Supporting Information For

Computer-Aided Screening of Bismuth Molybdates Nonlinear Optical Crystals γ-Bi_2MoO_6

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Table S1. The chemical formula, ICSD collection-code, space group, band gap (Eg), birefringence (Δn), second-order susceptibility ($\chi^{(2)}$), and the maximum $\chi^{(2)}$ tensor of 5 bismuth molybdates.

No.	Formula	ICSD	Space groups	Eg-GGA(eV)	Δn	$\chi^{(2)}$(pm/V)	$\lvert\chi^{(2)}\rvert_{max}$(pm/V)
1	Bi_2MoO_6	47139	$Pca2_1$	1.246	0.345	χ_{113}=-48.40; χ_{223}=125.05; χ_{333}=95.38	125.05
2	Bi_2MoO_6	201685	$Pca2_1$	1.251	0.354	χ_{113}=-48.54; χ_{223}=124.85; χ_{333}=94.79	124.85
3	Bi_2MoO_6	14266	$Pca2_1$	1.238	0.356	χ_{113}=-50.31; χ_{223}=124.58; χ_{333}=94.92	124.58
4	$Bi_{10}Mo_3O_{24}$	262963	C2	1.939	0.089	χ_{112}=-10.00; χ_{123}=16.41; χ_{222}=10.19; χ_{233}=11.43	16.41
5	$Bi_{10}Mo_3O_{24}$	173837	C2	1.948	0.079	χ_{112}=-9.67; χ_{123}=16.16; χ_{222}=8.41; χ_{233}=9.99	16.16
6	$Bi_{14}Mo_5O_{36}$	262964	C2	1.689	0.186	χ_{112}=0.06; χ_{123}=-9.85; χ_{222}=2.80; χ_{233}=0.71	9.85
7	$Cs_2NaBi(MoO_4)_3$	428061	R3c	2.475	0.042	χ_{113}=2.96; χ_{122}=0.52; χ_{222}=-0.02; χ_{223}=2.96; χ_{333}=-3.50;	3.50
8	$Cs_5Bi(MoO_4)_4$	20845	Cc	2.838	0.022	χ_{111}=0.45; χ_{113}=0.50; χ_{122}=-0.41; χ_{223}=-0.09; χ_{333}=-1.54	1.54

Table S2. Calculation of dipole moments of the Mo-O and Bi-O Polyhedra for γ-Bi_2MoO_6

	Species	Symmetry code of cations	dipole moment				
			x (a)	*y (b)*	*z (c)*	magnitude	
						debye	× 10^{-18} esu·cm/Å^3
γ-Bi_2MoO_6	$Mo(1)O_6$	1+x, y, 1+z	0.053	–2.657	7.505	7.962	0.016
		1/2–x, y, 1/2+z	–0.054	–2.658	7.506	7.963	0.016
		1–x, 1–y, 1/2+z	–0.054	2.659	7.504	7.961	0.016
		1/2+x,1–y,1+z	0.056	2.663	7.508	7.967	0.016
		∑$Mo(1)O_6$	0.001	0.007	30.024	30.036	0.061
	$Bi(1)O_6$	3/2–x, y, –1/2+z	–8.930	13.602	–6.180	17.405	0.036
		x,y,z	8.931	13.600	–6.177	17.404	0.036
		1–x, 1–y, –1/2+z	–8.932	–13.601	–6.179	17.405	0.036
		–1/2+x, 1–y, z	8.934	–13.600	–6.180	17.406	0.036
		∑$Bi(1)O_6$	0.003	0.001	–24.717	24.710	0.050
	$Bi(2)O_6$	x,y,z	–4.588	–12.895	–6.288	15.062	0.031
		1/2–x, y,–1/2+z	4.590	–12.894	–6.286	15.061	0.031
		1/2+x,1–y,z	–4.585	12.895	–6.287	15.061	0.031
		1–x,1–y,–1/2+z	4.588	12.895	–6.287	15.062	0.031
		∑$Bi(2)O_6$	0.004	0.001	–25.149	25.140	0.051
	∑Bi-O	/	0.008	0.003	–49.866	49.850	0.102
	Unit cell		0.009	0.009	–19.842	19.813	0.040

Table S3. Calculation of dipole moments of the Mo-O and Bi-O Polyhedra for $Bi_{10}Mo_3O_{24}$

