Supporting Information for

Broadening Frontiers of Infrared Nonlinear Optical Materials with π–Conjugated Trigonal Planar Groups

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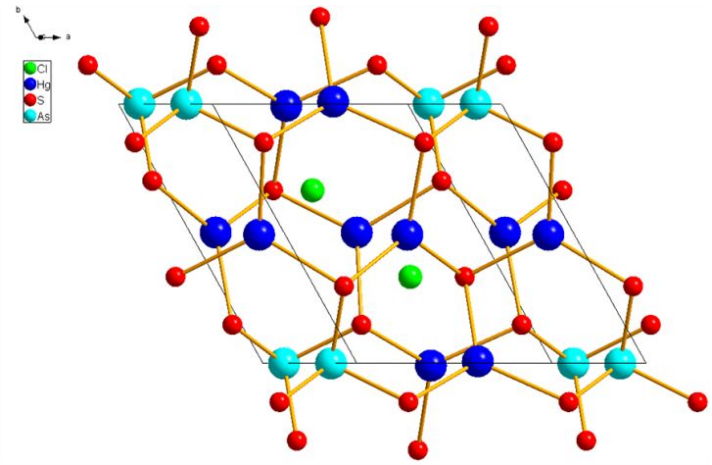

Figure S1. Crystal structure of Hg_3AsS_4Cl.

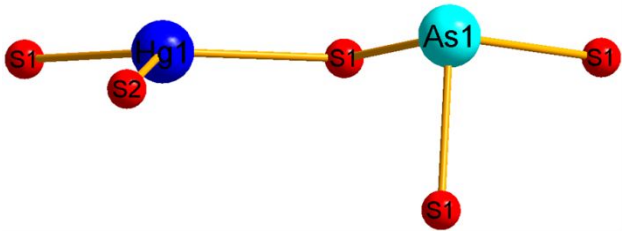

Figure S2. Coordination environment of Hg^{2+} and As^{3+} in Hg_3AsS_4Cl.

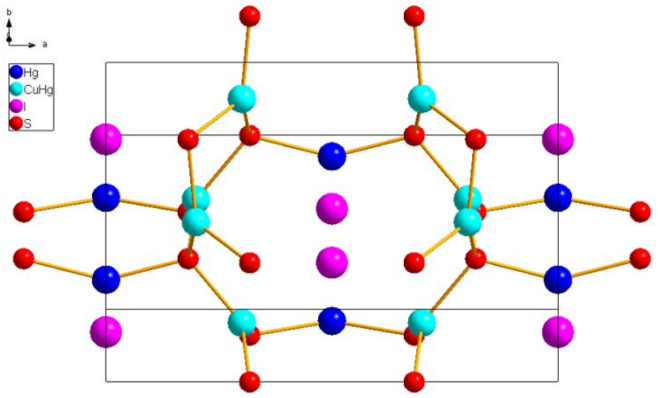

Figure S3. Crystal structure of $CuHg_2S_2I$.

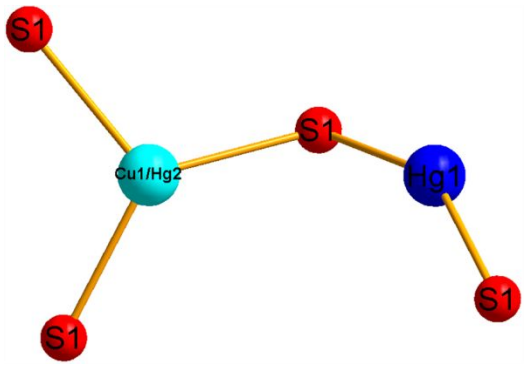

Figure S4. Coordination environment of $Cu1^{+}/Hg2^{2+}$ and $Hg1^{2+}$ in $CuHg_2S_2I$.

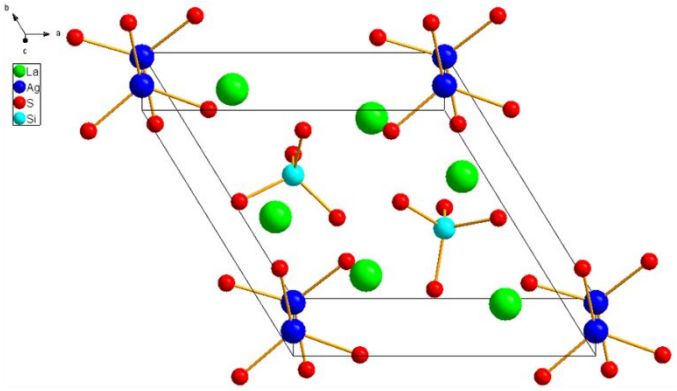

Figure S5. Crystal structure of La_3AgSiS_7.

