Supplementary Information for

Lone-pair, Electron-dominated, Nonlinear Optical Responses in Sulfur Clusters and Electric Tunability Properties

*Quanjie Zhong**

School of Materials Science and Physics, Nanhu Campus, China University of Mining and Technology, No.1 University Road, Xuzhou 221116, Jiangsu Province, China

E-mail address: quanjiezhong@cumt.edu.cn

1. Theory

1.1 (Hyper)polarizability[1–4]

The Energy of a system can be written as Taylor expansion with respect to a uniform external electric field.

$$E(F) = E(0) - \mu_0 F - (1/2)\alpha F^2 - (1/6)\beta F^3 - (1/24)\gamma F^4 - \cdots \quad \text{(S1)}$$

Where $\boldsymbol{\mu}_0$, $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ represent the permanent dipole moment, polarizability, and first- and second-order hyperpolarizability, respectively. Theses parameters can be obtained by taking the derivative of the energy with respect to the external electric field.

The orientationally average polarizability is defined as:

$$\alpha_{ave} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad \text{(S2)}$$

The orientationally average second-order hyperpolarizability is defined as:

$$\gamma_{ave} = (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz})/5 \quad \text{(S3)}$$

1.2 Second-order hyperpolarizability density[5–7]

The dipole moment and electron density can be described as follow:

$$\mu(F) = -\partial E/\partial F = \mu_0 + \alpha F + (1/2)\beta F^2 + (1/6)\gamma F^3 + \cdots \quad \text{(S4)}$$

$$\rho(r,F) = \rho^{(0)}(r) + \rho^{(1)}(r)F + (1/2)\rho^{(2)}(r)F^2 + (1/6)\rho^{(3)}(r)F^3 + \cdots \quad \text{(S5)}$$

The components of second-order hyperpolarizability density are defined as:

$$\rho_{ijk}^{(3)}(r) = [\partial^3 \rho(r)/(\partial F_i \partial F_j \partial F_k)]_{F=0} \quad \text{(S6)}$$

When using a numerical derivative, the components of the second-order hyperpolarizability density, such as $\rho_{xxx}^{(3)}$, can be calculated using the following formulas:

$$\rho_{xxx}^{(3)} = \left[\rho(2F_x) - 2\rho(F_x) + 2\rho(-F_x) - \rho(-2F_x)\right]/(2F_x^3) \quad \text{(S7)}$$

Furthermore, the local contribution to the second-order hyperpolarizability components is defined as:

$$\gamma_{ijkl} = \int -\rho_{ijk}^{(3)}(r) l dr \quad \text{(S8)}$$

where i, j, k and l represent one of the directions $\{x, y, z\}$.

2. Results

Table S1. Sum of electronic and zero-point energy (*E*) of sulfur clusters (I).

Clusters	**Symmetry**	***E* (au)**
S_5	C_s	−1991.135647
S_5^*	C_s	−1991.135663
S_6	D_{3d}	−2389.385409
S_6^*	D_{3d}	−2389.385415
S_7	C_s	−2787.622824
S_7^*	C_s	−2787.622796
S_8	D_{4d}	−3185.866058
S_8^*	D_{4d}	−3185.866058
S_9	C_2	−3584.093143
S_9^*	C_2	−3584.093142
S_{10}	D_2	−3982.326420
S_{10}^*	D_2	−3982.326421
S_{11}	C_2	−4380.561126
S_{11}^*	C_1	−4380.558742
S_{12}	D_{3d}	−4778.802658
S_{12}^*	D_{3d}	−4778.802665

a). Calculations are performed at the B3LYP-D3/def2-TZVP level.

b). The zero-point energy has not been corrected. Vibrational frequency scaling factor is 0.965 at the B3LYP/def2-TZVP level, according to CCCBDB (https://cccbdb.nist.gov/vibscalejust.asp, Access date August 2, 2023).

Table S2. Sum of electronic and zero-point energy (*E*) of sulfur clusters (II).

