Supplementary Information for "Size-dependent linear and nonlinear optical responses of silicon clusters"

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1. Theory

Energy of system is written as Taylor expansion with respect to uniform external electric field:[1]

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

Where μ_0, α, β and γ represent the permanent dipole moment, polarizability, first- and second-order hyperpolarizability, respectively. All these parameters are obtained through calculating the derivative of energy with respect to external electric field. Furthermore, the orientationally average polarizability and second-order hyperpolarizability are defined as:[2]

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

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

where α_{ii}, γ_{iiii}, and γ_{iijj} represent the components of the polarizability and second-order hyperpolarizability tensors.

Dipole moment and electron density of system are written as Taylor expansion with respect to uniform external electric field:[3]

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

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

Where μ_0, α, β and γ represent the permanent dipole moment, polarizability, first- and second-order hyperpolarizability, respectively. Therefore, the components of the polarizability, first- and second-order hyperpolarizability density are defined as:

$$\rho_i^{(1)}(r) = [\partial\rho(r)/(\partial F_i)]_{F=0} \quad \text{(S6)}$$

$$\rho_{ij}^{(2)}(r) = [\partial^2 \rho(r)/(\partial F_i \partial F_j)]_{F=0} \tag{S7}$$

$$\rho_{ijk}^{(3)}(r) = [\partial^3 \rho(r)/(\partial F_i \partial F_j \partial F_k)]_{F=0} \tag{S8}$$

Through numerical derivative, the components of the (hyper)polarizability density, such as $\rho_{xxx}^{(3)}$, are calculated using the following formulas:

$$\rho_{xxx}^{(3)} = [\rho(2F_x) - 2\rho(F_x) + 2\rho(-F_x) - \rho(-2F_x)]/(2F_x^3) \tag{S9}$$

Furthermore, the local contribution to the (hyper)polarizability components are defined as:

$$\alpha_{il} = \int -\rho_i^{(1)}(r) l \, dr \tag{S10}$$

$$\beta_{ijl} = \int -\rho_{ij}^{(2)}(r) l \, dr \tag{S11}$$

$$\gamma_{ijkl} = \int -\rho_{ijk}^{(3)}(r) l \, dr \tag{S12}$$

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

Table S1. Assessment for the structural optimization (I). Calculated frequency values (cm^{-1}) with their corresponding experimental values.

Cluster	Exp.	PBE	B3LYP	PBE0	B3PW91	B2PLYP	MP2
				def2-TZVP			
	252[a]	238(14)	242(10)	253(1)	248(4)	235(17)	235(17)
	300[a]	307(7)	317(17)	322(22)	326(26)	307(7)	295(5)
	386[a]	391(5)	387(1)	408(22)	401(15)	384(2)	384(2)
Si$_6$	404[a]	411(7)	394(10)	425(21)	414(10)	407(3)	438(34)
	458[a]	460(2)	463(5)	482(24)	484(26)	462(4)	465(7)
	464[b]	458(6)	457(7)	480(16)	475(11)	460(4)	474(10)
	289[a]	266(23)	214(75)	283(6)	236(53)	251(38)	304(15)
	340[a]	322(18)	286(54)	340(0)	312(28)	312(28)	342(2)
	340[a]	324(16)	318(22)	343(3)	318(22)	320(20)	356(16)
Si$_7$	358[a]	341(17)	344(14)	351(7)	330(28)	338(20)	356(2)
	417[b]	392(25)	398(19)	403(14)	372(45)	391(26)	435(18)
	435[a]	418(17)	415(20)	428(7)	404(31)	413(22)	451(16)

[a]ref. 4; [b]ref. 5.

Table S2. Assessment for the structural optimization (II). Calculated frequency values (cm^{-1}) with their corresponding experimental values.

