Supporting information

$SrCdSnQ_4$ (Q=S, Se): Infrared Nonlinear Optical Chalcogenides with Mixed NLO-Active and Synergetic Distorted Motifs.

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CONTENTS

Table S1. Chalcogenides containing both alkali-earth metal and d^{10} cations, for some of which SHG efficiency (d_{ij}) and band gaps (E_g) have been reported

Compounds	d_{ij} (×AGS)	E_g *(eV)*	***Compounds***	d_{ij} *(×AGS)*	E_g *(eV)*
$SrAg_2GeS_4$[9]	\	1.33	**$Ba_4Cd_3Nd_2Se_{10}$**[15]	\	3.0
$SrAg_2GeSe_4$[9]	\	0.68	**$Ba_4Cd_3Sm_2S_{10}$**[15]	\	~3.0
$SrAg_2SnS_4$[9]	\	1.08	**$Ba_4Cd_3Gd_2S_{10}$**[15]	\	~3.0
$SrAg_2SnSe_4$[9]	\	0.66	**$Ba4Cd_3Tb_2S_{10}$**[15]	\	~3.0
$Ba_6Ag_{3.92}Sn_{4.02}S_{16}$[1]	**8.72**	**1.58**	**$SrCu_2GeS_4$**[9]	\	2.49
$BaAg_2GeS_4$[9]	\	1.38	**$SrCu_2GeSe_4$**[9]	\	1.79
$BaAg_2GeSe_4$[9]	\	0.85	**$SrCu_2SnS_4$**[9]	\	1.73
$BaAg_2SnS_4$[9]	\	1.26	**$SrCu_2SnSe_4$**[9]	\	1.46
$BaAg_2SnSe_4$[9]	\	0.77	**$BaCu_2SnS_4$**[8]	**1.6**	**1.96**
Ba_2AgInS_4[10]	\	2.32	**$BaCu_2GeS_4$**[8]	**0.3**	**2.47**
$Ba_4AgGa_5Se_{12}$[10]	\	2.52	**$BaCu_2GeS_4$**[9]	\	2.46
$BaAgSbS_3$[11]	\	2.2	**$BaCu_2GeSe_4$**[9]	\	1.60
$Ba_2ZnGe_2S_6O$[2]	\	\	**$BaCu_2SnS_4$**[9]	\	1.74
$Ba_6Zn_6ZrS_{14}$[3]	\	\	**$BaCu_2SnSe_4$**[9]	\	1.50
$Ba_6Zn_7Ga_2S_{16}$[4]	**0.5**	**3.5**	**$BaCu_2SnSe_4$**[8]	**0.3**	**1.72**
$BaZnSnS_4$[5]	\	\	**$BaCu_2SiSe_4$**[8]	**0.3**	**2.62**
Ba_2ZnSe_3[12]	\	2.6	**$BaCu_2GeSe_4$**[8]	**0.3**	**1.88**
Ba_2ZnTe_3[12]	\	1.9	**$Ba_4CuGa_5S_{12}$**[13]	2.7	2.82
$BaCdSnS_4$[6]	**0.7**	**2.3**	**$Ba_4CuGa_5Se_{12}$**[13]	1.1	1.45
$Ba_3CdSn_2S_8$[6]	**0.1**	**2.75**	**$BaCuGdSe_3$**[14]	\	1.96
$BaCdSnSe_4$[7]	**1.6**	**1.79**			

Table S2. Atom coordinates and equivalent isotropic displacement parameters of **1** and **2**.

