Supporting Information

A series of pentanary inorganic supramolecular sulfides $(A_3X)[MB_{12}(MS_4)_3]$ (A = Na, K, Cs; X = Cl, Br, I; M = Ga, In, Gd) featuring $B_{12}S_{12}$ cluster

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Table S1. Selected bond distances (Å) for **1**–**6**.[a]

Bond	Dist.	Bond	Dist.
		1	
In(1)–S(1)	2.672(19)	B(1)–B(2)	1.803(12)
In(1)–S(1)#1	2.672(19)	B(1)–B(2)#2	1.789(12)
In(1)–S(1)#2	2.672(19)	B(1)–B(2)#10	1.775(11)
In(1)–S(1)#3	2.672(19)	B(2)–B(1)#3	1.789(12)
In(1)–S(1)#4	2.672(19)	B(2)–B(1)#10	1.775(11)
In(1)–S(1)#5	2.672(19)	B(2)–B(2)#2	1.787(14)
In(2)–S(1)	2.515(2)	B(2)–B(2)#10	1.775(11)
In(2)–S(1)#6	2.515(2)	K(1)–S(1)	3.511(7)
In(2)–S(2)	2.413(2)	K(1)–S(1)#6	3.511(7)
In(2)–S(2)#6	2.413(2)	K(1)–S(2)#9	3.552(5)
B(1)–S(2)	1.837(8)	K(1)–S(2)#10	3.552(5)
B(2)–S(1)	1.855(8)	K(1)–Cl(1)	3.563(6)
B(1)–B(1)#10	1.831(18)	K(1)–Cl(1)#11	3.563(6)
B(1)–B(1)#13	1.763(16)		
		2	
In(1)–S(1)	2.671(3)	B(1)–B(2)	1.80(2)
In(1)–S(1)#1	2.671(3)	B(1)–B(2)#2	1.82(2)
In(1)–S(1)#2	2.671(3)	B(1)–B(2)#10	1.78(18)
In(1)–S(1)#3	2.671(3)	B(2)–B(1)#5	1.82(2)
In(1)–S(1)#4	2.671(3)	B(2)–B(1)#10	1.78(18)
In(1)–S(1)#5	2.671(3)	B(2)–B(2)#10	1.83(3)
In(2)–S(1)	2.514(4)	B(2)–B(2)#12	1.77(3)

In(2)–S(1)#6	2.514(4)	K(1)–S(1)	3.473(9)
In(2)–S(2)	2.409(4)	K(1)–S(1)#6	3.473(9)
In(2)–S(2)#6	2.409(4)	K(1)–S(2)#10	3.519(7)
B(1)–S(1)	1.855(14)	K(1)–S(2)#11	3.519(7)
B(2)–S(2)	1.832(15)	K(1)–Br(1)	3.584(7)
B(1)–B(1)#2	1.78(2)	K(1)–Br(1)#9	3.584(7)
B(1)–B(1)#5	1.78(2)		
		3	
In(1)–S(1)	2.680(6)	B(1)–B(2)	1.79(3)
In(1)–S(1)#1	2.680(6)	B(1)–B(2)#3	1.76(4)
In(1)–S(1)#2	2.680(6)	B(1)–B(2)#10	1.75(3)
In(1)–S(1)#3	2.680(6)	B(2)–B(1)#4	1.79(3)
In(1)–S(1)#4	2.680(6)	B(2)–B(1)#10	1.75(3)
In(1)–S(1)#5	2.680(6)	B(2)–B(2)#10	1.83(3)
In(2)–S(1)	2.492(7)	B(2)–B(2)#12	1.76(3)
In(2)–S(1)#6	2.492(7)	K(1)–S(1)	3.403(12)
In(2)–S(2)	2.399(6)	K(1)–S(1)#6	3.403(12)
In(2)–S(2)#6	2.399(6)	K(1)–S(2)#10	3.490(9)
B(1)–S(1)	1.90(2)	K(1)–S(2)#11	3.490(9)
B(2)–S(2)	1.84(2)	K(1)–I(1)	3.668(10)
B(1)–B(1)#3	1.76(4)	K(1)–I(1)#9	3.668(10)
B(1)–B(1)#4	1.76(4)		
		4	
In(1)–S(1)	2.679(4)	B(1)–B(2)	1.80(2)
In(1)–S(1)#1	2.679(4)	B(1)–B(2)#4	1.82(2)
In(1)–S(1)#2	2.679(4)	B(1)–B(2)#13	1.79(2)
In(1)–S(1)#3	2.679(4)	B(2)–B(1)#5	1.82(2)
In(1)–S(1)#4	2.679(4)	B(2)–B(1)#13	1.79(2)
In(1)–S(1)#5	2.679(4)	B(2)–B(2)#13	1.85(4)
In(2)–S(1)	2.543(4)	B(2)–B(2)#15	1.78(4)
In(2)–S(1)#6	2.543(4)	Cs(1)–S(1) #7	5.078(3)
In(2)–S(2)	2.419(4)	Cs(1)–S(1)#8	5.078(3)
In(2)–S(2)#6	2.419(4)	Cs(1)–S(2)#13	3.568(4)
B(1)–S(1)	1.874(16)	Cs(1)–S(2)#14	3.568(4)
B(2)–S(2)	1.835(17)	Cs(1)–I(1)	3.714(15)
B(1)–B(1)#4	1.76(3)	Cs(1)–I(1)#12	3.714(15)
B(1)–B(1)#5	1.76(3)		
		5	
Ga(1)–S(2)	2.766(2)	B(1)–B(2)	1.771(12)
Ga(1)–S(2)#1	2.766(2)	B(1)–B(2)#2	1.796(12)
Ga(1)–S(2)#2	2.766(2)	B(1)–B(2)#7	1.776(11)
Ga(1)–S(2)#3	2.766(2)	B(2)–B(1)#5	1.776(11)
Ga(1)–S(2)#4	2.766(2)	B(2)–B(1)#7	1.776(11)