Clusters	Symmetry	*E* (au)
S_{13}	C_1	−5177.028082
S_{13}^*	C_2	−5177.032220
S_{14}	C_s	−5575.266790
S_{14}^*	C_1	−5575.269151
S_{15}	C_1	−5973.503390
S_{15}^*	C_2	−5973.499341
S_{16}	D_{4d}	−6371.727226
S_{16}^*	D_{4d}	−6371.727230
S_{17}	C_2	−6769.976591
S_{17}^*	C_1	−6769.967317
S_{18}	C_2	−7168.212789
S_{18}^*	C_2	−7168.203793
S_{19}	C_2	−7566.442150
S_{19}^*	C_1	−7566.443632
S_{20}	C_1	−7964.673368
S_{20}^*	C_1	−7964.681387

a). Calculations are performed at the B3LYP-D3/def2-TZVP level.

b). The zero-point energy has not been corrected. Vibrational frequency scaling factor is 0.965 at the B3LYP/def2-TZVP level, according to CCCBDB (https://cccbdb.nist.gov/vibscalejust.asp, Access date August 2, 2023).

Table S3. Vibration frequency of sulfur clusters (I).

Clusters	Frequency (cm^{-1})
S_5	91.04, 232.38, 287.41, 298.89, 334.17, 334.19, 426.24, 504.46, 510.94
S_6	164.15, 164.21, 204.32, 204.72, 267.37, 316.92, 349.34, 436.90, 437.82, 458.68, 458.73, 479.09
S_7	55.10, 132.26, 153.78, 170.70, 196.01, 236.56, 271.08, 293.93, 340.65, 370.53, 378.62, 452.60, 483.22, 527.73, 534.26
S_8	64.89, 70.19, 146.22, 146.27, 191.06, 191.06, 215.34, 243.24, 248.57, 248.57, 389.01, 415.49, 415.49, 462.03, 462.55, 467.76, 467.76, 476.24
S_9	45.25, 66.47, 91.49, 97.48, 143.80, 156.27, 176.39, 217.10, 218.27, 248.78, 256.69, 305.60, 387.41, 389.83, 422.86, 426.81, 453.88, 457.62, 458.48, 476.62, 480.84
S_{10}	37.47, 45.69, 68.39, 86.14, 89.54, 125.17, 137.29, 167.57, 218.44, 223.96, 224.17, 245.13, 249.23, 256.40, 375.22, 404.50, 404.62, 452.17, 456.23, 464.21, 467.23, 483.26, 484.22, 488.49
S_{11}	38.67, 48.56, 54.51, 64.45, 90.16, 93.43, 118.82, 163.21, 170.48, 174.61, 202.04, 212.94, 233.67, 247.74, 272.48, 288.97, 385.10, 387.60, 422.00, 425.02, 445.24, 454.54, 462.11, 467.99, 483.60, 485.54, 489.70
S_{12}	37.16, 38.98, 40.90, 41.65, 66.49, 72.62, 106.19, 141.35, 160.44, 160.54, 179.93, 179.97, 245.34, 245.99, 255.89, 256.26, 278.83, 296.06, 381.32, 401.23, 401.23, 434.56, 434.93, 459.01, 459.68, 459.93, 466.23, 466.58, 471.10, 471.23
S_{13}	37.48, 42.08, 57.08, 60.60, 66.14, 69.38, 74.64, 117.03, 127.61, 151.17, 173.41, 175.75, 189.45, 218.48, 236.17, 238.67, 239.62, 251.06, 261.85, 308.13, 356.20, 383.13, 398.84, 409.75, 428.32, 445.76, 453.55, 460.83, 461.71, 465.72, 474.31, 493.37, 499.62
S_{14}	20.66, 50.65, 52.19, 54.67, 59.53, 63.78, 70.83, 77.92, 125.97, 129.68, 154.80, 162.01, 173.83, 185.51, 188.96, 225.27, 235.35, 237.94, 245.59, 252.44, 258.37, 287.40, 375.30, 389.34, 393.26, 421.07, 425.74, 444.33, 452.90, 458.21, 464.02, 465.90, 466.98, 471.35, 476.25, 478.08

a). Calculations are performed at the B3LYP-D3/def2-TZVP level.

b). Frequency has not been corrected. According to CCCBDB, the vibrational frequency scaling factor at the B3LYP/def2-TZVP level is 0.965.

