Supporting Information (SI)

$Hg_3O_2(NO_3)F$: A mercury nitrate oxyfluoride with unprecedented $[(Hg_3O_2F)^+]_\infty$ cationic framework and excellent optical anisotropy

Yi-Lei Lv, [a] Lei Huai, [a] Yu-Long Wei, [a] Liang Ma, [a] Yue-Qi Wei, [a] Wenlong Liu, [a] Ru-Ling Tang*[a,b]

a. School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu 225002, P. R. China.

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

Supporting Information Index

Tables and Figures

Table S1. Important bond lengths (Å) and bond angles (°) for $Hg_3O_2(NO_3)F$.

Bond Length(Å)			
Hg(1)－O(1)[1]	2.121(5)	Hg(2)－O(1)[5]	2.067(4)
Hg(1)－O(1)	2.121(5)	Hg(2)[3]－O(1)	2.067(4)
Hg(1)－F(1)	2.383(5)	Hg(1)[6]－F(1)	2.328(6)
Hg(1)－F(1)[4]	2.328(6)	N(1)－O(2)	1.253(11)
Hg(1)[1]－O(1)	2.121(5)	N(1)－O(3)	1.249(10)
Hg(1)[1]－F(1)	2.383(5)	N(1)－O(4)	1.254(9)
Bond Angles (deg)			
O(1)[1]－Hg(1)－O(1)	177.7(2)	F(1)[4]－Hg(1)－F(1)	133.47(13)
F(1)[4]－Hg(1)－O(1)	90.46(12)	O(1)－Hg(2)－O(1)[5]	169.52
F(1)－Hg(1)－O(1)	88.90(11)	O(2)－N(1)－O(4)	119.6(11)
F(1)－Hg(1)－O(1)[1]	88.90(11)	O(3)－N(1)－O(2)	120.2(12)
F(1)[4]－Hg(1)－O(1)[1]	90.46(12)	O(3)－N(1)－O(4)	120.1(12)

[1]+X,1/2-Y,+Z; [2]1/2-X,-1/2+Y,1/2+Z; [3]1/2-X,1-Y,1/2+Z; [4]1/2+X,+Y,3/2-Z; [5]1/2-X,1-Y,-1/2+Z; [6]-1/2+X,+Y,3/2-z

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for N $Hg_3O_2(NO_3)F$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

atom	Wyckoff site	*x*	*y*	*z*	U_{eq}[a]/Å^2
Hg(1)	4c	3676.6(4)	2500	6318.7(4)	10.51(12)
Hg(2)	8d	2701.8(4)	5096.5(2)	3832.9(3)	12.48(11)
O(1)	8d	3659(6)	4430(4)	6378(5)	10.9(10)
F(1)	4c	1745(7)	2500	9015(8)	19.6(13)
N(1)	8d	4557(10)	2488(12)	11280(9)	15.2(16)
O(2)	8d	4793(16)	1372(9)	11020(18)	28(3)
O(3)	8d	5201(16)	3243(11)	10139(15)	29(3)
O(4)	8d	3588(13)	2839(8)	12629(12)	29(3)

Table S3. The reported inorganic nitrate halides. ("—" means no concrete data)