Atom	*x*	*y*	*z*	*U*eq(Å²)
		1		
Sn(1)	0.1255(1)	0.3627(1)	0.4413(1)	0.010(1)
Sn(2)	0.3748(1)	0.4313(1)	0.6509(1)	0.010(1)
Cd(1)	0.1241(1)	0.3881(1)	0.1900(1)	0.018(1)
Cd(2)	0.3751(1)	0.3247(1)	0.4676(1)	0.018(1)
Sr(1)	0.5000	0.5000	0.4407(3)	0.012(1)
Sr(2)	0	0.5000	0.4361(3)	0.012(1)
Sr(3)	0.2531(1)	0.4986(1)	0.4393(2)	0.013(1)
S(1)	0.3755(4)	0.5298(2)	0.5567(3)	0.009(1)
S(2)	0.3738(4)	0.4631(2)	0.8260(3)	0.012(1)
S(3)	0.2134(3)	0.3701(3)	0.3244(4)	0.014(1)
S(4)	0.4641(3)	0.3777(3)	0.5780(4)	0.013(1)
S(5)	0.0364(3)	0.3699(3)	0.3255(4)	0.013(1)
S(6)	0.2858(3)	0.3781(3)	0.5733(4)	0.012(1)
S(7)	0.1259(4)	0.4604(2)	0.5392(3)	0.011(1)
S(8)	0.3722(4)	0.2170(2)	0.5683(3)	0.014(1)
		2		
Sn(1)	0.43172(5)	0.62535(6)	0.68086(9)	0.0077(3)
Sn(2)	0.63604(6)	0.62535(5)	0.38879(8)	0.0082(3)
Cd(1)	.61248(7)	0.62379(6)	0.63869(10)	0.0161(3)
Cd(2)	0.57420(7)	0.62531(7)	0.10903(10)	0.0178(3)
Sr(1)	0.5000	0.5000	0.3946(2)	0.0111(6)
Sr(2)	0.49808(9)	0.74722(4)	0.89012(17)	0.0125(5)
Sr(3)	0.5000	0.5000	0.8894(2)	0.0121(6)
Se(1)	0.53179(7)	0.62407(9)	0.77674(13)	0.0104(5)
Se(2)	0.46415(7)	0.62689(9)	0.50333(14)	0.0095(4)
Se(3)	0.37739(8)	0.53398(8)	0.75432(16)	0.0113(5)

Se(4)	0.37776(7)	0.71549(8)	0.75763(17)	0.0108(5)
Se(5)	0.62920(8)	0.71469(8)	0.50739(16)	0.0114(5)
Se(6)	0.62941(8)	0.53484(8)	0.50432(16)	0.0110(5)
Se(7)	0.53693(7)	0.62544(9)	0.28946(13)	0.0084(5)
Se(8)	0.71635(7)	0.62697(9)	0.25803(14)	0.0109(4)

Table S3. Bond lengths [Å] in **1** and **2**.

1			
Sn(1)-S(8)#1	2.361(5)	Cd(1)-S(1)#2	2.454(4)
Sn(1)-S(3)	2.395(6)	Cd(1)-S(5)	2.577(6)
Sn(1)-S(5)	2.405(6)	Cd(1)-S(3)	2.592(6)
Sn(1)-S(7)	2.422(4)	Cd(1)-S(2)#3	2.601(4)
Sn(2)-S(4)	2.381(6)	Cd(2)-S(7)#4	2.446(4)
Sn(2)-S(2)	2.384(4)	Cd(2)-S(6)	2.580(6)
Sn(2)-S(6)	2.396(6)	Cd(2)-S(4)	2.606(7)
Sn(2)-S(1)	2.412(4)	Cd(2)-S(8)	2.623(4)
S(8)-Sn(1)#1	2.361(5)	S(1)-Cd(1)#12	2.454(4)
Cd(1)-S(1)#2	2.454(4)	S(2)-Cd(1)#13	2.601(4)
Cd(1)-S(5)	2.577(6)	S(7)-Cd(2)#11	2.446(4)

Symmetry transformations used to generate equivalent atoms:

#1 *–x* +1/2,-*y* +1/2,*z*	#2 *–x* +1/2,-*y* +1,*z* -1/2	#3 *x* -1/4,-*y* +3/4,*z* -3/4
#4 *x* +1/4,-*y* +3/4,*z* -1/4	#5 *–x* +1/4,*y* -1/4,*z* -1/4	#6 *–x* +1,-*y* +1,*z*
#7 *–x* +3/4,*y* +1/4,*z* -1/4	#8 -*x*,-*y* +1,*z*	#9 *x* -1/2,*y*,*z* -1/2
#10 *–x* +1/4,*y* +1/4,*z* +1/4	#11 *x* -1/4,-*y* +3/4,*z* +1/4	#12 *–x* +1/2,-*y* +1,*z* +1/2
#13 *x* +1/4,-*y* +3/4,*z* +3/4	#14 *x* +1/2,*y*,*z* +1/2	#15 *–x* +3/4,*y* -1/4,*z* +1/4

