Electronic Supplementary Information

Salt-inclusion sulfides $[K_4Cl][M^{II}_{11}In_9S_{26}]$ (M^{II} = Zn, Cd) displaying robust nonlinear optical activity

Yang-Ping Zhang,[1, 2] Shao-Min Pei,[1], Xiao-Ming Jiang,[1] Bin-Wen Liu,[1, *] and Guo-Cong Guo[1, *]

[1] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China.

[2] School of Physical Science and Technology, Shanghai Tech University, Shanghai 201210, P. R. China.

* Correspondence: bwliu@fjirsm.ac.cn, gcguo@fjirsm.ac.cn

SURPOTING INFORMATION

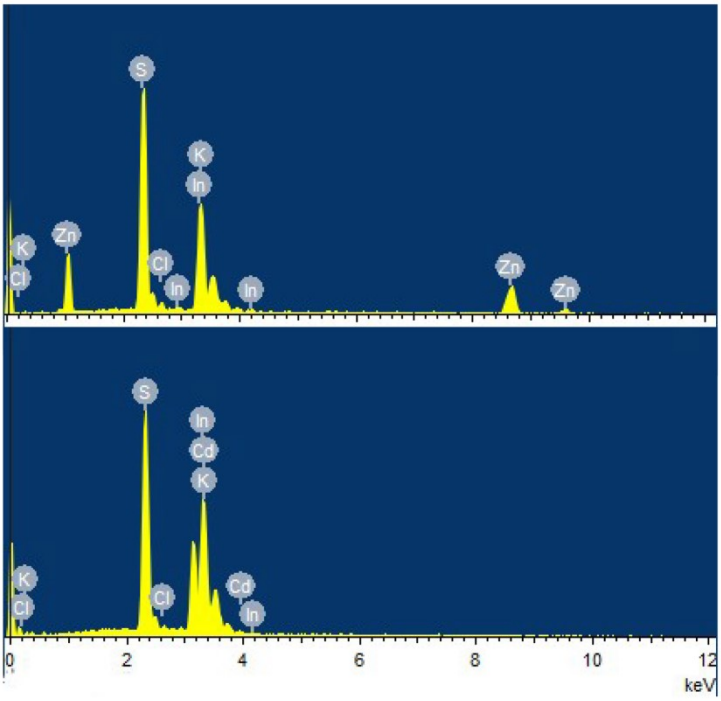

Fig. S1 The EDS results of compounds **1** and **2**.

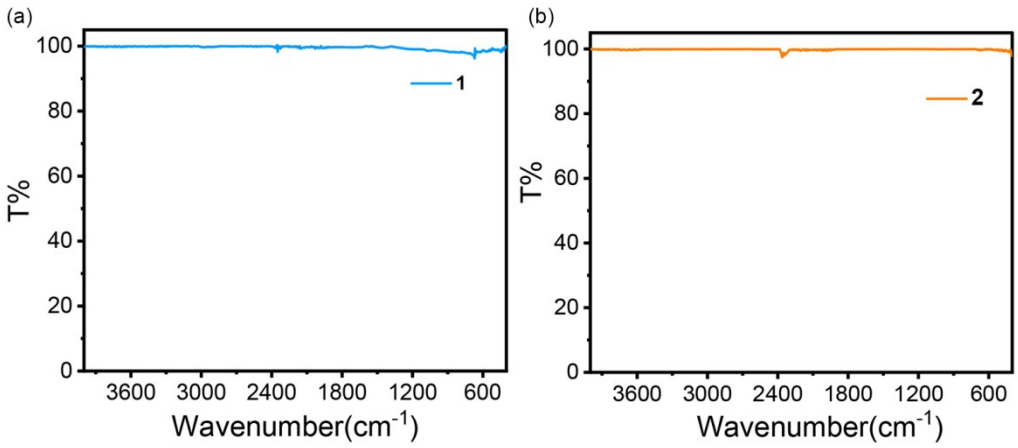

Fig. S2 The IR results of compounds **1** and **2**.

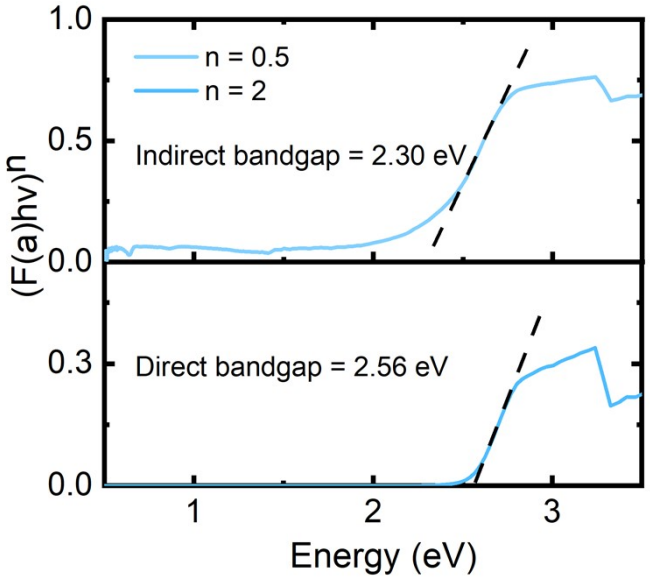

Fig. S3 The band gaps of **2** are determined by direct and indirect models.

