Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Two-dimensional two-photon absorptions and third-order nonlinear optical properties of I_h fullerenes and fullerene onions

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Supporting Information

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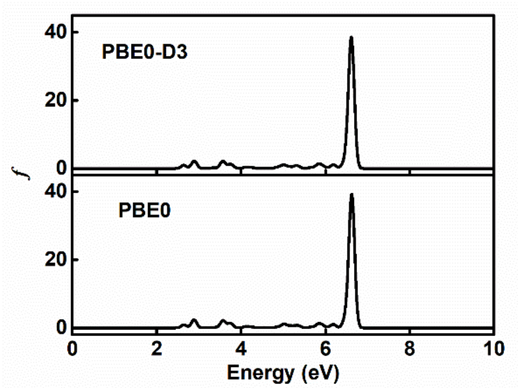
1. **Fig. S1** Electronic spectra of $C_{60}@C_{240}(I_h)$ [2117 (46×46) configurations] predicted with optimized geometry predicted with PBE0/6-31G(d) and PBE0-D3/6-31G(d), respectively.



Cartesian coordinates of $C_{60}@C_{240}(I_h)$ optimized with PBE0/6-31G(d) and PBE0-D3/6-31G(d):

PBE0/6-31G(d)				PBE0-D3/6-31G(d)			
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C	2.58807749	-1.57206029	1.82147058	C	2.59567900	-1.57558400	1.82661200
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C	4.58185401	1.48873461	5.15567005
C	4.58185401	3.94558913	3.63725046
C	6.02595687	3.47637166	1.18039595
C	6.91846150	0.72952482	1.18039595
C	6.02595687	-0.49890244	3.63725046
C	4.35720188	0.08356517	5.39547207
C	3.57416874	3.71073280	4.64317673
C	5.07267727	4.55601341	1.27043199
C	6.78183963	1.45125792	-0.06174355

C	-6.33262100	0.84747700	3.56036800
C	-6.77222200	1.45253500	2.35025200
C	-6.33262100	2.80548600	2.35025200
C	-5.62133300	3.03659800	3.56036800
C	-4.57638000	1.48695600	5.14811200
C	-6.01802200	-0.49729400	3.63228000
C	-6.90900600	0.72904000	1.17961100
C	-6.01802200	3.47120600	1.17961100
C	-4.57638000	3.93962400	3.63228000
C	-6.76779500	-0.70224300	1.26784900
C	-6.32640400	2.80651100	-0.06110600
C	-4.34830800	4.77818900	2.48289300
C	-3.56716800	2.48799900	5.38412600
C	-5.06249300	-0.89909500	4.63318800
C	-6.76779500	1.44805200	-0.06110600
C	-5.06249300	4.54613700	1.26784900
C	-3.56716800	3.70304200	4.63318800
C	-4.34830800	0.08389500	5.38412600
C	-6.32640400	-1.30976500	2.48289300
C	0.00000000	5.91061900	4.30826100
C	-1.15088900	6.28456600	3.56036800
C	-0.71128800	6.88962400	2.35025200
C	0.71128800	6.88962400	2.35025200
C	1.15088900	6.28456600	3.56036800
C	0.00000000	4.81189100	5.14811200
C	-2.33262600	5.56980700	3.63228000
C	-1.44164200	6.79614100	1.17961100
C	1.44164200	6.79614100	1.17961100
C	2.33262600	5.56980700	3.63228000
C	1.26391200	4.16141200	5.38412600
C	-2.41948700	4.53688100	4.63318800
C	-2.75923700	6.21955000	1.26784900
C	0.71418400	6.88402800	-0.06110600
C	3.20062700	5.61202900	2.48289300
C	-0.71418400	6.88402800	-0.06110600
C	2.75923700	6.21955000	1.26784900
C	2.41948700	4.53688100	4.63318800
C	-1.26391200	4.16141200	5.38412600
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C	5.62133300	1.82648200	4.30826100
C	5.62133300	3.03659800	3.56036800
C	6.33262100	2.80548600	2.35025200
C	6.77222200	1.45253500	2.35025200
C	6.33262100	0.84747700	3.56036800
C	4.57638000	1.48695600	5.14811200
C	4.57638000	3.93962400	3.63228000
C	6.01802200	3.47120600	1.17961100
C	6.90900600	0.72904000	1.17961100
C	6.01802200	-0.49729400	3.63228000
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C	3.56716800	3.70304200	4.63318800
C	5.06249300	4.54613700	1.26784900
C	6.76779500	1.44805200	-0.06110600

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C	6.33965150	2.81217298	-0.06174355	C	6.32640400	2.80651100	-0.06110600
C	6.78183963	-0.70424739	1.27043199	C	6.76779500	-0.70224300	1.26784900
C	5.07267727	-0.90120222	4.64317673	C	5.06249300	-0.89909500	4.63318800
C	3.57416874	2.49349336	5.39547207	C	3.56716800	2.48799900	5.38412600
C	4.35720188	4.78848545	2.48767143	C	4.34830800	4.77818900	2.48289300
C	-3.47452181	4.78226900	-4.30758554	C	-3.47417500	4.78179200	-4.30826100
C	-2.76374346	5.76057146	-3.56022896	C	-2.76288700	5.76079600	-3.56036800
C	-3.47452181	5.99151732	-2.35098061	C	-3.47417500	5.99190800	-2.35025200
C	-4.62458533	5.15594729	-2.35098061	C	-4.62506400	5.15573800	-2.35025200
C	-4.62458533	4.40859071	-3.56022896	C	-4.62506400	4.40784500	-3.56036800
C	-2.83174151	3.89755782	-5.15567005	C	-2.82835800	3.89290100	-5.14811200
C	-1.38763866	5.88519487	-3.63725046	C	-1.38671600	5.87715200	-3.63228000
C	-2.83174151	6.35441232	-1.18039595	C	-2.82835800	6.34557000	-1.17961100
C	-5.16834900	4.65676761	-1.18039595	C	-5.16098500	4.65081800	-1.17961100
C	-5.16834900	3.13834802	-3.63725046	C	-5.16098500	3.13498500	-3.63228000
C	-1.42592463	6.66753719	-1.27043199	C	-1.42349000	6.65356000	-1.26784900
C	-4.63359550	5.16035763	0.06174355	C	-4.62411700	5.14950800	0.06110600
C	-5.90056975	2.66422186	-2.48767143	C	-5.88802900	2.65894500	-2.48289300
C	-3.47593199	2.62870465	-5.39547207	C	-3.46854300	2.62374400	-5.38412600
C	-0.71044924	5.10288958	-4.64317673	C	-0.70930600	5.09255200	-4.63318800
C	-3.47593199	6.00144940	0.06174355	C	-3.46854300	5.98908300	0.06110600
C	-5.90056975	3.41651720	-1.27043199	C	-5.88802900	3.40988300	-1.26784900
C	-4.63359550	2.25255698	-4.64317673	C	-4.62411700	2.24827500	-4.63318800
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C	-0.71044924	6.43506512	-2.48767143	C	-0.70930600	6.42150800	-2.48289300
C	-5.62189437	-1.82666422	-4.30758554	C	-5.62133300	-1.82648200	-4.30826100
C	-6.33267271	-0.84836175	-3.56022896	C	-6.33262100	-0.84747700	-3.56036800
C	-6.77195788	-1.45298592	-2.35098061	C	-6.77222200	-1.45253500	-2.35025200
C	-6.33267271	-2.80496668	-2.35098061	C	-6.33262100	-2.80548600	-2.35025200
C	-5.62189437	-3.03591257	-3.56022896	C	-5.62133300	-3.03659800	-3.56036800
C	-4.58185401	-1.48873461	-5.15567005	C	-4.57638000	-1.48695600	-5.14811200
C	-6.02595687	0.49890244	-3.63725046	C	-6.01802200	0.49729400	-3.63228000
C	-6.91846150	-0.72952482	-1.18039595	C	-6.90900600	-0.72904000	-1.17961100
C	-6.02595687	-3.47637166	-1.18039595	C	-6.01802200	-3.47120600	-1.17961100
C	-4.58185401	-3.94558913	-3.63725046	C	-4.57638000	-3.93962400	-3.63228000
C	-6.78183963	0.70424739	-1.27043199	C	-6.76779500	0.70224300	-1.26784900
C	-6.33965150	-2.81217298	0.06174355	C	-6.32640400	-2.80651100	0.06110600
C	-4.35720188	-4.78848545	-2.48767143	C	-4.34830800	-4.77818900	-2.48289300
C	-3.57416874	-2.49349336	-5.39547207	C	-3.56716800	-2.48799900	-5.38412600
C	-5.07267727	0.90120222	-4.64317673	C	-5.06249300	0.89909500	-4.63318800
C	-6.78183963	-1.45125792	0.06174355	C	-6.76779500	-1.44805200	0.06110600
C	-5.07267727	-4.55601341	-1.27043199	C	-5.06249300	-4.54613700	-1.26784900
C	-3.57416874	-3.71073280	-4.64317673	C	-3.56716800	-3.70304200	-4.63318800
C	-4.35720188	-0.08356517	-5.39547207	C	-4.34830800	-0.08389500	-5.38412600
C	-6.33965150	1.31286711	-2.48767143	C	-6.32640400	1.30976500	-2.48289300
C	-0.00000000	-5.91120954	-4.30758554	C	0.00000000	-5.91061900	-4.30826100
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C	0.71077835	-6.88951201	-2.35098061	C	0.71128800	-6.88962400	-2.35025200
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C	1.44410285	-6.80528345	-1.18039595
C	2.33660749	-5.57685620	-3.63725046
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C	3.20767087	-5.62366860	-2.48767143
C	1.26697423	-4.16976830	-5.39547207
C	-2.42463773	-4.54591597	-4.64317673
C	-0.71547539	-6.89837610	0.06174355
C	2.76548276	-6.23228832	-1.27043199
C	2.42463773	-4.54591597	-4.64317673
C	-1.26697423	-4.16976830	-5.39547207
C	-3.20767087	-5.62366860	-2.48767143
C	5.62189437	-1.82666422	-4.30758554
C	5.62189437	-3.03591257	-3.56022896
C	6.33267271	-2.80496668	-2.35098061
C	6.77195788	-1.45298592	-2.35098061
C	6.33267271	-0.84836175	-3.56022896
C	4.58185401	-1.48873461	-5.15567005
C	4.58185401	-3.94558913	-3.63725046
C	6.02595687	-3.47637166	-1.18039595
C	6.91846150	-0.72952482	-1.18039595
C	6.02595687	0.49890244	-3.63725046
C	4.35720188	-0.08356517	-5.39547207
C	3.57416874	-3.71073280	-4.64317673
C	5.07267727	-4.55601341	-1.27043199
C	6.78183963	-1.45125792	0.06174355
C	6.33965150	1.31286711	-2.48767143
C	6.33965150	-2.81217298	0.06174355
C	6.78183963	0.70424739	-1.27043199
C	5.07267727	0.90120222	-4.64317673
C	3.57416874	-2.49349336	-5.39547207
C	4.35720188	-4.78848545	-2.48767143
C	3.47452181	4.78226900	-4.30758554
C	4.62458533	4.40859071	-3.56022896
C	4.62458533	5.15594729	-2.35098061
C	3.47452181	5.99151732	-2.35098061
C	2.76374346	5.76057146	-3.56022896
C	2.83174151	3.89755782	-5.15567005
C	5.16834900	3.13834802	-3.63725046
C	5.16834900	4.65676761	-1.18039595
C	2.83174151	6.35441232	-1.18039595
C	1.38763866	5.88519487	-3.63725046
C	1.42592463	4.11812218	-5.39547207
C	4.63359550	2.25255698	-4.64317673
C	5.90056975	3.41651720	-1.27043199
C	3.47593199	6.00144940	0.06174355
C	0.71044924	6.43506512	-2.48767143
C	4.63359550	5.16035763	0.06174355
C	1.42592463	6.66753719	-1.27043199
C	0.71044924	5.10288958	-4.64317673
C	3.47593199	2.62870465	-5.39547207
C	5.90056975	2.66422186	-2.48767143

C	-1.44164200	-6.79614100	-1.17961100
C	1.44164200	-6.79614100	-1.17961100
C	2.33262600	-5.56980700	-3.63228000
C	-2.75923700	-6.21955000	-1.26784900
C	0.71418400	-6.88402800	0.06110600
C	3.20062700	-5.61202900	-2.48289300
C	1.26391200	-4.16141200	-5.38412600
C	-2.41948700	-4.53688100	-4.63318800
C	-0.71418400	-6.88402800	0.06110600
C	2.75923700	-6.21955000	-1.26784900
C	2.41948700	-4.53688100	-4.63318800
C	-1.26391200	-4.16141200	-5.38412600
C	-3.20062700	-5.61202900	-2.48289300
C	5.62133300	-1.82648200	-4.30826100
C	5.62133300	-3.03659800	-3.56036800
C	6.33262100	-2.80548600	-2.35025200
C	6.77222200	-1.45253500	-2.35025200
C	6.33262100	-0.84747700	-3.56036800
C	4.57638000	-1.48695600	-5.14811200
C	4.57638000	-3.93962400	-3.63228000
C	6.01802200	-3.47120600	-1.17961100
C	6.90900600	-0.72904000	-1.17961100
C	6.01802200	0.49729400	-3.63228000
C	4.34830800	-0.08389500	-5.38412600
C	3.56716800	-3.70304200	-4.63318800
C	5.06249300	-4.54613700	-1.26784900
C	6.76779500	-1.44805200	0.06110600
C	6.32640400	1.30976500	-2.48289300
C	6.32640400	-2.80651100	0.06110600
C	6.76779500	0.70224300	-1.26784900
C	5.06249300	0.89909500	-4.63318800
C	3.56716800	-2.48799900	-5.38412600
C	4.34830800	-4.77818900	-2.48289300
C	3.47417500	4.78179200	-4.30826100
C	4.62506400	4.40784500	-3.56036800
C	4.62506400	5.15573800	-2.35025200
C	3.47417500	5.99190800	-2.35025200
C	2.76288700	5.76079600	-3.56036800
C	2.82835800	3.89290100	-5.14811200
C	5.16098500	3.13498500	-3.63228000
C	5.16098500	4.65081800	-1.17961100
C	2.82835800	6.34557000	-1.17961100
C	1.38671600	5.87715200	-3.63228000
C	1.42349000	4.10956200	-5.38412600
C	4.62411700	2.24827500	-4.63318800
C	5.88802900	3.40988300	-1.26784900
C	3.46854300	5.98908300	0.06110600
C	0.70930600	6.42150800	-2.48289300
C	4.62411700	5.14950800	0.06110600
C	1.42349000	6.65356000	-1.26784900
C	0.70930600	5.09255200	-4.63318800
C	3.46854300	2.62374400	-5.38412600
C	5.88802900	2.65894500	-2.48289300

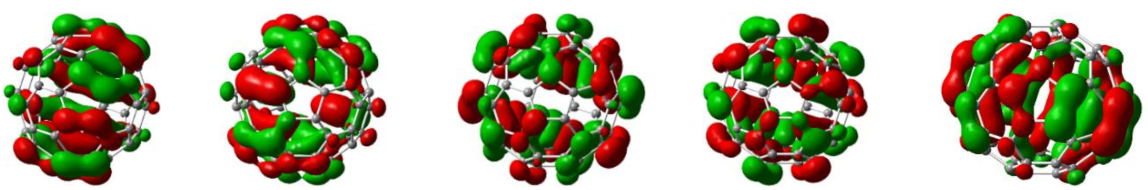
2. **Table S1** The longest and shortest interlayer distances of C_{60}@$C_{240}(I_h)$ and C_{60}@$C_{240}(I_h)$@C_{540} and the radius of C_{60}, C_{240}, C_{540}, C_{60}@$C_{240}(I_h)$, and C_{60}@$C_{240}(I_h)$@C_{540} at the PBE0/6-31G(d) level of theory. Three digitals after decimal point for shell distances are kept for comparison.