2			
Cd(1)-Se(13)	2.490(3)	Se(13)-Cd(2)#7	2.734(4)
Cd(1)-Se(15)	2.525(3)	Se(14)-Cd(4)#2	2.683(3)

Cd(1)-Se(4)	2.537(3)	Sn(4)-Se(17)	2.503(3)
Cd(1)-Se(18)	2.556(3)	Sn(4)-Se(9)	2.521(3)
Cd(2)-Se(18)	2.569(3)	Sn(4)-Se(16)	2.540(3)
Cd(2)-Se(6)#12	2.689(3)	Sn(4)-Se(10)	2.549(3)
Cd(2)-Se(5)#12	2.708(3)	Sn(1)-Se(1)	2.510(3)
Cd(2)-Se(13)#8	2.734(4)	Sn(1)-Se(6)	2.525(3)
Cd(3)-Se(2)	2.578(3)	Sn(1)-Se(5)	2.524(3)
Cd(3)-Se(9)	2.677(3)	Sn(1)-Se(11)	2.541(3)
Cd(3)-Se(16)	2.705(3)	Sn(2)-Se(12)	2.488(3)
Cd(3)-Se(12)#3	2.724(3)	Sn(2)-Se(14)	2.524(3)
Cd(3)-Sn(4)	3.3757(19)	Sn(2)-Se(8)	2.545(3)
Cd(4)-Se(10)	2.570(3)	Sn(2)-Se(2)	2.550(3)
Cd(4)-Se(14)#13	2.683(3)	Sn(3)-Se(11)	2.577(3)
Cd(4)-Se(8)#13	2.693(3)	Sn(3)-Se(15)	2.690(3)
Cd(4)-Se(17)#4	2.721(3)	Sn(3)-Se(4)	2.695(3)
Se(6)-Cd(2)#6	2.689(3)	Sn(3)-Se(1)#7	2.701(4)
Se(8)-Cd(4)#2	2.693(3)	Se(1)-Sn(3)#8	2.701(4)
Se(12)-Cd(3)#4	2.724(3)	Se(5)-Cd(2)#6	2.708(3)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,y+1/2,z+1/2	#2 x+1,-y+3/2,z+1/2	#3 x+0,-y+3/2,z-1/2
#4 x+0,-y+3/2,z+1/2	#5 x+1,y,z	#6 x+1/2,-y+1,z+1
#7 x+1/2,-y+1,z	#8 x-1/2,-y+1,z	#9 x,y,z+1
#10 x-1/2,y+1/2,z+1/2	#11 x-1/2,y-1/2,z-1/2	#12 x-1/2,-y+1,z-1
#13 x-1,-y+3/2,z-1/2	#14 x-1,y,z	#15 x+1/2,y-1/2,z-1/2
#16 x,y,z-1		

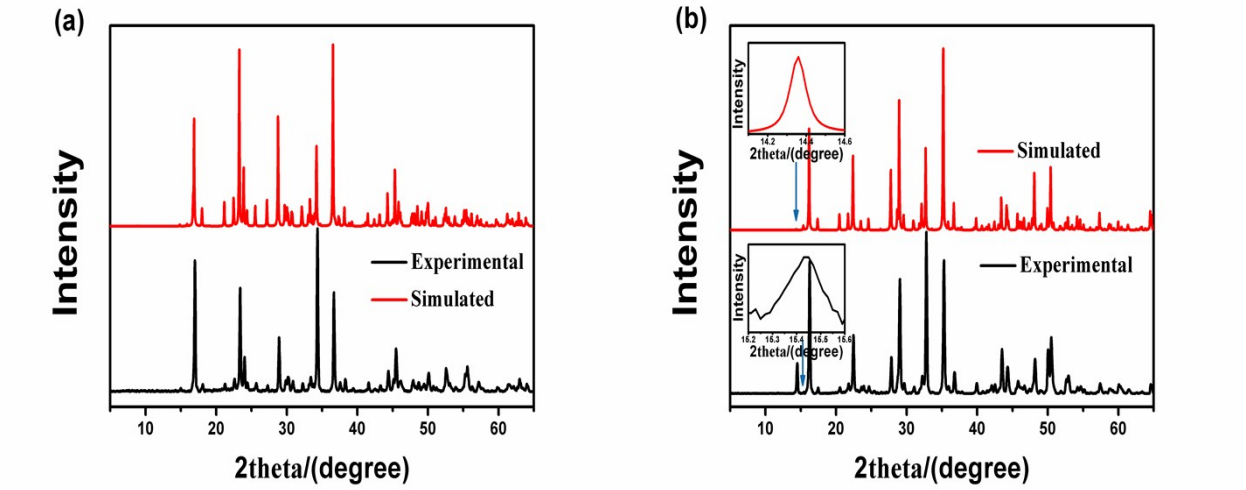

Figure S1. Experimental and simulated powder X-ray diffraction patterns of **1 (a)** and **2 (b)**.