	Compounds	Space group	Dimension	Birefringence
1	$Cs_2Pb(NO_3)_2Br_2$	$I4_1/amd$	1D	0.147@546 nm
2	$PbCdF(SeO_3)(NO_3)$	$Pca2_1$	2D	0.055@1064nm
3	$Pb_2(NO_3)_2(H_2O)F_2$	$Amm2$	3D	0.230@1064nm
4	$CsHgNO_3Cl_2$	$P6_3/mmc$	2D	0.145@546 nm
5	$Rb_2SbF_3(NO_3)_2$	$P2_1$	3D	0.06@1064nm
6	$RbSnF_2NO_3$	$C2/m$	3D	0.05@1064nm
7	$(NH_4)_3SbF_3(NO_3)_3$	$P2_1$	0D	0.098@546nm
8	$(NH_4)_3SbF_4(NO_3)_2$	$Pnma$	0D	0.164@546nm
9	$Na_3Rb_6(CO_3)_3(NO_3)_2Cl\cdot(H_2O)_6$	$P6_3/mcm$	3D	0.14 @ 546 nm
10	$Cs_2PbCl_2(NO_3)_2$	$I4_1/amd$	2D	——
11	$(NH_4)_2SiF_6\cdot NH_4NO_3$	$P6_3/mmc$	0D	——
12	$(NH_4)_2Sn_2F_4(NO_3)_2$	$C2$	0D	——
13	$[((NH_3)_5Co)_2O_2](NO_3)_2Cl_3\cdot 2H_2O$	$Pnnm$	0D	——
14	Ag_2ClNO_3	$Pnma$	3D	——
15	Ag_2INO_3	$P2_12_12_1$	3D	——
16	$CaClNO_3\cdot 2H_2O$	$Pbca$	2D	——
17	$HgINO_3$	$Pnma$	2D	——
18	$K_2SbF_3(NO_3)_2\cdot KNO_3$	$Cmc2_1$	3D	——
19	$NaSbF_3NO_3\cdot H_2O$	$Pbca$	2D	——
20	$Pb_3F_5NO_3$	$P\bar{1}$	2D	——
21	$Rb_3CoCl_4NO_3$	$Pnma$	3D	——
22	$Cs_3Sb_2F_6(NO_3)_3$	$C2/_C$	3D	——
23	$K_3Sb_2F_7(NO_3)_2$	$C2/_C$	3D	——
24	$K_4Sb_2F_6(NO_3)_3$	$Pbcn$	3D	——
25	$Rb_4Sb_2F_6(NO_3)_4$	$P2_1$	3D	——
26	$RbTeF_4(NO_3)$	$P1$	3D	——
27	$RbTeF_4(NO_3)$	$P\bar{1}$	3D	——
28	$Co(NH_3)_5NO_2Cl(NO_3)$	$Pna2_1$	0D	——
29	$KBiCl_3(NO_3)$	$P2_1/_C$	3D	——
30	$Ag_3I(NO_3)_2$	$P2_12_12_1$	3D	——
31	$Ag_2HgI_2(NO_3)_2\cdot H_2O$	$Pbam$	3D	——

32	$KSbF_3NO_3$	*Pbca*	2D	——
33	$(NH_4)_2(HF_2)(NO_3)$	$Pmc2_1$	0D	——
34	$K_3(HF_2)(NO_3)_2$	*Pbam*	0D	——
35	$Rb_3SbF_3(NO_3)_3$	$P2_1$	3D	——
36	$Cs_3MI_4NO_3$ (M = Zn, Co, Cd)	*Pnma*	3D	——
37	$K_3ZnCl_4NO_3$	*Pnma*	3D	——
38	$[(UO_2)_4F_{13}][Sr_3(H_2O)_8](NO_3)\cdot H_2O$	$P\bar{1}$	2D	——
39	$K_2TeF_5NO_3$	*P*4/*nmm*	3D	——
40	$K_2SiF_6\cdot KNO_3$	$P6_3/mmc$	2D	——
41	Cs_3 $((Sn_3F_6)_2H)$ $(NO_3)_4$	$P\bar{1}$	2D	——
42	$Cu_{36.6}Cl_{6.7}(NO_3)_{2.6}(OH)_{63.9}\cdot 2.1H_2O$	$P6_3/mmc$	3D	——
43	$(OsNO(NH_3)_4NO_3)Cl_2\cdot 0.5(H_2O)$	$C2/_C$	0D	——
44	$[Rb_2Cd(Cl)(NO_3)(C_2O_4)(H_2O)]$	*Pbca*	3D	——
45	Ag_2BrNO_3	*Pnma*	3D	——
46	$BrNO_3$	$P2_12_12_1$	0D	——

Table S4. The birefringence of some Hg-based compounds.

