Supporting Information

Heterovalent cations substitution to design asymmetric chalcogenides with promising nonlinear optical performances

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Table S1. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (U_{eq}[a], Å^2 × 10^3) for **1** and **2**.

Atom	Wyck. site	*x*	*y*	*z*	U_{eq}/Å^2
			Compound 1		
Ba(1)	16*b*	7493.6(3)	4982.6(2)	-622.7(11)	13.1(2)
Ba(2)	8*a*	7500	2500	-616.9(11)	12.8(2)
Ba(3)	8*a*	7500	2500	4361.1(12)	12.8(2)
Sn(1)	16*b*	5699.7(4)	3749.4(4)	9765.4(5)	11.58(19)
Sn(2)	16*b*	6127.9(4)	3755.9(4)	4371.8(4)	10.83(18)
Zn(1)	16*b*	6392.0(6)	3746.6(6)	6850.9(10)	16.5(3)
Zn(2)	16*b*	6769.7(6)	3751.9(7)	1505.0(9)	15.1(3)
S(1)	16*b*	7043.2(12)	3759.1(19)	3263(2)	12.2(7)
S(2)	16*b*	7781.1(11)	3741.5(18)	678(2)	12.6(5)
S(3)	16*b*	6244.8(12)	4573.4(15)	10608(3)	12.2(10)
S(4)	16*b*	5481.7(12)	3742.0(16)	7952(2)	12.3(5)
S(5)	16*b*	7183.4(11)	3739(2)	8072(2)	15.0(6)
S(6)	16*b*	6241.4(13)	2928.8(15)	625(3)	13.2(10)
S(7)	16*b*	6244.4(13)	2931.6(15)	5599(3)	13.7(11)
S(8)	16*b*	6256.2(13)	4569.8(15)	5622(3)	12.4(10)
			Compound 2		
Ba(1)	8*a*	5000	5000	2601(3)	12.8(4)
Ba(2)	8*a*	7500	2500	5090(3)	12.8(4)
Ba(3)	16*b*	4998.7(5)	2481.9(3)	2601(2)	13.8(4)
Se(1)	16*b*	5427.9(8)	3739.1(16)	3725.6(15)	10.4(5)
Sn(1)	16*b*	6356.2(6)	3744.8(7)	2592.9(11)	9.7(3)
Zn(1)	16*b*	8617.0(10)	3743.0(11)	7624(2)	19.1(6)
Sn(2)	16*b*	6804.9(6)	3750.7(6)	7180.9(11)	12.4(3)

Se(2)	16*b*	4706.8(8)	3762.0(15)	6328.6(16)	14.5(4)
Zn(2)	16*b*	5725.2(10)	3744.8(11)	5484.8(17)	14.9(5)
Se(3)	16*b*	3740.6(10)	4586.4(14)	3829(2)	12.7(7)
Se(4)	16*b*	7835.6(7)	3741.4(17)	6352.7(16)	11.4(4)
Se(5)	16*b*	6253.9(9)	2905.5(14)	6354(2)	12.5(7)
Se(6)	16*b*	6250.3(10)	4590.0(14)	6329(2)	12.1(7)
Se(7)	16*b*	3748.9(10)	2908.3(14)	3858(2)	12.4(7)
Se(8)	16*b*	4542.9(9)	3738.6(15)	1532.5(15)	12.9(5)