Ga(1)–S(1)#5	2.766(2)	B(2)–B(2)#2	1.784(14)
Ga(2)–S(1)	2.220(2)	B(2)–B(2)#5	1.784(14)
Ga(2)–S(1)#6	2.220(2)	K(1)–S(1) #7	3.556(3)
Ga(2)–S(2)	2.319(2)	K(1)–S(1)#8	3.556(3)
Ga(2)–S(2)#6	2.319(2)	K(1)–S(2)	3.265(4)
B(1)–S(1)	1.854(9)	K(1)–S(2)#6	3.265(4)
B(2)–S(2)	1.865(8)	K(1)–I(1)	3.611(3)
B(1)–B(1)#7	1.831(17)	K(1)–I(1)#9	3.611(3)
B(1)–B(1)#16	1.742(15)		
		6	
Gd(1)–S(2)	2.790(3)	B(1)–B(2)	1.84(7)
Gd(1)–S(2)#1	2.790(3)	B(1)–B(2)#4	1.77(5)
Gd(1)–S(2)#2	2.790(3)	B(1)–B(2)#13	1.78(5)
Gd(1)–S(2)#3	2.790(3)	B(2)–B(1)#2	1.79(4)
Gd(1)–S(2#4	2.790(3)	B(2)–B(1)#13	1.78(4)
Gd(1)–S(2)#5	2.790(3)	B(2)–B(2)#2	1.79(4)
Ga(1)–S(1)	2.229(2)	B(2)–B(2)#4	1.78(4)
Ga(1)–S(1)#11	2.229(2)	K(1)–S(1) #12	1.81(4)
Ga(1)–S(2)	2.344(3)	K(1)–S(1)#14	1.81(4)
Ga(1)–S(2)#11	2.344(3)	K(1)–S(2)	3.558(4)
B(1)–S(1)	1.836(4)	K(1)–S(2)#11	3.558(4)
B(2)–S(2)	1.868(3)	K(1)–I(1) #6	3.272(4)
B(1)–B(1)#13	1.84(7)	K(1)–I(1)#12	3.272(4)
B(1)–B(1)#16	1.77(5)		