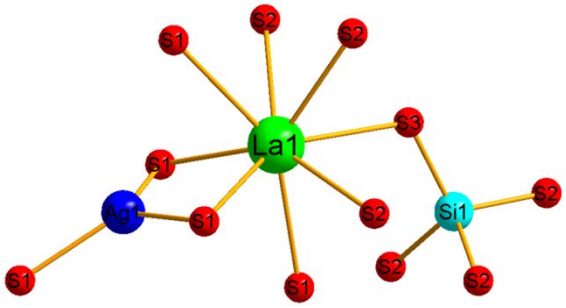

Figure S6. Coordination environment of Ag^{+}, La^{3+} and Si^{4+} in La_3AgSiS_7.

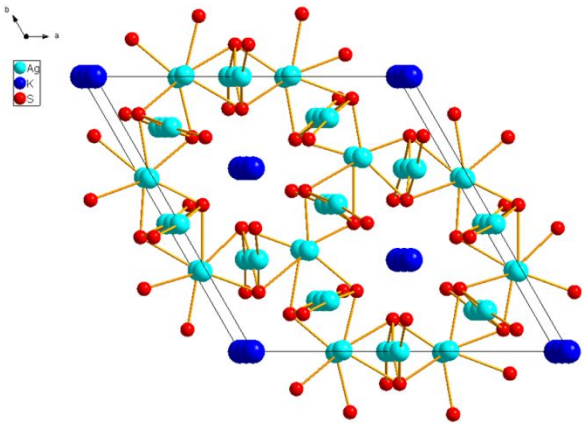

Figure S7. Crystal structure of KAg_5S_3.

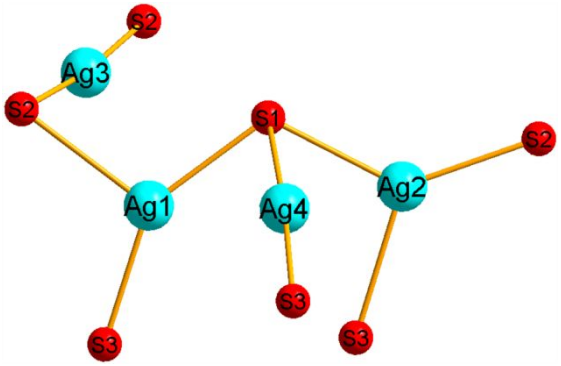

Figure S8. Coordination environment of Ag^+ in KAg_5S_3.

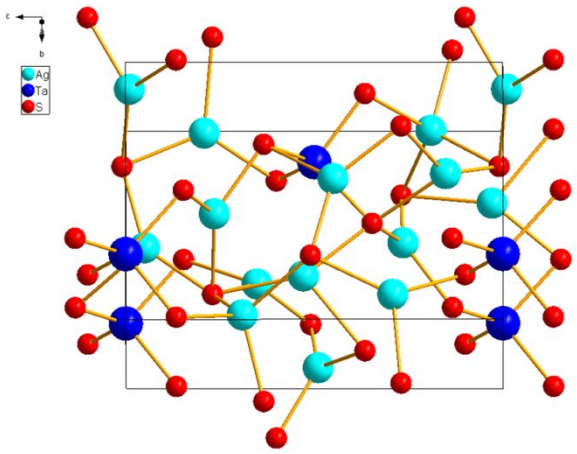

Figure S9. Crystal structure of Ag_7TaS_6 (*Pn* space group).

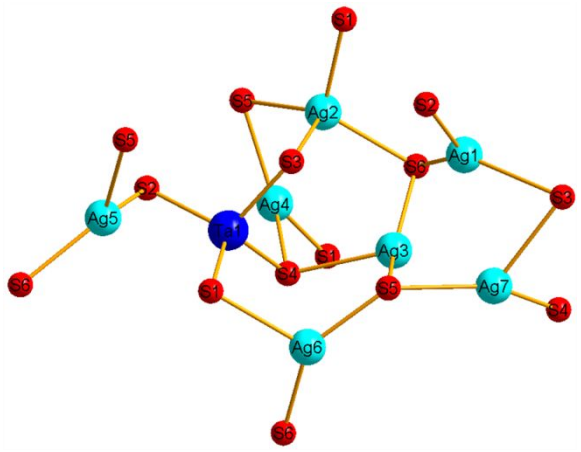

Figure S10. Coordination environment of Ag^{+} and Ta^{5+} in Ag_7TaS_6.

