Electronic Supplementary Information:

Synergism of Multiple Functional Chromophores Significantly Enhancing the Birefringence in Layered Non-Centrosymmetric Chalcohalide

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Contents

Figure S5 Electron localization function (ELF) of Hg_3AsS_4Cl (a), Hg_3AsS_4Br (b), Hg_3AsSe_4Br (c), and Hg_3AsSe_4I (d).

Figure S6 Calculated dielectric function of Hg_3AsS_4Cl (a), Hg_3AsS_4Br (b), Hg_3AsSe_4Br (c), and Hg_3AsSe_4I (d).

Figure S7 Calculated frequency-dependent SHG coefficients of $AgGaS_2$ ($\chi^{(2)}_{312} = 2d_{36}$) from sum-over-states (SOS) approximation by the *ab-initio* method.

Figure S8 SHG-density of occupied (left) and unoccupied (right) of Hg_3AsS_4Cl (a, b), Hg_3AsS_4Br (c, d), Hg_3AsSe_4Br (e, f), and Hg_3AsSe_4I (g, h) in the VE process.

Table S1 Materials with experimentally measured birefringence larger than 0.100 and visible transmittance, which are containing one and two functional chromophores.

Compounds	Space groups	Δ*n*	Band gap (eV)
One functional chromophore			
$NaNO_2$ [1]	*Im*2*m*	0.30	3.32
$Y_2C_{12}N_{12}O_{24}H_{30}$ [2]	*P*-1	0.274 (@ 3482 nm)	5.20
$Gd_2C_{12}N_{12}O_{24}H_{30}$ [2]	*P*-1	0.264 (@ 3874 nm)	5.29
TiO_2 [3]	$P4_2/mnm$	0.256 (@ 1530 nm)	3.10
$LaC_6N_6O_9H_9$ [2]	$P2_1/c$	0.233 (@ 1912 nm)	5.00
$TbVO_4$ [4]	$I4_1/amd$	0.22 (@ 1064 nm)	2.79
$RbNa(HC_3N_3O_3)\cdot 2H_2O$ [5]	$Pna2_1$	0.194 (@ 1922 nm)	5.10
$LiNa_5Mo_9O_{30}$ [6]	*Fdd*2	0.1935 (@ 1062.6 nm)	3.47
$KLi(HC_3N_3O_3)\cdot 2H_2O$ [7]	$Pna2_1$	0.186 (@ 514 nm)	5.23
$C_6H_7O_6Li\cdot H_2O$ [8]	$P2_12_12_1$	0.174□ (@ 1064 nm)	4.20
$CaCO_3$ [9]	*R*-3*c*	0.172 (@ 1064 nm)	5.39
$Sn_2B_5O_9Cl$ [10]	*Pnn*2	0.168 (@ 546 nm)	3.53
α-$LiIO_3$ [11]	*P*63	0.1401 (@ 1064 nm)	4~4.5
$KNbO_3$ [12]	*Amm*2	0.1323 (@ 1064 nm)	3.1□0
KIO_3 [13, 11b]	*R*3*m*	0.1276 (@ 1064 nm)	3~4.5
$Ca(BO_2)_2$ [14]	*Pbcn*	0.124 (@ 1064 nm)	7.34
$Ba_2Ca(B_3O_6)_2$ [15]	*R*-3	0.1241 (@ 589.3 nm)	6.97
$GdAl_3(BO_3)_4$ [16]	*R*32	0.12	7.09
$RbBaYB_6O_{12}$ [17]	*R*-3	0.120 (@ 589 nm)	6.36
$CsBaYB_6O_{12}$ [17]	*R*-3	0.120 (@ 589 nm)	6.39
α-BaB_2O_4 [9a]	*R*-3*c*	0.116 (@ 1064 nm)	6.56
$Na_3Ba_2(B_3O_6)_2F$ [18]	$P6_3/m$	0.1149 (@ 532 nm)	7.09
β-BaB_2O_4 [19, 11b]	*R*3*c*	0.1125 (@ 1064 nm)	7.00
$Te_2P_2O_9$ [20]	*Cc*	0.10615 (@ 1013.98 nm)	4.30
$KTiOAsO_4$ [19, 11b]	$Pna2_1$	0.106 (@ 1064 nm)	3.60
$KSrCO_3F$ [21]	*P*-6*m*2	0.1049 (@ 1064 nm)	6.36
$Ba_2Mg(BO_3)_2$ [22]	*R*-3*m*	0.10422 (@ 546 nm)	6.63
Two functional chromophores			
$Sb[NH_2CSNH_2]_2Br_3$ [23]	$Cmc2_1$	0.428 (@ 589.3 nm)	4.96□
SbB_3O_6 [24]	*C*2	0.290 (@ 546 nm)	3.95
α-$BaTeW_2O_9$ [25]	*Pnma*	0.247 (@ 404.7 nm)	3.42
β-$BaTeMo_2O_9$ [26]	$P2_1$	0.226 (@ 1068 nm)	3.10
$CdTeMoO_6$ [27]	$P\text{-}42_1m$	0.2222 (@ 1311 nm)	3.59
α-$BaTeMo_2O_9$ [28]	$Pca2_1$	0.20689 (@ 1064 nm)	3.12
α-BiB_3O_6 [29]	*C*2	0.1747 (@ 1064 nm)	4.32
$Cs_2TeW_3O_{12}$ [30]	$P6_3$	0.1648 (@ 1013.98 nm)	3.02
$Cs_2TeMo_3O_{12}$ [31]	$P6_3$	0.1476 (@ 1014 nm)	2.88
$Na_2TeW_2O_9$ [32]	*Cc*	0.1471 (@1062.6 nm)	3.47
YVO_4 [9a]	$I4_1/amd$	0.208 (@ 1064 nm)	3.1□0