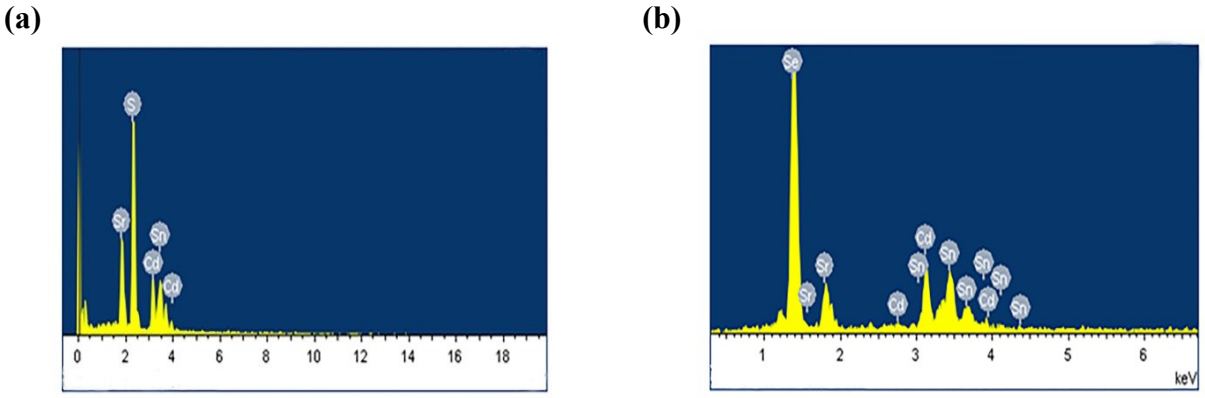

Figure S2. EDS spectra of single-crystals of **1 (a)** and **2 (b)**.

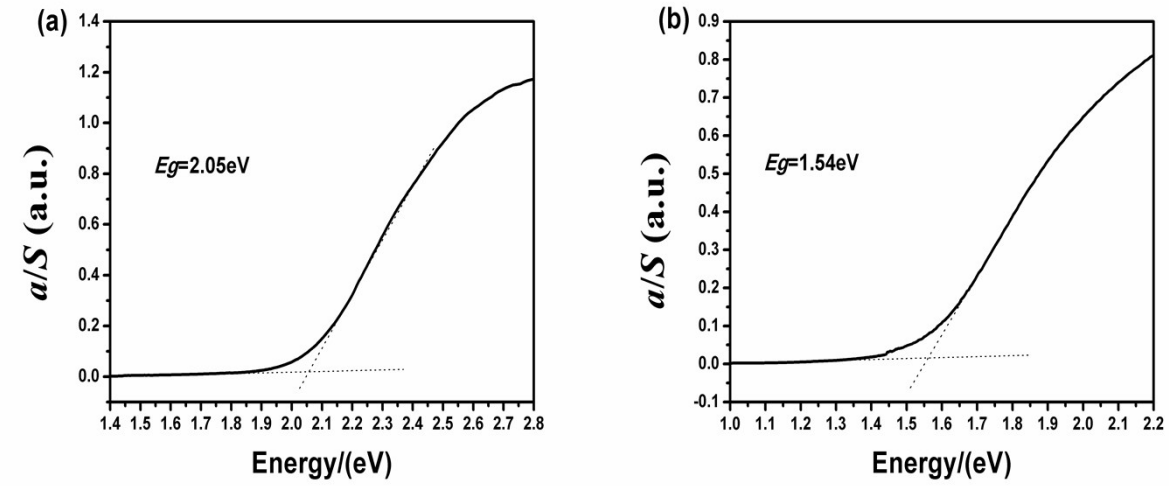

Figure S3. UV – Vis diffuse reflectance spectra of **1(a)** and **2 (b)**.