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

Table S2. Important bond lengths (Å) for **1** and **2**

Bond	Dist./Å	Bond	Dist./Å
Compound 1			
Ba(1)–S(1)#1	3.249(4)	Ba(3)–S(8)#4	3.254(3)
Ba(1)–S(2)	3.236(4)	Ba(3)–S(8)#9	3.254(3)
Ba(1)–S(3)#2	3.223(3)	Sn(1)–S(3)	2.398(3)
Ba(1)–S(4)#3	3.238(3)	Sn(1)–S(4)	2.350(3)
Ba(1)–S(5)#2	3.253(4)	Sn(1)–S(5)#11	2.404(2)
Ba(1)–S(6)#4	3.235(3)	Sn(1)–S(6)#10	2.399(3)
Ba(1)–S(7)#3	3.259(3)	Sn(2)–S(1)	2.413(2)
Ba(1)–S(8)#1	3.258(3)	Sn(2)–S(2)#11	2.363(2)
Ba(2)–S(2)#5	3.231(4)	Sn(2)–S(7)	2.396(4)
Ba(2)–S(3)#6	3.254(3)	Sn(2)–S(8)	2.401(4)
Ba(2)–S(3)#7	3.254(3)	Zn(1)–S(4)	2.399(3)
Ba(2)–S(5)#8	3.252(4)	Zn(1)–S(5)	2.297(3)
Ba(2)–S(5)#2	3.252(4)	Zn(1)–S(7)	2.409(4)
Ba(2)–S(6)#5	3.259(3)	Zn(1)–S(8)	2.400(4)
Ba(3)–S(1)#5	3.238(4)	Zn(2)–S(1)	2.309(3)
Ba(3)–S(4)#9	3.248(3)	Zn(2)–S(2)	2.406(2)
Ba(3)–S(4)#4	3.248(3)	Zn(2)–S(3)#2	2.405(4)
Ba(3)–S(7)#5	3.253(3)	Zn(2)–S(6)	2.401(4)
Compound 2			

Ba(1)–Se(1)#1	3.362(4)	Ba(3)–Se(2)	3.340(3)
Ba(1)–Se(3)#1	3.369(3)	Sn(1)–Se(1)	2.549(2)
Ba(1)–Se(7)#2	3.356(3)	Zn(2)–Se(1)	2.414(3)
Ba(1)–Se(7)#3	3.356(3)	Sn(1)–Se(2)#2	2.498(2)
Ba(1)–Se(8)	3.351(3)	Sn(1)–Se(3)#2	2.532(3)
Ba(1)–Se(8)#1	3.350(3)	Sn(1)–Se(7)#2	2.531(3)
Ba(2)–Se(2)#2	3.331(3)	Zn(1)–Se(3)#7	2.505(4)
Ba(2)–Se(2)#4	3.331(3)	Zn(1)–Se(4)	2.416(3)
Ba(2)–Se(4)#5	3.359(4)	Zn(1)–Se(7)#7	2.516(4)
Ba(2)–Se(5)#5	3.363(3)	Zn(1)–Se(8)#7	2.513(3)
Ba(2)–Se(6)#4	3.371(3)	Sn(2)–Se(4)	2.540(2)
Ba(2)–Se(6)#2	3.371(3)	Sn(2)–Se(5)	2.525(3)
Ba(3)–Se(1)	3.356(4)	Sn(2)–Se(6)	2.533(3)
Ba(3)–Se(2)#6	3.351(3)	Sn(2)–Se(8)#8	2.500(3)
Ba(3)–Se(3)#2	3.378(3)	Zn(2)–Se(2)	2.524(2)
Ba(3)–Se(4)#4	3.349(4)	Zn(2)–Se(5)	2.516(4)
Ba(3)–Se(5)#6	3.354(3)	Zn(2)–Se(6)	2.508(4)
Ba(3)–Se(6)#4	3.340(3)	Zn(1)–Se(3)#12	2.504(4)
Ba(3)–Se(7)	3.379(3)		

Symmetry transformations used to generate equivalent atoms for **1**: #1 3/2-*y*, 1-*y*, -1/2+*z*; #2+*x*, +*y*, -1+*z*; #3 5/4-*x*, 1/4+*y*, -3/4+*z*; #4 1/4+*x*, 3/4-*y*, -1/4+*z*; #5 3/2-*x*, 1/2-*y*, +*z*; #6 5/4-*x*, -1/4+*y*, -5/4+*z*; #7 1/4+*x*, 3/4-*y*, -5/4+*z*; #8 3/2-*x*, 1/2-*y*, -1+*z*; #9 5/4-*x*, -1/4+*y*, -1/4+*z*; 10+*x*, +*y*, 1+*z*; #11 -1/4+*x*, 3/4-*y*, 1/4+*z*.

Symmetry transformations used to generate equivalent atoms for **2** : #1 1-*x*, 1-*y*, +*z*; #2 1/4+*x*, 3/4-

y, -1/4+*z*; #3 3/4-*x*, 1/4+*y*, -1/4+*z*; #4 5/4-*x*, -1/4+*y*, -1/4+*z*; #5 3/2-*x*, 1/2-*y*, +*z*; #6 1-*x*, 1/2-*y*, -1/2+*z*; #7 1/2+*x*, +*y*, 1/2+*z*; #8 1/4+*x*, 3/4-*y*, 3/4+*z*; #12 -1/2+*x*, +*y*, -1/2+*z*;

Table S3. Calculated bond valences for **1** and **2**.