Compounds	Space groups	Δ*n*	Band gap (eV)
$NH_4B_4O_6F$ [33]	*Pna*2$_1$	0.1171 (@ 1064 nm)	7.95
CsB_4O_6F [34]	*Pna*2$_1$	0.114 (@ 1064 nm)	8.00
$[Al(H_2O)_6](IO_3)_2(NO_3)$ [35]	*P*-3*m*1	0.253 (@ 546 nm)	4.00

Table S2 Calculated band gaps and experimental volumes of Hg_3AsQ_4X (Q = S, Se; X = Cl, Br, I).

Compounds	Band gap (eV)			Volume (Å^3)
	LDA	GGA	HSE06	
Hg_3AsS_4Cl	1.34	1.83	2.34	430.539
Hg_3AsS_4Br	1.42	1.84	2.44	447.682
Hg_3AsSe_4Br	1.24	1.77	2.02	487.034
Hg_3AsSe_4I	1.39	1.68	1.93	510.496

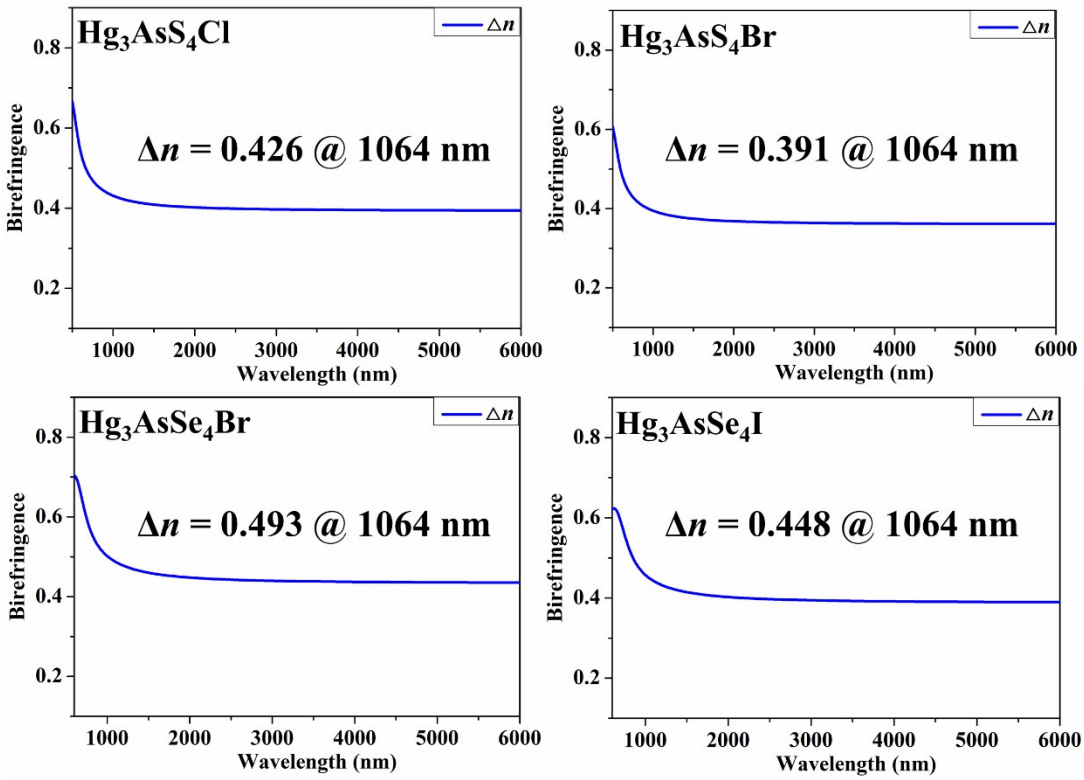


Figure S1 Calculated birefringence for Hg_3AsQ_4X (Q = S, Se; X = Cl, Br, I).