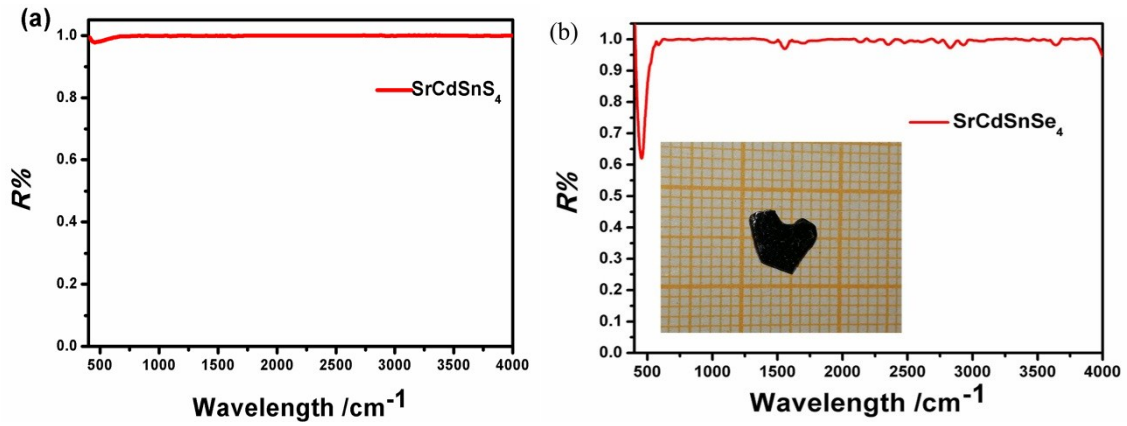

Figure S4. IR spectra of **1 (a)** and **2 (b)**. IR spectrum of **2** was measured using single crystal while that of **1** was measured using powder sample.

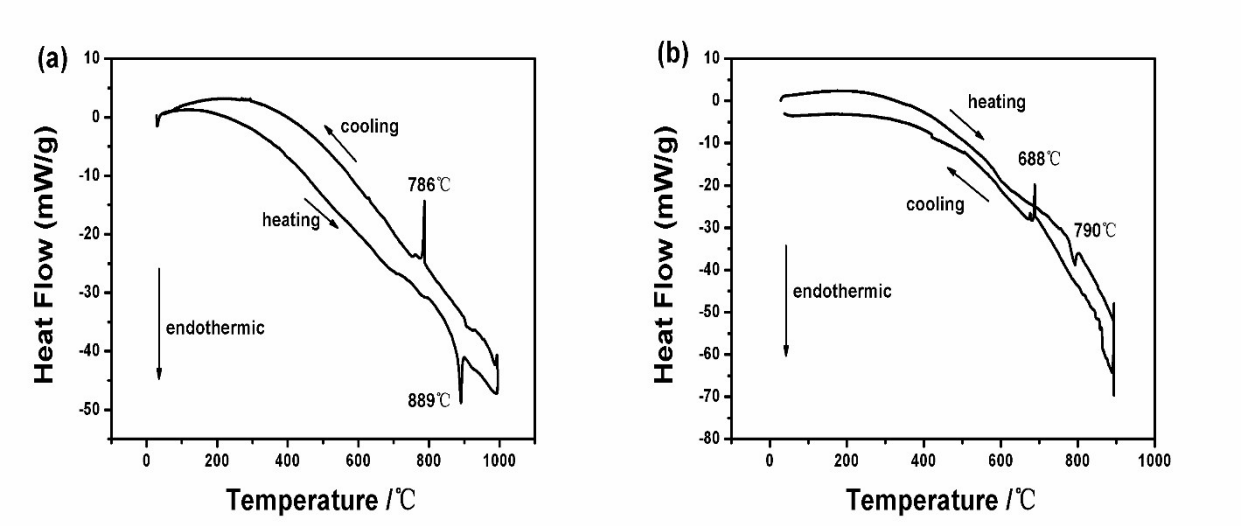

Figure S5. DSC curves of **1 (a)** and **2 (b)**.