Table S4. Vibration frequency of sulfur clusters (II).

Clusters	Frequency (cm^{-1})
S_{15}	17.67, 25.49, 27.56, 47.03, 49.59, 57.85, 62.09, 66.72, 75.97, 100.63, 114.03, 153.74, 157.33, 168.90, 180.72, 189.59, 206.26, 228.46, 237.85, 245.89, 259.47, 263.52, 269.97, 301.83, 385.08, 391.50, 406.19, 407.87, 431.04, 437.94, 451.08, 454.62, 457.88, 462.04, 465.74, 469.56, 473.67, 478.44, 482.84
S_{16}	4.77, 10.00, 24.44, 26.17, 44.94, 44.94, 45.62, 45.62, 54.20, 63.77, 88.29, 130.62, 130.62, 159.66, 170.46, 170.46, 192.06, 192.33, 207.98, 208.01, 246.13, 246.13, 246.88, 246.88, 265.35, 266.54, 380.82, 393.15, 393.15, 418.37, 419.24, 443.09, 443.09, 455.83, 460.60, 466.61, 467.92, 467.92, 469.74, 469.74, 472.85, 473.10
S_{17}	21.95, 24.07, 38.89, 44.90, 47.90, 51.48, 52.16, 53.49, 61.86, 64.80, 74.89, 108.47, 109.20, 128.66, 140.97, 158.61, 169.63, 186.56, 208.33, 217.64, 225.36, 233.61, 252.92, 262.40, 270.21, 273.98, 281.35, 288.73, 385.21, 386.29, 402.71, 404.59, 427.33, 429.43, 449.67, 450.59, 454.24, 455.16, 459.32, 463.31, 464.36, 466.16, 472.09, 480.04, 480.21
S_{18}	19.74, 28.70, 33.95, 37.49, 42.91, 49.60, 50.90, 60.48, 64.25, 64.54, 66.94, 87.14, 92.49, 112.95, 129.33, 156.67, 157.99, 168.69, 186.25, 197.45, 206.97, 227.34, 237.27, 248.19, 255.74, 261.27, 268.80, 277.05, 283.12, 290.30, 381.07, 389.29, 390.94, 409.90, 411.80, 431.82, 436.01, 451.86, 453.09, 459.63, 460.16, 462.51, 465.43, 465.79, 466.35, 467.36, 473.27, 473.69
S_{19}	13.90, 19.20, 23.83, 32.73, 35.12, 44.00, 46.48, 52.20, 57.14, 63.93, 65.84, 73.88, 81.73, 88.02, 111.09, 120.37, 144.86, 155.66, 169.67, 175.64, 187.32, 196.90, 220.64, 230.89, 242.55, 253.04, 260.91, 265.26, 270.90, 272.29, 285.14, 303.09, 383.84, 385.23, 397.29, 402.00, 420.04, 423.32, 439.47, 443.55, 449.37, 454.78, 456.89, 459.86, 462.58, 465.60, 466.62, 466.96, 469.61, 478.50, 481.25
S_{20}	24.30, 30.95, 41.25, 45.88, 46.59, 51.67, 55.52, 58.04, 60.75, 62.88, 69.13, 81.36, 87.33, 89.77, 99.82, 117.51, 130.45, 150.85, 159.64, 165.44, 173.40, 180.56, 191.76, 215.31, 223.80, 226.64, 233.82, 237.07, 238.70, 250.85, 256.66, 263.37, 265.88, 277.51, 380.46, 386.70, 390.65, 402.46, 410.72, 424.53, 426.06, 438.84, 445.06, 452.79, 458.68, 461.45, 463.90, 466.52, 468.19, 470.47, 474.24, 480.55, 481.17, 483.84

a). Calculations are performed at the B3LYP-D3/def2-TZVP level.

b). Frequency has not been corrected. According to CCCBDB, the vibrational frequency scaling factor at the B3LYP/def2-TZVP level is 0.965.