Isolated fullerenes and Onions	Distances (Å)		Radius (Å)	
	longest	shortest	longest	shortest
C_{60}	—	—	3.536 (C_{60})	
C_{240}	—	—	7.318 (C_{240})	6.926 (C_{240})
C_{540}	—	—	11.321 (C_{540})	10.197 (C_{540})
C_{60}@$C_{240}(I_h)$	3.901 (C_{60}-C_{240}) 3.892 (C_{60}-C_{240})[a]	3.551 (C_{60}-C_{240}) 3.528 (C_{60}-C_{240})[a]	3.534 (C_{60}) 3.544 (C_{60})[a] 7.314 (C_{240}) 7.314 (C_{240})[a]	 6.936 (C_{240}) 6.921 (C_{240})[a]
C_{60}@$C_{240}(I_h)$@C_{540}	3.896 (C_{60}-C_{240}) 4.042 (C_{240}-C_{540})	3.524 (C_{60}-C_{240}) 3.389 (C_{240}-C_{540})	3.533 (C_{60}) 7.308 (C_{240}) 11.314 (C_{540})	 6.908 (C_{240}) 10.249 (C_{540})

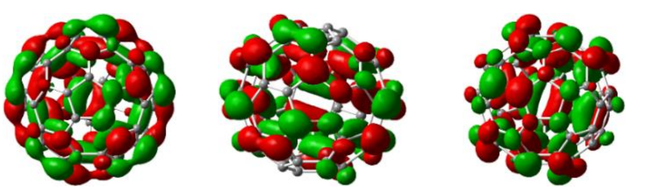
[a] The distances and radius of C_{60}@$C_{240}(I_h)$ are predicted with PBE0-D3/6-31G(d).

3. **Fig. S2** The frontier molecular orbitals (five degenerate HOMO and three degenerate LUMO) of a) C_{60}, b) C_{240}, c) C_{60}@$C_{240}(I_h)$, d) C_{540}, and e) C_{60}@$C_{240}(I_h)$@C_{540}. (single-point computation from zindo). The m in HOMO(m) [LMUMO(m)] stand for the numbering of degenerate orbitals. The number in square brackets is the orbital energy. All HOMOs are five-fold degenerate and all LUMOs are three-fold degenerate.

a) C_{60}

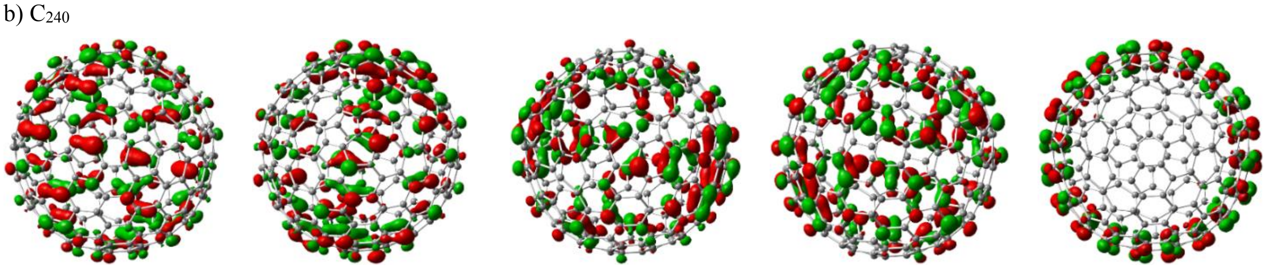


HOMO(5-1) HOMO(5-2) HOMO(3) HOMO(4) HOMO(5) [−6.80 eV]

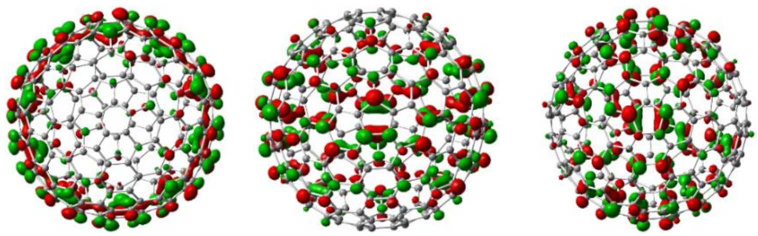


LUMO(1) LUMO(2) LUMO(3) [−1.36 eV]

b) C_{240}

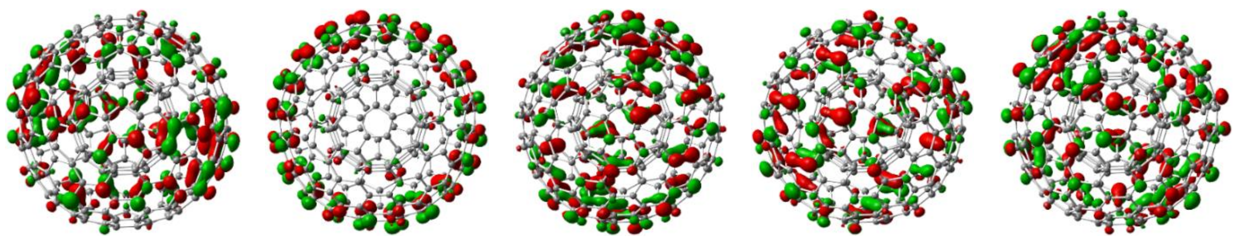


HOMO(1) HOMO(2) HOMO(3) HOMO(4) HOMO(5) [−6.35 eV]



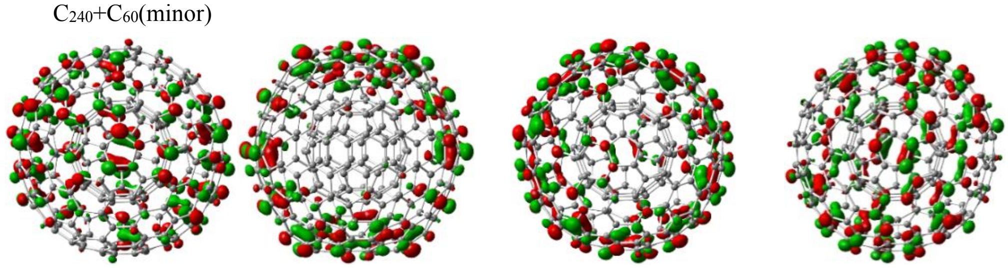
LUMO(1) LUMO(2) LUMO(3) [–2.01 eV]

c) C_{60}@C_{240}(I_h)



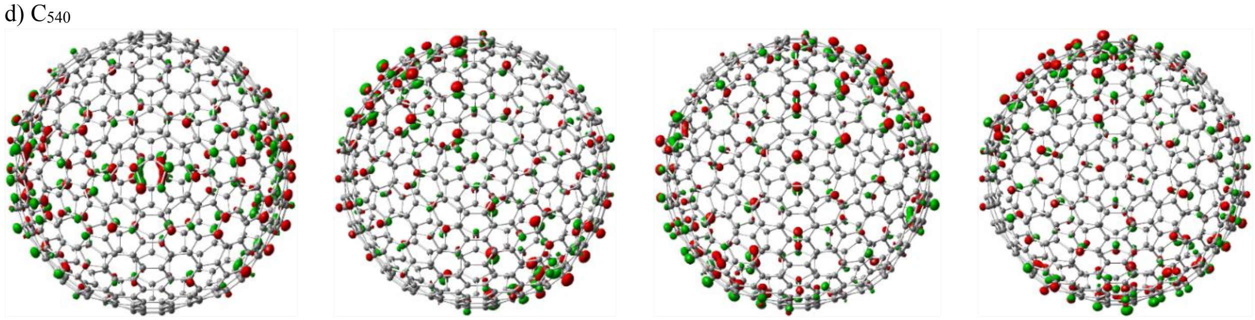
HOMO(1) HOMO(2) HOMO(3) HOMO(4) HOMO(5) [–6.30 eV]

C_{240}+C_{60}(minor)

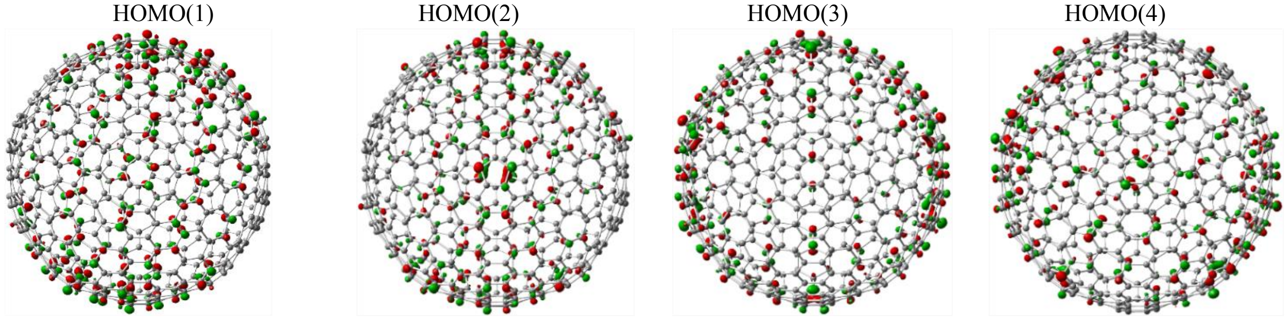


LUMO(1) LUMO(2) LUMO(3) [–2.02 eV] C_{240}

d) C_{540}

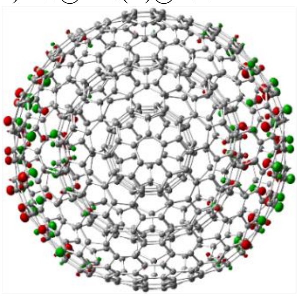


HOMO(1) HOMO(2) HOMO(3) HOMO(4)

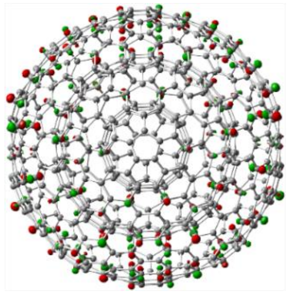


HOMO(5) [–5.89 eV] LUMO(1) LUMO(2) LUMO(3) [–2.44 eV]

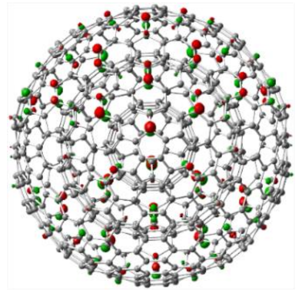
e) $C_{60}@C_{240}(I_h)@C_{540}$



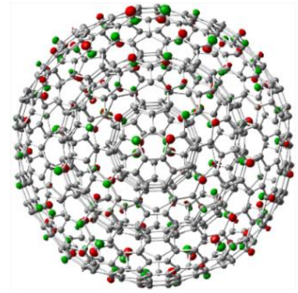
HOMO(1)



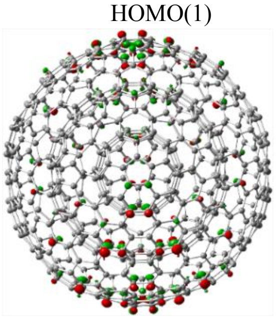
HOMO(2)



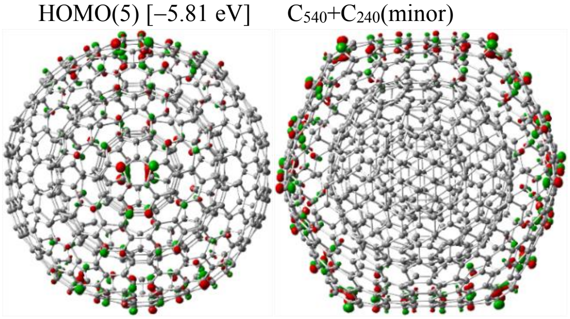
HOMO(3)



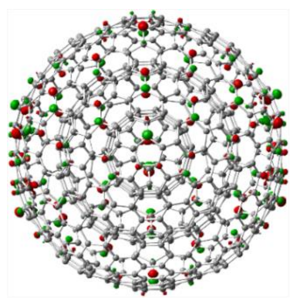
HOMO(4)



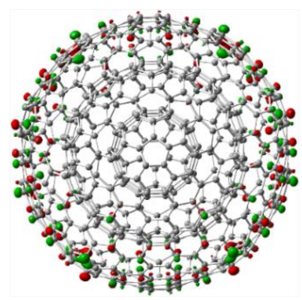
HOMO(5) [−5.81 eV] $C_{540}+C_{240}$(minor)



LUMO(1)

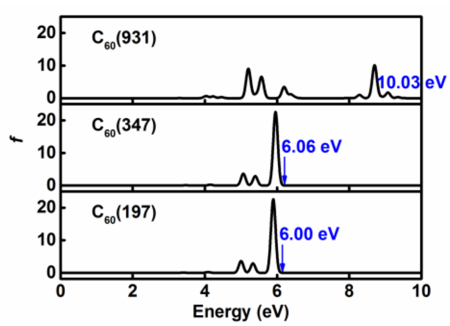


LUMO(2)

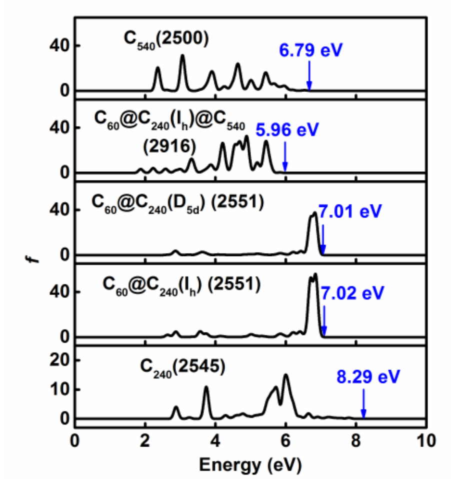


LUMO(3) [−2.46 eV] C_{540}

4. **Fig. S3** Electronic spectra of C_{60} with 197 (14×14), 347 (196 single-electron excitation and 150 double-electron excitation), and 931(31×30) configurations. f is the oscillator strength. The numbers in blue are the predicted highest electron transition energies.



5. **Fig. S4** Electronic spectra of C_{240} [2545 (48×53) configurations], C_{540} [2500 (49×51) configurations], $C_{60}@C_{240}(I_h)$ [2551 (50×51) configurations], $C_{60}@C_{240}(D_{5d})$ [2551 (50×51) configurations], and $C_{60}@C_{240}(I_h)@C_{540}$ [2916 (55×53) configurations]. f is the oscillator strength. The numbers in blue are the predicted highest electron transition energies.