Compounds	Space group	Hg polyhedra	Birefringence
Ba_2HgTe_5	*Pnma*	$HgTe_2$	0.643@2090 nm
HgB_2S_4	$P2_1/n$	HgS_2	0.52@1064nm
HgS	$P3_221$	HgS_2	0.29@2100nm
$BaHgGeSe_4$	*Ama2*	$HgSe_4$	0.27@2090 nm
$EuHgGeS_4$	*Ama2*	HgS_4	0.25@2090 nm
$Cs_2HgI_2Cl_2$	$P2_1$	$HgCl_2I_2$	0.198@1064nm
$Hg_3(Te_3O_8)(SO_4)$	$P2_1/m$	HgO_5,HgO_7	0.166@1064nm
$BaHgSe_2$	$Pmc2_1$	$HgSe_3$, $HgSe_2$	0.1473@2090 nm
$CsHgNO_3Cl_2$	$P6_3/mmc$	HgO_6Cl_2	0.145@546 nm
$CsHgClSO_4{\cdot}H_2O$	*Pmmn*	HgO_5Cl	0.12@546 nm
$Hg_3(SeO_3)_2(SO_4)$	$P2_1$	HgO_5,HgO_7,HgO_8	0.118@546 nm
$CuHgPS_4$	$Pna2_1$	HgS_4	0.11@2090 nm
$AgHgPS_4$	*Pn*	HgS_4	0.11@2090 nm
$Hg_3O_2SO_4$	$P3_221$	HgO_6	0.10@546 nm
$HgTeO_2F(OH)$	$Pca2_1$	HgO_2	0.09@1064 nm
$BaHgS_2$	$Pmc2_1$	HgS_4, HgS_2	0.07@2090 nm
$LiHgPO_4$	$P\bar{4}21m$	HgO_6	0.068@1064 nm
$Hg_3P_2S_8$	*Aba2*	HgS_4	0.05@2090 nm

Figure S1. The crystal structure of $Hg_3O_2(NO_3)_2$.