Atom	**bond valence**	**Atom**	**bond valence**
Compound 1		**Compound 2**	
Ba(1)	2.216	Ba(1)	2.191
Ba(2)	2.187	Ba(2)	2.211
Ba(3)	2.191	Ba(3)	2.214
Zn(1)	1.859	Zn(1)	1.955
Zn(2)	1.835	Zn(2)	1.940
Sn(1)	4.059	Sn(1)	3.964
Sn(2)	4.002	Sn(2)	3.997
S(1)	2.055	Se(1)	2.075
S(2)	2.080	Se(2)	2.384
S(3)	1.972	Se(3)	2.237
S(4)	2.111	Se(4)	2.377
S(5)	2.083	Se(5)	2.268
S(6)	1.963	Se(6)	2.251
S(7)	1.949	Se(7)	2.210
S(8)	1.946	Se(8)	2.370

Table S4. NLO properties about a series compounds of $AM^{II}M^{IV}Q_4$.

Compound	Space group	*a* (Å)	*b* (Å)	*c* (Å)	Band gap (eV)	SHG (× AGS)	LIDT	*Δ*n
$SrCdGeS_4$	*Ama*2	10.3325	10.2335	6.4408	2.60	2.0	/	/
$SrCdGeSe_4$	*Ama*2	10.8245	10.6912	6.6792	1.90	5.0	/	/
$SrHgSnS_4$	*Ama*2	10.4072	10.4873	6.5578	2.72	1.9	/	/
$SrHgGeS_4$	*Ama*2	10.838	10.746	6.638	2.42	4.8	/	/
$BaZnSiSe_4$	*Ama*2	11.3055	11.2344	6.1994	2.71	1/3	/	/
$BaZnGeSe_4$	*Ama*2	11.3255	11.2527	6.2917	2.46	1.0	/	/
$BaHgGeSe_4$	*Ama*2	11.255	11.033	6.6847	2.49	4.7	/	/
β-$BaHgSnS_4$	*Ama*2	10.8450	10.8042	6.6178	2.77	2.8	/	/
$SrZnSnS_4$	*Fdd*2	12.6336	20.9242	20.8591	2.83	1.0×$LiGaS_2$	/	/
$SrCdSnS_4$	*Fdd*2	20.9017	21.0626	13.0676	2.05	1.3	0.22	10AGS
$SrCdSnSe_4$	*Fdd*2	21.8908	21.8945	13.5407	1.54	1.5	0.33	5AGS
$SrHgSnSe_4$	*Fdd*2	21.9027	21.9059	13.5010	2.07	5.0	/	/
$BaCdSnS_4$	*Fdd*2	21.566	21.760	13.110	2.30	0.7	/	/
$BaCdSnSe_4$	*Fdd*2	22.381	22.711	13.588	1.79	1.6	/	/
$BaMnSnS_4$	*Fdd*2	21.547	21.796	12.981	1.90	1.2	0.17	10AGS
$BaCdGeS_4$	*Fdd*2	21.285	21.691	12.786	2.58	0.3	0.15	13AGS
$BaHgSnSe_4$	*Fdd*2	22.441	22.760	13.579	1.98	5.0	/	/
$BaZnSnS_4$	*Fdd*2	21.398	21.865	12.707	3.25	0.6	0.17	5.7AGS
$BaZnSnSe_4$	*Fdd*2	22.240	22.705	13.197	1.88	1.0	0.26	9.8AGS