6. **Table S2** The transition nature of the major electron excitations in C_{60}, C_{240}, $C_{60}@C_{240}(I_h)$, C_{540}, and $C_{60}@C_{240}(I_h)@C_{540}$. The numbering of molecular orbitals is in Fig. S4.

Molecules	signs[a]	λ/nm (eV)	f_{total}	f		Transition nature	$\langle\gamma_0\rangle_{contribution}$	$\langle\gamma_0\rangle_{total}$
C_{60} (931)	6_A	376.3		0.006	$S_0\to S_{28}$	H(4)→L+3(3)(15.16%)H(3)→L+3(1)(15.08%)H(1)→L+1(1)(12.82%)	0.00	–10.00
		376.3	0.018	0.006	$S_0\to S_{29}$	H(2)→L+3(4)(10.90%)	0.00	
		376.3		0.006	$S_0\to S_{30}$	NO	0.00	
		(3.29 eV)						
	—	238.3		3.016	$S_0\to S_{193}$	NO	–0.34	
		238.3	9.048	3.016	$S_0\to S_{194}$	NO	–0.52	
		238.3		3.016	$S_0\to S_{195}$	NO	–0.71	
		(5.20 eV)						
	6_B	235.5		0.000	$S_0\to S_{209}$	H–1(5)→L+2(3)(23.63%)H–1(3)→L+2(2)(21.74%)H–1(5)→L+2(1)(18.04%)H–1(4)→L+2(2)(18.03%)	0.00	
		235.5	0.000	0.000	$S_0\to S_{210}$	H–1(4)→L+2(1)(32.56%)H–1(2)→L+2(3)(30.14%)	0.00	
		235.5		0.000	$S_0\to S_{211}$	H–1(1)→L+2(3)(28.20%)H–1(3)→L+2(2)(21.86%)H–1(5)→L+2(1)(12.64%)H–1(4)→L+2(2)(11.09%)	0.00	
		235.5		0.000	$S_0\to S_{212}$	H–1(1)→L+2(2)(35.57%)H–1(2)→L+2(1)(30.54%)H–1(3)→L+2(1)(10.96%)	0.00	
		(5.26 eV)						
	6_C	222.7		2.181	$S_0\to S_{256}$	H–2(4)→L+2(1)(38.78%)H–2(3)→L+2(2)(19.65%)	–0.88	
		222.7	6.543	2.181	$S_0\to S_{257}$	H–2(3)→L+2(2)(25.72%)H–2(2)→L+2(3)(21.41%)H–2(2)→L+2(1)(19.72%)	–1.01	
		222.7		2.181	$S_0\to S_{258}$	H–2(1)→L+2(3)(41.37%)H–2(2)→L+2(2)(10.15%)	–1.14	
		(5.57 eV)						
	—	200.1		1.151	$S_0\to S_{305}$	H–6(5)→L(1)(14.93%)H–6(4)→L(2)(14.72%)H–6(1)→L(3)(14.71%)	–0.55	
		200.1	3.453	1.151	$S_0\to S_{306}$	H–6(4)→L(1)(16.10%)H–6(2)→L(2)(12.24%)	–0.57	
		200.1		1.151	$S_0\to S_{307}$	H–6(5)→L(3)(16.23%)H–6(1)→L(1)(16.10%)H–6(3)→L(2)(10.83%)	–0.58	
		(6.19 eV)						
	—	142.5		3.373	$S_0\to S_{663}$	H–4(5)→L+5(1)(11.93%)	–0.76	
		142.5	10.119	3.373	$S_0\to S_{664}$	NO	–0.78	
		142.5		3.373	$S_0\to S_{665}$	H–4(3)→L+5(2)(11.11%)H–4(1)→L+5(1)(11.10%)H–6(2)→L+4(2)(11.07%)	–0.80	
		(8.70 eV)						
C_{240} (1600)	—	425.8		2.242	$S_0\to S_{40}$	H(2)→L+1(2)(16.39%)H(4)→L+1(3)(14.90%)H(1)→L+1(1)(13.00%)	–1.69	–332.43
		425.8	6.726	2.242	$S_0\to S_{41}$	H(3)→L+1(2)(21.22%)H(2)→L+1(1)(16.57%)H(5)→L+1(3)(16.57%)	–3.93	
		425.8		2.242	$S_0\to S_{42}$	H(5)→L+1(2)(16.39%)H(1)→L+1(3)(12.75%)	–6.18	
		(2.91 eV)						
	—	327.6		6.461	$S_0\to S_{144}$	H(5)→L+2(2)(16.75%)	–27.45	
		327.6	19.383	6.461	$S_0\to S_{145}$	NO	–32.49	
		327.6		6.461	$S_0\to S_{146}$	H(2)→L+2(5)(13.96%)H(3)→L+2(1)(13.68%)	–37.54	
		(3.78 eV)						

	—	224.7		2.231	$S_0 \rightarrow S_{777}$	NO	−6.36	
		224.7	6.693	2.231	$S_0 \rightarrow S_{778}$	NO	−6.40	
		224.7		2.231	$S_0 \rightarrow S_{779}$	NO	−6.44	
		(5.52 eV)						
	—	209.1		3.958	$S_0 \rightarrow S_{938}$	H−9(3)→L+5(13.54%)H−5(2)→L+8(2)(13.47%)H−5(3)→L+8(1)(13.47%)	−12.13	
		209.1	11.874	3.958	$S_0 \rightarrow S_{939}$	H−5(3)→L+8(3)(15.63%)H−9(2)→L+5(13.41%)H−5(1)→L+8(3)(12.84%)	−12.33	
		209.1		3.958	$S_0 \rightarrow S_{940}$	H−5(2)→L+8(3)(15.63%)H−9(1)→L+5(13.41%)H−5(1)→L+8(1)(12.83%)	−12.53	
		(5.93 eV)						
	2_A	203.8		2.665	$S_0 \rightarrow S_{1027}$	H−3(3)→L+6(4)(21.96%)	−8.35	
		203.8	7.995	2.665	$S_0 \rightarrow S_{1028}$	H−3(1)→L+6(2)(23.11%)	−8.54	
		203.8		2.665	$S_0 \rightarrow S_{1029}$	H−3(2)→L+6(3)(14.18%)H−3(2)→L+6(1)(11.39%)	−8.74	
		(6.08 eV)						
	—	197.2		4.677	$S_0 \rightarrow S_{1138}$	NO	−15.68	
		197.2	14.031	4.677	$S_0 \rightarrow S_{1139}$	NO	−15.88	
		197.2		4.677	$S_0 \rightarrow S_{1140}$	NO	−16.09	
		(6.29 eV)						
	2_B	187.5		0.007	$S_0 \rightarrow S_{1317}$	H−7(1)→L+7(5)(13.10%)	0.01	
		187.5	0.021	0.007	$S_0 \rightarrow S_{1318}$	H−7(3)→L+7(4)(10.44%)	0.01	
		187.5		0.007	$S_0 \rightarrow S_{1319}$	H−7(1)→L+7(1)(12.87%)H−7(2)→L+7(2)(10.06%)	0.01	
		(6.61 eV)						
	2_C	187.1		0.000	$S_0 \rightarrow S_{1332}$	NO	0.00	
		187.1		0.000	$S_0 \rightarrow S_{1333}$	H−6(1)→L+7(1)(14.33%)H−6(4)→L+7(5)(13.86%)	0.00	
		187.1	0.000	0.000	$S_0 \rightarrow S_{1334}$	H−6(1)→L+7(2)(10.16%)	0.00	
		187.1		0.000	$S_0 \rightarrow S_{1335}$	NO	0.00	
		187.1		0.000	$S_0 \rightarrow S_{1336}$	H−6(1)→L+7(4)(12.13%)H−6(2)→L+7(2)(12.01%)	0.00	
		(6.63 eV)						
C_{60}@C_{240}(I_h) (2117)	—	469.1		0.701	$S_0 \rightarrow S_{56}$	H−1(5)(C_{60})→L+1(3)(C_{240})(11.23%)H(4)(C_{60} and C_{240})→L+1(2)(C_{240})(10.48%)	0.37	−306.17
		469.1	2.103	0.701	$S_0 \rightarrow S_{57}$	H(3)(C_{60} and C_{240})→L+1(1)(C_{240})(13.15%)H(1)(C_{60} and C_{240})→L+1(3)(C_{240})(11.57%) H(5)(C_{60} and C_{240})→L+1(2)(C_{240})(11.57%)	−0.05	
		469.1		0.701	$S_0 \rightarrow S_{58}$	H−1(3)(C_{60})→L+1(3)(C_{240})(15.17%)	−0.47	
		(2.64 eV)						
	6@2	430.0		1.876	$S_0 \rightarrow S_{85}$	H−1(2)(C_{60})→L+1(1)(C_{240})(14.18%)	−4.43	
		430.0	5.628	1.876	$S_0 \rightarrow S_{86}$	NO	−6.26	
		430.0		1.876	$S_0 \rightarrow S_{87}$	H−1(3)(C_{60})→L+1(3)(C_{240})(13.13%)	−8.10	
		(2.88 eV)						
	—	347.3	5.076	1.692	$S_0 \rightarrow S_{198}$	H(4)(C_{60} and C_{240})→L+3(1)(C_{240})(18.08%)H(2)(C_{60} and C_{240})→L+3(2)(C_{240})(14.98%)	−6.32	
		347.3		1.692	$S_0 \rightarrow S_{199}$	H(5)(C_{60} and C_{240})→L+3(4)(C_{240})(18.95%)H(4)(C_{60} and C_{240})→L+3(5)(C_{240})(11.48%)	−6.91	

					H(3)(C_{60} and C_{240})→L+3(5)(C_{240})(10.50%)	
	347.3		1.692	$S_0 \rightarrow S_{200}$	H(3)(C_{60} and C_{240})→L+3(3)(C_{240})(17.65%)H(1)(C_{60} and C_{240})→L+3(2)(C_{240})(16.17%)	−7.49
	(3.57 eV)					
—	331.2	3.189	1.063	$S_0 \rightarrow S_{258}$	H−1(2)(C_{60})→L+3(1)(C_{240})(12.89%)H−1(3)(C_{60})→L+3(2)(C_{240})(10.40%)	−6.28
	331.2		1.063	$S_0 \rightarrow S_{259}$	H−1(5)(C_{60})→L+3(3)(C_{240})(12.56%)H−1(1)(C_{60})→L+3(2)(C_{240})(10.75%)	−6.46
	331.2		1.063	$S_0 \rightarrow S_{260}$	H−1(4)(C_{60})→L+3(4)(C_{240})(21.61%)H−1(2)(C_{60})→L+3(5)(C_{240})(14.32%) H−1(3)(C_{60})→L+3(3)(C_{240})(12.42%)	−6.63
	(3.74 eV)					
6_A	326.6	0.000	0.000	$S_0 \rightarrow S_{285}$	H−1(2)(C_{60})→L+12(1)(C_{60})(15.25%)H−1(5)(C_{60})→L+12(2)(C_{60})(14.71%)	0.00
	326.6		0.000	$S_0 \rightarrow S_{286}$	H−1(4)(C_{60})→L+12(3)(C_{60})(14.17%)	0.00
	326.6		0.000	$S_0 \rightarrow S_{287}$	H−1(3)(C_{60})→L+12(5)(C_{60})(11.53%)H−1(4)(C_{60})→L+12(2)(C_{60})(10.99%)	0.00
	326.6		0.000	$S_0 \rightarrow S_{288}$	H−1(1)(C_{60})→L+12(5)(C_{60})(18.28%)H−1(3)(C_{60})→L+12(3)(C_{60})(13.70%)	0.00
	(3.80 eV)					
6_B	247.1	2.379	0.793	$S_0 \rightarrow S_{1002}$	H−6(3)(C_{60})→L+10(1)(C_{60})(10.99%)H−6(4)(C_{60})→L+10(1)(C_{60})(10.21%)	−1.33
	247.1		0.793	$S_0 \rightarrow S_{1003}$	H−6(5)(C_{60})→L+10(2)(C_{60})(14.55%)	−1.34
	247.1		0.793	$S_0 \rightarrow S_{1004}$	H−6(2)(C_{60})→L+10(3)(C_{60})(15.82%)	−1.36
	(5.02 eV)					
6_C	230.4	0.000	0.000	$S_0 \rightarrow S_{1263}$	H−7(4)(C_{60})→L+10(2)(C_{60})(12.95%)H−7(2)(C_{60})→L+10(1)(C_{60})(12.94%)	0.00
	230.4		0.000	$S_0 \rightarrow S_{1264}$	H−7(4)(C_{60})→L+10(3)(C_{60})(12.18%)	0.00
	230.4		0.000	$S_0 \rightarrow S_{1265}$	H−7(2)(C_{60})→L+10(3)(C_{60})(12.18%)	0.00
	230.4		0.000	$S_0 \rightarrow S_{1266}$	H−7(2)(C_{60})→L+10(2)(C_{60})(12.95%)H−7(4)(C_{60})→L+10(1)(C_{60})(12.94%)	0.00
	(5.38 eV)					
2_A	200.3	2.247	0.749	$S_0 \rightarrow S_{1866}$	H−4(3)(C_{240})→L+8(1)(C_{240})(30.02%)H−4(2)(C_{240})→L+8(3)(C_{240})(11.79%)	−1.41
	200.3		0.749	$S_0 \rightarrow S_{1867}$	H−4(1)(C_{240})→L+8(2)(C_{240})(23.82%)H−4(3)(C_{240})→L+8(3)(C_{240})(11.92%) H−8(2)(C_{240})→L+11(2)(C_{240})(11.81%)	−1.44
	200.3		0.749	$S_0 \rightarrow S_{1868}$	H−4(2)(C_{240})→L+8(4)(C_{240})(26.53%)H−8(3)(C_{240})→L+11(2)(C_{240})(11.81%) H−4(1)(C_{240})→L+8(3)(C_{240})(10.35%)	−1.48
	(6.19 eV)					
—	192.1	3.195	1.065	$S_0 \rightarrow S_{19\,71}$	H−9(4)(C_{240})→L+12(1)(C_{60})(20.31%)H−9(2)(C_{240})→L+12(5)(C_{60})(12.13%) H−9(3)(C_{240})→L+12(4)(C_{60})(10.46%)	−1.73
	192.1		1.065	$S_0 \rightarrow S_{1972}$	H−9(5)(C_{240})→L+12(3)(C_{60})(28.90%)H−9(2)(C_{240})→L+12(1)(C_{60})(21.68%)	−1.76
	192.1		1.065	$S_0 \rightarrow S_{1973}$	H−9(1)(C_{240})→L+12(2)(C_{60})(27.08%)H−9(3)(C_{240})→L+12(4)(C_{60})(19.32%) H−9(4)(C_{240})→L+12(3)(C_{60})(10.37%)	−1.80
	(6.45 eV)					
2_B	190.0	6.567	2.189	$S_0 \rightarrow S_{2031}$	H−10(2)(C_{240})→L+9(2)(C_{240})(33.01%)H−10(1)(C_{240})→L+9(1)(C_{240})(14.04%)	−3.59
	190.0		2.189	$S_0 \rightarrow S_{2032}$	H−10(3)(C_{240})→L+9(5)(C_{240})(31.12%)H−10(1)(C_{240})→L+9(1)(C_{240})(26.95%)	−3.61
	190.0		2.189	$S_0 \rightarrow S_{2033}$	H−10(3)(C_{240})→L+9(4)(C_{240})(27.69%)H−10(1)(C_{240})→L+9(3)(C_{240})(21.66%) H−10(2)(C_{240})→L+9(5)(C_{240})(12.82%)	−3.63