Symmetry codes: #1 1+*y*-*x*, +*y*, 3/2-*z*; #2 1+*x*-*y*, 1-*x*, +*z*; #3 1-*y*, +*x*-*y*, +*z*; #4 +*x*, +*x*-*y*, 3/2-*z*; #5 1-*y*, 1-*x*, 3/2-*z*; #6 -*y*+*x*, -*y*, 1-*z*; #7 2+*y*-*x*,1-*x*,+*z*; #8 1-*y*,-1+*x*-y,+*z*; #9 1-*x*, -*y*, 1/2+*z*; #10 1+*y*-*x*, +*y*, 1/2-*z*; #11 –*y*+*x*, -1+*x*, -1/2+*z*; #12 1-*x*, -*y*, -1/2+*z*; #13 +*x*, +*x*-*y*, 1/2+*z*; #14 –*y*+*x*, -1+*x*, 1/2+*z*; #15 1+*y*, 1-*x*+*y*, 1/2+*z*; #16 2-*x*, -*y*, 1/2+*z* for **1.** #1+*x*, +*x*-*y*, 1/2-z; #2 1-*y*, 1-*y*, +*z*; #3 1+*y*-*x*, 1-*x*, +*z*; #4 1+*y*-*x*, +*y*, 1/2-*z*; #5 1-*y*, 1-*x*, 1/2-*z*; #6 +*y*, +*x*, 1-*z*; #7 2-*y*, 1+*x*-*y*, +*z*; #8 1+*y*-*x*, 2-*x*, +*z*; #9 2-*x*, 2-*y*, -1/2+*z*; #10 1-*x*, 1-*y*, -1/2+*z*; #11 1-*y*, 1-*x*, 3/2-*z*; #12 +*x*, +*x*-*y*, 3/2-*z*; #13 +*y*, 1-*x*+*y*, 1/2+*z*; #14 1-*y*+*x*, +*x*, 1/2+*z*; #15 2-*x*, 2-*y*, 1/2+*z*; #16 1-*x*, 1-*y*, 1/2+*z* for **2.** #1 +*x*, 1+*x*-*y*, 3/2-*z*; #2 1-*y*, 1-*x*, 3/2-*z*; #3 1-*y*, 1-*x*, +*z*; #4 +*y*-*x*, +*y*, 3/2-*z*; #5 +*y*-*x*, 1-*x*, +*z*; #6 +*y*, +*x*, 1-*z*; #7 -*y*, +*x*-*y*, +*z*; #8 -*y*, +*x*-*y*, +*z*; #9 -*x*, -*y*, 1/2+*z*; #10 1-*x*, 1-*y*, 1/2+*z*; #11 1-*y*, 1-*x*, 1/2+*z*; #12 +*x*, 1+*x*-*y*, 1/2-*z*; #13 -*x*, -*y*, -1/2+*z*; #14 -*y*+*x*, +*x*, -1/2+*z*; #15 +*y*, -*x*+*y*, -1/2+*z*; #16 1-*x*, 1-*y*, -1/2+*z* for **3.** #1 +*x*, 1+*x*-*y*, 3/2-*z*; #2 1-*y*, 1+*x*-*y*, +*z*; #3 +*y*-*x*, +*y*, 3/2-*z*; #4 1-*y*, 1-*x*, 3/2-*z*; #5 +*y*-*x*, 1-*x*, +*z*; #6 +*y*, +*x*, 1-*z*; #7 -*y*, +*x*-*y*, +*z*; #8 -*y*, +*x*-*y*, +*z*; #9 +*y*, -*x*+*y*, -1/2+*z*; #10 –*y*+*x*, +*x*, -1/2+*z*; #11 +*y*, -*x*-*y*, 1/2+*z*; #12 –*y*+*x*, +*x*, 1/2+*z*; #13 1-*y*, 1-*x*, 1/2+*z*; #14 1-*x*, 1-*y*, 1/2+*z*; #15 +*x*, 1+*x*-*y*, 1/2-*z*; #16 -*x*, -*y*, -1/2+*z*; #17 1-*x*, 1-*y*, -1/2+*z* for **4.** #1 *x*, *x*-*y*+1, -*z*+1/2; #2 -*x*+*y*, -*x*+1, *z*; #3 -*y*+1, -*x*+1, -*z*+1/2; #4 -*x*+*y*, *y*, -*z*+1/2; #5 -*y*+1, *x*-*y*+1, *z* #6 -*x*, -*x*+*y*, -*z*+1; #7 *x*, *x*-*y*+1, -*z*+3/2; #8 -*x*, -*y*+1, *z*-1/2; #9 -*x*, -*y*, *z*-1/2 #10 -*y*, x-*y*, *z*; #11 -*x*+*y*, -*x*, *z*; #12 *y*, -*x*+*y*, *z*+1/2; #13 -*x*, -*y*, *z*+1/2; #14 *x*-*y*, *x*, *z*+1/2; #15 -*x*, -*y*+1, *z*+1/2; #16 -*y*+1, -*x*+1, -*z*+3/2 for **5.** #1 +*x*, 1+*x*-*y*, 1/2-*z*; #2 +*y*-*x*, 1-*x*, +*z*; #3 1-*y*, 1-*x*+*y*, +*z*; #4 1-*y*, 1-*x*, 1/2-*z*; #5 +*y*-*x*, +*y*, 1/2-*z*; #6 -*y*, +*x*-*y*, +*z*; #7 -*y*+*x*, +*x*, 1/2+*z*; #8 +*y*-*x*, -*x*, +*z*; #9 +*y*, -*x*+*y*, 1/2+*z*; #10 -*x*, -*y*, 1/2+*z*; #11 -*x*, -*x*+*y*, 1-*z*; #12 -*x*, -*y*, -1/2+*z*; #13 +*x*, 1+*x*-*y*, 3/2-*z*; #14 -*x*, 1-*y*, -1/2+*z*; #15 -*x*, 1-*y*, 1/2+*z*; #16 1-*y*, 1-*x*, 3/2-*z* for **6.**

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (U_{eq}[a], Å^2 × 10^3) for **1–6**.