Table S1. Selected bond distances (Å) in compounds **1** and **2**.

bond	distance/Å	bond	distance/Å
		compound 1	
K1-Cl1	2.930(7)	Zn6-S4	2.399(3)
K2-Cl1×2	2.932(5)	Zn6-S8	2.387(3)
K3-Cl1	2.896(8)	Zn6-S15	2.389(3)
Zn1-S3	2.411(5)	Zn7-S2	2.387(4)
Zn1-S4	2.417(3)	Zn7-S4	2.352(3)
Zn1-S4	2.417(3)	Zn7-S5	2.377(3)
Zn1-S9	2.431(5)	Zn7-S13	2.412(3)
Zn2-S1	2.400(3)	Zn8-S6	2.373(3)
Zn2-S6	2.435(4)	Zn8-S11	2.366(4)
Zn2-S11	2.374(3)	Zn8 S13	2.405(3)
Zn2-S14	2.428(3)	Zn8-S15	2.364(3)
Zn3-S5	2.434(3)	Zn9-S10	2.383(3)
Zn3-S7	2.431(3)	Zn9-S11	2.343(3)
Zn3-S10	2.445(4)	Zn9-S12	2.355(3)
Zn3-S15	2.406(3)	Zn9-S13	2.426(4)
Zn4-S2	2.414(3)	Zn10-S7	2.390(3)
Zn4-S3	2.431(3)	Zn10-S9	2.360(3)
Zn4-S7	2.434(4)	Zn10-S12	2.369(4)
Zn4-S12	2.384(3)	Zn10-S13	2.400(3)
Zn5-S6	2.420(3)	Zn11-S1	2.390(3)
Zn5-S6	2.420(3)	Zn11-S2	2.403(3)
Zn5-S8	2.419(5)	Zn11-S5	2.426(4)
Zn5-S14	2.450(5)	Zn11-S10	2.400(3)
Zn6-S1	2.375(4)		
		compound 2	
K1-Cl1	2.985(4)	Cd6-S11	2.4781(19)
K2-Cl1×2	2.993(3)	Cd6-S12	2.4805(18)
K3-Cl1	2.977(5)	Cd6-S13	2.533(2)
Cd1-S5	2.4723(18)	In1-S4	2.4794(19)
Cd1-S10	2.492(2)	In1-S9	2.469(3)
Cd1-S15	2.4635(19)	In1-S4	2.4795(19)
Cd1-S7	2.4784(19)	In1-S3	2.457(3)
Cd2-S6	2.4686(18)	In2-S6	2.508(2)
Cd2-S14	2.490(3)	In2-S1	2.4865(19)
Cd2-S6	2.4686(18)	In2-S14	2.5127(17)
Cd2-S8	2.460(3)	In2-S11	2.4684(18)
Cd3-S1	2.478(2)	In3-S7	2.5219(19)
Cd3-S8	2.5197(18)	In3-S12	2.503(2)
Cd3-S15	2.5134(19)	In3-S13	2.5285(18)
Cd4-S13	2.5364(18)	In4-S1	2.4920(19)

Cd4-S5	2.5200(19)	In4-S2	2.4892(18)
Cd4-S4	2.493(2)	In4-S5	2.509(2)
Cd4-S2	2.510(3)	In4-S10	2.5054(19)
Cd5-S11	2.505(2)	In5-S2	2.493(2)
Cd5-S13	2.5352(17)	In5-S3	2.5208(15)
Cd5-S15	2.4931(19)	In5-S7	2.514(2)
Cd5-S6	2.5180(19)	In5-S12	2.480(2)
Cd6-S10	2.5217(19)		