Table S5. Basis sets assess to evaluate the second-order hyperpolarizability of sulfur clusters.

Method	Basis set	α_{xx} (au)			γ_{xxxx} (au)
		F_x=−0.001au	F_x=0 au	F_x=0.001 au	
MP2	aug-cc-pVDZ	198.0682334	198.0417312	198.0682334	5.30E+04
	aug-cc-pVTZ	200.0160253	199.9875330	200.0160253	5.70E+04
	aug-cc-pVQZ	200.3876208	200.3577807	200.3876208	5.97E+04
	daug-cc-pVDZ	199.8760760	199.8443396	199.8760760	6.35E+04
	daug-cc-pVTZ	200.3369236	200.3057955	200.3369236	6.23E+04
Method	**Basis set**	α_{zz} (au)			γ_{zzzz} (au)
		F_z=−0.001au	F_z=0 au	F_z=0.001 au	
MP2	aug-cc-pVDZ	115.4795506	115.4691537	115.4795724	2.08E+04
	aug-cc-pVTZ	117.9165769	117.9034754	117.9166002	2.62E+04
	aug-cc-pVQZ	118.1824699	118.1676215	118.1824941	2.97E+04
	daug-cc-pVDZ	118.1451105	118.1282871	118.1451356	3.37E+04
	daug-cc-pVTZ	118.4915433	118.4749094	118.4915683	3.33E+04

a). S_8 cluster serve as the evaluated system; energies were converged to 1×10^{-6} Ha; gamma components were calculated using the finite-field method.

b). Given the symmetry of S_8 cluster, the values of γ_{xxxx} and γ_{yyyy} are exactly the same, so the γ_{yyyy} is not listed here.

Table S6. Functionals assess to evaluate the second-order hyperpolarizability of sulfur clusters (I).

		F_x (−0.001 au)	F_x (0 au)	F_x (0.001 au)	
MP2	α_{xx}	199.8760760	199.8443396	199.8760760	6.35E+04 (γ_{xxxx})
	α_{yy}	199.8549156	199.8443396	199.8549156	2.12E+04 (γ_{yyxx})
	α_{zz}	118.1347540	118.1282871	118.1347540	1.29E+04 (γ_{zzxx})
		F_z (−0.001 a.u.)	F_z (0 au)	F_z (0.001 au)	
	α_{xx}	199.8507946	199.8443396	199.8508123	1.29E+04 (γ_{xxzz})
	α_{yy}	199.8507946	199.8443396	199.8508123	1.29E+04 (γ_{yyzz})
	α_{zz}	118.1451105	118.1282871	118.1451356	3.37E+04 (γ_{zzzz})

a). S_8 cluster serve as the evaluated system; energies were converged to 1×10^{-6} Ha; gamma components were calculated using the finite-field method; polarizability and second-order hyperpolarizability values are expressed in atomic units.

b). In the calculation, MP2 method was combined with daug-cc-pVDZ basis set.

c). Given the symmetry, S_8 cluster responds equally to the electric field along the *x* and *y* directions, so γ_{yyxx}, γ_{yyyy}, and γ_{zzyy} are not listed.

Table S7. Functionals assess to evaluate the second-order hyperpolarizability of sulfur clusters

(II).

	MP2	PBE0	Error	PBE30	Error	PBE35	Error
γ_{xxxx}	6.35E+04	6.31E+04	−0.57%	5.95E+04	−6.26%	5.61E+04	−11.58%
γ_{yyxx}	2.12E+04	2.10E+04	−0.48%	1.98E+04	−6.19%	1.87E+04	−11.52%
γ_{zzxx}	1.29E+04	1.23E+04	−4.68%	1.17E+04	−9.88%	1.10E+04	−14.69%
γ_{xxzz}	1.29E+04	1.23E+04	−4.63%	1.17E+04	−9.84%	1.10E+04	−14.65%
γ_{yyzz}	1.29E+04	1.23E+04	−4.63%	1.17E+04	−9.84%	1.10E+04	−14.65%
γ_{zzzz}	3.37E+04	3.01E+04	−10.57%	2.86E+04	−15.14%	2.71E+04	−19.40%
γ_{ave}	5.10E+04	4.96E+04	−2.75%	4.68E+04	−8.19%	4.42E+04	−13.27%

a). S_8 cluster serve as the evaluated system; second-order hyperpolarizability values are expressed in atomic units.