Atom	*x*	*y*	*z*	U_{eq}/Å^2
		1		
In1	6667	3333	7500	18.5(3)
In2	4723.1(6)	0	5000	25.4(2)
S1	6660(2)	1753.7(18)	5656(2)	17.3(4)
S2	3974.1(18)	704.4(18)	3075(2)	25.7(5)
B1	5380(8)	2065(7)	2842(8)	11.1(17)
B2	6663(8)	2549(8)	3973(9)	15.5(18)
K1	7921(6)	0	5000	234(6)
Cl1	10000	0	7500	189(8)
		2		
In1	6667	3333	2500	15.1(6)
In2	4709.6(10)	4709.6(10)	5000	20.9(4)
S1	6657(4)	4907(3)	4346(4)	14.7(7)
S2	3957(3)	3256(4)	6922(4)	21.3(8)
B1	6647(15)	4106(13)	6027(15)	10(3)
B2	5369(14)	3317(14)	7164(14)	11(3)
K1	7895(7)	7895(7)	5000	126(3)
Br1	10000	10000	7500	86.0(18)
		3		
In1	3333	6667	7500	30.3(12)
In2	5290.7(19)	5290.7(19)	5000	26.9(8)
S1	3366(6)	5101(5)	5654(6)	16.5(13)
S2	6036(6)	6738(6)	3094(6)	22.2(14)
B1	3360(20)	5910(20)	3930(20)	9(5)
B2	4620(20)	6690(20)	2840(20)	10(6)
K1	2181(10)	2181(10)	5000	94(4)
I1	0	0	2500	52.4(14)
		4		
In1	3333	6667	7500	13.7(6)
In2	5279.4(11)	5279.4(11)	5000	16.8(4)
S1	3386(4)	5148(3)	5658(4)	11.3(8)
S2	5976(4)	6723(4)	3099(4)	18.3(9)
B1	3356(16)	5925(14)	3971(17)	6(3)
B2	4610(15)	6686(16)	2835(16)	11(4)
Cs1	2173.0(13)	2173.0(13)	5000	57.2(7)
I1	0	0	2500	35.9(7)
		5		
Ga1	3333	6667	2500	29(1)
Ga2	0	5376(1)	5000	22(1)
S1	625(2)	6723(2)	6778(2)	15(1)

S2	1603(2)	5083(2)	4420(2)	14(1)
B1	2036(7)	6692(7)	7159(8)	9(2)
B2	2512(8)	5874(8)	6054(8)	9(2)
K1	0	2172(3)	5000	73(2)
I1	0	0	7500	36(1)
		6		
Gd1	3333	6667	2500	26.07(9)
Ga1	0	5397.1(3)	5000	14.38(9)
S1	640.2(5)	6732.8(5)	6794.8(6)	13.86(15)
S2	1600.3(5)	5073.5(5)	4435.8(7)	12.60(15)
B1	2027(2)	6686(2)	7148(3)	10.7(7)
B2	2509(2)	5860(2)	6068(3)	9.0(6)
K1	0	2166.1(9)	5000	62.3(4)
I1	0	0	7500	34.36(12)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