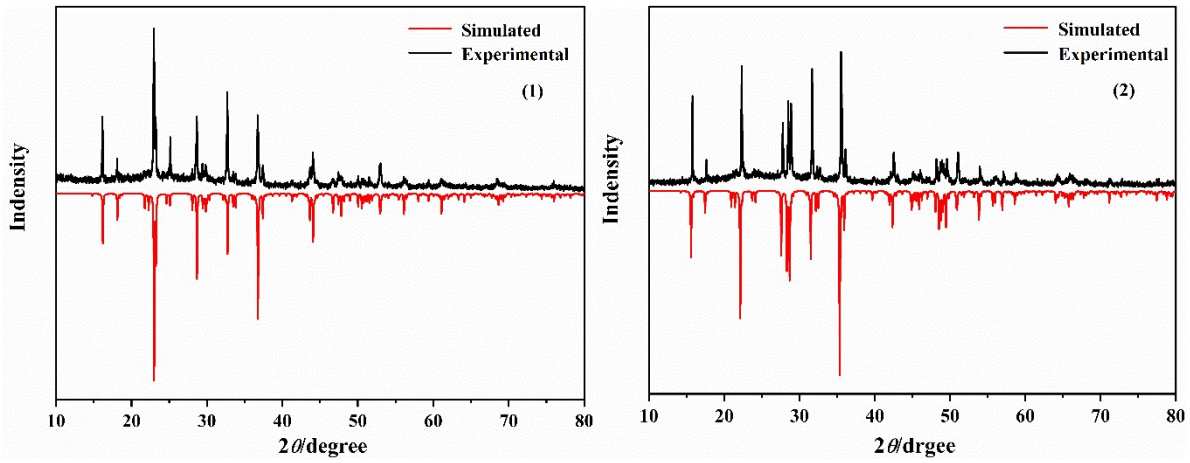

Figure S1. Powder XRD patterns for **1** and **2**.

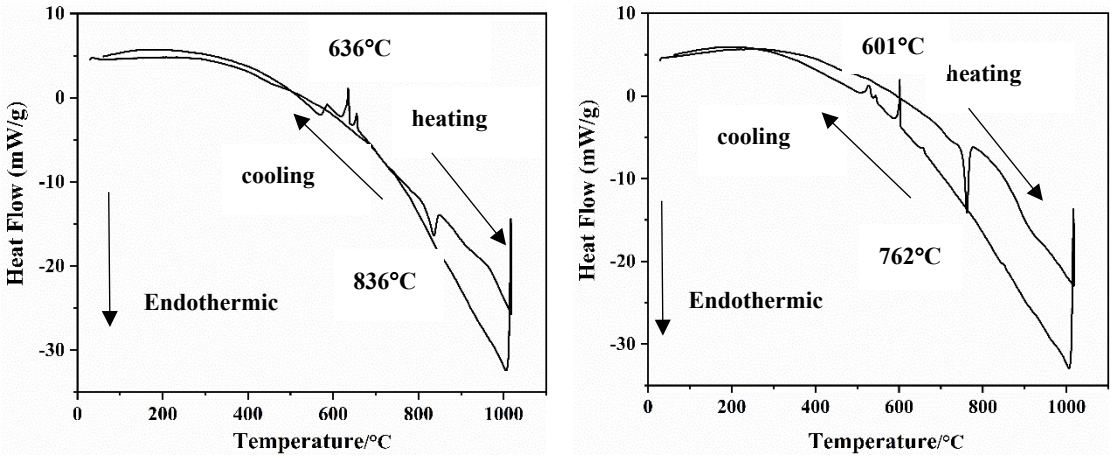

Figure S2. DSC curves of **1** (a) and **2** (b).

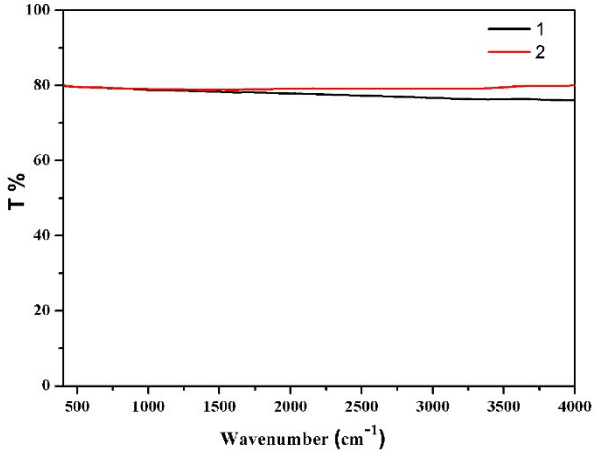

Figure S3. FT-IR spectra for **1** and **2**.