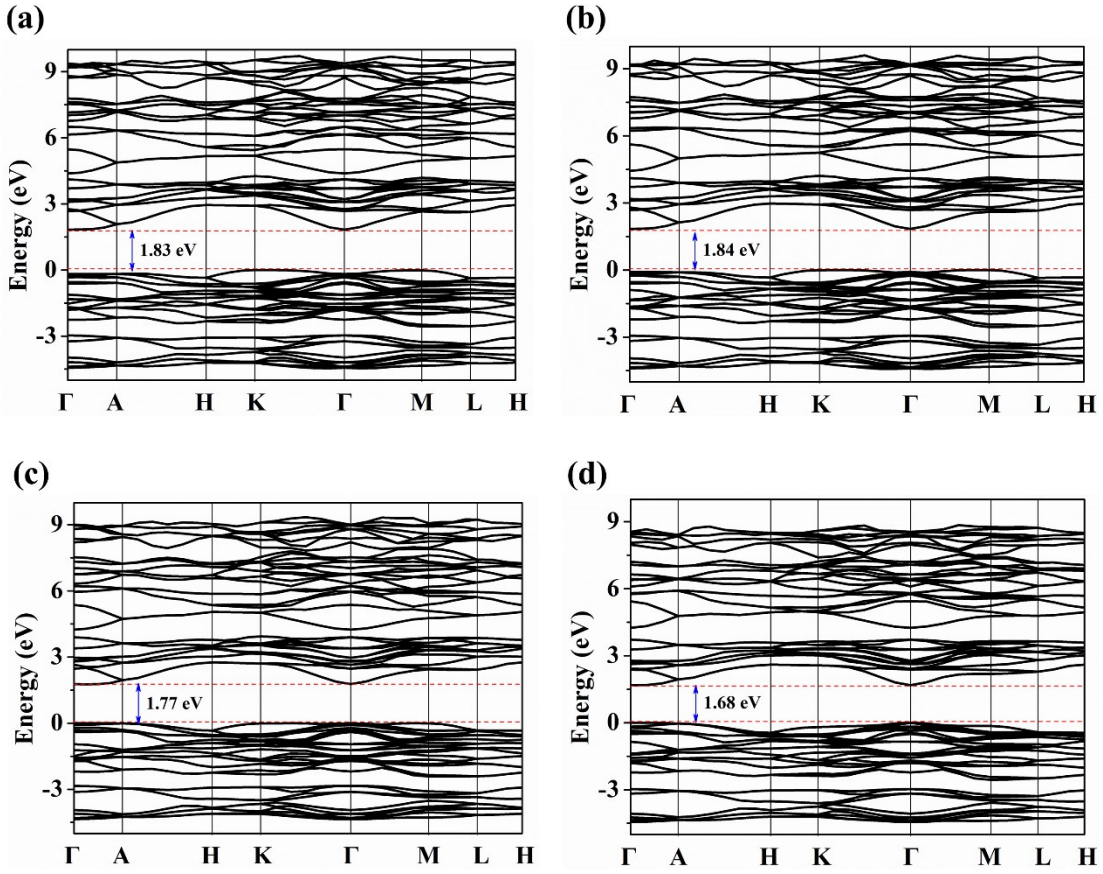


Figure S2 Calculated band gaps of Hg_3AsS_4Cl (a), Hg_3AsS_4Br (b), Hg_3AsSe_4Br (c), and Hg_3AsSe_4I (d) by the GGA functional.