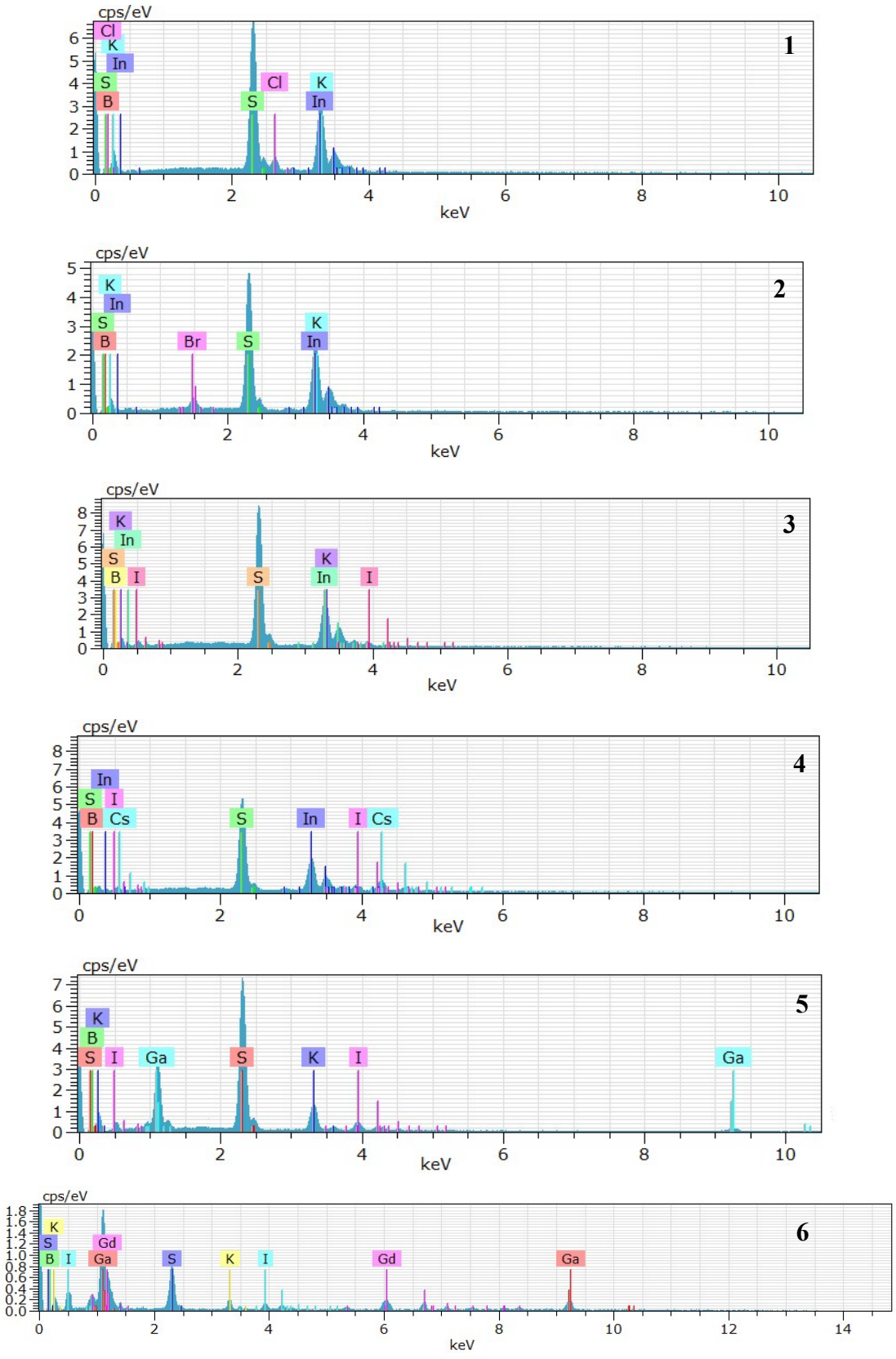

Fig. S1. EDS analyses for **1–6**.

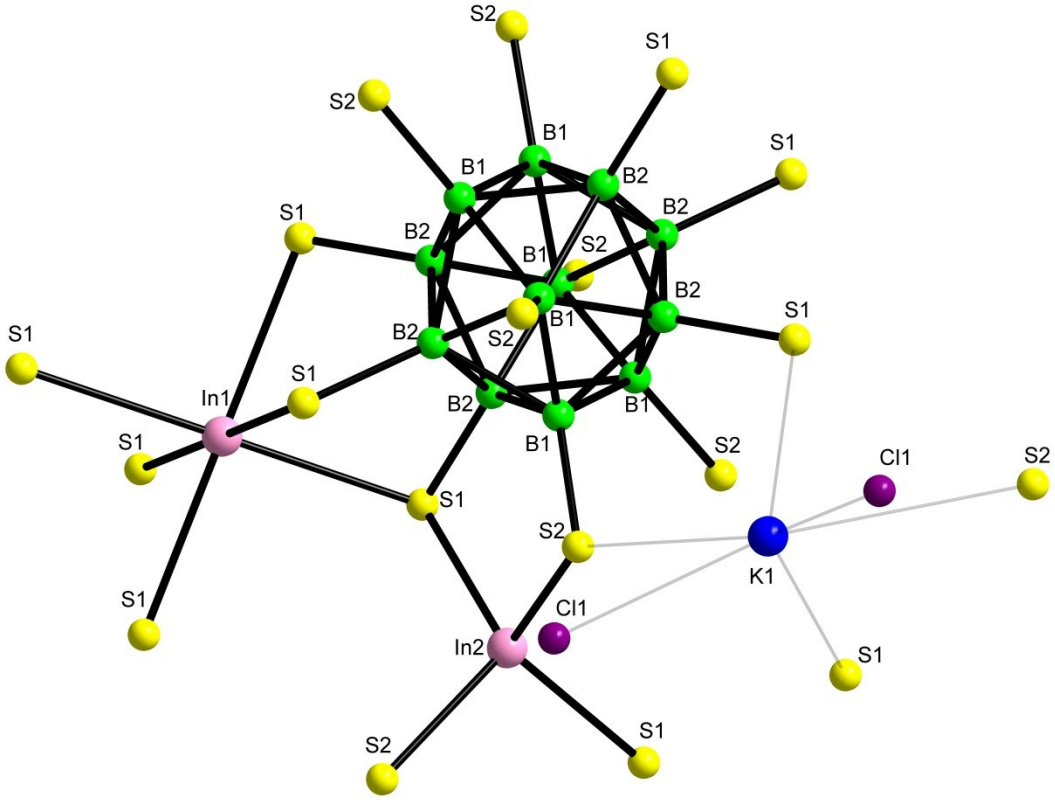

Fig. S2. Coordination geometry of **1**.