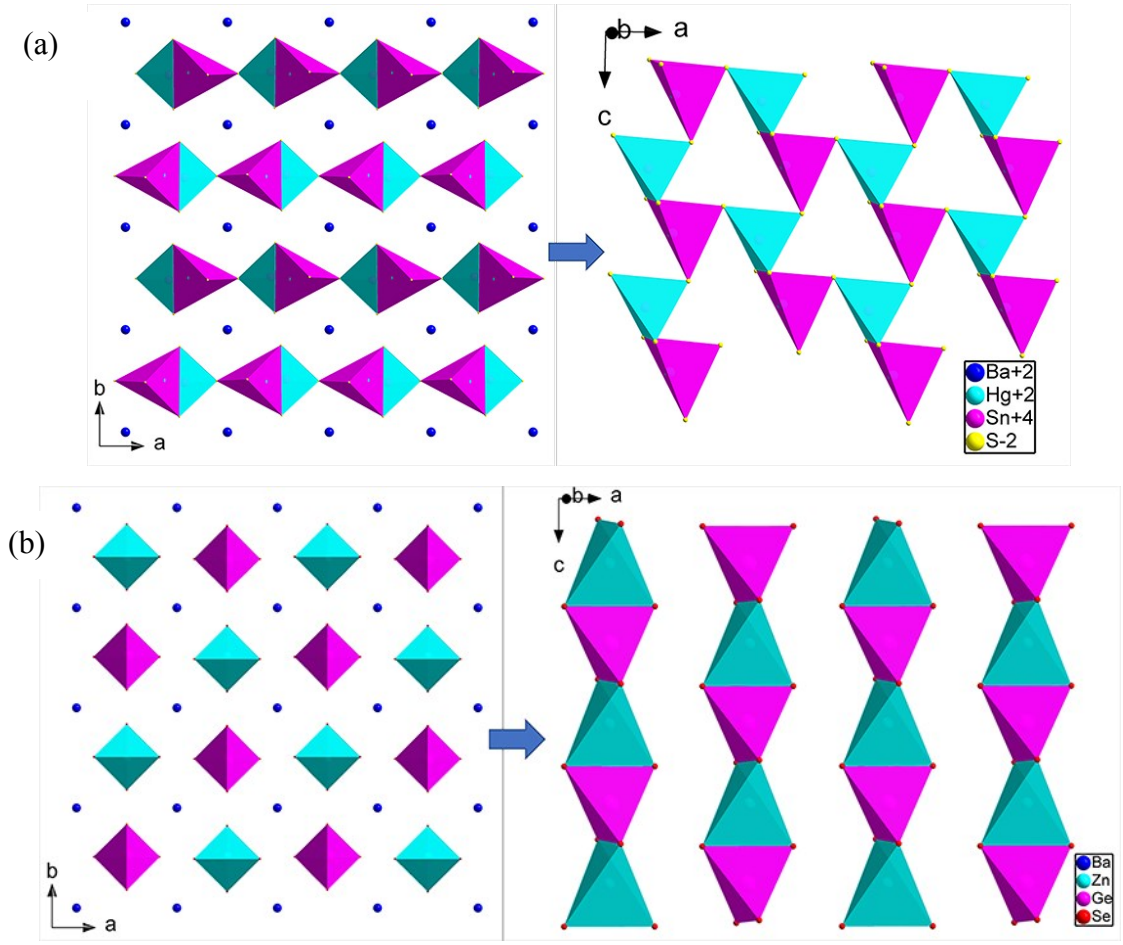

Figure S4. (a) The overall structure of $BaZnGeSe_4$ and the chain structure of $BaZnGeSe_4$. (b) Structure of β−$BaHgSnS_4$ viewed along the c direction and view of one $_\infty$[Hg−Sn−S] layer along the *a* direction.