b). In the calculation, MP2 and DFT methods were combined with daug-cc-pVDZ basis set.

c). PBE30 (30% HF exchange, 70% PBE GGA exchange, and PBE GGA correlation); PBE35 (35% HF exchange, 65% PBE GGA exchange, and PBE GGA correlation)

Table S8. Functionals assess to evaluate the second-order hyperpolarizability of sulfur clusters

(III).

		F_x (−0.001 au)	F_x (0 au)	F_x (0.001 au)	
MP2	α_{xx}	437.6345231	437.5435950	437.6345231	1.82E+05 (γ_{xxxx})
	α_{yy}	437.5738942	437.5435950	437.5738942	6.06E+04 (γ_{yyxx})
	α_{zz}	255.0674827	255.0519605	255.0674827	3.10E+04 (γ_{zzxx})
		F_z (−0.001 a.u.)	F_z (0 au)	F_z (0.001 au)	
	α_{xx}	437.5591051	437.5435950	437.5591188	3.10E+04 (γ_{xxzz})
	α_{yy}	437.5591051	437.5435950	437.5591188	3.10E+04 (γ_{yyzz})
	α_{zz}	255.0825735	255.0519605	255.0825869	6.12E+04 (γ_{zzzz})

a). S_{16} cluster serve as the evaluated system; energies were converged to 1×10^{-6} Ha; gamma components were calculated using the finite-field method; polarizability and second-order hyperpolarizability values are expressed in atomic units.

b). In the calculation, MP2 method was combined with daug-cc-pVDZ basis set.

c). Given the symmetry, S_{16} cluster responds equally to the electric field along the *x* and *y* directions, so γ_{yyxx}, γ_{yyyy}, and γ_{zzyy} are not listed.

Table S9. Functionals assess to evaluate the second-order hyperpolarizability of sulfur clusters

(IV).

	MP2	PBE0	Error	PBE30	Error	PBE35	Error
γ_{xxxx}	1.82E+05	2.22E+05	21.92%	2.04E+05	12.05%	1.88E+05	3.15%
γ_{yyxx}	6.06E+04	7.39E+04	21.91%	6.79E+04	12.02%	6.25E+04	3.12%
γ_{zzxx}	3.10E+04	3.08E+04	−0.66%	2.89E+04	−6.75%	2.72E+04	−12.37%
γ_{xxzz}	3.10E+04	3.08E+04	−0.62%	2.89E+04	−6.72%	2.72E+04	−12.34%
γ_{yyzz}	3.10E+04	3.08E+04	−0.62%	2.89E+04	−6.72%	2.72E+04	−12.34%
γ_{zzzz}	6.12E+04	5.74E+04	−6.25%	5.43E+04	−11.37%	5.14E+04	−16.10%
γ_{ave}	1.34E+05	1.54E+05	15.16%	1.43E+05	6.42%	1.32E+05	−1.49%

a). S_{16} cluster serve as the evaluated system; second-order hyperpolarizability values are expressed in atomic units.

b). In the calculation, MP2 and DFT methods were combined with daug-cc-pVDZ basis set.

c). PBE30 (30% HF exchange, 70% PBE GGA exchange, and PBE GGA correlation); PBE35 (35% HF exchange, 65% PBE GGA exchange, and PBE GGA correlation)

Table 10. Static second-order hyperpolarizability of sulfur clusters (I).