Table S2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for A. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
		compound 1		
K1	0	6373(3)	2731(5)	51.6(15)
K2	3750(2)	3459(2)	2704(4)	51.0(11)
K3	0	2225(4)	4685(5)	56.9(17)
Zn1	0	3323.2(7)	775.8(16)	10.3(3)
Zn2	1011.1(5)	556.2(5)	3215.6(12)	13.6(2)
Zn3	2957.7(5)	1649.1(5)	689.8(9)	15.4(2)
Zn4	1028.4(5)	3927.3(5)	3196.9(12)	14.6(2)
Zn5	0	36.7(8)	679.5(15)	10.6(3)
Zn6	980.2(5)	1690.9(5)	796.9(13)	18.3(3)
Zn7	1984.2(6)	3308.0(7)	686.2(14)	17.7(3)
Zn8	1964.6(5)	19.3(7)	715.5(14)	13.4(3)
Zn9	2963.9(5)	545.6(5)	3144.0(15)	18.8(3)
Zn10	991.0(5)	4991.6(7)	690.7(14)	15.5(2)
Zn11	2005.2(5)	2213.5(5)	3213.7(12)	17.5(2)
S1	940.2(17)	1705.2(15)	2680(3)	17.4(7)
S2	2046.3(17)	3344.6(14)	2576(3)	15.4(7)
S3	0	3303(2)	2688(4)	15.9(9)
S4	4005.7(15)	2221.9(15)	4994(3)	14.7(7)
S5	3044.2(16)	2811.7(15)	136(3)	13.1(7)
S6	995.7(14)	616.9(17)	5145(3)	14.0(7)
S7	4035.3(16)	1130.9(16)	123(3)	13.6(6)
S8	0	1166(2)	-4(4)	15.7(9)
S9	0	4442(2)	24(4)	14.8(9)
S10	3053.9(16)	1687.1(14)	2623(3)	14.7(7)
S11	3015.0(15)	4947.8(15)	2589(3)	16.0(7)
S12	4005.5(14)	50.5(16)	2568(3)	15.3(7)
S13	2022.9(14)	4448.5(14)	68(3)	13.0(7)
S14	0	60(2)	7617(4)	15.7(9)
S15	1933.8(16)	1113.3(15)	9(3)	16.7(7)

Cl1	0	2241(2)	6982(5)	29.5(10)
In1	0	3323.2(7)	775.8(16)	10.3(3)
In2	1011.1(5)	556.2(5)	3215.6(12)	13.6(2)
In3	2957.7(5)	1649.1(5)	689.8(9)	15.4(2)
In4	1028.4(5)	3927.3(5)	3196.9(12)	14.6(2)
In5	0	36.7(8)	679.5(15)	10.6(3)
In6	980.2(5)	1690.9(5)	796.9(13)	18.3(3)
In7	1984.2(6)	3308.0(7)	686.2(14)	17.7(3)
In8	1964.6(5)	19.3(7)	715.5(14)	13.4(3)
In9	2963.9(5)	545.6(5)	3144.0(15)	18.8(3)
In10	991.0(5)	4991.6(7)	690.7(14)	15.5(2)
In11	2005.2(5)	2213.5(5)	3213.7(12)	17.5(2)
		compound 2		
K1	0	3596.8(15)	3069.0(3)	66.6(10)
K2	1254.3(13)	1555.0(12)	3117.0(2)	66.4(7)
K3	0	2251.2(16)	6070.0(3)	64.6(11)
Cd1	2974.1(2)	1667.1(2)	101.1(5)	15.7(1)
Cd2	0	15.1(4)	80.6(8)	15.9(2)
Cd3	4031.7(2)	3309.5(2)	4980.6(6)	18.7(1)
Cd4	1978.1(3)	3294.2(2)	76.6(6)	20.6(2)
Cd5	1940.0(2)	37.8(3)	70.2(7)	20.0(1)
Cd6	2032.2(2)	4466.3(2)	2654.1(7)	19.1(1)
In1	0	3327.2(3)	0000.0(8)	17.3(2)
In2	4008.6(2)	4438.7(2)	2540.7(6)	19.6(1)
In3	4027.9(2)	6.9(3)	85.4(6)	20.5(1)
In4	3006.0(2)	2781.0(2)	2549.9(6)	20.1(1)
In5	3981.2(2)	1089.5(2)	2562.2(6)	19.7(1)
S1	4083.4(9)	3287.0(8)	3075.4(18)	19.4(4)
S2	2941.7(10)	1640.4(8)	3151.8(18)	19.6(4)
S3	0	6718.1(12)	3110.0(2)	18.2(6)
S4	9623.0(9)	2779.7(8)	827.5(19)	19.2(4)
S5	3078.8(9)	2811.9(8)	622.8(16)	17.9(4)
S6	963.9(8)	649.4(9)	5616.2(17)	17.4(4)
S7	4049.2(9)	1175.9(9)	634.9(17)	18.2(4)
S8	0	1112.3(11)	811.0(2)	20.4(6)
S9	0	4403.7(11)	820.0(2)	16.7(5)
S10	1951.7(9)	3296.9(8)	3187.7(17)	20.1(4)
S11	1953.9(8)	79.2(9)	3150.9(17)	20.2(4)
S12	948.1(8)	4952.9(9)	3160.7(16)	16.7(4)
S13	2024.9(8)	4454.2(8)	704.5(16)	15.2(4)
S14	0	71.2(13)	3169.0(2)	19.0(6)
S15	1960.9(9)	1152.3(8)	799.5(18)	19.6(4)
Cl1	0	2224.4(12)	3779.0(3)	33.0(6)