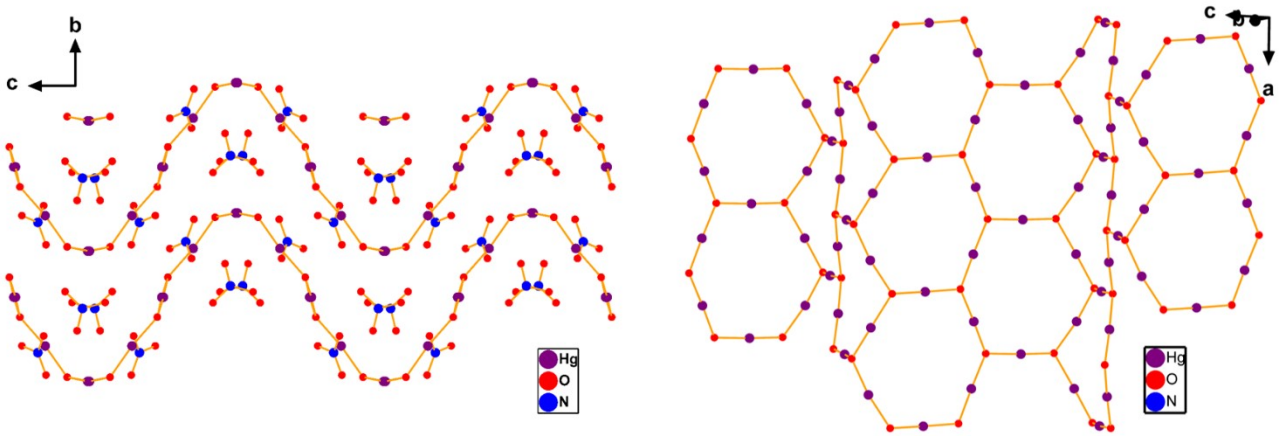
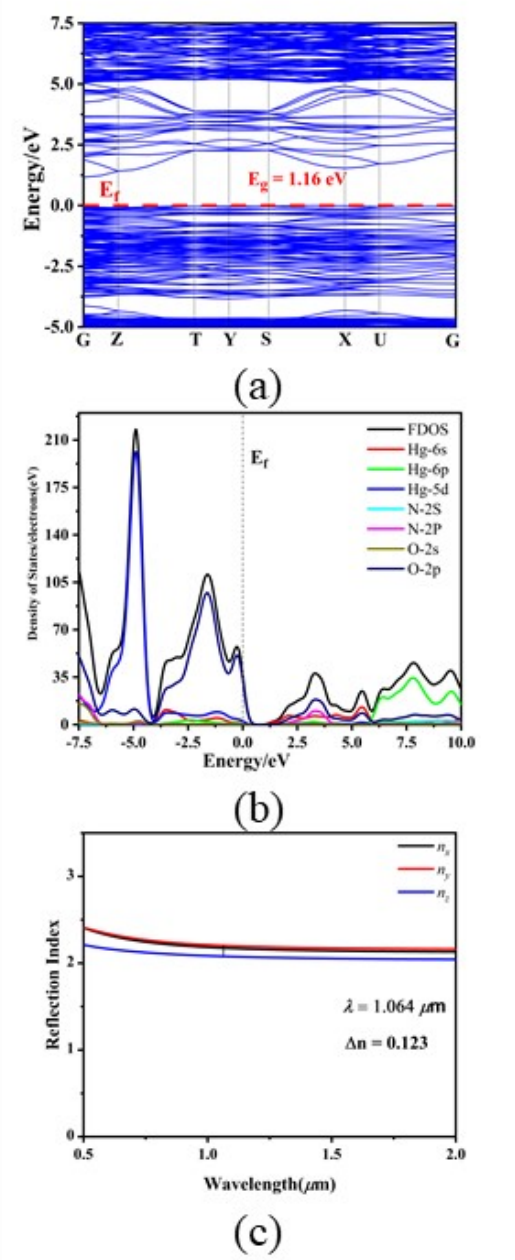
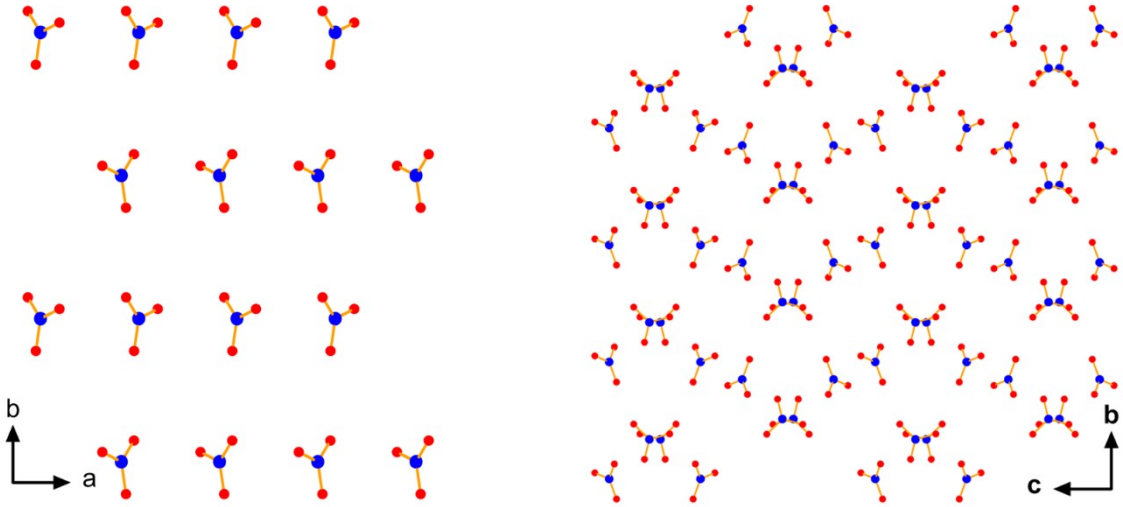


Figure S2. Theoretical calculations of $Hg_3O_2(NO_3)_2$.