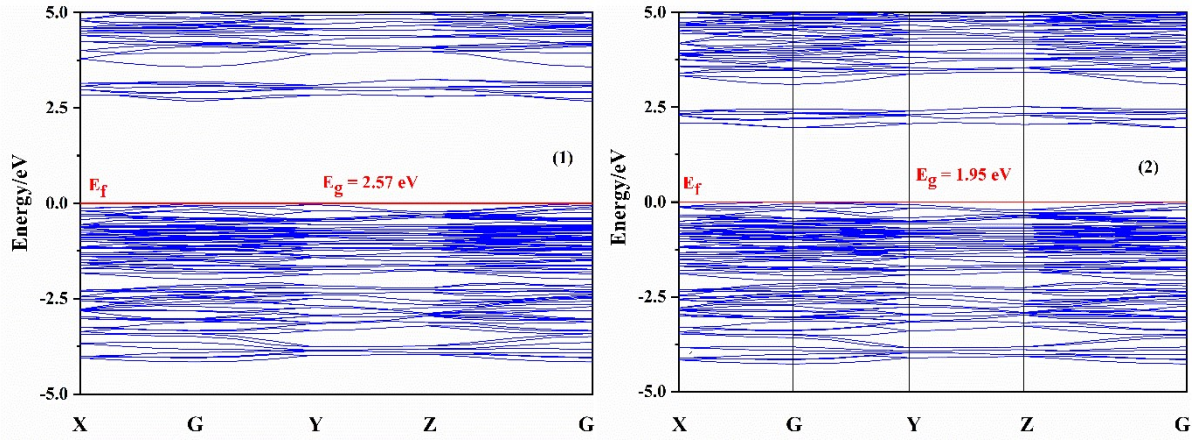

Figure S5. The calculated band structures for **1** and **2**. The Fermi level is chosen at 0 eV.

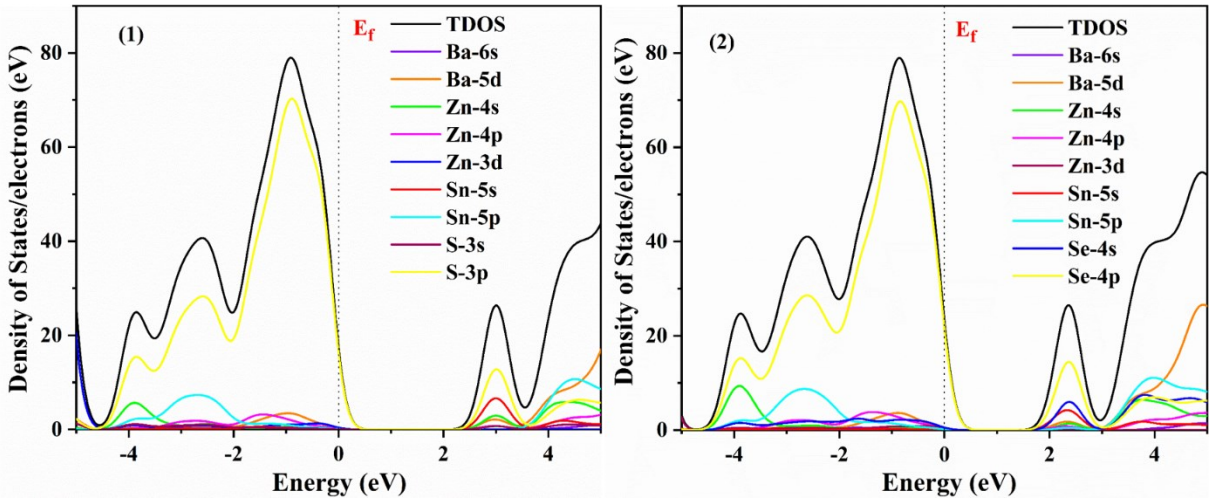

Figure S6. The calculated DOS for **1** and **2**. The Fermi level is chosen at 0 eV.