Clusters	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{ave}	Volume	Factor
S_5	3.22E+04	3.79E+04	2.14E+04	3.07E+04	144.96	211.80
S_6	3.67E+04	3.80E+04	2.68E+04	3.31E+04	171.36	193.04
S_7	5.99E+04	4.60E+04	2.46E+04	4.31E+04	199.34	216.26
S_8	5.95E+04	5.95E+04	2.86E+04	4.68E+04	229.33	203.97
S_9	7.14E+04	6.82E+04	3.27E+04	5.65E+04	254.19	222.29
S_{10}	9.68E+04	6.99E+04	3.67E+04	6.57E+04	284.22	231.10
S_{11}	1.02E+05	7.30E+04	4.32E+04	7.24E+04	310.81	232.91
S_{12}	1.02E+05	1.02E+05	4.22E+04	7.99E+04	343.02	232.81
S_{13}	1.01E+05	9.44E+04	5.18E+04	8.37E+04	362.82	230.58
S_{14}	1.11E+05	8.93E+04	6.04E+04	8.89E+04	391.50	227.12
S_{15}	1.46E+05	1.28E+05	5.56E+04	1.06E+05	423.33	250.21
S_{16}	2.04E+05	2.04E+05	5.43E+04	1.43E+05	459.00	310.76
S_{17}	2.33E+05	1.03E+05	6.44E+04	1.29E+05	478.07	270.49
S_{18}	2.58E+05	1.31E+05	6.92E+04	1.44E+05	505.59	285.61
S_{19}	2.93E+05	1.56E+05	6.54E+04	1.59E+05	532.44	298.34
S_{20}	1.83E+05	1.33E+05	9.81E+04	1.38E+05	550.23	250.19

a). Second-order hyperpolarizabilities were calculated at the PBE30/daug-cc-pVDZ level.

b). Second-order hyperpolarizability values, volume of clusters, and second-order hyperpolarizability factor units are au, $Å^3$, and au $Å^{-3}$.

Table 11. Static second-order hyperpolarizability of sulfur clusters (II).

Clusters	γ_{xxyy}	γ_{xxzz}	γ_{yyzz}
S_5	1.11E+04	1.02E+04	9.75E+03
S_6	1.26E+04	9.94E+03	9.44E+03
S_7	2.01E+04	1.13E+04	1.11E+04
S_8	1.98E+04	1.17E+04	1.17E+04
S_9	2.23E+04	1.78E+04	1.50E+04
S_{10}	2.69E+04	1.68E+04	1.88E+04
S_{11}	3.13E+04	2.14E+04	1.92E+04
S_{12}	3.40E+04	2.12E+04	2.13E+04
S_{13}	3.58E+04	2.59E+04	2.37E+04
S_{14}	3.74E+04	2.88E+04	2.57E+04
S_{15}	4.45E+04	2.87E+04	2.69E+04
S_{16}	6.79E+04	2.89E+04	2.89E+04
S_{17}	5.58E+04	3.92E+04	2.79E+04
S_{18}	6.00E+04	4.03E+04	3.14E+04
S_{19}	6.84E+04	3.98E+04	3.18E+04
S_{20}	5.46E+04	4.19E+04	4.06E+04

a). Second-order hyperpolarizabilities were calculated at the PBE30/daug-cc-pVDZ level.

b). Second-order hyperpolarizability values, volume of clusters, and second-order hyperpolarizability factor units are au, $Å^3$, and au $Å^{-3}$.

c). The values of γ_{xxyy} and γ_{yyxx}, γ_{xxzz} and γ_{zzxx}, γ_{yyzz} and γ_{zzyy} are the same, so the γ_{yyxx}, γ_{zzxx}, and γ_{zzyy} are not listed.

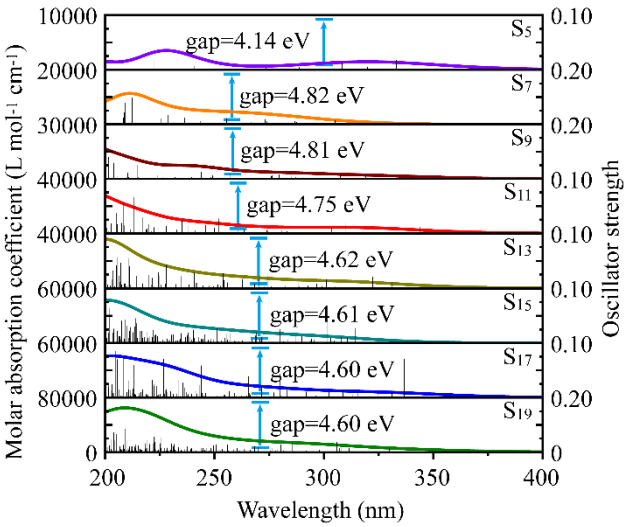

Figure S1. Simulated ultraviolet spectra of odd-numbered sulfur clusters (S_{2n+1}, where n=2–9).