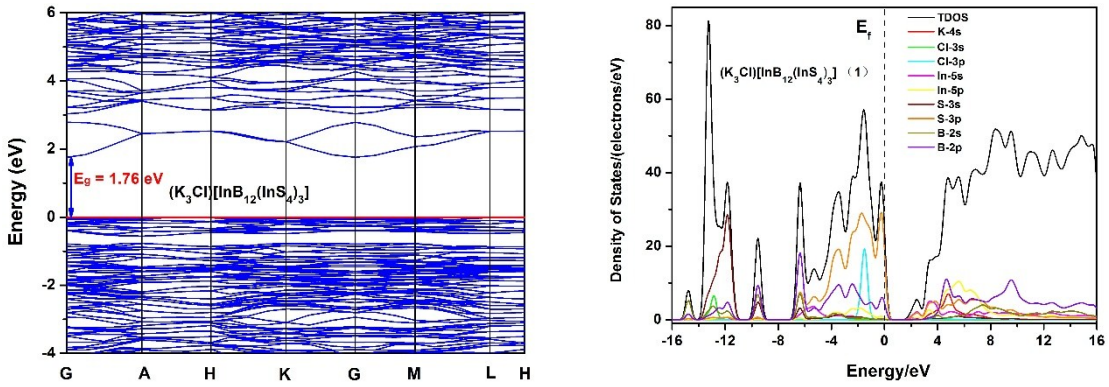

Fig. S3. Calculated band structure (left) and DOS (right) of **1**. The Fermi level is chosen as the energy reference at 0 eV.

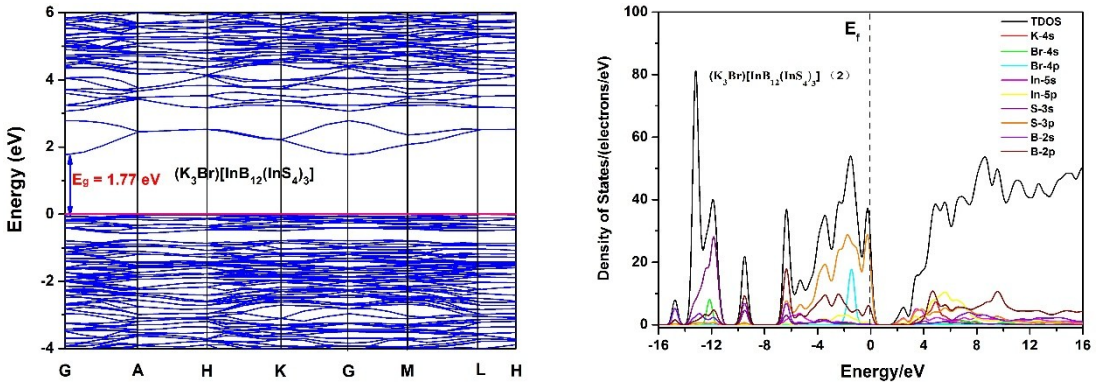

Fig. S4. Calculated band structure (left) and DOS (right) of **2**. The Fermi level is chosen as the energy reference at 0 eV.

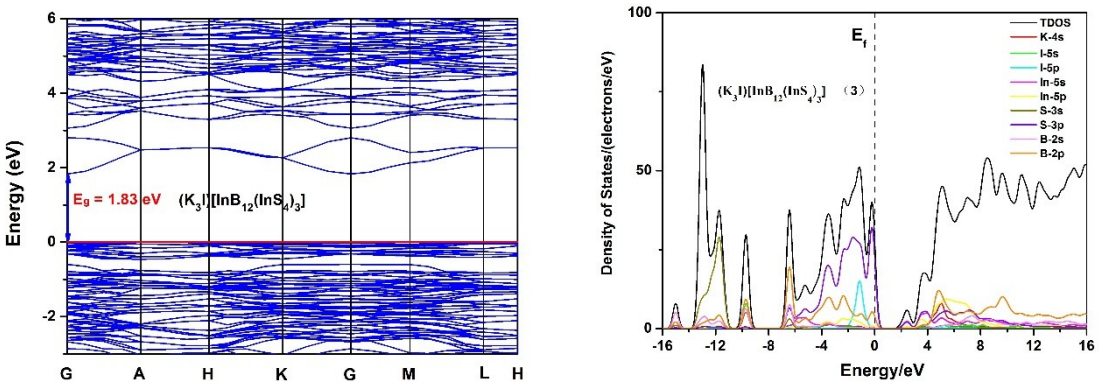

Fig. S5. Calculated band structure (left) and DOS (right) of **3**. The Fermi level is chosen as the energy reference at 0 eV.