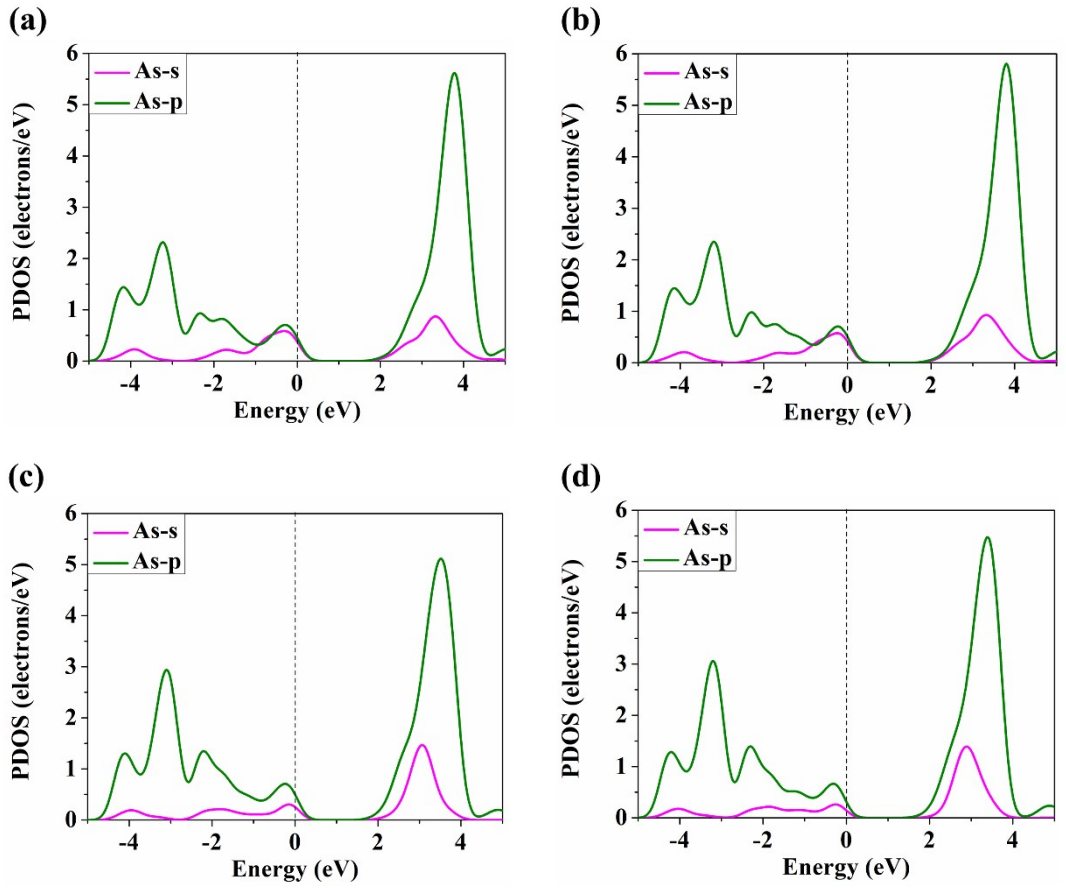


Figure S3 Partial density of states of As 4*s*4*p* orbitals of Hg_3AsS_4Cl (a), Hg_3AsS_4Br (b), Hg_3AsSe_4Br (c), and Hg_3AsSe_4I (d) by the GGA functional.

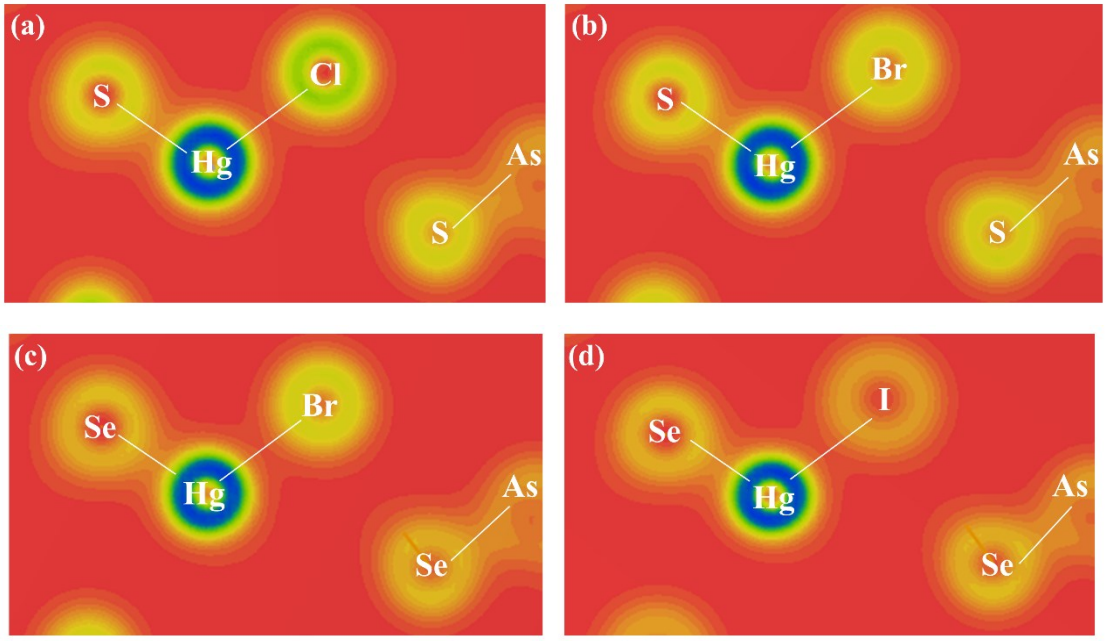
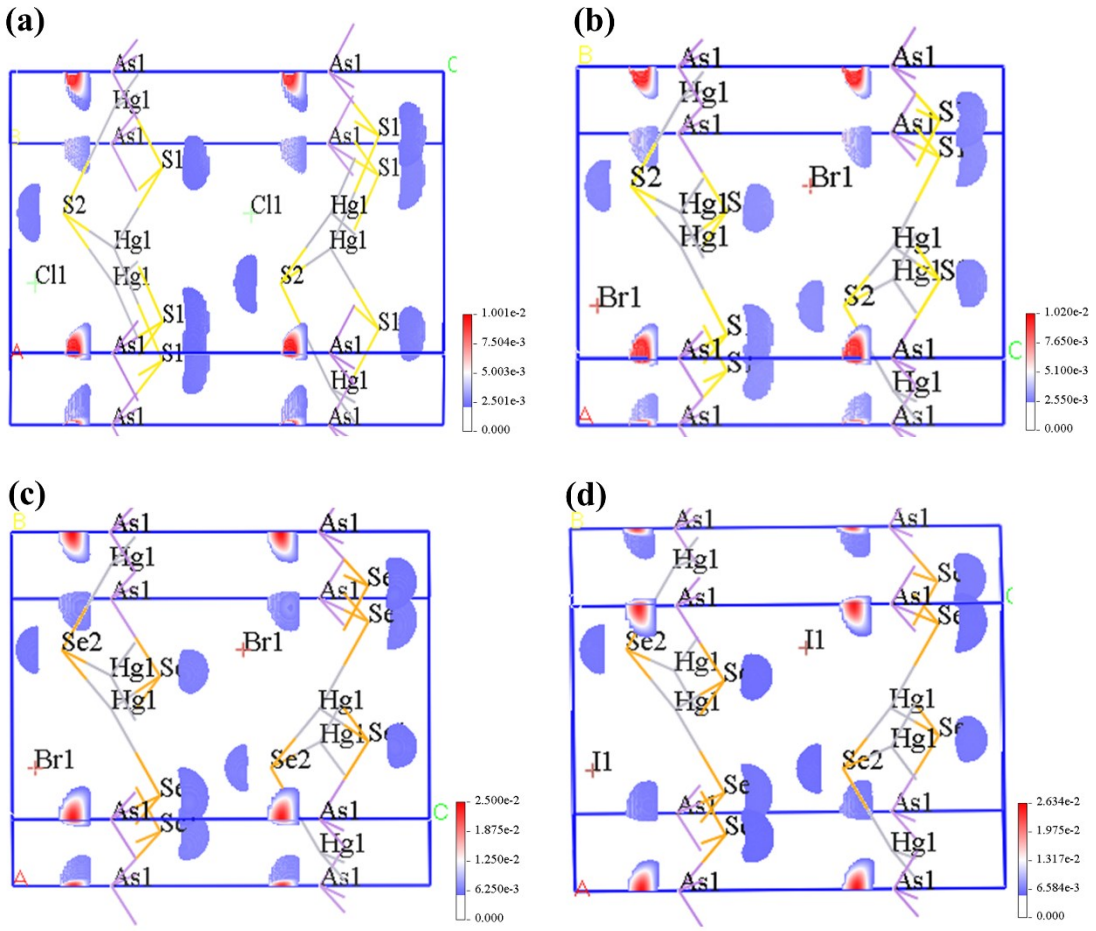