		(6.53 eV)						
	—	187.8		10.463	$S_0 \rightarrow S_{2061}$	H−10(1)(C_{240})→L+12(1)(C_{60})(18.65%)H−10(2)(C_{240})→L+12(3)(C_{60})(12.75%)	−19.12	
		187.8	31.387	10.462	$S_0 \rightarrow S_{2062}$	H−10(3)(C_{240})→L+12(5)(C_{60})(22.57%)H−10(2)(C_{240})→L+12(3)(C_{60})(12.49%)	−19.82	
		187.8		10.462	$S_0 \rightarrow S_{2063}$	H−10(3)(C_{240})→L+12(2)(C_{60})(17.97%)H−10(2)(C_{240})→L+12(4)(C_{60})(15.31%)	−20.52	
		(6.60 eV)						
	—	187.2		8.251	$S_0 \rightarrow S_{2071}$	H−10(1)(C_{240})→L+12(1)(C_{60})(15.43%)H−8(1)(C_{240})→L+11(3)(C_{240})(10.31%)	−18.67	
		187.2	24.752	8.250	$S_0 \rightarrow S_{2072}$	H−10(3)(C_{240})→L+12(2)(C_{60})(11.77%)H−10(2)(C_{240})→L+12(4)(C_{60})(10.03%)	−19.09	
		187.2		8.251	$S_0 \rightarrow S_{2073}$	H−10(3)(C_{240})→L+12(5)(C_{60})(14.09%)H−10(2)(C_{240})→L+12(3)(C_{60})(12.07%) H−8(1)(C_{240})→L+11(1)(C_{240})(10.31%)	−19.50	
		(6.62 eV)						
	2_C	186.5		13.108	$S_0 \rightarrow S_{2084}$	H−9(1)(C_{240})→L+9(4)(C_{240})(23.97%)H−9(3)(C_{240})→L+9(5)(C_{240})(14.64%)	−31.95	
		186.4	39.327	13.109	$S_0 \rightarrow S_{2085}$	H−9(4)(C_{240})→L+9(1)(C_{240})(15.45%)H−9(3)(C_{240})→L+9(3)(C_{240})(11.61%)	−33.50	
		186.4		13.110	$S_0 \rightarrow S_{2086}$	H−9(5)(C_{240})→L+9(2)(C_{240})(22.30%)H−9(2)(C_{240})→L+9(1)(C_{240})(14.01%)	−35.06	
		(6.65 eV)						
C_{540} (1850)	—	523.3		7.108	$S_0 \rightarrow S_{40}$	H(2)→L+1(1)(21.64%)H(4)→L+1(3)(13.84%)H(3)→L+1(2)(10.83%)	−72.60	−3266.74
		523.3	21.324	7.108	$S_0 \rightarrow S_{41}$	H(5)→L+1(2)(10.83%)	−137.54	
		523.3		7.108	$S_0 \rightarrow S_{42}$	H(1)→L+1(2)(13.02%)H(3)→L+1(3)(10.72%)H(5)→L+1(1)(10.72%)	−202.47	
		(2.37 eV)						
	—	402.2		10.963	$S_0 \rightarrow S_{137}$	H(2)→L+2(4)(10.74%)	−349.46	
		402.2	32.889	10.963	$S_0 \rightarrow S_{138}$	H(4)→L+2(1)(10.07%)	−389.43	
		402.2		10.963	$S_0 \rightarrow S_{139}$	H(1)→L+2(3)(12.54%)H(5)→L+2(5)(11.70%)	−429.40	
		(3.08 eV)						
	5_A	319.4		2.709	$S_0 \rightarrow S_{387}$	NO	−64.53	
		319.4	8.127	2.709	$S_0 \rightarrow S_{388}$	H−2(4)→L+3(2)(10.05%)	−65.29	
		319.4		2.709	$S_0 \rightarrow S_{389}$	NO	−66.04	
		(3.88 eV)						
	—	313.8		3.428	$S_0 \rightarrow S_{430}$	H−6(1)→L+1(1)(12.02%)H−7(3)→L(1)(11.54%)H−7(2)→L(2)(11.43%)	−71.59	
		313.8	10.284	3.428	$S_0 \rightarrow S_{431}$	H−7(1)→L(1)(11.54%)H−7(2)→L(3)(11.43%)	−72.66	
		313.8		3.428	$S_0 \rightarrow S_{432}$	H−7(1)→L(2)(11.84%)H−7(3)→L(3)(11.84%)H−6(4)→L+1(2)(10.62%)	−73.75	
		(3.95 eV)						
	5_B	276.2		0.056	$S_0 \rightarrow S_{730}$	H−2(4)→L+4(1)(12.49%)	−1.73	
		276.2	0.168	0.056	$S_0 \rightarrow S_{731}$	NO	−1.73	
		276.2		0.056	$S_0 \rightarrow S_{732}$	H−2(2)→L+4(3)(14.31%)	−1.73	
		(4.49 eV)						
	—	269.1		7.716	$S_0 \rightarrow S_{789}$	NO	−145.42	
		269.1	23.148	7.716	$S_0 \rightarrow S_{790}$	NO	−147.95	
		269.1		7.716	$S_0 \rightarrow S_{791}$	NO	−150.50	

		(4.61 eV)						
	—	227.3		3.407	$S_0\rightarrow S_{1331}$	NO	−49.35	
		227.3	10.221	3.407	$S_0\rightarrow S_{1332}$	H−5(3)→L+8(4)(11.81%)	−49.56	
		227.3		3.407	$S_0\rightarrow S_{1333}$	H−5(2)→L +8(2)(13.15%)	−49.78	
		(5.45 eV)						
C_{60}@C_{240} (I_h)@C_{540} (1057)	—	651.0	3.636	1.212	$S_0\rightarrow S_{23}$	H(5)(C_{240} and C_{540})→L+1(1)(C_{540})(14.51%)H(3)(C_{240} and C_{540})→L+1(3)(C_{540})(12.91%)H−1(5)(C_{540})→L(1)(C_{540})(10.93%) H(4)(C_{240} and C_{540})→L+1(2)(C_{540})(10.39%)	−7.61	−2921.44
		651.0		1.212	$S_0\rightarrow S_{24}$	H(1)(C_{240} and C_{540})→L+1(3)(C_{540})(12.91%)H(2)(C_{240} and C_{540})→L+1(2)(C_{540})(12.55%)	−12.99	
		651.0		1.212	$S_0\rightarrow S_{25}$	H(1)(C_{240} and C_{540})→L+1(2)(C_{540})(12.98%)H(3)(C_{240} and C_{540})→L+1(1)(C_{540})(12.98%) H(2)(C_{240} and C_{540})→L+1(3)(C_{540})(11.80%)	−18.38	
		(1.90 eV)						
	6@2	429.0		0.420	$S_0\rightarrow S_{273}$	H−3(3)(C_{60})→L+3(3)(C_{240})(22.44%)H−3(2)(C_{60})→L+3(2)(C_{240})(18.75%) H−3(5)(C_{60})→L+3(1)(C_{240})(12.50%)	−6.22	
		429.0	1.260	0.420	$S_0\rightarrow S_{274}$	H−3(1)(C_{60})→L+3(2)(C_{240})(18.74%)H−3(5)(C_{60})→L+3(1)(C_{240})(10.88%) H−3(4)(C_{60})→L+3(3)(C_{240})(10.47%)H−3(3)(C_{60})→L+3(1)(C_{240})(10.18%)	−6.29	
		429.0		0.420	$S_0\rightarrow S_{275}$	H−3(4)(C_{60})→L+3(2)(C_{240})(16.26%)H−3(2)(C_{60})→L+3(3)(C_{240})(15.57%) H−3(1)(C_{60})→L+3(1)(C_{240})(15.56%)	−6.37	
		(2.89 eV)						
	—	354.7		4.344	$S_0\rightarrow S_{559}$	H−4(5)(C_{240})→L+8(1)(C_{60})(12.19%)H−1(5)(C_{540})→L+8(1)(C_{60}) (11.48%)	−68.19	
		354.7	13.032	4.344	$S_0\rightarrow S_{560}$	H−4(2)(C_{240})→L+8(3)(C_{60})(10.04%)	−71.39	
		354.7		4.344	$S_0\rightarrow S_{561}$	NO	−74.60	
		(3.50 eV)						
	—	339.1		5.685	$S_0\rightarrow S_{633}$	NO	−99.91	
		339.1	17.056	5.685	$S_0\rightarrow S_{634}$	NO	−104.29	
		339.1		5.686	$S_0\rightarrow S_{635}$	NO	−108.68	
		(3.66 eV)						
	5_A	311.9		9.921	$S_0\rightarrow S_{844}$	H−5(2)(C_{540})→L+5(2)(C_{540})(18.87%)H−5(1)(C_{540})→L+5(1)(C_{540})(16.36%)	−205.23	
		311.9	29.763	9.921	$S_0\rightarrow S_{845}$	H−5(1)(C_{540})→L+5(5)(C_{540})(15.65%)H−5(3)(C_{540})→L+5(2)(C_{540})(10.95%) H−5(4)(C_{540})→L+5(1)(C_{540})(10.68%)	−214.02	
		311.9		9.921	$S_0\rightarrow S_{846}$	H−5(4)(C_{540})→L+5(4)(C_{540})(16.64%)H−5(2)(C_{540})→L+5(3)(C_{540})(10.33%)	−222.80	
		(3.98 eV)						
	—	297.8		5.160	$S_0\rightarrow S_{926}$	H−4(5)(C_{240})→L+6(3)(C_{540})(17.94%)H−4(2)(C_{240})→L+6(1)(C_{540})(11.25%)	−117.99	
		297.8	15.479	5.159	$S_0\rightarrow S_{927}$	H−4(4)(C_{240})→L+6(1)(C_{540})(22.48%)H−4(2)(C_{240})→L+6(2)(C_{540})(12.99%)	−119.88	
		297.8		5.160	$S_0\rightarrow S_{928}$	H−4(1)(C_{240})→L+6(2)(C_{540})(20.11%)H−4(3)(C_{240})→L+6(3)(C_{540})(11.65%)	−121.75	
		(4.16 eV)						
	5_B	286.4	25.413	8.471	$S_0\rightarrow S_{999}$	H−5(2)(C_{540})→L+6(1)(C_{540})(33.45%)H−5(2)(C_{540})→L+6(3)(C_{540})(18.55%)	−193.56	
		286.4		8.471	$S_0\rightarrow S_{1000}$	H−5(1)(C_{540})→L+6(3)(C_{540})(50.45%)H−5(3)(C_{540})→L+6(2)(C_{540})(13.37%)	−197.74	

286.4 (4.33 eV)	8.471	$S_0 \rightarrow S_{1001}$	H−5(4)(C_{540})→L+6(2)(C_{540})(43.12%)H−5(3)(C_{540})→L+6(1)(C_{540})(30.42%)	−201.91

[a] The numbers 6, 2, 5, and 6@2 stand for C_{60}, C_{240}, C_{540}, and C_{60}@C_{240}, respectively and subscripts A, B, and C denote three different electronic excitations states of systems.

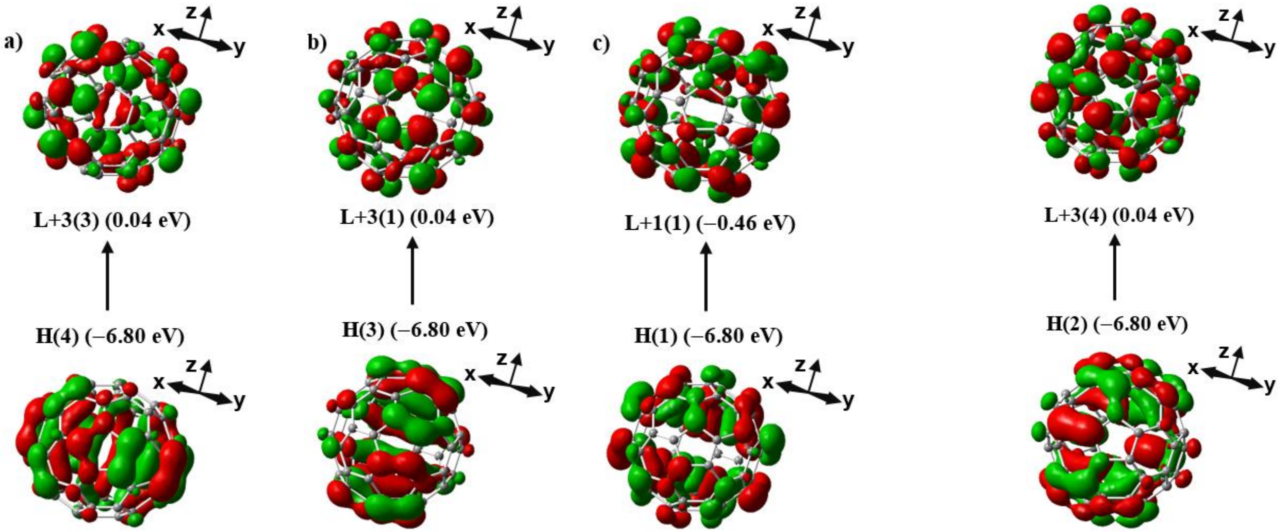
7. **Fig. S5** The molecular orbitals associated with major electron transitions in C_{60}, C_{240}, C_{60}@C_{240}(I_h), C_{540}, and C_{60}@C_{240}(I_h)@C_{540}. In the Cartesian coordinate system, the thin line arrow indicates parallel to the paper surface, the thick arrow indicates outward, and the dotted arrow indicates inward. H denotes HOMO and L denotes LUMO.

1) C_{60} (931) (Isosurface value=0.02) [HOMO–6, HOMO–4, HOMO–1, HOMO and LUMO+3 are five-fold degenerate. LUMO, LUMO+1, LUMO+2, and LUMO+5 are three-fold degenerate. HOMO–2 is four-fold degenerate.]

a. The lowest electronic excitation: 6_A—Corresponding to the transition at 3.80 eV (326.6 nm) in C_{60}@C_{240}.