	Species	Symmetry code of cations	dipole moment				
			x (a)	*y (b)*	*z (c)*	magnitude	
						debye	× 10^{-18} esu·cm/Å^3
$Bi_{10}Mo_3O_{24}$	$Mo(1)O_4$	1–x, y, 1–z	5.082	–1.940	–1.972	5.961	0.005
		x, y, z	–5.085	–1.937	1.970	5.962	0.005
		1/2+x, 1/2+y, z	–5.083	–1.938	1.973	5.962	0.005
		1/2–x, 1/2+y, 1–z	5.082	–1.941	–1.972	5.961	0.005
		∑$Mo(1)O_4$	–0.004	–7.757	–0.001	7.766	0.007
	$Mo(2)O_4$	1+x, y, 1+z	–0.002	–1.716	–0.001	1.716	0.001
		1/2+x, 1/2+y, 1+z	–0.001	–1.714	0.000	1.714	0.001
		∑$Mo(2)O_4$	–0.004	–3.430	–0.001	3.438	0.003
	∑Mo-O	/	–0.008	–11.187	–0.003	11.204	0.010
	$Bi(1)O_5$	1–x, y, 1–z	9.329	–1.501	18.527	19.929	0.017
		x, y, z	–9.318	–1.502	–18.517	19.916	0.017
		1/2+x, 1/2+y, z	–9.323	–1.503	–18.523	19.923	0.017
		1/2–x, 1/2+y, 1–z	9.322	–1.503	18.522	19.922	0.017
		∑$Bi(1)O_5$	0.011	–6.009	0.010	5.977	0.005
	$Bi(2)O_4$	1–x, –1+y, 1–z	0.915	18.293	–4.364	18.850	0.016
		x, –1+y, z	–0.915	18.293	4.364	18.850	0.016
		1/2+x, –1/2+y, z	–0.915	18.293	4.364	18.850	0.016
		1/2–x, –1/2+y, 1–z	0.915	18.293	–4.364	18.850	0.016
		∑$Bi(2)O_4$	0.000	73.173	0.000	73.173	0.063
	$Bi(3)O_5$	1–x, y, 1–z	–3.893	8.212	–12.164	14.862	0.013
		x, y, z	3.891	8.210	12.165	14.861	0.013
		1/2+x,1/2+y, z	3.891	8.210	12.165	14.861	0.013
		1/2–x, 1/2+y, 1–z	–3.894	8.210	–12.165	14.862	0.013
		∑$Bi(3)O_5$	–0.004	32.842	0.001	32.837	0.028
	$Bi(4)O_6$	1–x, –1+y, 1–z	–0.758	–7.215	13.370	15.280	0.013
		x, –1+y, z	0.758	–7.213	–13.370	15.279	0.013
		1/2+x, –1/2+y, z	0.761	–7.214	–13.368	15.278	0.013
		1/2–x, –1/2+y, 1–z	–0.756	–7.216	13.372	15.282	0.013
		∑$Bi(4)O_6$	0.004	–28.859	0.003	28.847	0.025
	$Bi(5)O_5$	1–x, y, 1–z	3.271	–6.099	15.107	16.310	0.014
		x, y, z	–3.271	–6.095	–15.108	16.310	0.014
		1/2+x, 1/2+y, z	–3.272	–6.097	–15.107	16.309	0.014
		1/2–x, 1/2+y, 1–z	3.271	–6.097	15.109	16.311	0.014
		∑$Bi(5)O_5$	–0.001	–24.388	0.001	24.388	0.021
	∑Bi-O	/	0.009	46.759	0.015	46.797	0.040
	Unit cell		0.001	35.572	0.013	35.594	0.031

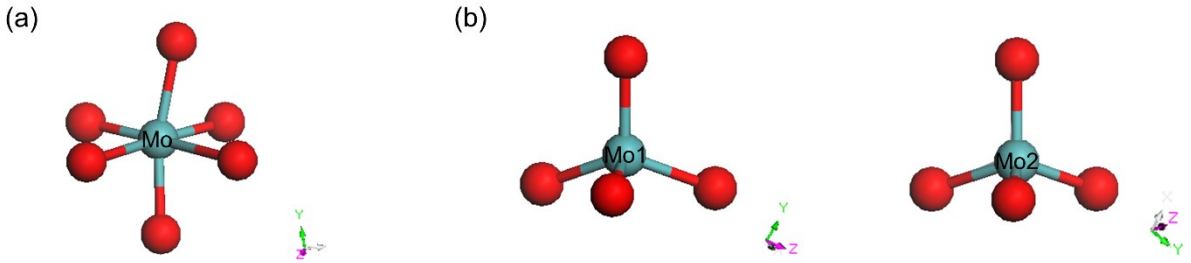

Figure S1. The Mo respective coordination polyhedra of γ-Bi_2MoO_6 (a) and $Bi_{10}Mo_3O_{24}$ (b).