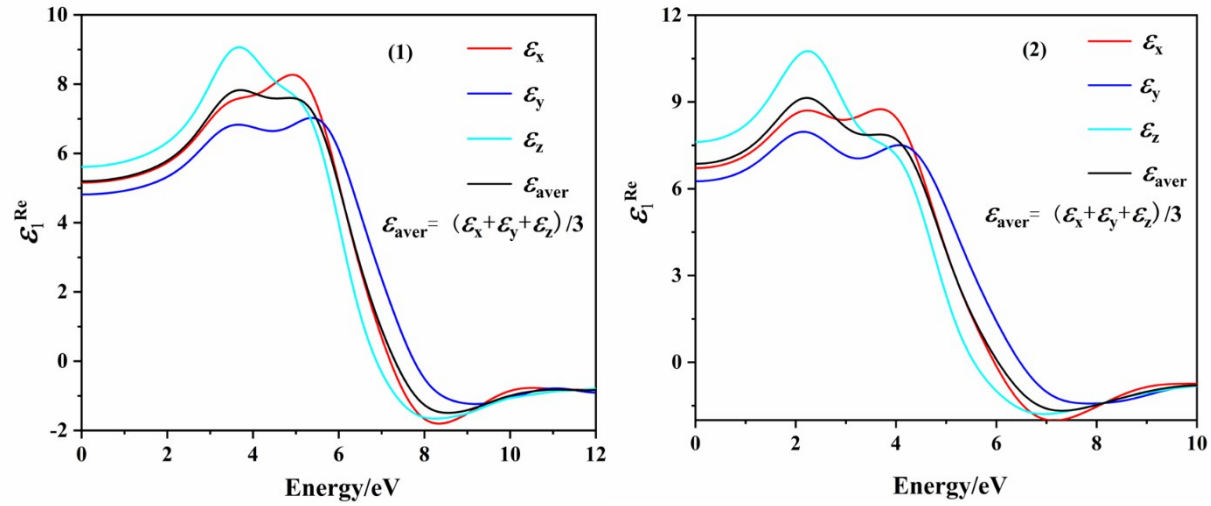

Figure S7. Calculated real parts of the optical dielectric functions for **1** and **2**.

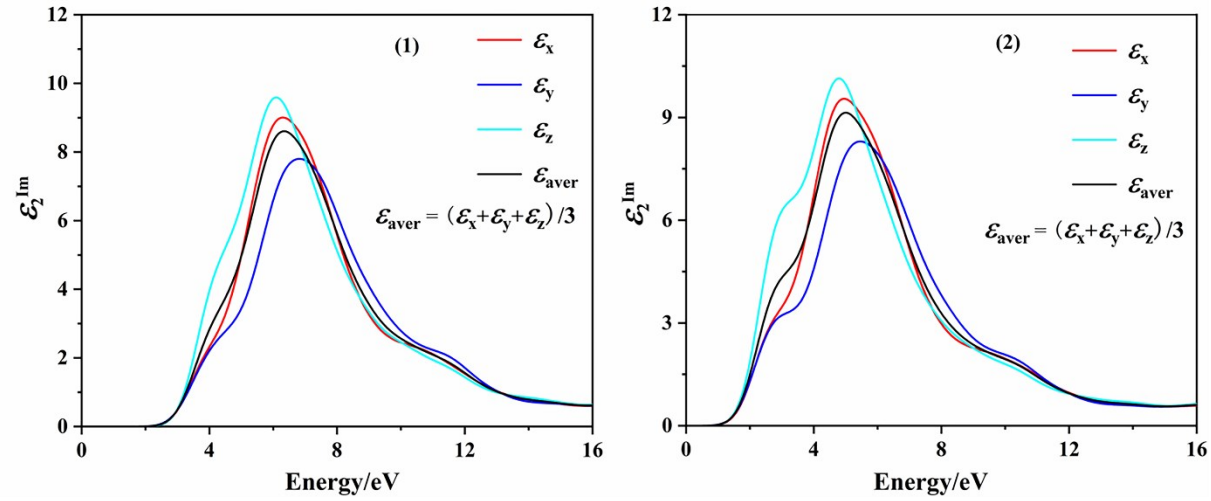

Figure S8. Calculated imaginary parts of the optical dielectric functions for **1** and **2**.

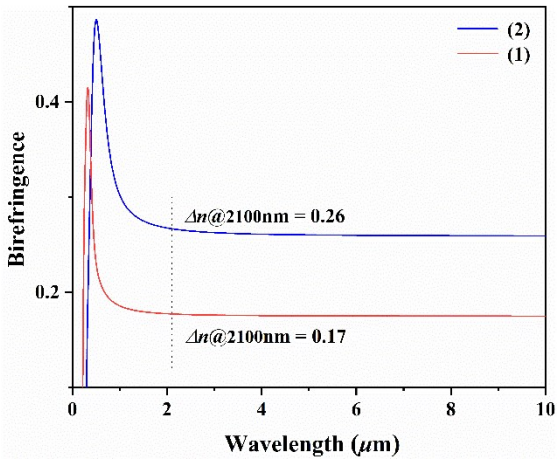

Figure S9. Calculated wavelength-dependent birefringence *Δn* for **1** and **2**.