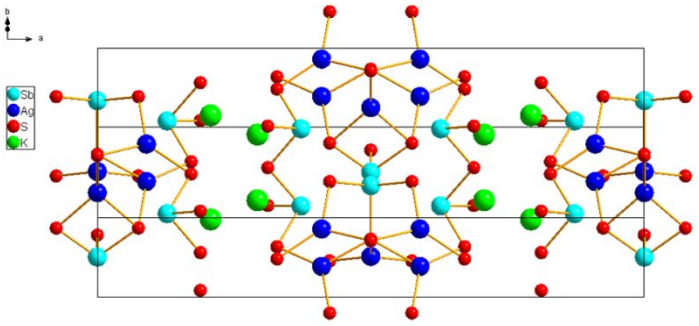

Figure S11. Crystal structure of $K_2Ag_3Sb_3S_7$.

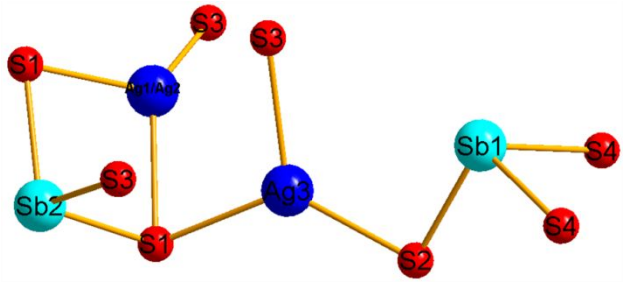

Figure S12. Coordination environment of Ag^{+} and Sb^{3+} in $K_2Ag_3Sb_3S_7$.

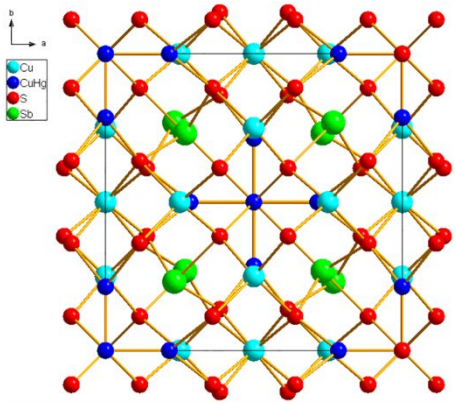

Figure S13. Crystal structure of $Cu_{10}Hg_2Sb_4S_{13}$.

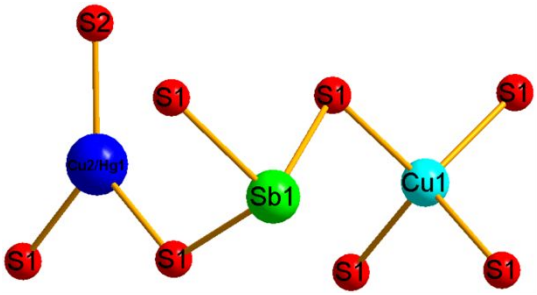

Figure S14. Coordination environment of ($Cu2^{+}$/$Hg1^{2+}$)、Sb^{3+}和 $Cu1^{+}$ in $Cu_{10}Hg_2Sb_4S_{13}$.

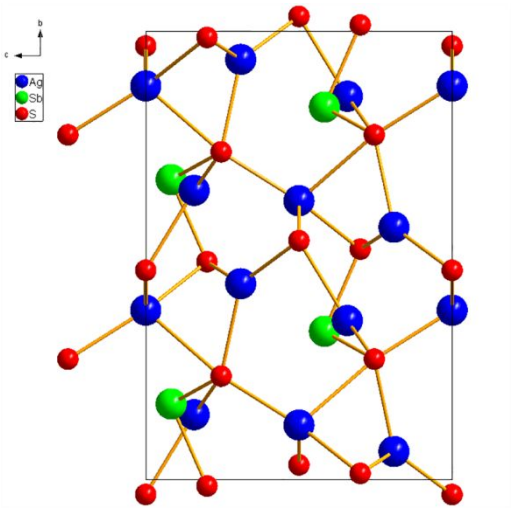

Figure S15. Crystal structure of Ag_5SbS_4.

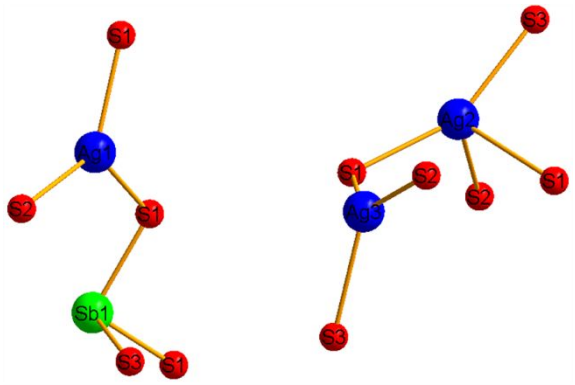

Figure S16. Coordination environment of Ag^{+} and Sb^{3+} in Ag_5SbS_4.