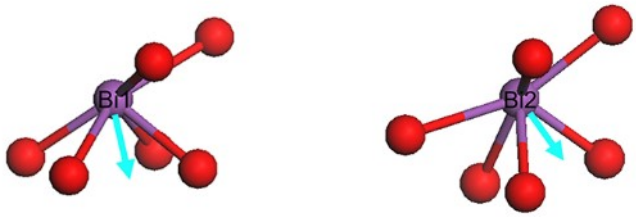

Figure S2. The Bi respective coordination polyhedra of γ-Bi_2MoO_6, with purple arrows indicating the directions of the group's dipole moments.

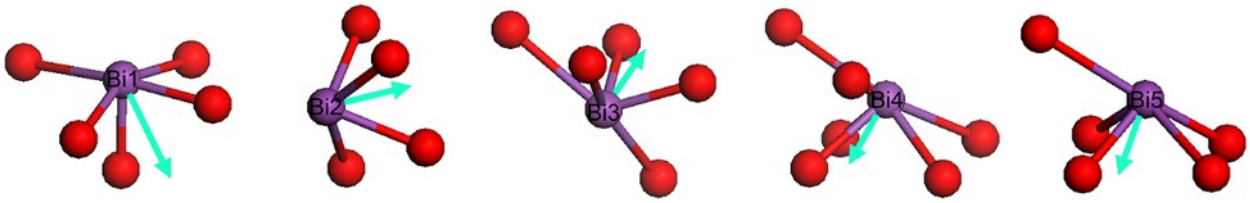

Figure S3. The Bi respective coordination polyhedra of $Bi_{10}Mo_3O_{24}$, with purple arrows indicating the directions of the group's dipole moments.

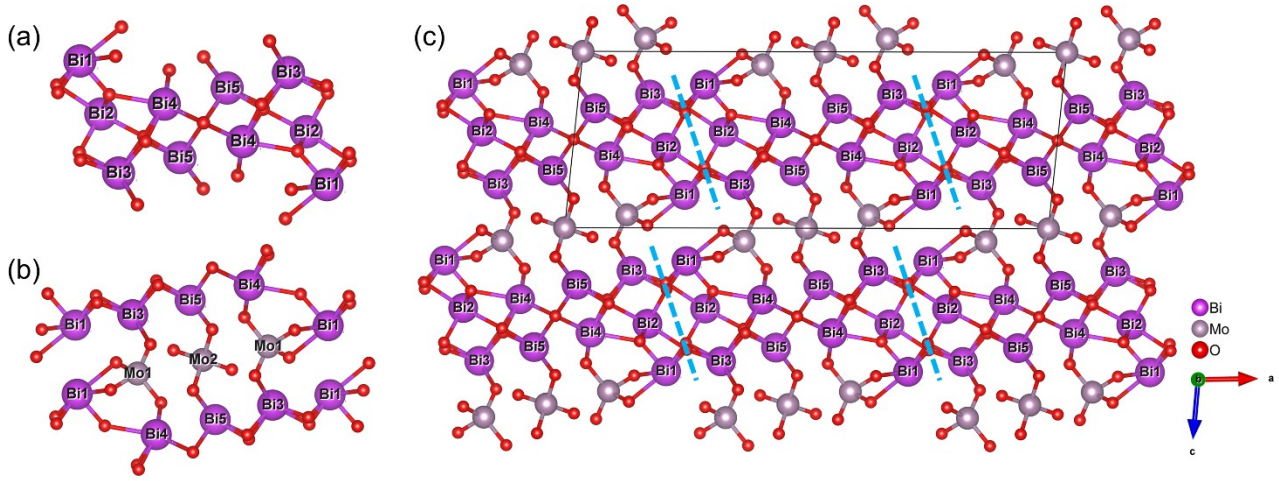

Figure S4. The $[Bi_{10}O_{12}]n$ layer (a). The ten-membered ring channels (b). Projection of $Bi_{10}Mo_3O_{24}$ crystal structure on to (010) plane (c).