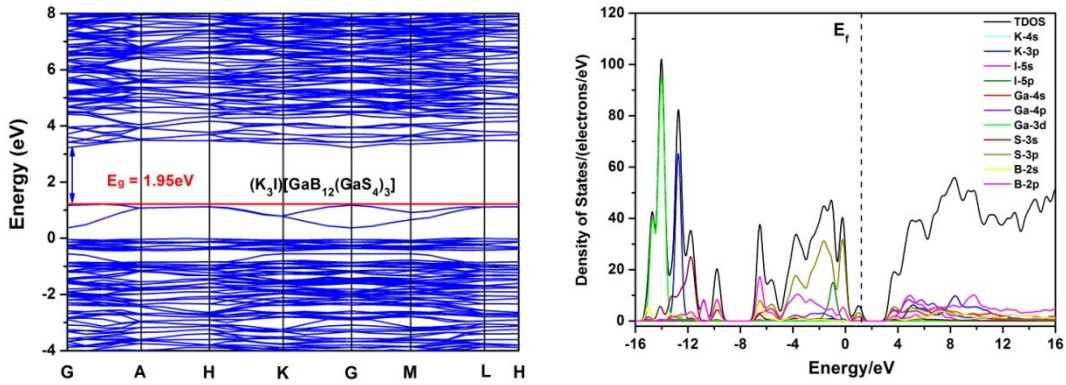

Fig. S6. Calculated band structure (left) and DOS (right) of **5**. The Fermi level is chosen as the energy reference at 0 eV.

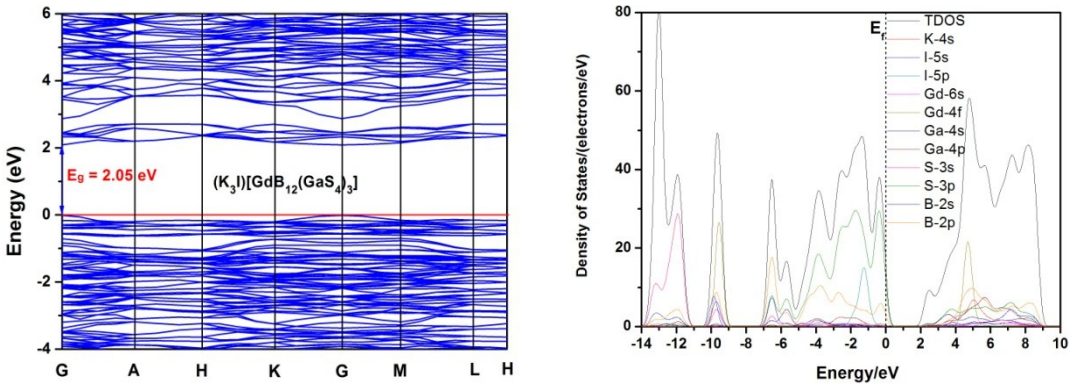

Fig. S7. Calculated band structure (left) and DOS (right) of **6**. The Fermi level is chosen as the energy reference at 0 eV.

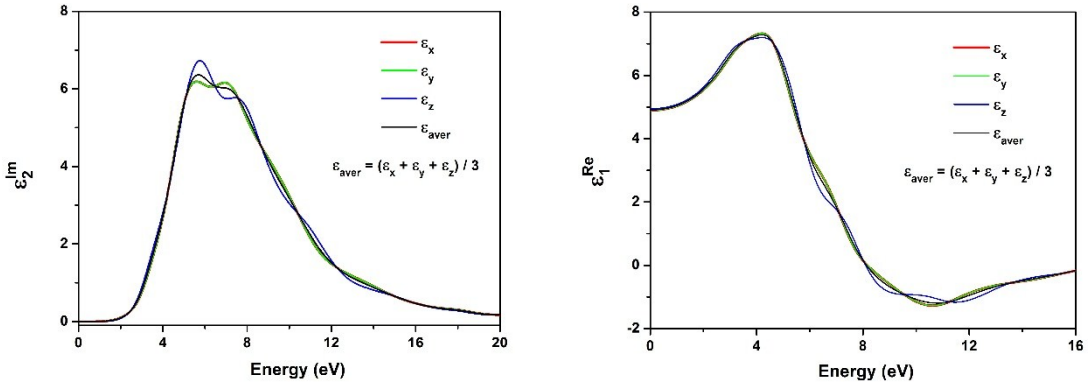

Fig. S8. Calculated real and imaginary parts of optical dielectric functions of **1** in different directions.

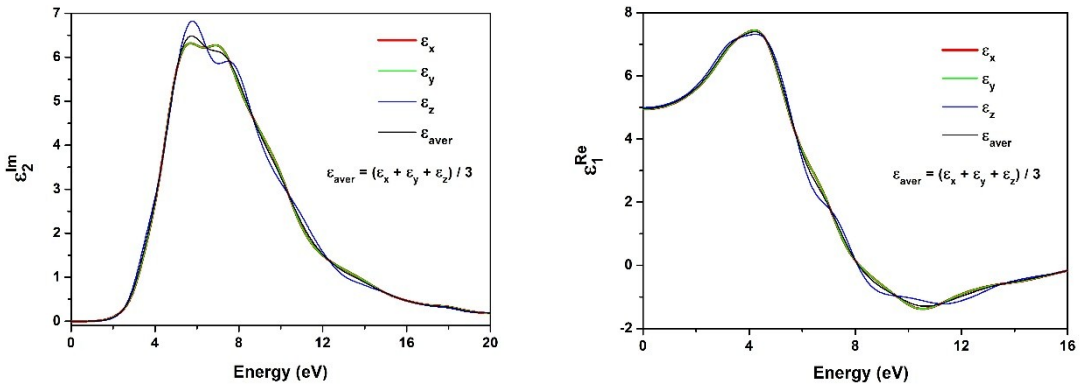

Fig. S9. Calculated real and imaginary parts of optical dielectric functions of **2** in different directions.