Cluster	Exp.	PBE0		
		def2-SVP	def2-TZVP	def2-QZVP
Si$_6$	252[a]	249(3)	253(1)	252(0)
	300[a]	325(25)	322(22)	321(21)
	386[a]	405(19)	408(22)	407(21)
	404[a]	422(18)	425(21)	424(20)
	458[a]	474(16)	482(24)	481(23)
	464[b]	471(7)	480(16)	479(15)
Si$_7$	289[a]	277(12)	283(6)	282(7)
	340[a]	336(4)	340(0)	339(1)
	340[a]	337(3)	343(3)	342(2)
	358[a]	354(4)	351(7)	350(8)
	417[b]	399(18)	403(14)	402(15)
	435[a]	422(13)	428(7)	427(8)

[a]ref. 4; [b]ref. 5.

Table S3. Assessment for the electronic absorption spectra calculation (I). Calculated

adiabatic ionization potential (eV) with their corresponding experimental values.

Cluster	Exp.	PBE	B3LYP	PBE0	B3PW91	B2PLYP	MP2
				def2-TZVP			
Si_6	7.9[a]	7.49	7.48	7.58	7.59	7.49	7.62
Si_7	7.9[a]	7.68	7.64	7.78	7.76	7.70	8.06

[a]ref. 6.

Table S4. Assessment for the electronic absorption spectra calculation (II). Calculated

adiabatic ionization potential (eV) with their corresponding experimental values.

Cluster	Exp.	PBE0		
		def2-SVP	def2-TZVP	def2-QZVP
Si_6	7.9[a]	7.77	7.58	7.57
Si_7	7.9[a]	7.98	7.78	7.77

[a]ref. 6.

Table S5. Assessment for the second-order hyperpolarizability calculation. Calculated second-order hyperpolarizability values (au).

Clu.	Com.	CCSD(T)	CAM-B3LYP	PBE0	PBE20
			aug-cc-pVTZ		
	γ_{xxxx}	9.75E+04	1.01E+05(3.24%)	9.87E+04(1.21%)	1.01E+05(3.40%)
Si$_5$	γ_{yyyy}	9.63E+04	1.01E+05(4.57%)	9.88E+04(2.56%)	1.01E+05(4.79%)
	γ_{zzzz}	7.16E+04	7.05E+04(-1.52%)	7.18E+04(0.27%)	7.37E+04(2.94%)
	γ_{xxxx}	1.60E+05	1.49E+05(-7.28%)	1.60E+05(-0.49%)	1.66E+05(3.37%)
Si$_6$	γ_{yyyy}	1.60E+05	1.49E+05(-7.28%)	1.60E+05(-0.49%)	1.66E+05(3.37%)
	γ_{zzzz}	6.91E+04	6.58E+04(-4.77%)	6.57E+04(-5.01%)	6.73E+04(-2.62%)
	γ_{xxxx}	1.58E+05	1.41E+05(-11.0%)	1.49E+05(-5.92%)	1.54E+05(-2.63%)
Si$_7$	γ_{yyyy}	1.52E+05	1.41E+05(-7.39%)	1.49E+05(-2.11%)	1.54E+05(1.32%)
	γ_{zzzz}	7.16E+04	6.66E+04(-7.00%)	6.65E+04(-7.19%)	6.82E+04(-4.81%)
	γ_{xxxx}	2.44E+05	2.22E+05(-9.30%)	2.38E+05(-2.46%)	2.47E+05(1.18%)
Si$_8$	γ_{yyyy}	1.35E+05	1.29E+05(-4.10%)	1.30E+05(-3.71%)	1.33E+05(-0.96%)
	γ_{zzzz}	9.14E+04	8.35E+04(-8.56%)	8.44E+04(-7.59%)	8.69E+04(-4.90%)
	γ_{xxxx}	1.36E+05	1.24E+05(-8.52%)	1.28E+05(-5.82%)	1.32E+05(-3.10%)
Si$_9$	γ_{yyyy}	1.60E+05	1.46E+05(-8.77%)	1.53E+05(-4.64%)	1.58E+05(-1.49%)
	γ_{zzzz}	1.62E+05	1.49E+05(-7.61%)	1.56E+05(-3.30%)	1.62E+05(-0.01%)
	γ_{xxxx}	1.69E+05	1.50E+05(-11.6%)	1.57E+05(-7.21%)	1.62E+05(-4.12%)
Si$_{10}$	γ_{yyyy}	1.57E+05	1.40E+05(-11.0%)	1.45E+05(-7.24%)	1.50E+05(-4.24%)
	γ_{zzzz}	1.69E+05	1.50E+05(-11.5%)	1.57E+05(-7.14%)	1.62E+05(-4.05%)