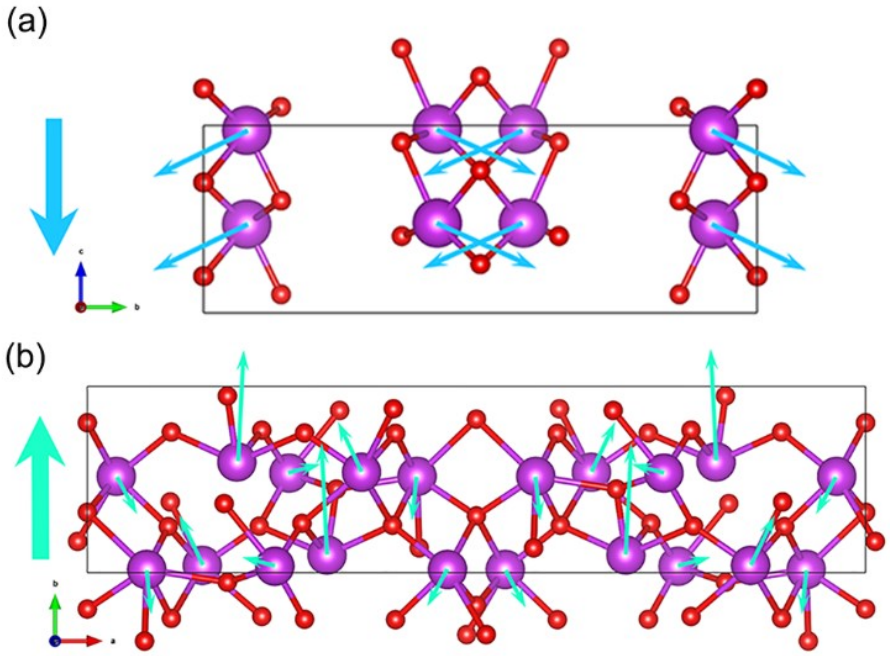

Figure S5. The dipole moment directions generated by the asymmetric Bi-O groups in γ-Bi_2MoO_6 (a) and $Bi_{10}Mo_3O_{24}$ (b). (γ-Bi_2MoO_6 is along the c-axis, $Bi_{10}Mo_3O_{24}$ is along the b-axis.)

