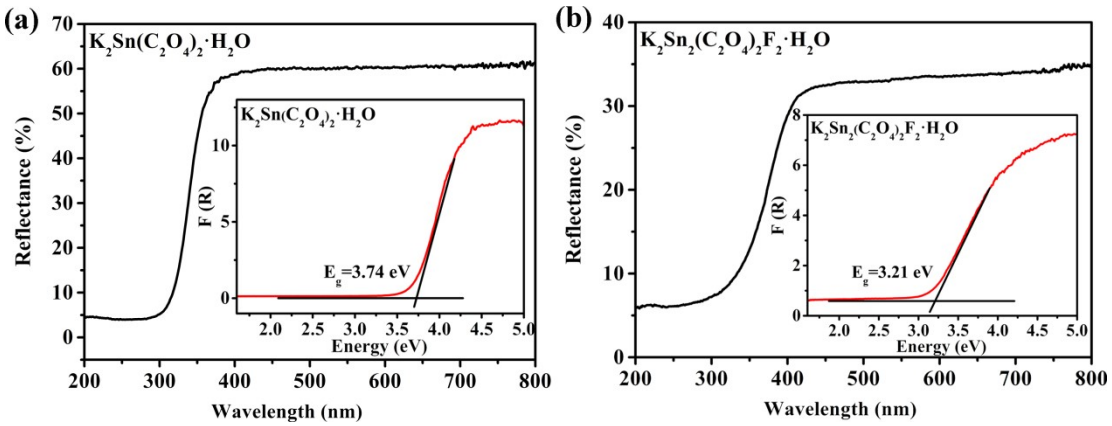

Fig. S5 The UV-vis-NIR diffuse reflectance spectrum and band gap of (a) $K_2Sn(C_2O_4)_2·H_2O$ and (b) $K_2Sn_2(C_2O_4)_2F_2·H_2O$.

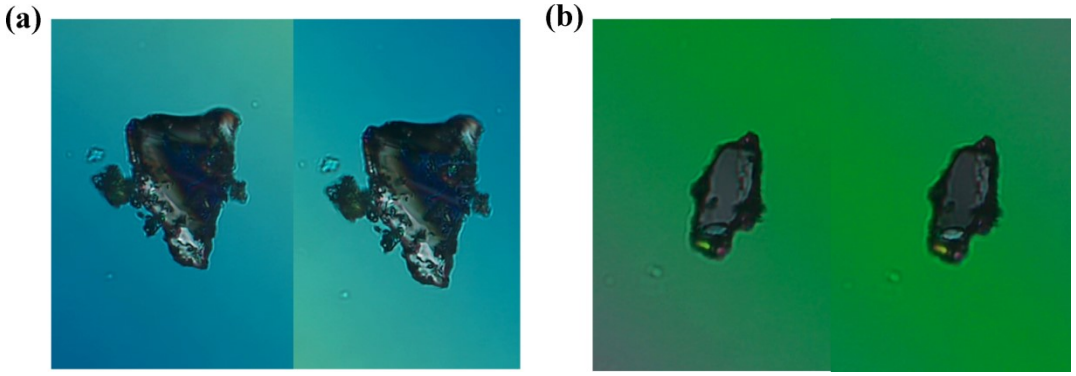

Fig. S6 Birefringence measurement photo of (a) $K_2Sn(C_2O_4)_2·H_2O$ and (b) $K_2Sn_2(C_2O_4)_2F_2·H_2O$.