Electronic supplementary information

Theoretical Studies on Oxidation-Switchable Second-Order Nonlinear Optical Responses of Metallosalen-Keggin Polyoxometalate Derivatives

Teng-Ying Ma,[ab] Ting Zhang,[b] Bo Zhu,[b] Li- Kai Yan*[b] and Zhong-Min Su*[ab]

E-mail: yanlk924@nenu.edu.cn; zmsu@nenu.edu.cn

Content

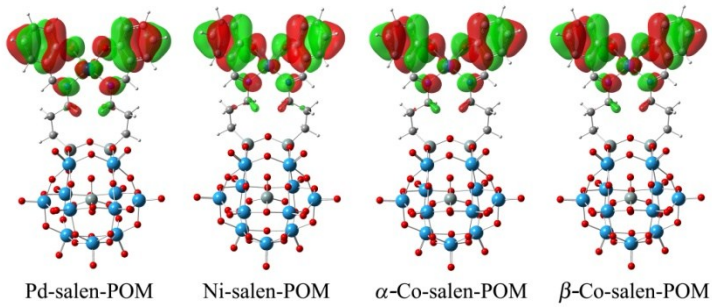

Figure S1.The highest occupied molecular orbitals (HOMO) of **Pd-salen-POM**, **Ni-salen-POM** and **Co-salen-POM**.

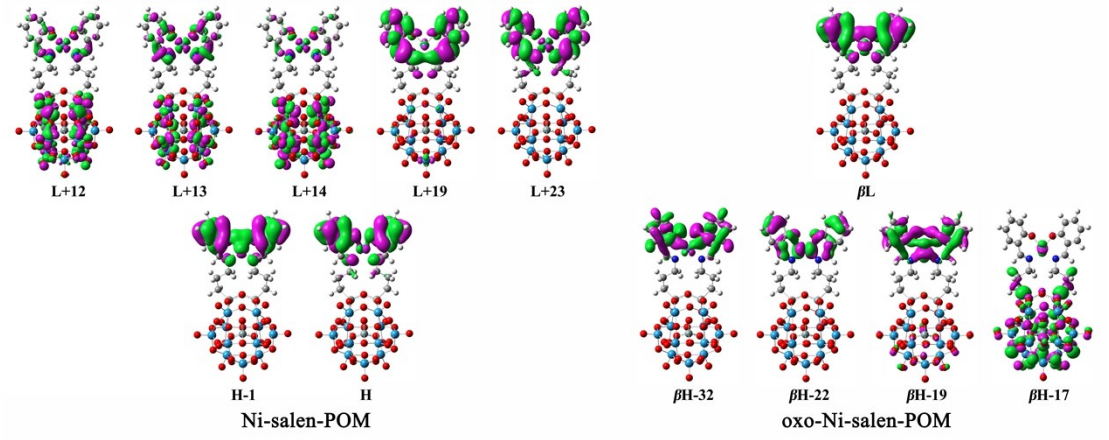

Figure S2. Molecular orbitals of **Ni-salen-POM** and **oxo-Ni-salen-POM** involved in the crucial excited states.

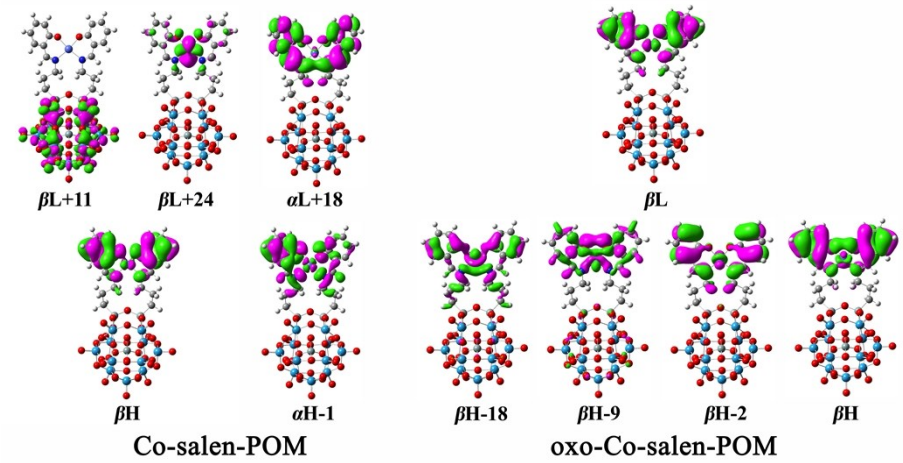

Figure S3. Molecular orbitals of **Co-salen-POM** and **oxo-Co-salen-POM** involved in the crucial excited states.

Table S1. The relative energies Δ*E* (eV) of the **Pd−salen−POM**, **oxo−Pd−salen−POM**, **Ni−salen−POM**, **oxo−Ni−salen−POM**, **Co−salen−POM** and **oxo−Co−salen−POM** compounds for several spin configurations have been calculated by different functionals.

Compounds	spin configuration	B3LYP (eV)	M06-2X (eV)	CAM-B3LYP (eV)	LC-BLYP (eV)	PBE0 (eV)
Pd−salen−POM	1	0	0	0	0	0
	3	1.980	2.069	2.141	2.070	2.102
oxo−Pd−salen−	2	0	0	0	0	0
POM	4	1.628	1.384	0.788	1.470	1.551
Ni−salen−POM	1	0	0	0	0	0
	3	0.801	3.089	2.649	0.211	0.879
oxo−Ni−salen−	2	0	0	0	0	0
POM	4	0.235	0.277	0.390	0.396	0.032
Co−salen−POM	2	0.190	0.301	0.270	0.381	0.096
	4	0	0	0	0	0
oxo−Co−salen−	1	0.886	1.185	1.372	1.878	1.300
POM	3	0	0	0	0	0
	5	0.246	0.143	0.122	0.513	0.117

Table S2. The transition energies Δ*E* (eV), maximum absorption wavelengths λ_{max} (nm), oscillator strengths *f*, and major contribution of all compounds obtained by PBE0 functional.

Compounds	Excited state	Δ*E* (eV)	λ_{max}/nm	*f*	Major contribution
Pd−salen	S24	3.518	352.4	0.148	H→L+21 (34%), H-1→L+19 (31%)
−POM			382.0[a]		H→L+7 (8%)
Ni−salen	S33	3.641	340.6	0.200	H-1→L+19 (65%), H→L+23 (16%)
−POM	S32	3.618	342.7	0.037	H-1→L+13 (29%), H-1→L+12 (18%)
			370.0[a]		H-1→L+14 (12%), H→L+19 (10%)
Co−salen	S60	3.431	361.4	0.027	*β*H→*β*L+24 (59%), *β*H→*β*L+11 (7%)
−POM			358.0[a]		*α*H-1→*α*L+18 (5%)
oxo-Pd-	S4	1.539	805.4	0.027	*β*H-1→*β*L (98%)
salen-POM	S19	2.655	467.1	0.035	*β*H-38→*β*L (41%), *α*H-1→*α*L+4 (12%)
					*α*H-39→*α*L+4 (8%)
oxo-Ni-salen	S13	1.740	712.4	0.019	*β*H-19→*β*L (82%), *β*H-17→*β*L (5%)
-POM	S15	2.010	616.8	0.049	*β*H-32→*β*L (82%), *β*H-22→*β*L (6%)
oxo-Co-	S10	1.603	773.6	0.106	*β*H-18→*β*L (45%), *β*H-9→*β*L (23%)
salen-POM					*β*H→*β*L (712%), *β*H-2→*β*L (11%)

[a] The experimental data of maximum absorption wavelengths.