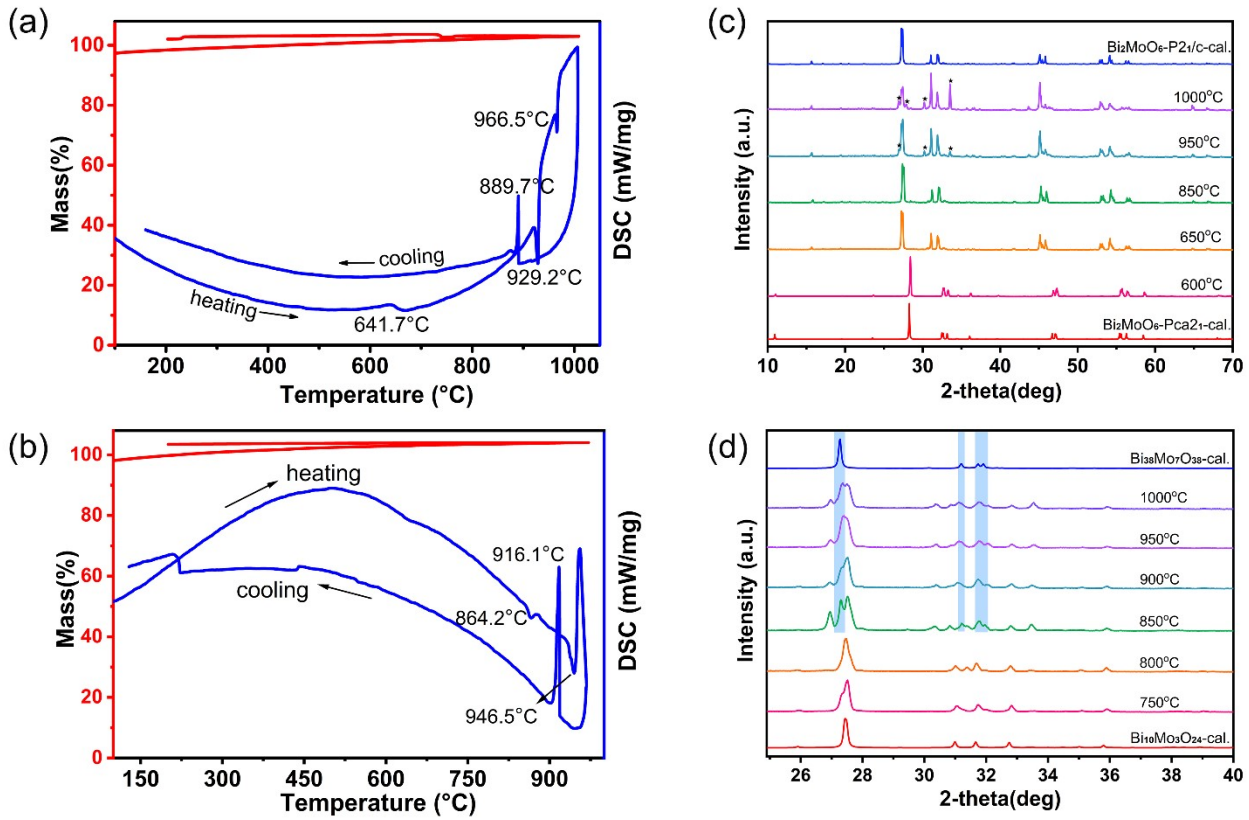

Figure S6. The TG-DSC curves of γ-Bi_2MoO_6 (a) and $Bi_{10}Mo_3O_{24}$ (c). The XRD patterns of the γ-Bi_2MoO_6 (b) and $Bi_{10}Mo_3O_{24}$ (d) samples obtained at different calcination temperatures.

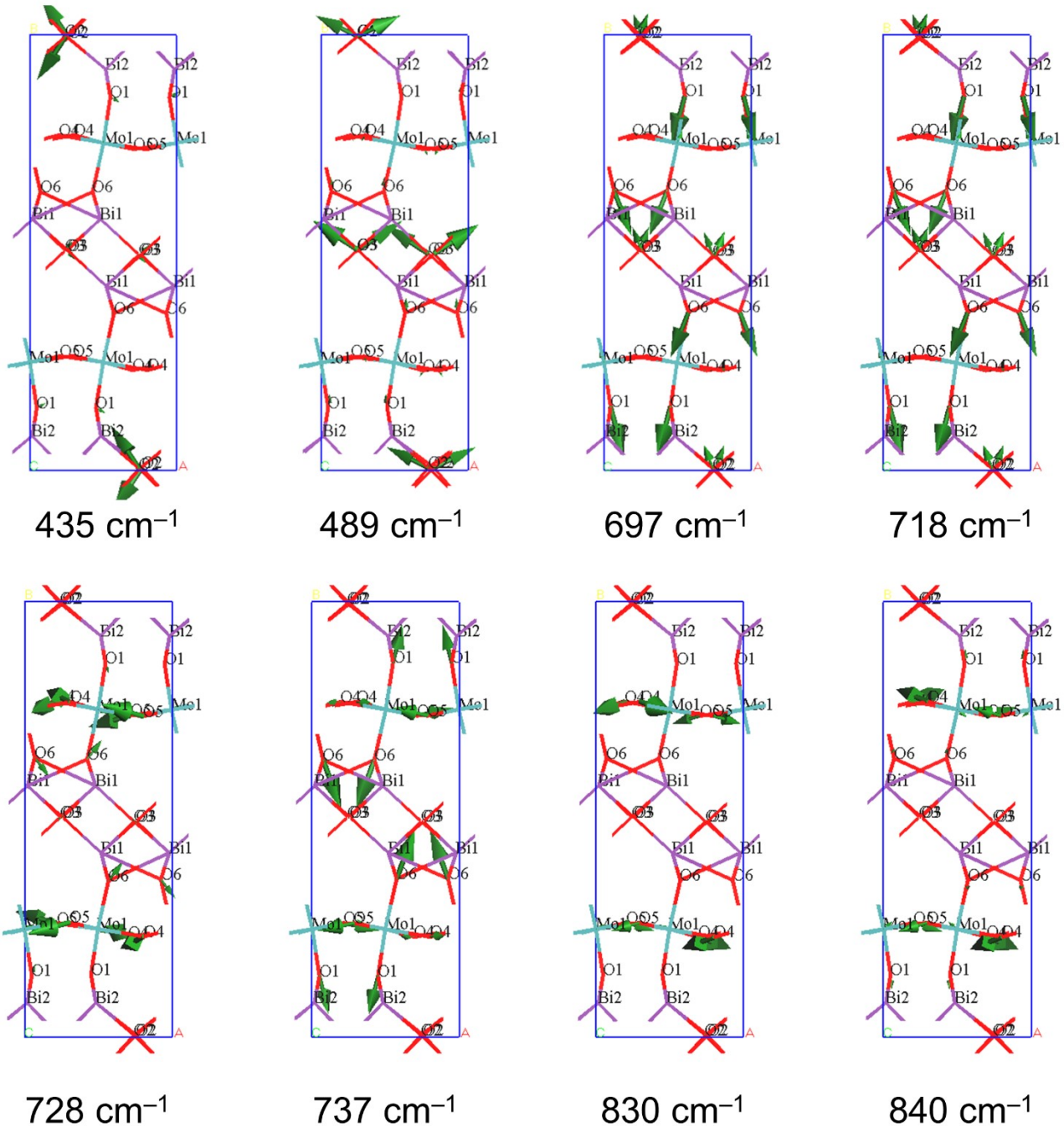

Figure S7. The infrared vibration mode of γ-Bi_2MoO_6.