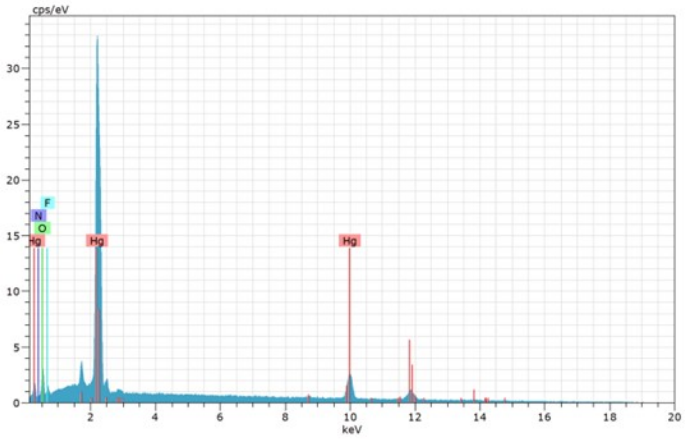
(a) Calculated band gap; (b) Density of states (DOS). the fermi level is set at 0 eV; and (c) Calculated refractive index dispersion curves of $Hg_3O_2(NO_3)_2$.

Figure S3. The arrangement of NO_3 groups in $Hg_3O_2(NO_3)F$ (a) and $Hg_3O_2(NO_3)_2$ (b).



(a) (b)

Figure S4. EDS images and results of $Hg_3O_2(NO_3)F$.



The molar ratio of Hg : O : N : F from the EDS results.

Compound		**Molar ratio**
1	Hg : O : N : F	29.89 : 49.93 : 10.05 : 10.13=2.97 : 4.97 : 1 : 1
2	Hg : O : N : F	29.97 : 50.10 : 9.93 : 10=3.01 : 5.04 : 1 : 1
3	Hg : O : N : F	30.08 : 49.94 : 9.89 : 10.09=3.04 : 5.04 : 1 : 1.02

References:

1. M. K. Kim, V. Jo and K. M. Ok, New variant of highly symmetric layered perovskite with coordinated NO_3^- ligand: hydrothermal synthesis, structure, and characterization of $Cs_2PbCl_2(NO_3)_2$, *Inorg. Chem.*, 2009, **48**, 7368–7372.
2. Leclaire, M. M. Borel, Identification et Structure du Chlorure Nitrate de Calcium Dihydrate, *Acta Cryst*, 1978, **34**, 902–904.
3. L. J. Jouffret, J. M. Hiltbrunner, M. Rivenet, N. Sergent, S. Obbade, D. Avignant, and M. Dubois, L. J. Jouffret, J. M. Hiltbrunner, M. Rivenet, N. Sergent, Saïd Obbade, *Inorg. Chem.*, 2016, **55**, 12185−12192.
4. R. Vaidhyanathan, S. Natarajan, and C. N. R. Rao, Open-Framework Rubidium Halides Incorporated in Cadmium Oxalate Host Lattices, *J. Solid State Chem.*, 2002, **167**, 274–281.
5. M. Bourgault, B. Ducourant, D. Mascherpa-corral et R. Fourcade, Structure cristalline et moleculaire de $KSbF_3NO_3$, *J. Fluorine Chem.*, 1981, **17,** 215–224.
6. R. Ouarsal, M. Lachkar, M. Bolte and B. El Bali, Trirubidium cobalt tetrachloride nitrate(V), $Rb_3CoCl_4NO_3$, *Acta Crystallogr. E Structure Report*, 2005, **61**, i44–i45.
7. Leclaire and M. M. Borel, Identification et structure du chlorure nitrate de calcium dihydraté, *Acta Cryst. B Structural Crystallography and Crystal Chemistry*, 1978, **34**, 902–904.
8. S. Farhadi and J. Safabakhsh, Solid-state thermal decomposition of the $[Co(NH_3)_5CO_3]NO_3{\cdot}0.5H_2O$ complex: A simple, rapid and low-temperature synthetic route to Co_3O_4 nanoparticles, *J. Alloys Compd.*, 2012, **515**, 180–185.
9. M. Cheng, W. Q. Jin, Z. H. Yang and S. L. Pan, Large optical anisotropy-oriented construction of a carbonate-nitrate chloride compound as a potential ultraviolet birefringent material, *Chem. Sci.*, 2022, **13**, 13482–13488.
10. Z. Chen, H. Zeng, S. J. Han, Z. H. Yang and S. L. Pan, From $BaCl_2$ to $Ba(NO_3)Cl$: significantly enhanced birefringence derived from π-conjugated $[NO_3]$, *New J. Chem.*, 2021, **45**, 17544–17550.
11. V. M. Miskowski, B. D. Szntarsiero, W. P. Schaefer, G. E. Ansok, and H. B. Gray, Crystal Structure and Polarized Electronic Spectra of a (u-Superoxo) dicobalt(III) Complex: $[((NH_3)_5Co)_2O_2](NO_3)_2Cl_3{\cdot}2H_2O$, *lnorg. Chem.*, 1984, **23**, 172–176.
12. D. T. Tran, P. Y. Zavalij, S. R. J. Oliver, $Pb_3F_5NO_3$, a Cationic Layered Material for Anion-Exchange, *J. Am. Chem. Soc,* 2002, **124**, 3966–3969.
13. M. Bourgault, B. Ducourant, D. M. Corral, R. Fourcade, Structure Cristalline de $NaSbF_3NO_3{\cdot}H_2O$. Etude de La Liaison Hydrogene O-H-X (X=Cl, Br, NO_3), *J. Fluorine Chem.*, 1981, **17**, 305–315.
14. M. Bourgault, B. Ducourant, R. Fourcade, Sur un nouveau compose doubleur de frequence, synthese, et structure du nitrate-bis-nitratotrifluoroantimonate de potassium $K_2SbF_3(NO_3)_2{\cdot}KNO_3$, *J. Solid-State Chem.*, 1983, **50**, 79–85.
15. K. Persson, The Crystal Structure of Ag_2INO_3, *Acta Cryst*, 1979, **35**, 302–306.
16. K. Persson, Structure of Disilver Chloride Nitrate, *Acta Cryst*, 1979, **35**, 1432–1435.
17. N. Buchholz, R. Mattes, The Double Sale $(NH_4)_2SiF_6{\cdot}NH_4NO_3$, *Mat. Res. Bull,* 1988**, 23**, 755–758.
18. G. Peng, Y. Yang, Y. H. Tang, M. Luo, T. Yan, Y. Q. Zhou, C. S. Lin, Z. S. Lin and N. Ye, Collaborative enhancement from Pb^{2+} and F^- in $Pb_2(NO_3)_2(H_2O)F_2$ generates the largest second harmonic generation effect among nitrates, *Chem Commun.*, 2017, **53**, 9398–9401.
19. L. Wang, H. M. Wang, D. Zhang, D. J. Gao, J. Bi, L. Huang and G. H. Zou, Centrosymmetric $RbSnF_2NO_3$. noncentrosymmetric $Rb_2SbF_3(NO_3)_2$, *Inorg. Chem. Front.*, 2021, **8**, 3317–3324.
20. L. Wang, F. Yang, X. Y. Zhao, L. Huang, D. J. Gao, J. Bi, X. Wang and G. H. Zou, $Rb_3SbF_3(NO_3)_3$: an excellent antimony nitrate nonlinear optical material with a strong second harmonic generation response