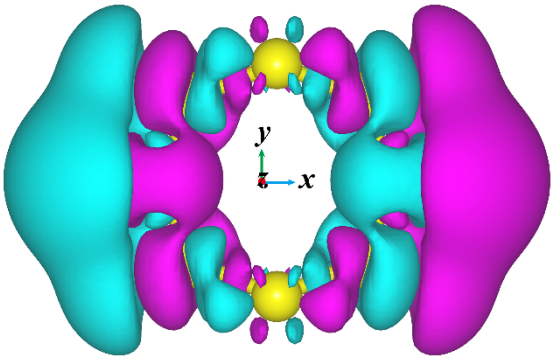

Figure S2. Local contribution to the first-order hyperpolarizability β_{xxx} of S_8 cluster. Note: cyan and magenta represent positive and negative regions, respectively; the values of isosurface is 1 au; the $\beta_{xxx}(+)$ and $\beta_{xxx}(-)$ represent the positive and negative contribution to first-order hyperpolarizability β_{xxx}, respectively; the values of $\beta_{xxx}(+)$ and $\beta_{xxx}(-)$ are 1584.3 and −1584.4 au, respectively.

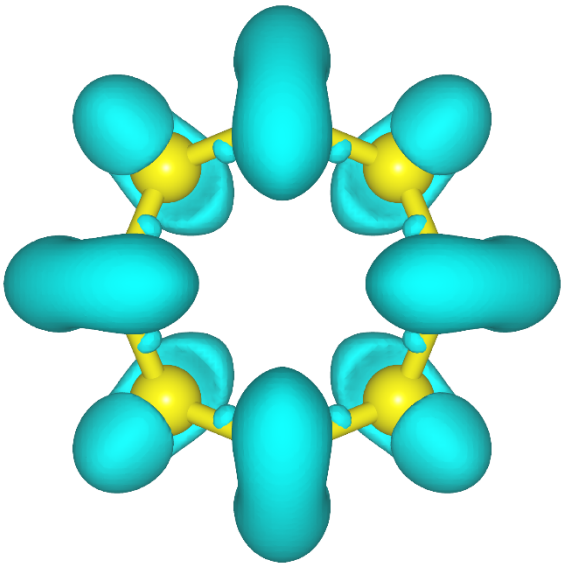

Figure S3. Electron localization function of S_8 cluster.

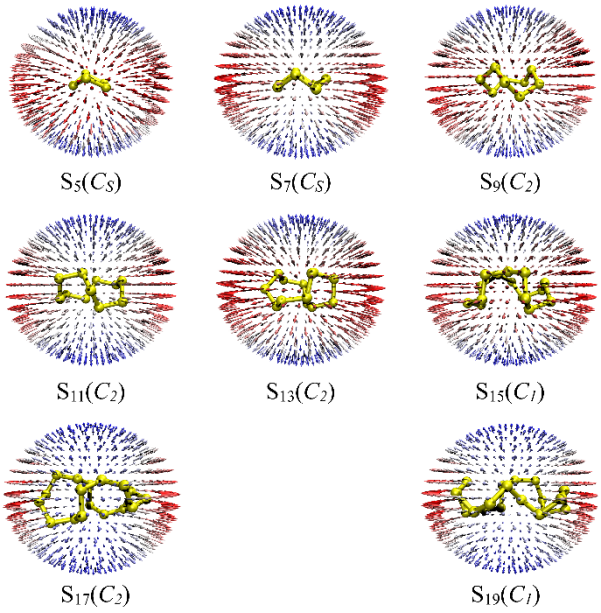

Figure S4. Three-dimensional visualization of the second-order hyperpolarizability tensor of odd-numbered sulfur clusters (S_{2n+1}, where n=2–9). Note: the color of the arrows on the sphere varies from blue to white to red, with shorter arrows becoming bluer and longer arrows becoming redder, and the actual length of the arrows corresponds to modulus of the $\gamma_{eff}(\theta,\Phi)$ vector multiplied by a factor. Here, the longest arrow on each sphere is forced the same length for aesthetics, which means the $\gamma_{eff}(\theta,\Phi)$ vector of various sulfur clusters are multiplied various coefficients.