Table S6. Molecular orbital (MO) transitions in ground state to first excited state.

Excited state	Clusters	MO transitions[a]
$S_0 \rightarrow S_1$	Si_5	HOMO→LUMO (99.7%)
	Si_6	HOMO−1→LUMO (61.9%); HOMO→LUMO (38.0%)
	Si_7	HOMO→LUMO (99.9%)
	Si_8	HOMO→LUMO (99.6%)
	Si_9	HOMO→LUMO (99.3%)
	Si_{10}	HOMO→LUMO (97.4%)
	Si_{11}	HOMO→LUMO (99.1%)
	Si_{12}	HOMO→LUMO (93.1%)
	Si_{13}	HOMO→LUMO (99.7%)
	Si_{14}	HOMO→LUMO (94.1%)
	Si_{15}	HOMO−1→LUMO (95.2%)
	Si_{16}	HOMO→LUMO (99.0%)
	Si_{17}	HOMO→LUMO (99.0%)
	Si_{18}	HOMO→LUMO (99.8%)
	Si_{19}	HOMO→LUMO (94.9%)
	Si_{20}	HOMO→LUMO (87.0%); HOMO−2→LUMO+1(7.2%)

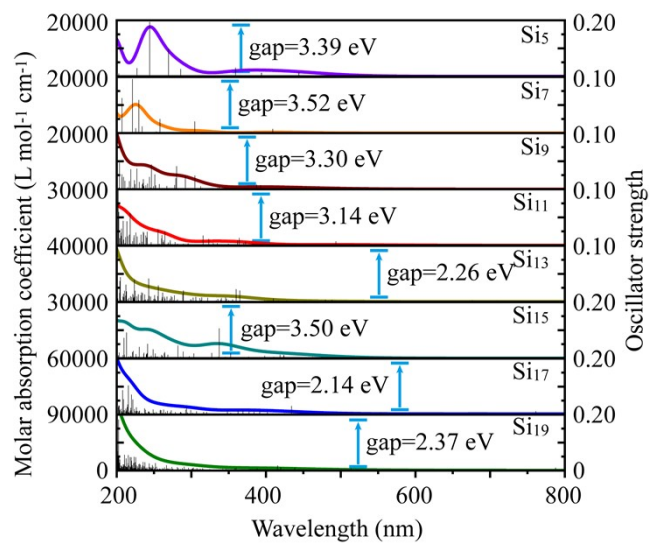[a]MO transitions with absolute contribution more than 5.0% are listed.

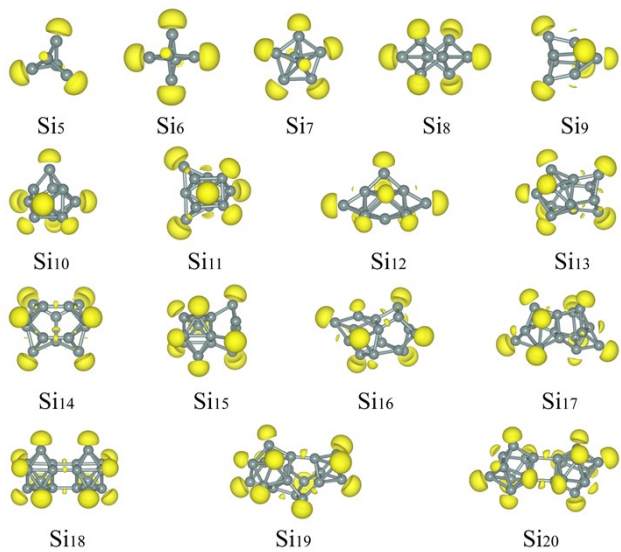**Figure S1.** Simulated ultraviolet–visible–near-infrared spectra of odd-numbered silicon clusters.