fabricated by a rational multi-component design, *Dalton Trans.*, 2019, **48**, 15144–15150.
21. Y. Long, X. H. Dong, H. M. Zeng, Z. Lin and G. H. Zou, Layered Perovskite-like Nitrate $Cs_2Pb(NO_3)_2Br_2$ as a Multifunctional Optical Material, *Inorg. Chem.*, 2022, **61**, 4184–4192.
Y. V. Kokunov, D. G. Detkov, Y. E. Gorbunova, M. M. Ershova, Y. N. Mikhailov, and Academician Yu. A. Buslaev, Crystal Structure of $(NH_4)_2Sn_2F_4(NO_3)_2$: The First Example of Dimeric $[Sn_2F_4E_2]$ Complexes in Tin(II) Fluorides, *Dokl. Chem.*, 2001, **378**, 135–138.
22. K. Penneth, B. Holmbeerg, Structure of Mercury Disilver Diiodide Dinitrate Monohydrate, *Acta Cryst*, 1982, **38**, 904–907.
23. M. L. Zhou, Y. Yang, Y. W. Guo, Z. S. Lin, J. Y. Yao, Y. C. Wu and C. T. Chen, Hg-Based Infrared Nonlinear Optical Material KHg4Ga5Se12 Exhibits Good Phase-Matchability and Exceptional Second Harmonic Generation Response, *Chem. Mater.*, 2017, **29**, 7993−8002.
24. M. Yan, Z. D. Sun, W. D. Yao, W. Zhou, W. L. Liu and S. P. Guo, A highly distorted HgS_4 tetrahedron-induced moderate second-harmonic generation response of $EuHgGeS_4$, *Inorg. Chem. Front.*, 2020, **7**, 2451−2458.
25. W. H. Xing, N. Z. Wang, C. L. Tang, C. X. Li, Z. S. Lin, J. Y. Yao, W. L. Yin and B. Kang, From $AgGaS_2$ to $AgHgPS_4$: vacancy defects and highly distorted HgS_4 tetrahedra double-induced remarkable second-harmonic generation response, *J. Mater. Chem. C*, 2021, **9**, 1062−1068.
26. K. Wu, X. Su, S. L. Pan and Z. H. Yang, Synthesis and characterization of mid-infrared transparency compounds: acentric $BaHgS_2$ and centric $Ba_8Hg_4S_5Se_7$, *Inorg. Chem.*, 2015, **54**, 2772−2779.
27. B. L. Wu, C. L. Hu, F. F. Mao, R. L. Tang and J. G. Mao, Highly Polarizable Hg^{2+} Induced a Strong Second Harmonic Generation Signal and Large Birefringence in $LiHgPO_4$, *J. Am. Chem. Soc.*, 2019, **141**, 10188−10192.
28. C. Li, W. L. Yin, P. F. Gong, X. S. Li, M. L. Zhou, A. Mar, Z. S. Lin, J. Y. Yao, Y. C. Wu and C. T. Chen, Trigonal Planar $[HgSe_3]^{4-}$ Unit: A New Kind of Basic Functional Group in IR Nonlinear Optical Materials with Large Susceptibility and Physicochemical Stability, *J. Am. Chem. Soc.*, 2016, **138**, 6135−6138.
29. Y. Huang, Y. Zhang, D. D. Chu, Z. H. Yang, G. M. Li and S. L. Pan, HgB_2S_4: A d^{10} Metal Thioborate with Giant Birefringence and Wide Band Gap, *Chem. Mater.*, 2023, **35**, 4556−4563.
30. Y. W. Guo, F. Liang, W. L. Yin, Z. Li, X. Y. Luo, Z. S. Lin, J. Y. Yao, A. Mar and Y. C. Wu, $BaHgGeSe_4$ and $SrHgGeSe_4$: Two New Hg-Based Infrared Nonlinear Optical Materials, *Chem. Mater.*, 2019, **31**, 3034−3040.
31. M. R. Sun and J. Y. Yao, Ba_2HgTe_5: a Hg-based telluride with giant birefringence induced by linear $[HgTe_2]$ units, *Inorg. Chem. Front.*, 2022, **9**, 5024−5031.
32. W. Carrillo-Cabrera , F. Menzel , W. Brockner, Crystal structure of copper mercury tetrathiophosphate, $CuHgPS_4$**,** *Z. Krist. Cryst. Mater.*, 1992, **202**, 152−153.
33. G. Zhang, Y. J. Li, K. Jiang, H. Y. Zeng, T. Liu, X. G. Chen, J. G. Qin, Z. S. Lin, P. Z. Fu, Y. C. Wu and C. T. Chen, A new mixed halide, $Cs_2HgI_2Cl_2$: molecular engineering for a new nonlinear optical material in the infrared region, *J. Am. Chem. Soc.*, 2012, **134**, 14818−14822.
34. X. H. Dong, L. Huang, H. M. Zeng, Z. Lin, K. M. Ok and G. H. Zou, High-Performance Sulfate Optical Materials Exhibiting Giant Second Harmonic Generation and Large Birefringence, *Angew. Chem., Int. Ed.*, 2022, **61**, e202116790.
35. P. F. Li, C. L. Hu, Y. P. Gong, F. Kong and J. G. Mao, $Hg_3(Te_3O_8)(SO_4)$: a new sulfate tellurite with a novel structure and large birefringence explored from d^{10} metal compounds, *Chem. Commun*, 2021, **57**, 7039−7042.