$S_0 \rightarrow S_{28}$: 376.3 nm (3.29 eV) $S_0 \rightarrow S_{29}$: 376.3 nm (3.29 eV) $S_0 \rightarrow S_{30}$: 376.3 nm (3.29 eV) (NO)

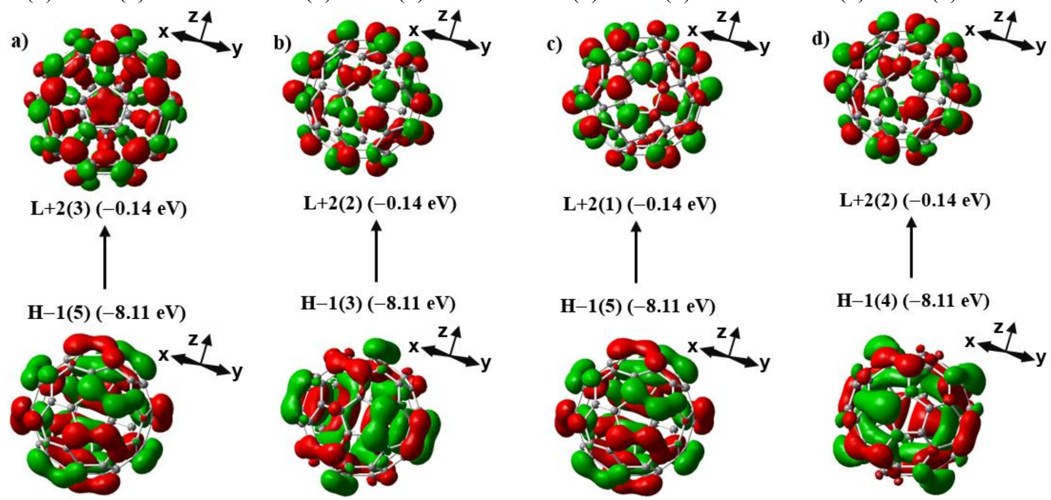
H(4)→L+3(3) 15.16% H(3)→L+3(1) 15.08% H(1)→L+1(1) 12.82% H(2)→L+3(4) 10.90%



b. 6_B—Corresponding to the transition at 5.02 eV (247.1 nm) in $C_{60}@C_{240}$.

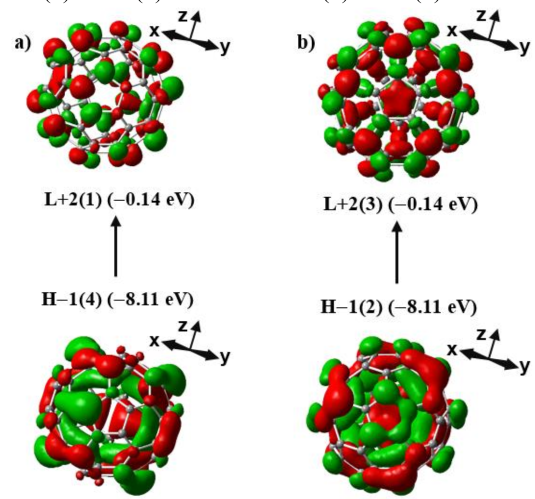
$S_0 \rightarrow S_{209}$: 235.5 nm (5.26 eV)

H−1(5)→L+2(3) 23.63% H−1(3)→L+2(2) 21.74% H−1(5)→L+2(1) 18.04% H−1(4)→L+2(2) 18.03%



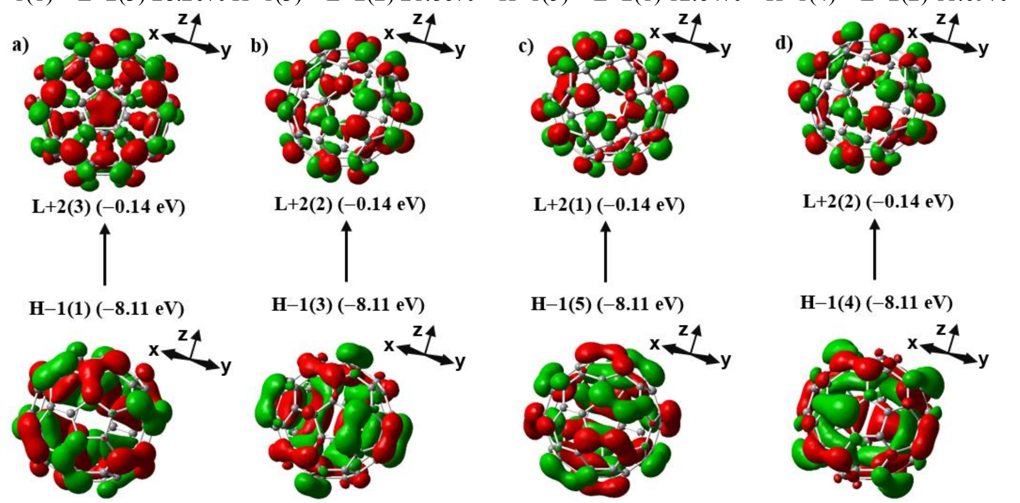
$S_0 \rightarrow S_{210}$: 235.5 nm (5.26 eV)

H−1(4)→L+2(1) 32.56% H−1(2)→L+2(3) 30.14%



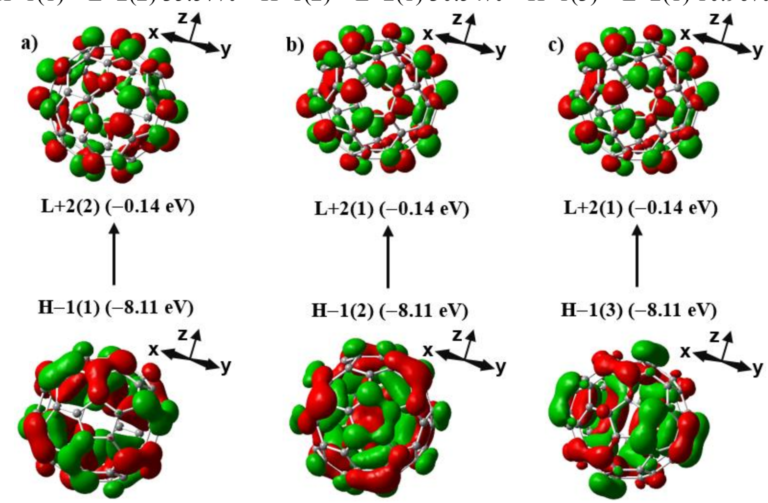
$S_0 \rightarrow S_{211}$: 235.5 nm (5.26 eV)

H−1(1)→L+2(3) 28.20% H−1(3)→L+2(2) 21.86% H−1(5)→L+2(1) 12.64% H−1(4)→L+2(2) 11.09%



$S_0 \rightarrow S_{212}$: 235.5 nm (5.26 eV)

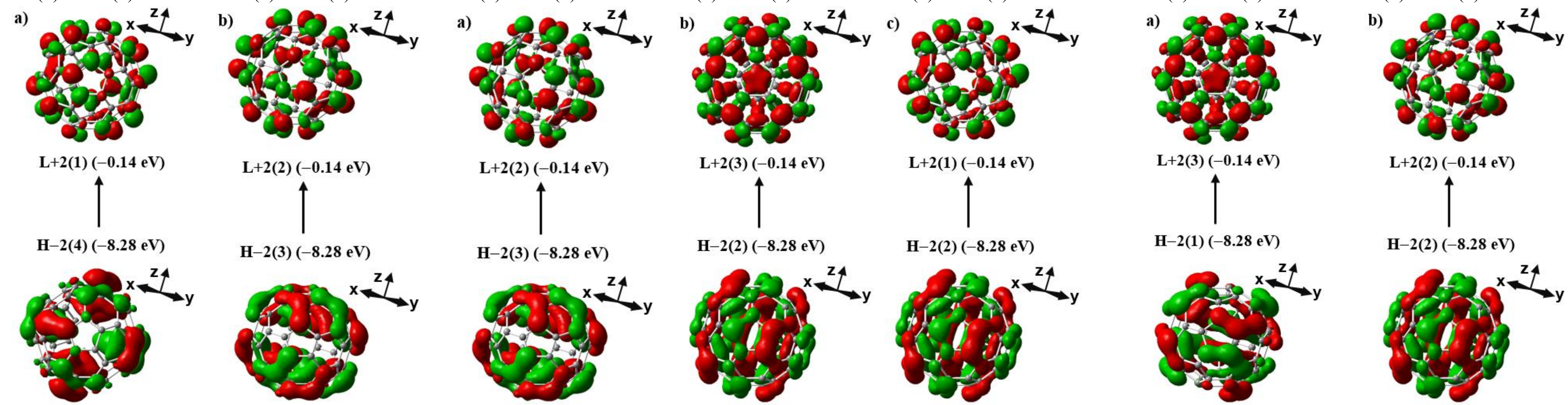
H−1(1)→L+2(2) 35.57% H−1(2)→L+2(1) 30.54% H−1(3)→L+2(1) 10.96%



c. 6C—Corresponding to the transition at 5.37 eV (231.0 nm) in $C_{60}@C_{240}$.

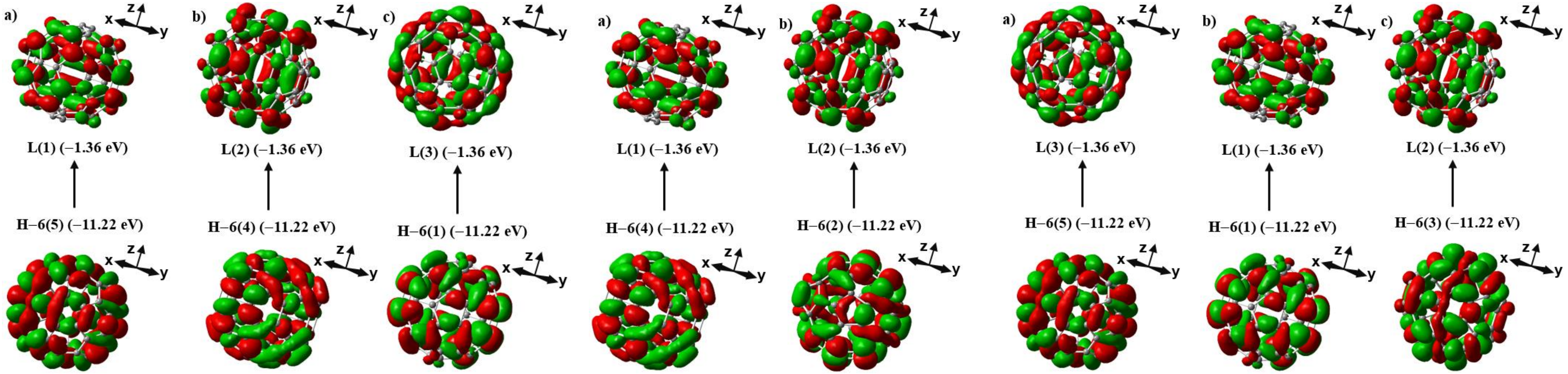
$S_0 \rightarrow S_{256}$: 222.7 nm (5.57 eV) | $S_0 \rightarrow S_{257}$: 222.7 nm (5.57 eV) | $S_0 \rightarrow S_{258}$: 222.7 nm (5.57 eV)

H−2(4)→L+2(1) 38.78% H−2(3)→L+2(2) 19.65% H−2(3)→L+2(2) 25.72% H−2(2)→L+2(3) 21.41% H−2(2)→L+2(1) 19.72% H−2(1)→L+2(3) 41.37% H−2(2)→L+2(2) 10.15%



d. $S_0 \rightarrow S_{305}$: 200.1 nm (6.19 eV) | $S_0 \rightarrow S_{306}$: 200.1 nm (6.19 eV) | $S_0 \rightarrow S_{307}$: 200.1 nm (6.19 eV)

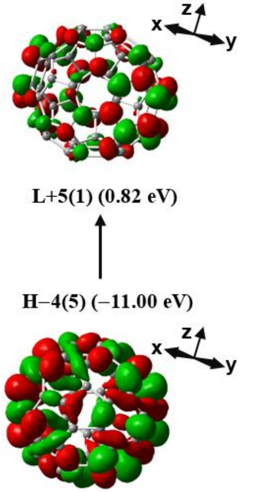
H−6(5)→L(1) 14.93% H−6(4)→L(2) 14.72% H−6(1)→L(3) 14.71% H−6(4)→L(1) 16.10% H−6(2)→L(2) 12.24% H−6(5)→L(3) 16.23% H−6(1)→L(1) 16.10% H−6(3)→L(2) 10.83%



e. The strongest oscillator strength:

$S_0 \rightarrow S_{663}$: 142.5 nm (8.70 eV)

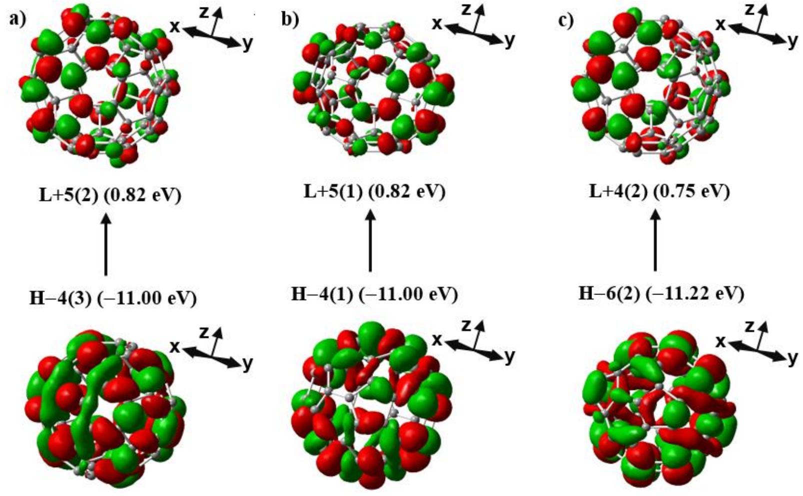
$H-4(5) \rightarrow L+5(1)$ 11.93%



$S_0 \rightarrow S_{664}$: 142.5 nm (8.70 eV) (NO)

$S_0 \rightarrow S_{665}$: 142.5 nm (8.70 eV)

$H-4(3) \rightarrow L+5(2)$ 11.11% $H-4(1) \rightarrow L+5(1)$ 11.10% $H-6(2) \rightarrow L+4(2)$ 11.07%



2) C_{240} (1600) (Isosurface value=0.02) [HOMO−6, HOMO, LUMO+2, and LUMO+7 are five-fold degenerate. HOMO−9, HOMO−7, HOMO−5, HOMO−3, LUMO+1, and LUMO+8 are three-fold degenerate. LUMO+6 is four-fold degenerate. LUMO+5 has no degenerate orbitals.]