Figure S2. Electron localization function of silicon clusters. The isosurface value was set
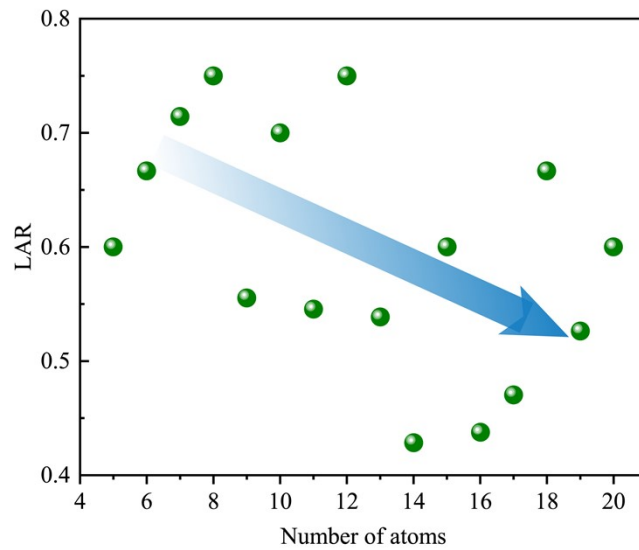
to 0.9.

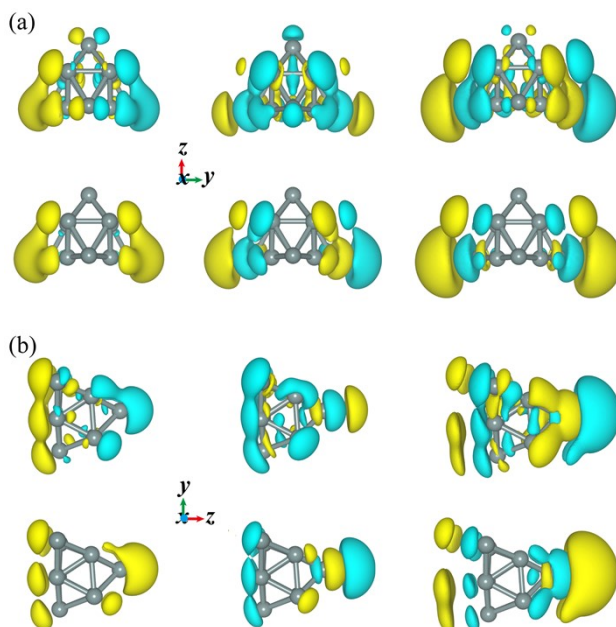**Figure S3.** Evolution behaviors of LAR value with size in silicon clusters.

Figure S4. Responses of Si_{11} cluster to external electric fields. (a) Polarizability density (upper left) $\rho_y^{(1)}$, first-order hyperpolarizability (upper middle) $\rho_{yy}^{(2)}$, second-order hyperpolarizability (upper right) $\rho_{yyy}^{(3)}$, local contribution to the polarizability (lower left) α_{yy}, local contribution to the first-order hyperpolarizability (lower middle) β_{yyy}, local contribution to the second-order hyperpolarizability (lower right) γ_{yyyy}. (b) Polarizability density (upper left) $\rho_z^{(1)}$, first-order hyperpolarizability (upper middle) $\rho_{zz}^{(2)}$, second-order hyperpolarizability (upper right) $\rho_{zzz}^{(3)}$, local contribution to the polarizability (lower left) α_{zz}, local contribution to the first-order hyperpolarizability (lower middle) β_{zzz}, local contribution to the second-order hyperpolarizability (lower right) γ_{zzzz}.

References

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