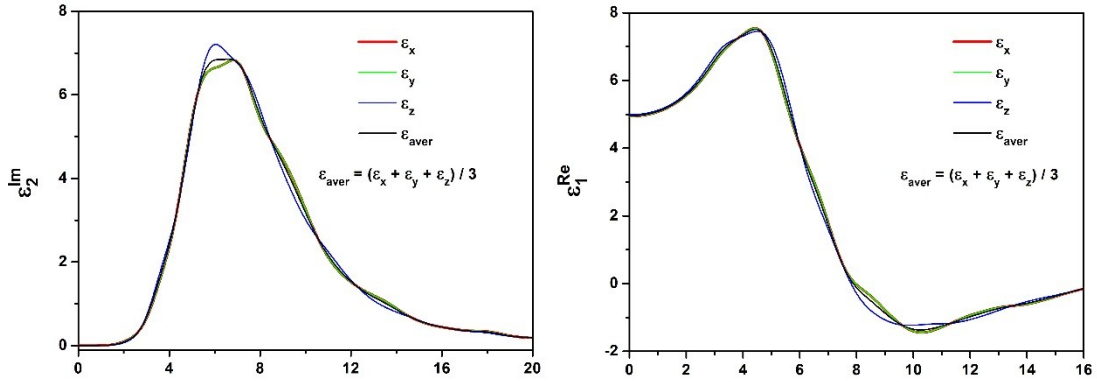

Fig. S10. Calculated real and imaginary parts of optical dielectric functions of **3** in different directions.

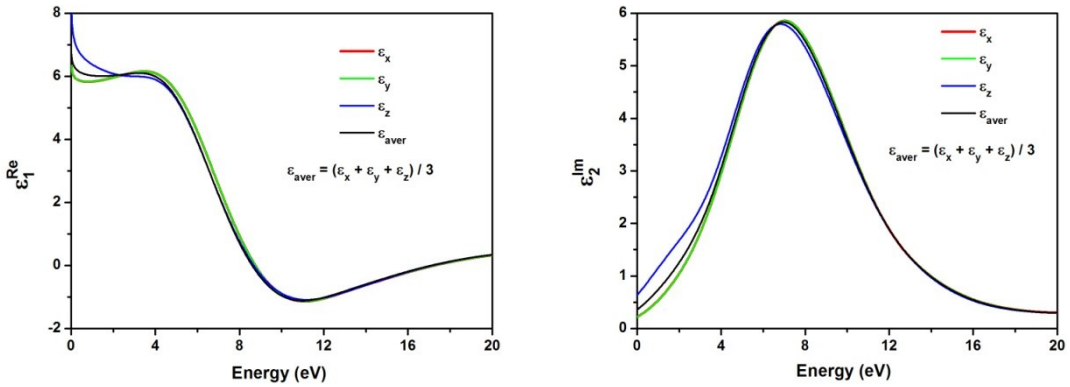

Fig. S11. Calculated real and imaginary parts of optical dielectric functions of **5** in different directions.

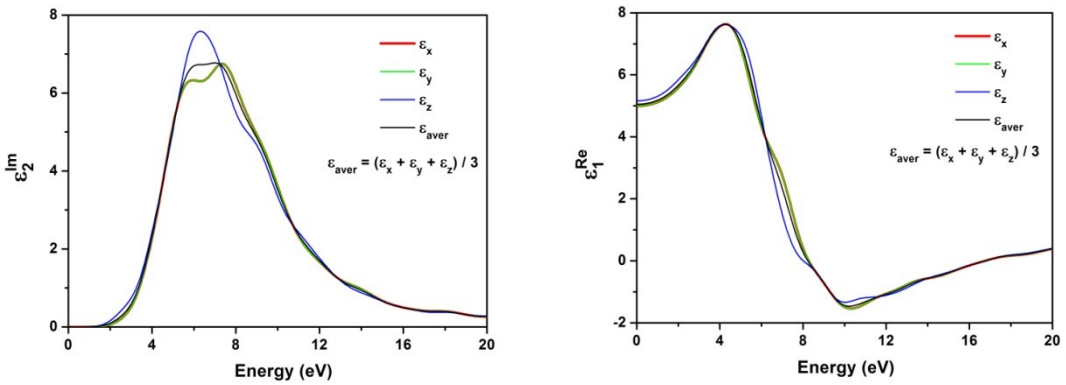

Fig. S12. Calculated real and imaginary parts of optical dielectric functions of **6** in different directions.