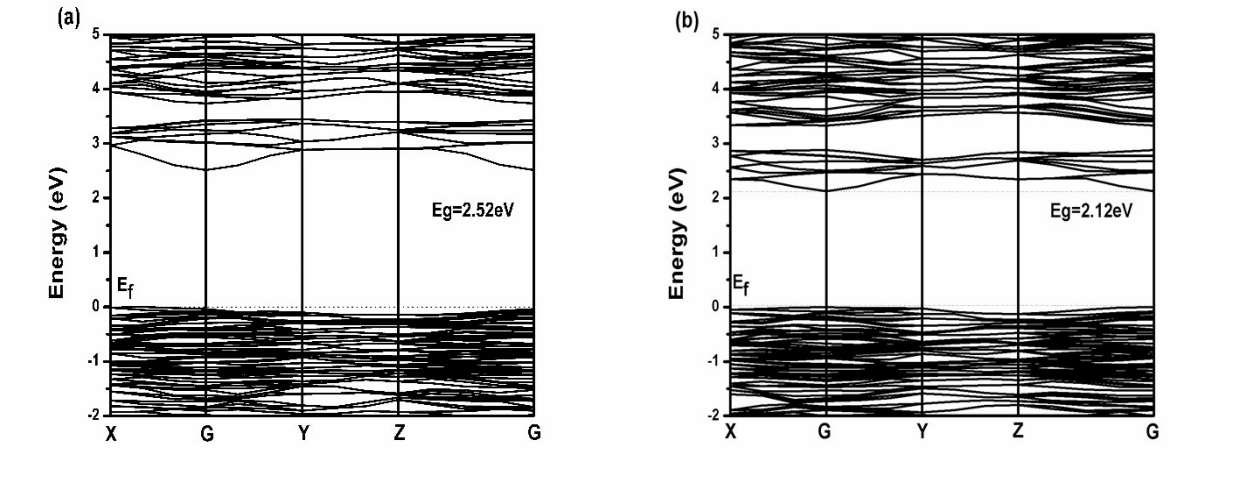

Figure S6. Band structures of **1 (a)** and **2 (b)**. The Fermi level is set at 0 eV for all of the band structures.

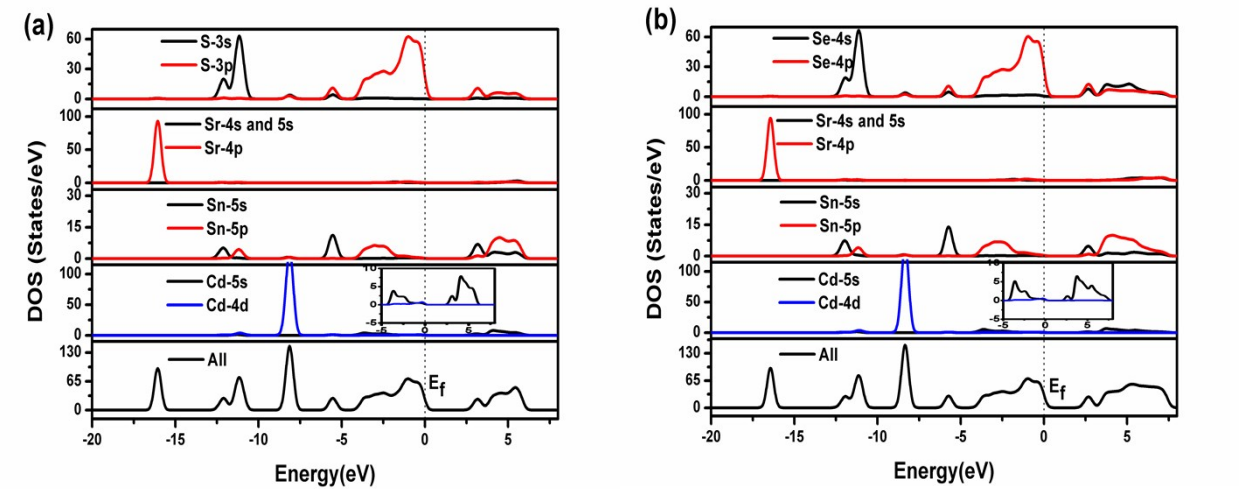

Figure S7. Total and partial DOSs of **1 (a)** and **2 (b)**. The Fermi level is set at 0 eV for all of the DOS.