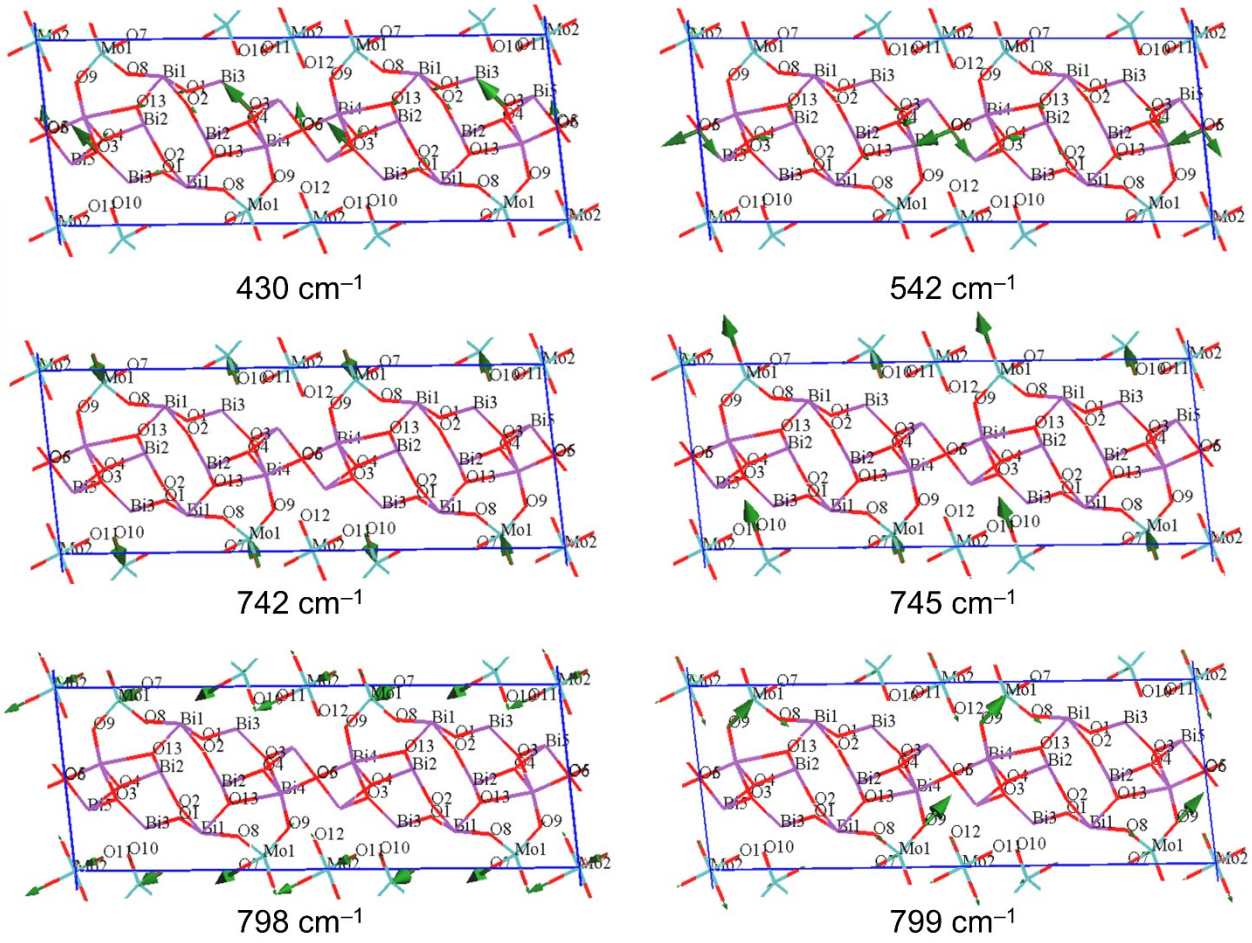

Figure S8. The infrared vibration mode of $Bi_{10}Mo_3O_{24}$.