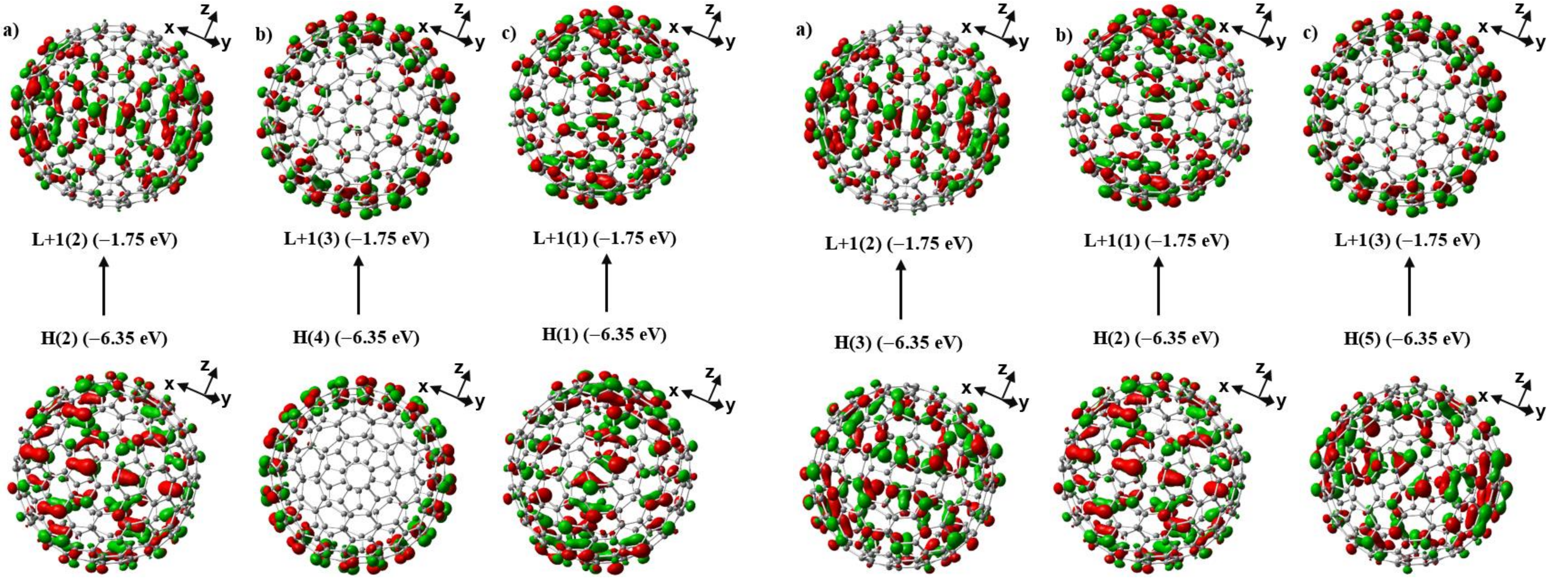
a. The lowest electronic excitation:

$S_0 \rightarrow S_{40}$: 425.8 nm (2.91 eV)

H(2)→L+1(2) 16.39% H(4)→L+1(3) 14.90% H(1)→L+1(1) 13.00%

$S_0 \rightarrow S_{41}$: 425.8 nm (2.91 eV)

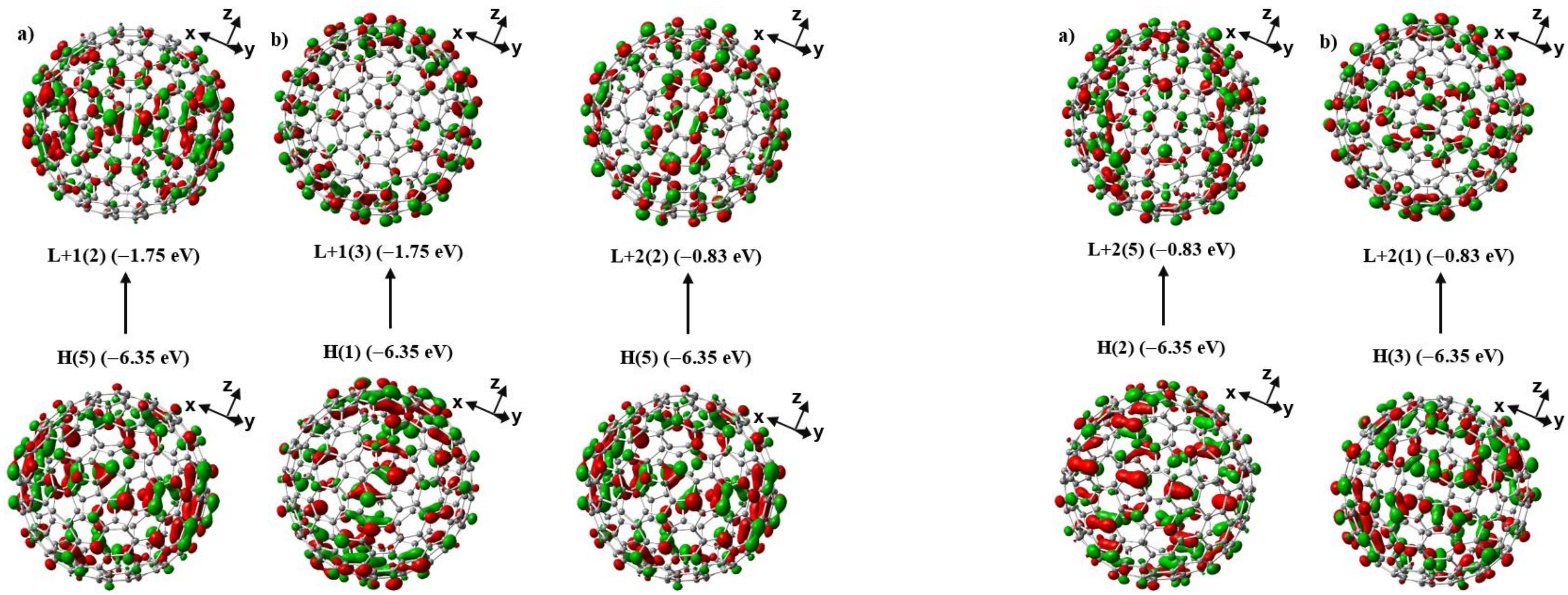
H(3)→L+1(2) 21.22% H(2)→L+1(1) 16.57% H(5)→L+1(3) 16.57%



b. The strongest oscillator strength:

$S_0 \rightarrow S_{42}$: 425.8 nm (2.91 eV) $S_0 \rightarrow S_{144}$: 327.6 nm (3.78 eV) $S_0 \rightarrow S_{145}$: 327.6 nm (3.78 eV) (NO) $S_0 \rightarrow S_{146}$: 327.6 nm (3.78 eV)

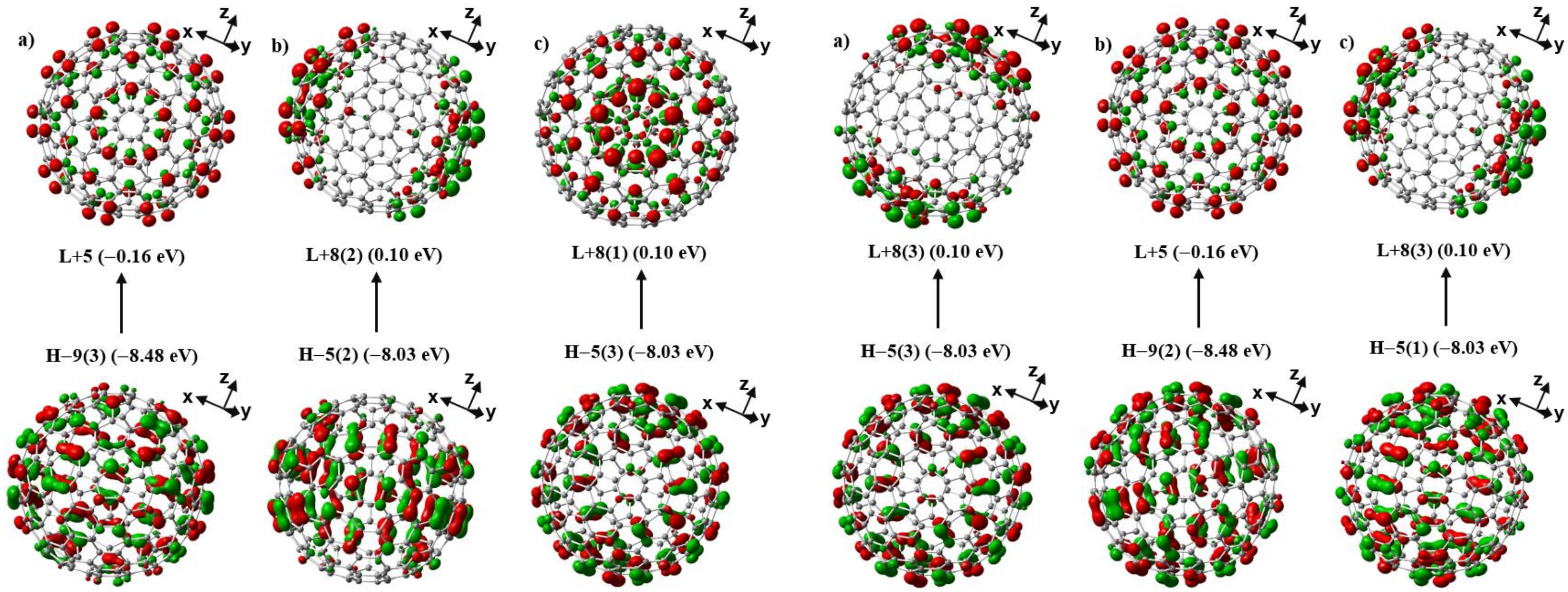
H(5)→L+1(2) 16.39% H(1)→L+1(3) 12.75% H(5)→L+2(2) 16.75% H(2)→L+2(5) 13.96% H(3)→L+2(1) 13.68%

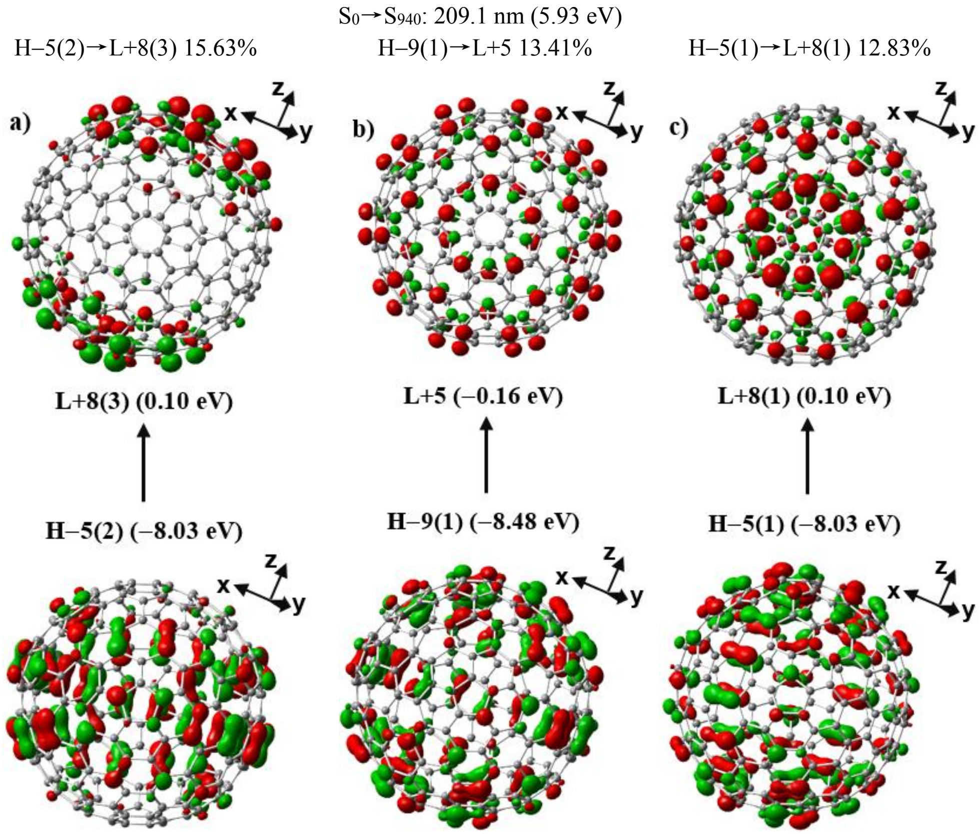


c.

S$_0$→S$_{938}$: 209.1 nm (5.93 eV) S$_0$→S$_{939}$: 209.1 nm (5.93 eV)

H−9(3)→L+5 13.54% H−5(2)→L+8(2) 13.47% H−5(3)→L+8(1) 13.47% H−5(3)→L+8(3) 15.63% H−9(2)→L+5 13.41% H−5(1)→L+8(3) 12.84%

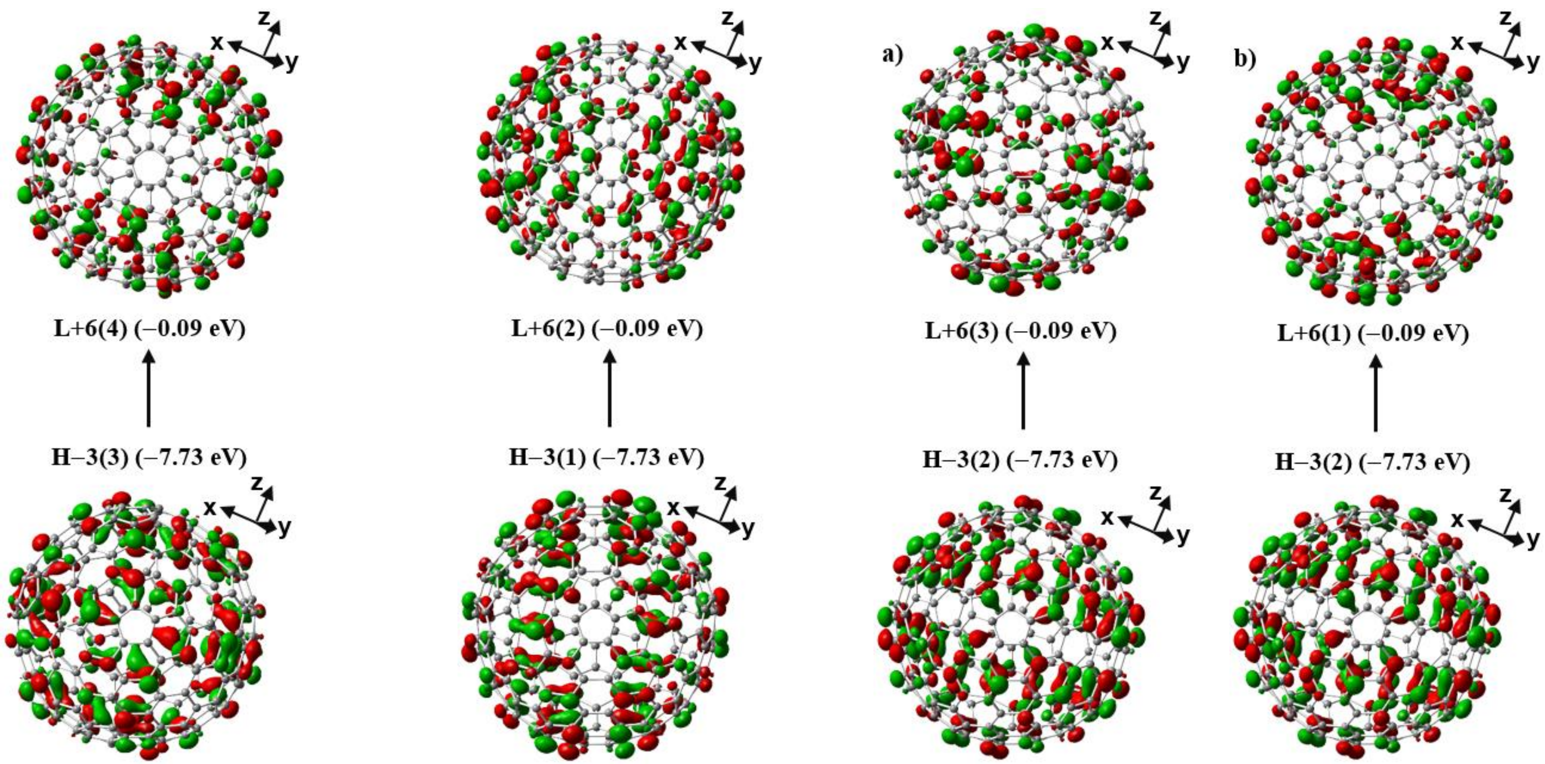



S0→S940: 209.1 nm (5.93 eV)
H−5(2)→L+8(3) 15.63%
H−9(1)→L+5 13.41%
H−5(1)→L+8(1) 12.83%
a)
b)
c)
L+8(3) (0.10 eV)
L+5 (−0.16 eV)
L+8(1) (0.10 eV)
H−5(2) (−8.03 eV)
H−9(1) (−8.48 eV)
H−5(1) (−8.03 eV)
x
y
z

d. 2_A—Corresponding to the transition at 6.19 eV (200.3 nm) in $C_{60}@C_{240}$.