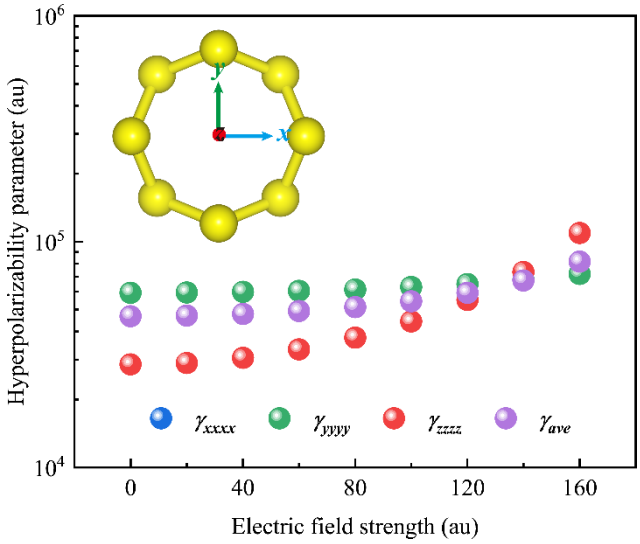

Figure S5. External electric field (along the *z* direction) with various field strength tunning the second-order hyperpolarizability of S_8 cluster.

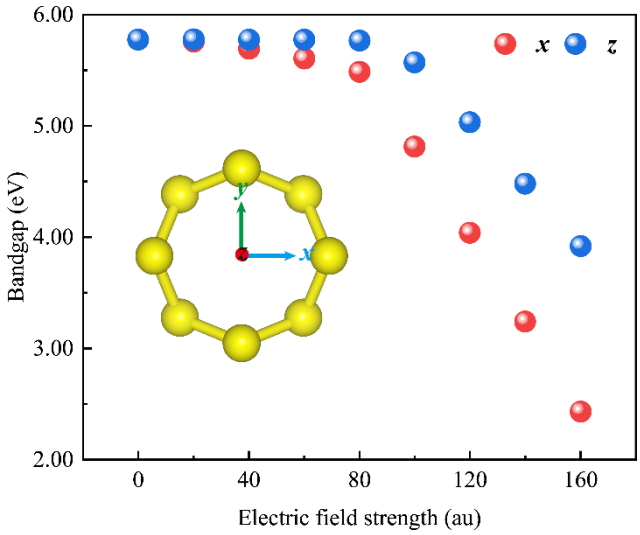

Figure S6. External electric field (along the *x* and *z* directions, respectively) with various field strength tunning the bandgap of S_8 cluster.

References

1 Y. R. Shen, The Principles of Nonlinear Optics, John Wiley & Sons, New York, 1984.

2 R. W. Boyd, Nonlinear Optics, Academic Press, San Diego, 1992.

3 M. G. Papadopoulos, A. J. Sadlej and J. Leszczynski, Non-Linear Optical Properties of Matter, Springer, Dordrecht, 2006.

4 M. T. Zhao, B. P. Singh and P. N. Prasad, *J. Chem. Phys.*, 1988, **89**, 5535.

5 M. Nakano, I. Shigemoto, S. Yamada and K. Yamaguchi, *J. Chem. Phys.*, 1995, **103**, 4175–4191.

6 S. Yamada, M. Nakano, I. Shigemoto, S. Kiribayashi and K. Yamaguchi, *Chem. Phys. Lett.*, 1997, **267**, 445–451.

7 H. Wu, A. Chaudhari and S. Lee, *J. Comput. Chem.*, 2005, **26**, 1543–1564.