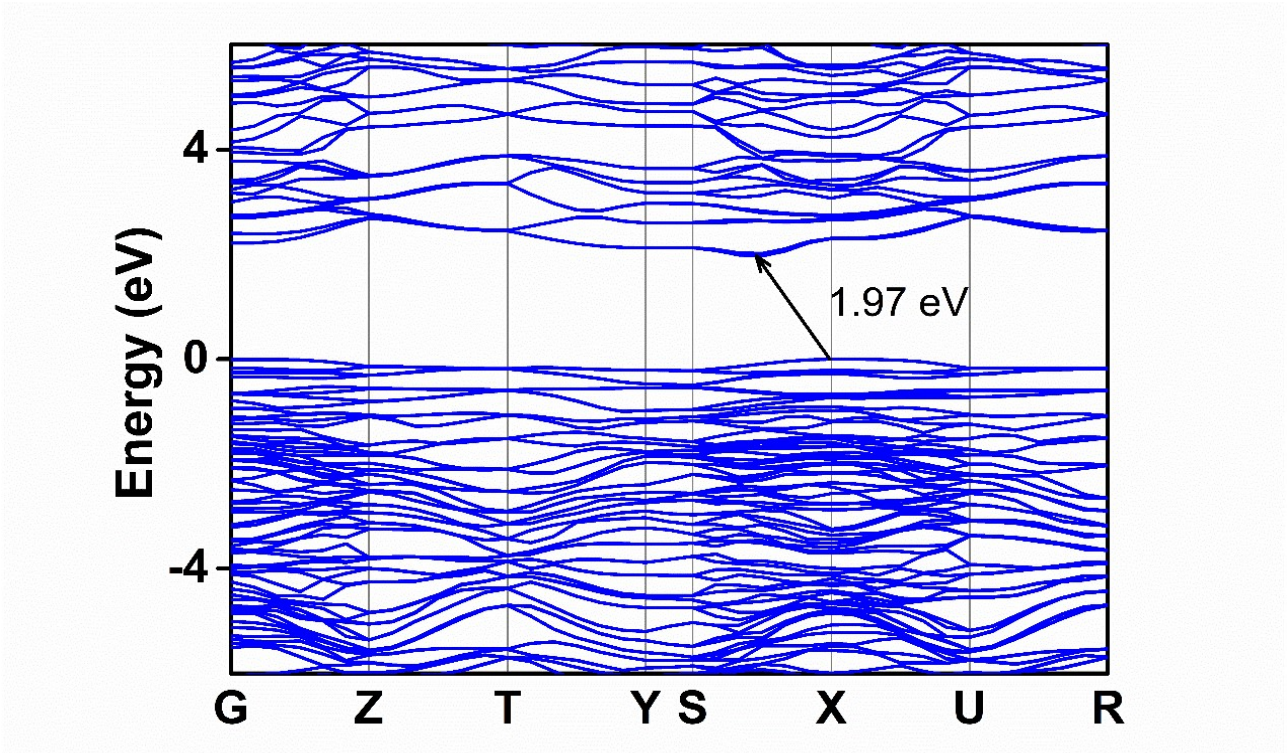

Figure S9. The bandgap of γ-Bi_2MoO_6 calculated using the HSE06 method.