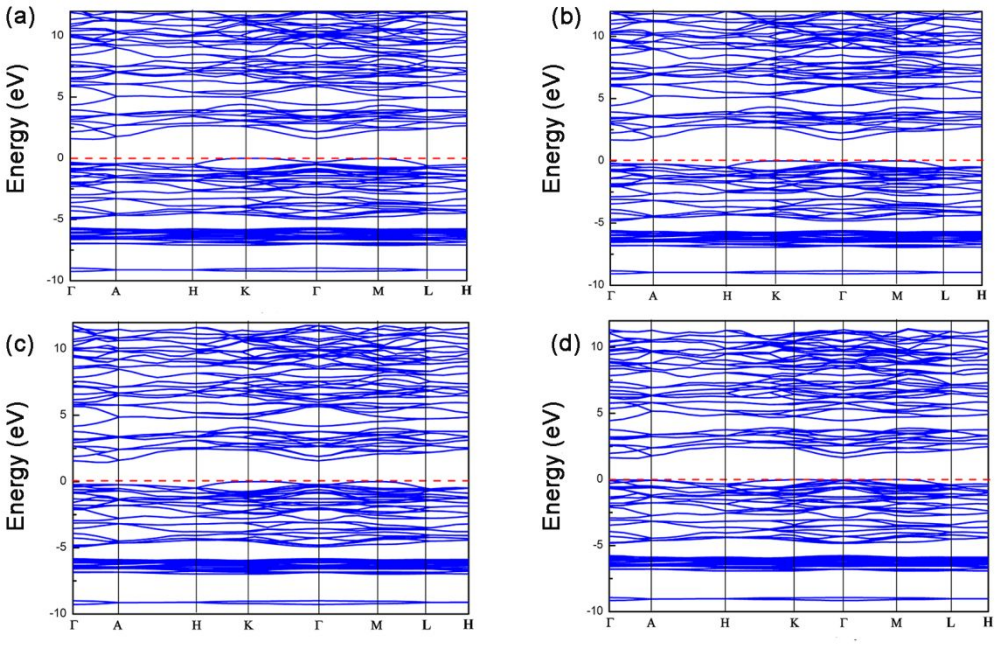

Figure S17. Electronic band structure of Hg_3AsS_4Cl (a), Hg_3AsS_4Br (b), Hg_3AsSe_4Br (c), Hg_3AsSe_4I (d).

Table S1. Band gap, the second−order polarization tensor and the contribution of different building blocks to NLO effect of Hg_3AsQ_4X (Q = S，Se；X = Cl，Br，I).

	E_g (Sx−LDA)	E_g (GGA)	SHG tensors	[Hg(S/Se)$_3$] trigonal planar unit	[As(S/Se)$_3$] pyramidal
Hg_3AsS_4Cl	1.975	1.550	d_{31} = 11.029 d_{33} = −6.939	d_{31} = 12.561 d_{33} = 0.162	d_{31} = 5.855 d_{33} = −4.865
Hg_3AsS_4Br	2.020	1.653	d_{31} = 13.93 d_{33} = −4.88	d_{31} = 14.94 d_{33} = 1.145	d_{31} = 7.535 d_{33} = −2.871
Hg_3AsSe_4Br	1.792	1.447	d_{31} = 21.117 d_{33} = −4.318	d_{31} = 23.406 d_{33} = 5.417	d_{31} = 10.328 d_{33} = −4.014
Hg_3AsSe_4I	1.875	1.598	d_{31} = 27.993 d_{33} = 3.088	d_{31} = 26.992 d_{33} = 8.575	d_{31} = 13.038 d_{33} = 0.772

Table S2. Space group, SHG coefficient and birefringence of several benchmark crystals and compounds that contain trigonal planar units (marked in red).

Compounds	Space group	d_{ij} (pm/V)	Δn
$AgGaS_2$	$I\bar{4}2d$	13.4	0.034
$BaGa_4S_7$	$Pmn2_1$	16.6	0.063
$BaGa_4Se_7$	Pc	24	0.06
$BaGa_2GeS_6$	$R3$	12.0	0.068
$BaGa_2GeSe_6$	$R3$	27.4	0.15
$LiGaGe_2Se_6$	$Fdd2$	18.6	0.04
$BaHgSe_2$	$Pmc2_1$	39.87	0.1649
$Ag_6HgSiSe_6$	$Pmn2_1$	43.22	0.233
$Ag_6HgGeSe_6$	$Pmn2_1$	21.36	0.207