$S_0 \rightarrow S_{1027}$: 203.8 nm (6.08 eV) | $S_0 \rightarrow S_{1028}$: 203.8 nm (6.08 eV) | $S_0 \rightarrow S_{1029}$: 203.8 nm (6.08 eV)

H−3(3)→L+6(4) 21.96% | H−3(1)→L+6(2) 23.11% | H−3(2)→L+6(3) 14.18% | H−3(2)→L+6(1) 11.39%

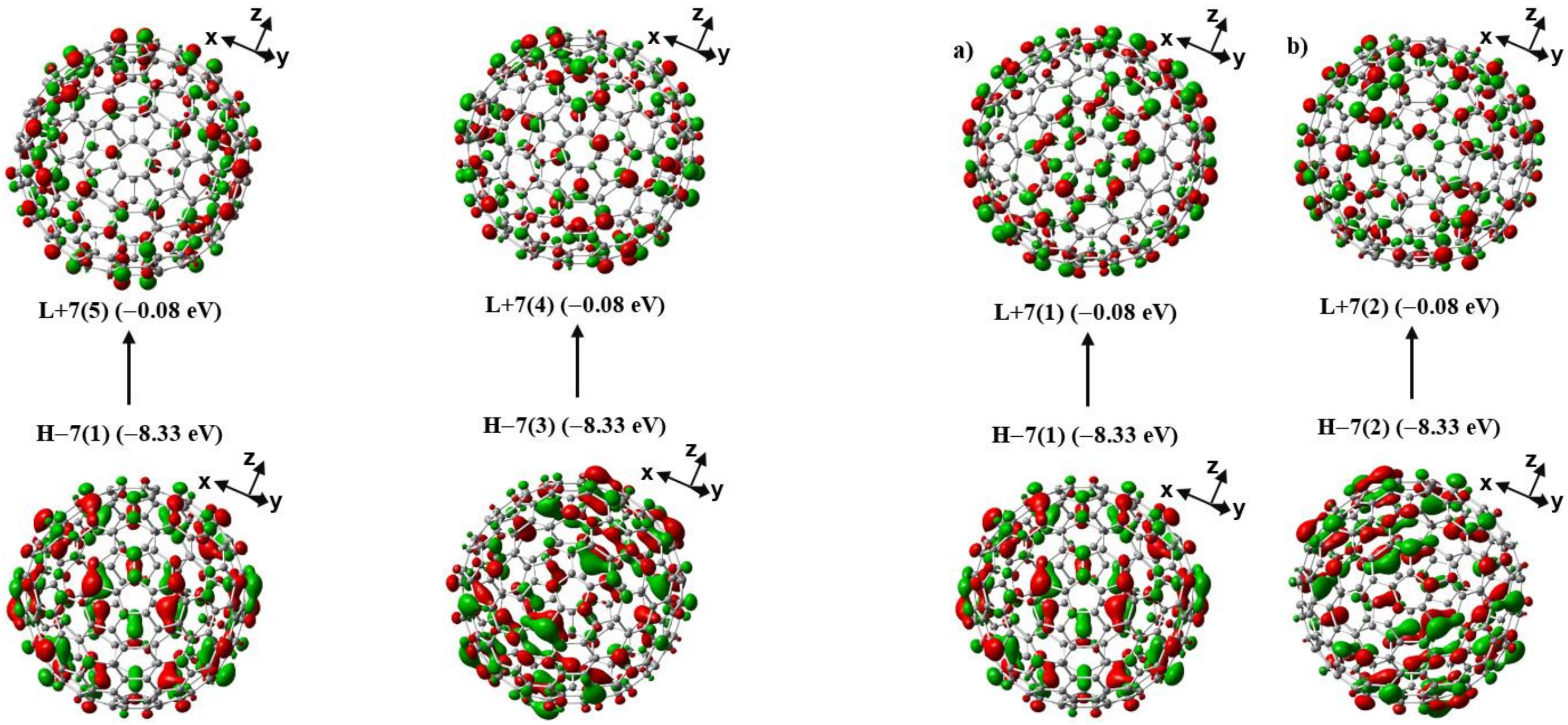


e. 2_B—Corresponding to the transition at 6.53 eV (190.0 nm) in $C_{60}@C_{240}$.

$S_0 \rightarrow S_{1317}$: 187.5 nm (6.61 eV)
H−7(1)→L+7(5) 13.10%

$S_0 \rightarrow S_{1318}$: 187.5 nm (6.61 eV)
H−7(3)→L+7(4) 10.44%

$S_0 \rightarrow S_{1319}$: 187.5 nm (6.61 eV)
H−7(1)→L+7(1) 12.87%   H−7(2)→L+7(2) 10.06%



f. 2c—Corresponding to the transition at 6.65 eV (186.4 nm) in $C_{60}@C_{240}$.

$S_0 \rightarrow S_{1332}$: 187.1 nm (6.63 eV) (NO)

$S_0 \rightarrow S_{1333}$: 187.1 nm (6.63 eV)

H−6(1)→L+7(1) 14.33% H−6(4)→L+7(5) 13.86%

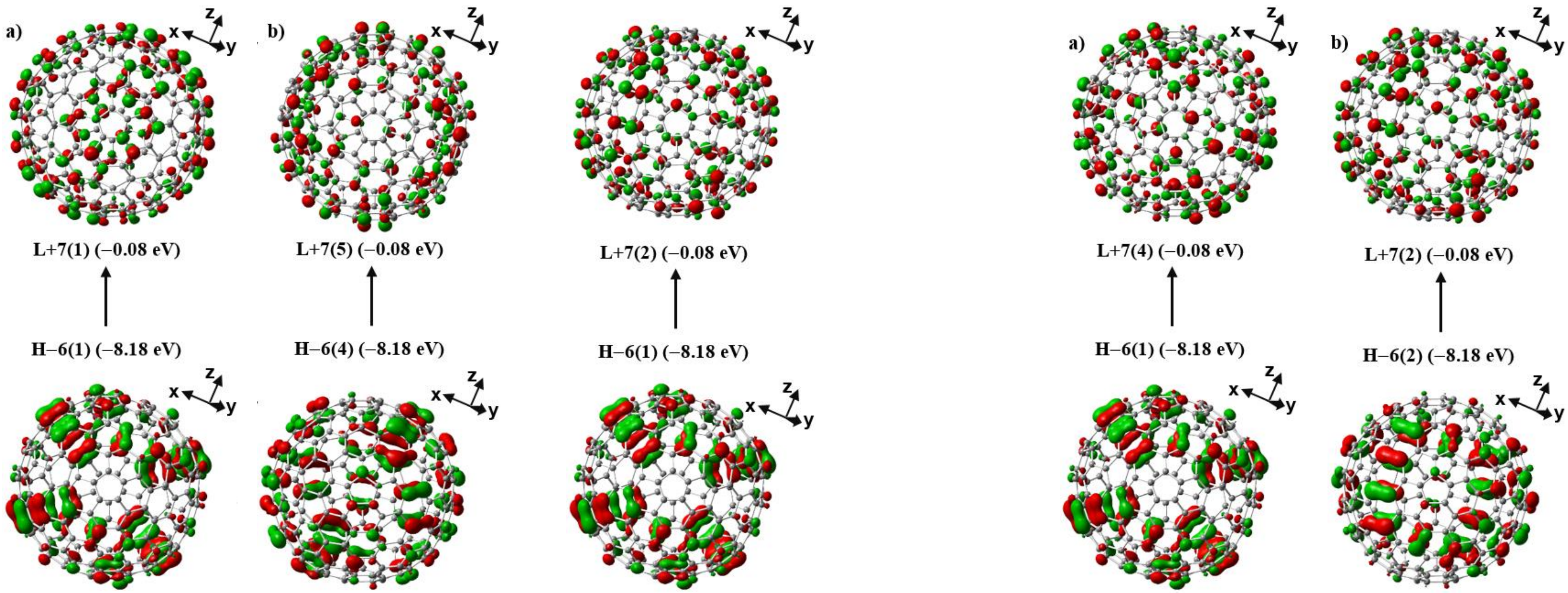
$S_0 \rightarrow S_{1334}$: 187.1 nm (6.63 eV)

H−6(1)→L+7(2) 10.16%

$S_0 \rightarrow S_{1335}$: 187.1 nm (6.63 eV) (NO)

$S_0 \rightarrow S_{1336}$: 187.1 nm (6.63 eV)

H−6(1)→L+7(4) 12.13% H−6(2)→L+7(2) 12.01%

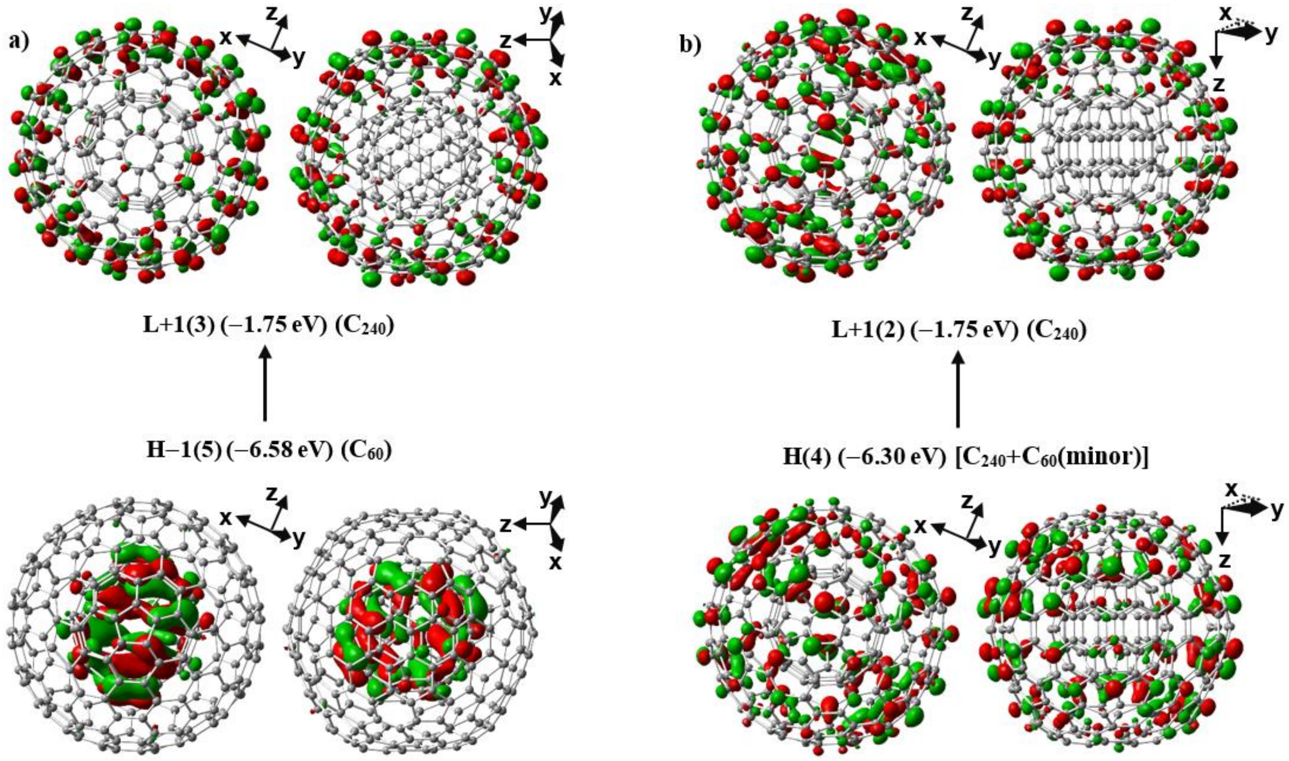


3) $C_{60}@C_{240}$ (2117) (Isosurface value=0.02) [HOMO−9, HOMO−6, HOMO−1, HOMO, LUMO+3, LUMO+9, and LUMO+12 are five-fold degenerate. HOMO−10, HOMO−8, HOMO−4, LUMO+1, LUMO+10, and LUMO+11 are three-fold degenerate. HOMO−7 and LUMO+8 are four-fold degenerate.]

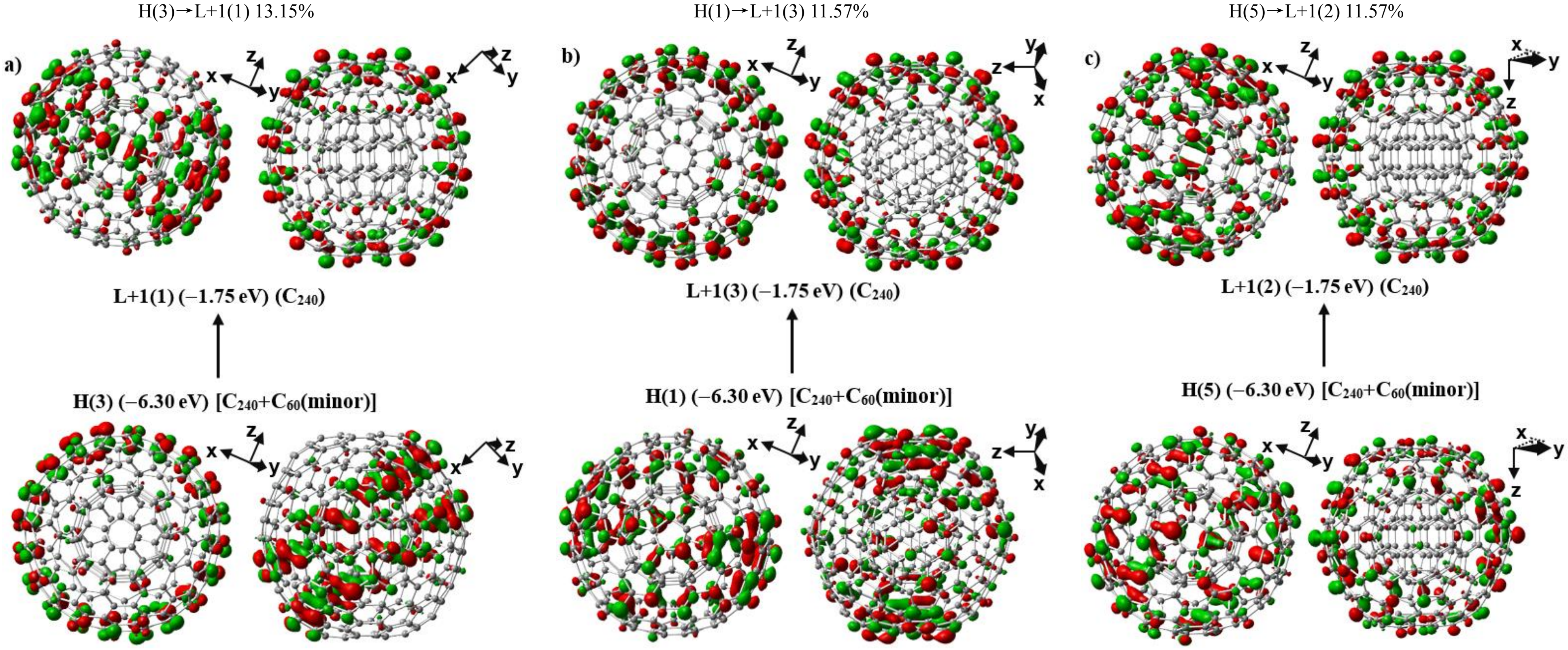
a. The lowest electronic excitation:

$S_0 \rightarrow S_{56}$: 469.1 nm (2.64 eV)

H−1(5)→L+1(3) 11.23% H(4)→L+1(2) 10.48%



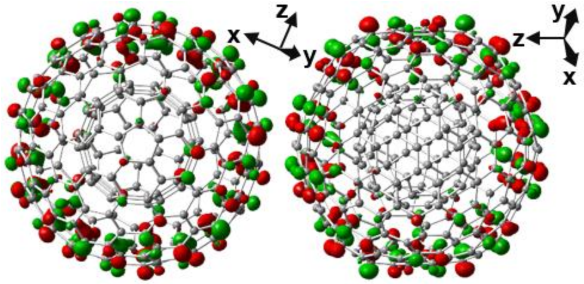
$S_0 \rightarrow S_{57}$: 469.1 nm (2.64 eV)



b. 6@2—Corresponding to the transition at 2.89 eV (429.0 nm) in $C_{60}@C_{240}@C_{540}$.