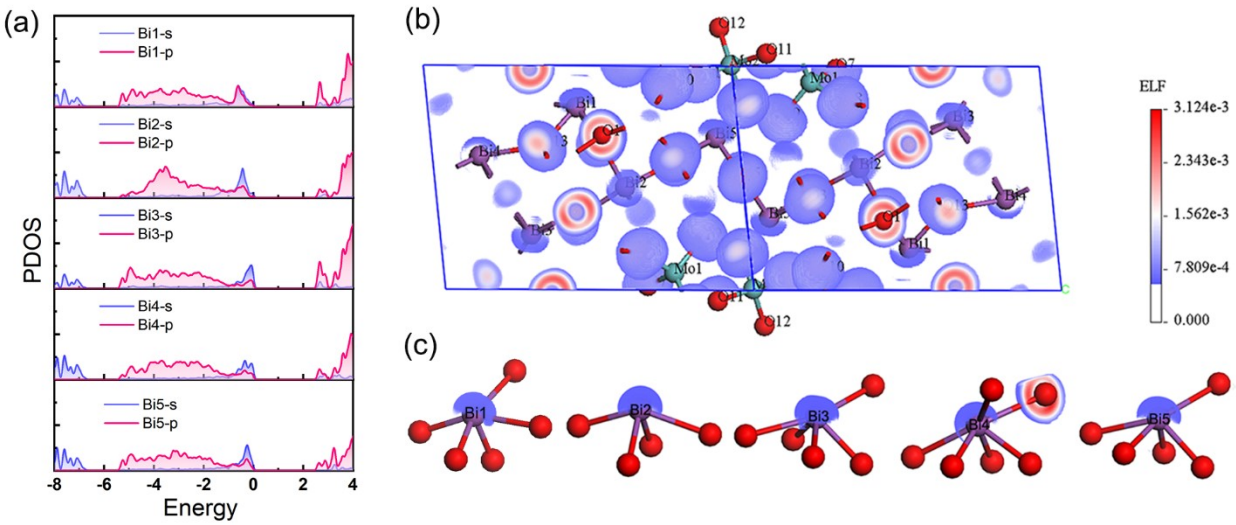

Figure S10. Partial DOSs of Bi1-Bi5 atoms from $Bi_{10}Mo_3O_{24}$ (a). The ELF of $Bi_{10}Mo_3O_{24}$ (b). The ELF for five independent Bi atoms in $Bi_{10}Mo_3O_{24}$ (c).

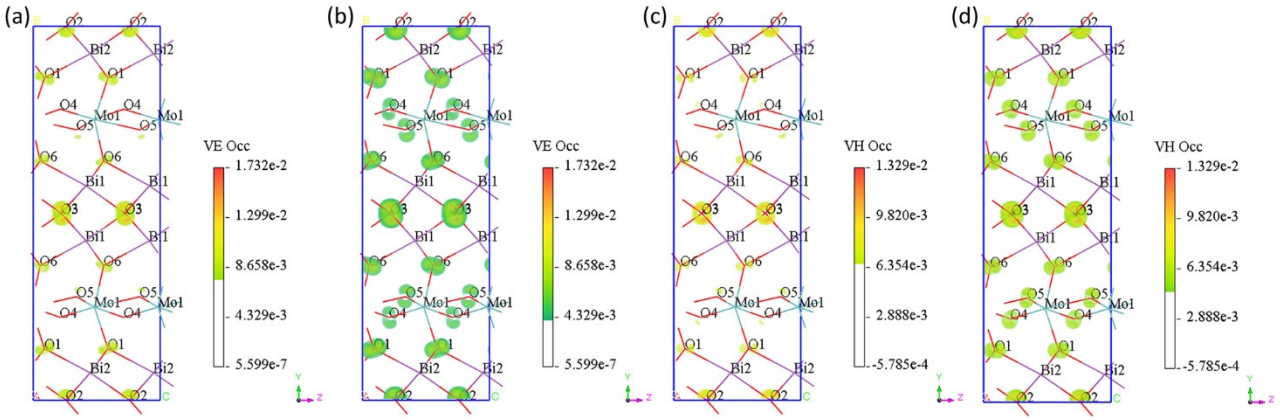

Figure S11. SHG density maps of occupied orbitals of the largest SHG coefficient d_{24} of γ-Bi_2MoO_6 in different density color scale.

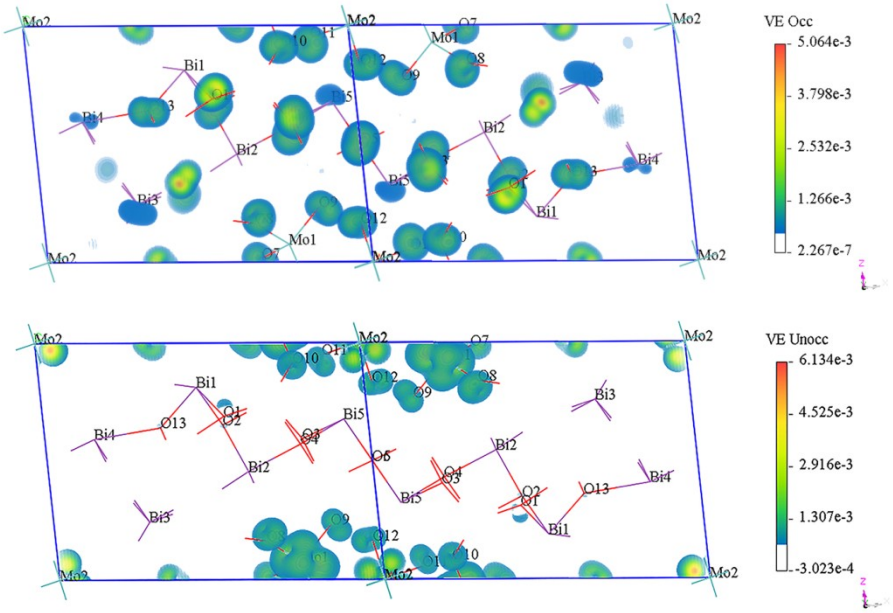

Figure S12. SHG density maps of occupied and unoccupied orbitals of the largest SHG coefficient d_{22} for $Bi_{10}Mo_3O_{24}$.