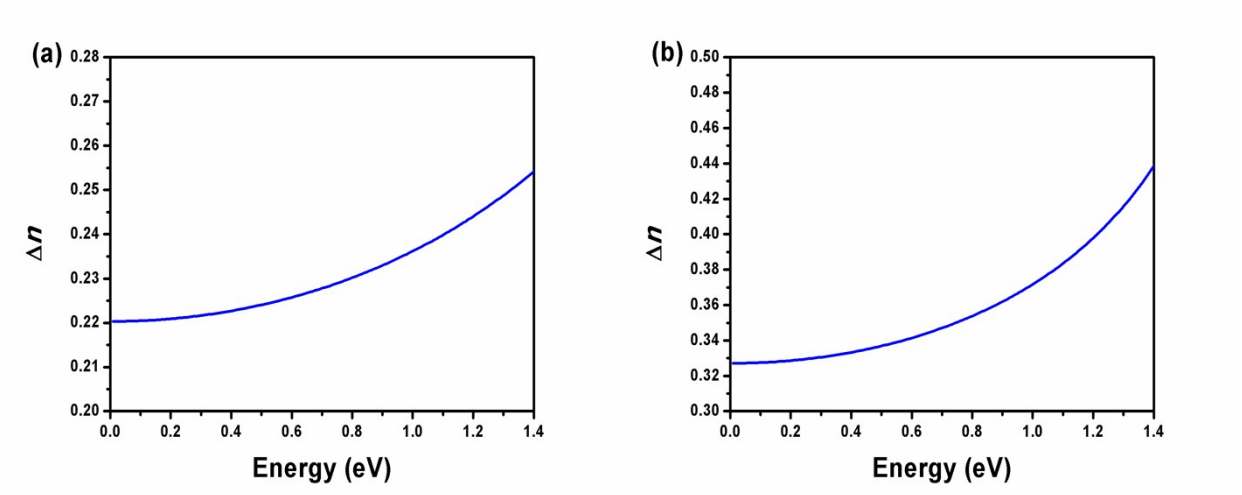

Figure S8. Calculated birefringence Δ*n* of **1 (a)** and **2 (b)**.

REFERENCES

1 W. H. Lai, A. S. Haynes, L. Frazer, Y. M. Chang, T. K. Liu, J. F. Lin, I. C. Liang, H. S. Sheu, J. B. Ketterson, M. G. Kanatzidis, K. F. Hsu, *Chem. Mater.*, 2015, **27,** 1316.

2 C. L. Teske, *Z. Naturforsch.*, 1980, **85b,** 672.

3 X. Zhang, J. Q. He, W. Chen, K. T. Zhang, C. Zheng, J. L. Sun, F. H. Liao, J. H. Lin, F. Q. Huang, *Chem. Eur. J.*, 2014, **20,** 5977.

4 Y. Y. Li, P. F. Liu, L. M. Wu, *Chem. Mater.*, 2017, **29,** 5259.

5 C. L. Teske, *Z. Naturforsch.*, 1980, **35b,** 509.

6 N. Zhen, K. Wu, Y. Wang, Q. Li, W. H. Gao, D. W. Hou, Z. H. Yang, H. D. Jiang, Y. J. Dong, S. L. Pan, *Dalton Trans.*, 2016, **45,** 10681.

7 K. Wu, X. Su, Z. H. Yang, S. L. Pan, *Dalton Trans.*, 2015, **44,** 19856.

8 L. Y. Nian, J. B. Huang, K. Wu, Z. Su, Z. H. Yang, S. L. Pan, *RSC Adv.*, 2017, **7,** 29378.

9 T. Zhu, W. P. Huhn, G. C. Wessler, D. Shin, B. Saparov, D. B. Mitzi, V. Blum, *Chem. Mater.*, 2017, **29,** 7868.

10 W. L. Yin, K. Feng, D. J. Mei, J. Y. Yao, P. Fu, Y. C. Wu, *Dalton Trans.* 2012, **41,** 2272.

11 C. Liu, Y. Y. Shen, P. P. Hou, M. J. Zhi, C. M. Zhou, W. X. Chai, J. W. Cheng, Y. Liu, *Inorg. Chem.*, 2015, **54 (18),** 8931.

12 J. Prakash, A. Mesbah, J. Beard, D. Rocca, S. Lebègue, C. D. Malliakas, J. A. Ibers, *Z. Naturforsch.*, 2016; **71(5)b,** 425.

13 S. M. Kuo, Y. M. Chang, I. Chung, J. I. Jang, B. H. Her, S. H. Yang, J. B. Ketterson, M. G. Kanatzidis, K. F. Hsu, *Chem. Mater.*, 2013, **25 (12),** 2427.

14 F. Q. Huang, K. Mitchell, J. A. Ibers, *Inorg. Chem.*, 2001, **40,** 20.

15 Y. T. Yang, J. A. Ibers, *J. Solid. State. Chem.*, 2000, **149,** 384.