Figure S4 Calculated charge density of Hg_3AsS_4Cl (a), Hg_3AsS_4Br (b), Hg_3AsSe_4Br (c), and Hg_3AsSe_4I (d).



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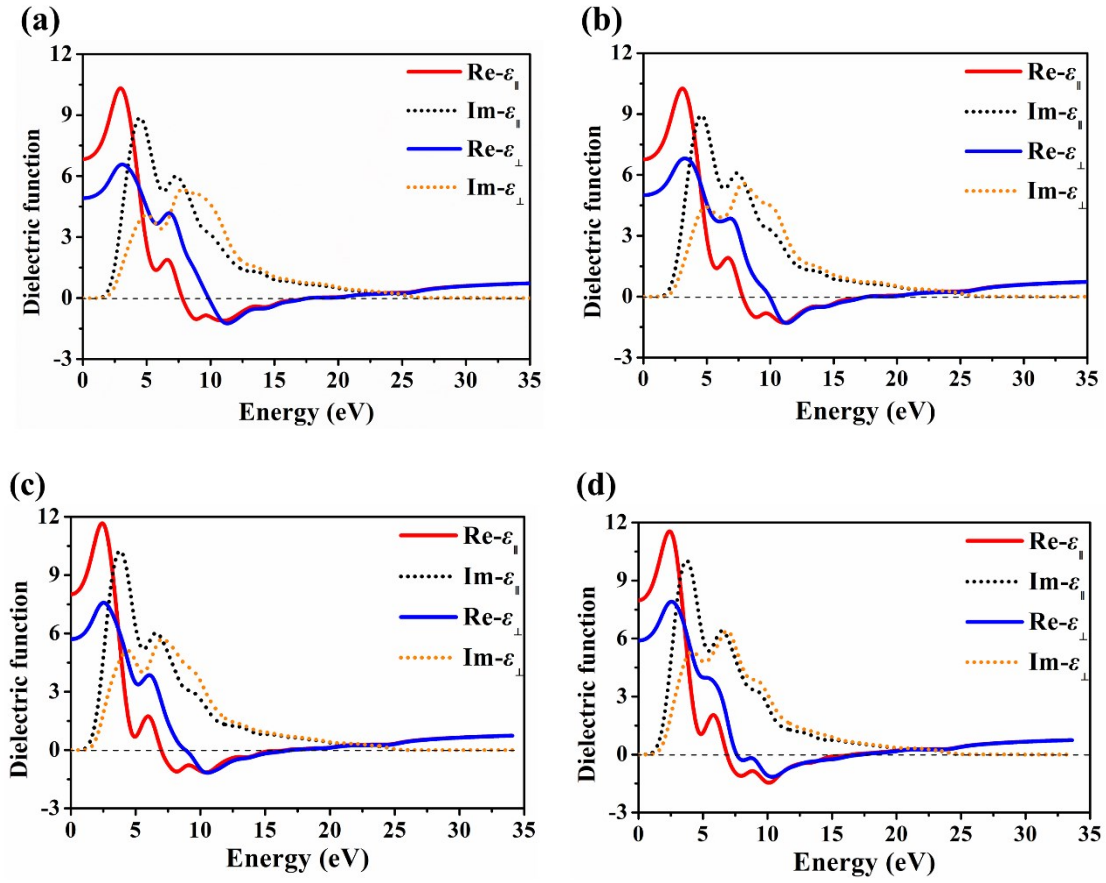
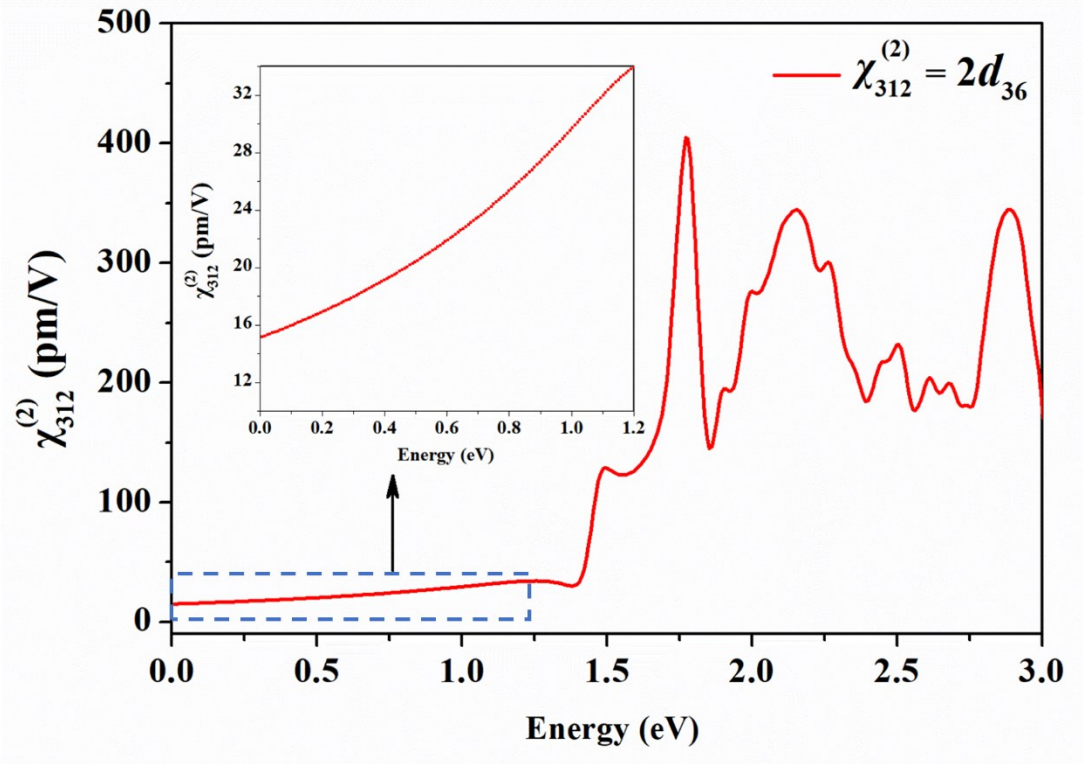


Figure S6 Calculated dielectric function of Hg_3AsS_4Cl (a), Hg_3AsS_4Br (b), Hg_3AsSe_4Br (c), and Hg_3AsSe_4I (d).



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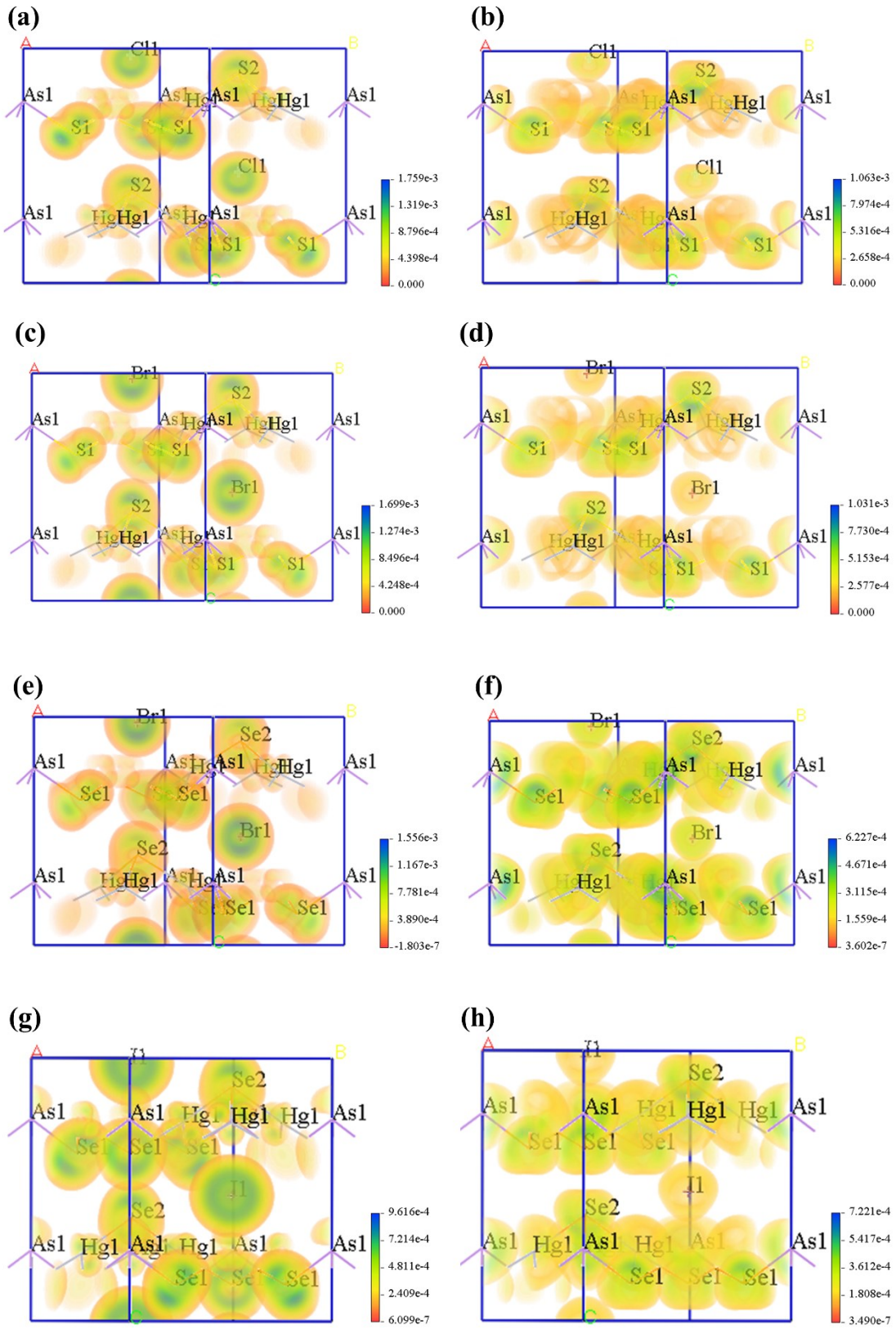

Figure S8 SHG-density of occupied (left) and unoccupied (right) of Hg_3AsS_4Cl (a, b), Hg_3AsS_4Br (c, d), Hg_3AsSe_4Br (e, f), and Hg_3AsSe_4I (g, h) in the VE process.

Reference

1 (a) K. C. Wu and C. T. Chen, *Appl. Phys. A*, 1992, **54,** 209-220. (b) K. C. Wu and C. T. Chen, *J. Cryst. Growth*, 1996, **166,** 533-536.

2 X. Hao, M. Luo, C. S. Lin, D. H. Lin, L. L. Cao and N. Ye, *Dalton Trans.*, 2019, **48,** 12296-12302.

3 J. R. Devore, *J. Opt. Soc. Am.*, 1951, **41,** 416-419.

4 Y. Y. Zhu, H. Tu, L. S. Jia, Y. C. Yue, Y. Zhao and Z. G. Hu, *Opt. Mater.*, 2017, **65,** 106-111.

5 Y. X. Song, D. H. Lin, M. Luo, C. S. Lin, Q. L. Chen and N. Ye, *Inorg. Chem. Front.*, 2020, **7,** 150-156.

6 W. G. Zhang, H. W. Yu, J. Cantwell, H. P. Wu, K. R. Poeppelmeier and P. S. Halasyamani, *Chem. Mater.*, 2016, **28,** 4483-4491.

7 D. H. Lin, M. Luo, C. S. Lin, F. Xu and N. Ye, *J. Am. Chem. Soc.*, 2019, **141,** 3390-3394.

8 K. R. Rao, C. Aneesh, H. L. Bhat, S. Elizabeth, M. S. Pavan and T. N. G. Row, *Cryst. Growth Des.*, 2013, **13,** 97-105.

9 (a) G. Q. Zhou, J. Xu, X. D. Chen, H. Y. Zhong, S. T. Wang, K. Xu, P. Z. Deng and F. X. Gan, *J. Cryst. Growth*, 1998, **191,** 517-519. (b) G. Ghosh, *Opt. Commun.*, 1999, **163,** 95-102.

10 J. Y. Guo, T. Abudukadi, S. J. Han, Z. H. Yang and S. L. Pan, *Angew. Chem. Int. Ed.*, 2019, **58,** 17675-17678.

11 (a) P. Hermet, *Comp. Mater. Sci.*, 2017, **138,** 199-203. (b) K. C. Zhang and X. M. Wang, Nonlinear Optics Crystal Materials Science. Science Press, 2006.

12 (a) T. Fukuda and Y. Uematsu, *Jpn. J. Appl. Phys.*, 1972, **11,** 163-169. (b) M. Sheik-Bahae and M. Ebrahimzadeh, *Opt. Commun.*, 1997, **142,** 294-298.

13 B. Erdinc and H. Akkus, *J. Phys.*: *Condens. Matter.*, 2009, **21,** 125503-125509.

14 X. L. Chen, B. B. Zhang, F. F. Zhang, Y. Wang, M. Zhang, Z. H. Yang, K. R. Poeppelmeier and S. L. Pan, *J. Am. Chem. Soc.*, 2018, **140,** 16311-16319.

15 Z. Jia, N. N. Zhang, Y. Y. Ma, L. W. Zhao, M. J. Xia and R. K. Li, *Cryst. Growth Des.*, 2017, **17,** 558-562.

16 Y. C. Yue, Y. Y. Zhu, Y. Zhao, H. Tu and Z. G. Hu, *Cryst.* Grow*th Des.*, 2016, **16,** 347-350.

17 X. L. Chen, F. F. Zhang, Y. J. Shi, Y. Z. Sun, Z. H. Yang and S. L. Pan, *Dalton Trans.*, 2018, **47,** 750-757.

18 H. Zhang, M. Zhang, S. L. Pan, Z. H. Yang, Z. Wang, Q. Bian, X. L. Hou, H. W. Yu, F. F. Zhang, K. Wu, F. Yang, Q. J. Peng, Z. Y. Xu, K. B. Chang and K. R. Poeppelmeier, *Cryst. Growth Des.*, 2015, **15,** 523-529.

19 H. P. Li, C. H. Kam, Y. L. Lam and W. Ji, *Opt. Mater.*, 2001, **15,** 237-242.

20 W. M. Dong, Q. Yao, J. Y. Zhang, L. T. Liu, J. Li and J. Y. Wang, *Cryst. Growth Des.*, 2018, **18,** 5919-5926.

21 W. G. Zhang and P. S. Halasyamani, *CrystEngComm.*, 2017, **19,** 4742-4748.

22 X. S. Lv, P. Wang, H. J. Yu, Y. Y. Hu, H. D. Zhang, C. C. Qiu, J. Li, X. P. Wang, B. Liu and Y. Y. Zhang, *Opt. Mater. Express*, 2019, **9,** 3835-3842.

23 N. Karthick, R. Sankar, R. Jayavel and S. Pandi, *J. Cryst. Growth*, 2009, **312,** 114-119.

24 Y. C. Liu, X. M. Liu, S. Liu, Q. R. Ding, Y. Q. Li, L. N. Li, S. G. Zhao, Z. S. Lin, J. H. Luo and M. C. Hong, *Angew. Chem. Int. Ed.*, 2020, **59,** 7793-7796.

25 Z. H. Zhang, X. T. Tao, J. J. Zhang, Y. X. Sun, C. Q. Zhang and B. Li, *CrystEngComm.*, 2013, **15,** 10197-10204.

26 W. G. Zhang, X. T. Tao, C. Q. Zhang, Z. L. Gao, Y. Z. Zhang, W. T. Yu, X. F. Cheng, X. S. Liu and M. H. Jiang, *Cryst*. *Growth Des*., 2008, **8,** 304-307.

27 C. G. Li, X. X. Tian, Z. L. Gao, Q. Wu, P. Zhao, Y. X. Sun, C. Q. Zhang, S. J. Zhang, D. L. Cui and X. T. Tao, *Cryst*. *Growth Des*., 2018, **18,** 3376-3384.

28 Z. L. Gao, Q. Wu, X. T. Liu, Y. X. Sun and X. T. Tao, *Opt*. *Express*, 2015, **23,** 3851-3860.

29 H. Hellwig, J. Liebertz and L. Bohatý, *J*. *Appl*. *Phys*., 2000, **88,** 240-244.

30 P. Zhao, Q. Wu, C. L. Li, S. J. Zhang, Y. X. Sun, C. Q. Zhang, S. Q. Xia, Z. L. Gao and X. T. Tao, *Opt*. *Mater*. *Express*, 2016, **6,** 451-458.

31 (a) J. J. Zhang, X. T. Tao, Y. X. Sun, Z. H. Zhang, C. Q. Zhang, Z. L. Gao, H. B. Xia and S. Q. Xia, *Cryst*. *Growth Des*., 2011, **11,** 1863-1868. (b) X. X. Feng, J. J. Zhang, Z. L. Gao, S. J. Zhang, Y. X. Sun and X. T. Tao, *Appl*. *Phys*. *Lett*., 2014, **104,** 081912-081915.

32 H. W. Yu, W. G. Zhang and P. S. Halasyamani, *Cryst*. *Growth Des*., 2016, **16,** 1081-1087.

33 G. Q. Shi, Y. Wang, F. F. Zhang, B. B. Zhang, Z. H. Yang, X. L. Hou, S. L. Pan and K. R. Poeppelmeier, *J*. *Am*. *Chem*. *Soc*., 2017, **139,** 10645-10648.

34 X. F. Wang, Y. Wang, B. B. Zhang, F. F. Zhang, Z. H. Yang and S. L. Pan, *Angew*. *Chem*. *Int*. *Ed*., 2017, **56,** 14119-14123.

35 Z. Y. Bai, C. L. Hu, D. M. Wang, L. H. Liu, L. Z. Zhang, Y. S. Huang, F. F. Yuan and Z. B. Lin, *Chem*. *Commun*., 2020, **56,** 11629-11632.