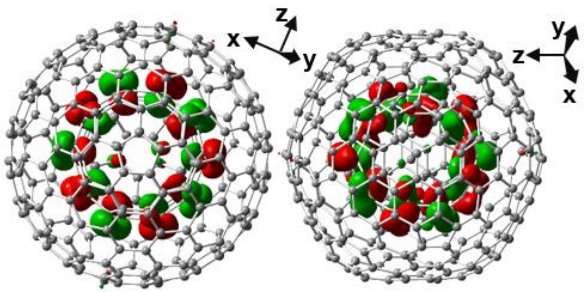
$S_0 \rightarrow S_{58}$: 469.1 nm (2.64 eV)

H−1(3)→L+1(3) 15.17%



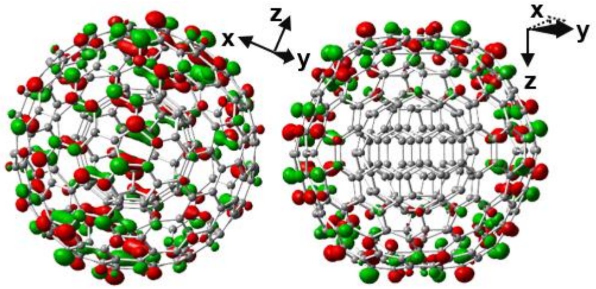
L+1(3) (−1.75 eV) (C_{240})

H−1(3) (−6.58 eV) (C_{60})



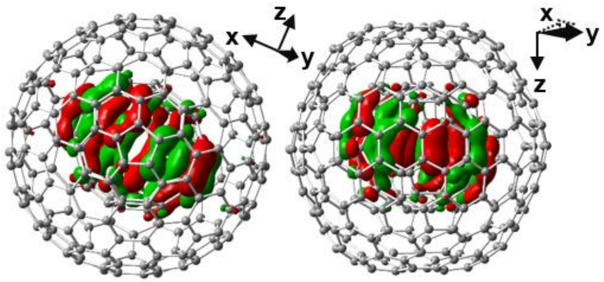
$S_0 \rightarrow S_{85}$: 430.0 nm (2.88 eV)

H−1(2)→L+1(1) 14.18%



L+1(1) (−1.75 eV) (C_{240})

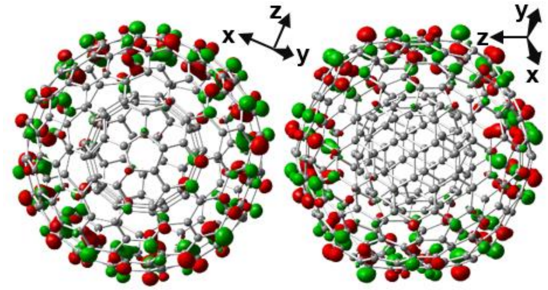
H−1(2) (−6.58 eV) (C_{60})



$S_0 \rightarrow S_{86}$: 430.0 nm (2.88 eV) (NO)

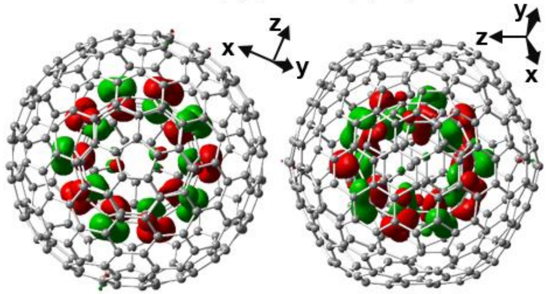
$S_0 \rightarrow S_{87}$: 430.0 nm (2.88 eV)

H−1(3)→L+1(3) 13.13%



L+1(3) (−1.75 eV) (C_{240})

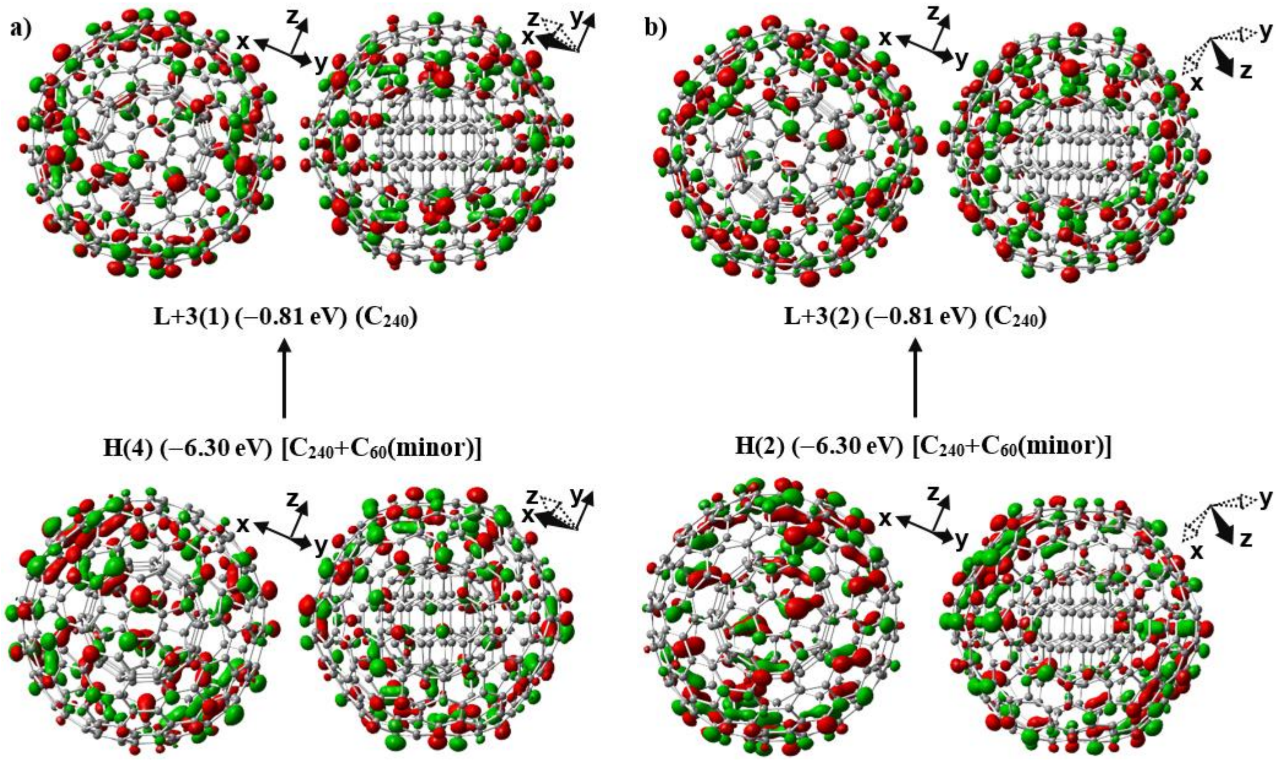
H−1(3) (−6.58 eV) (C_{60})



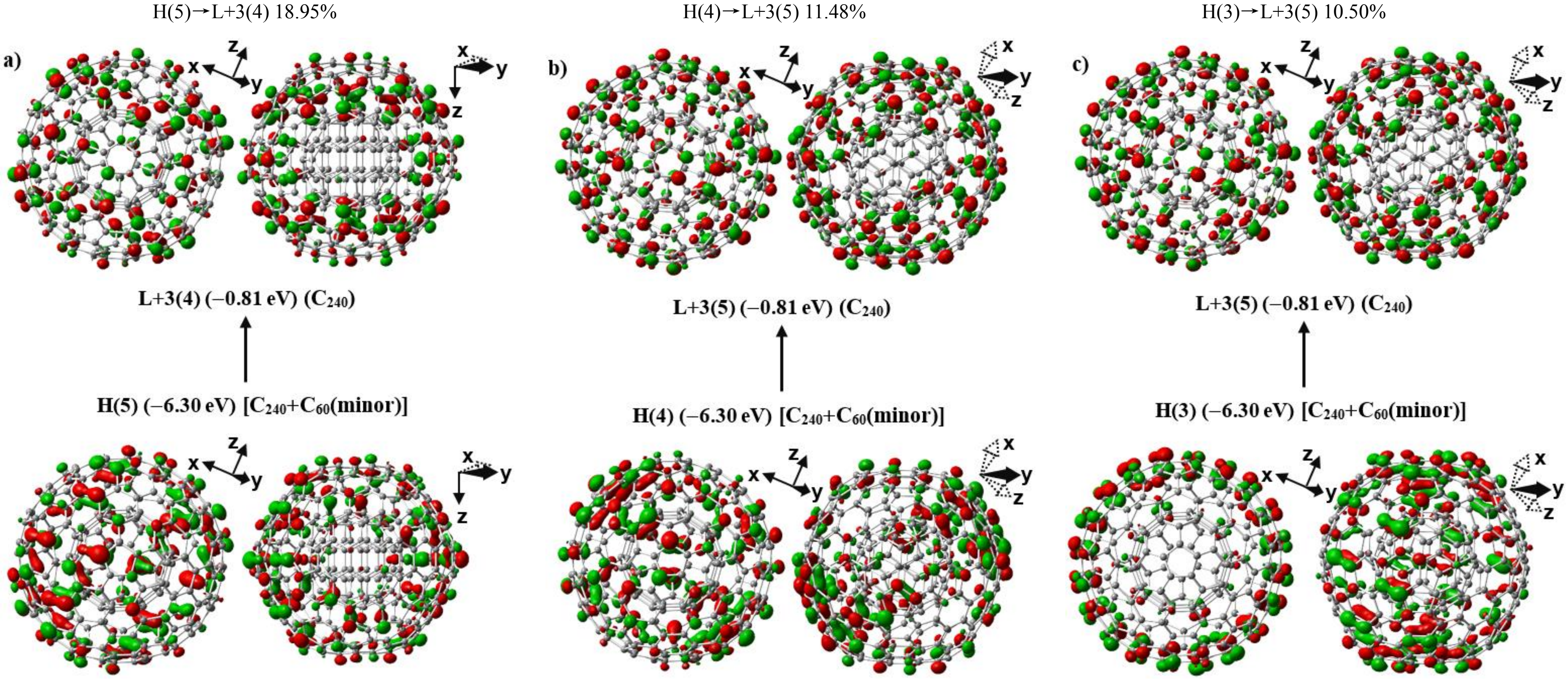
c. $S_0 \rightarrow S_{198}$: 347.3 nm (3.57 eV)

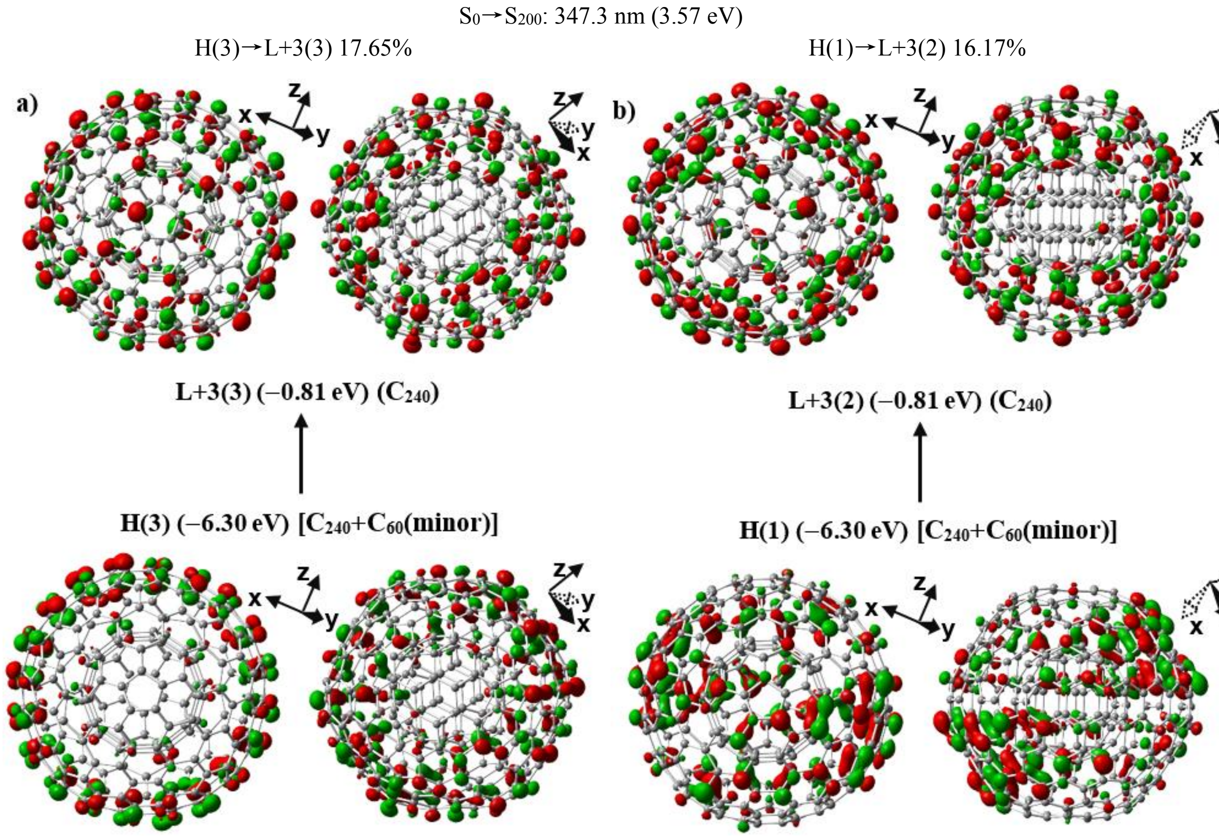
H(4)→L+3(1) 18.08%

H(2)→L+3(2) 14.98%



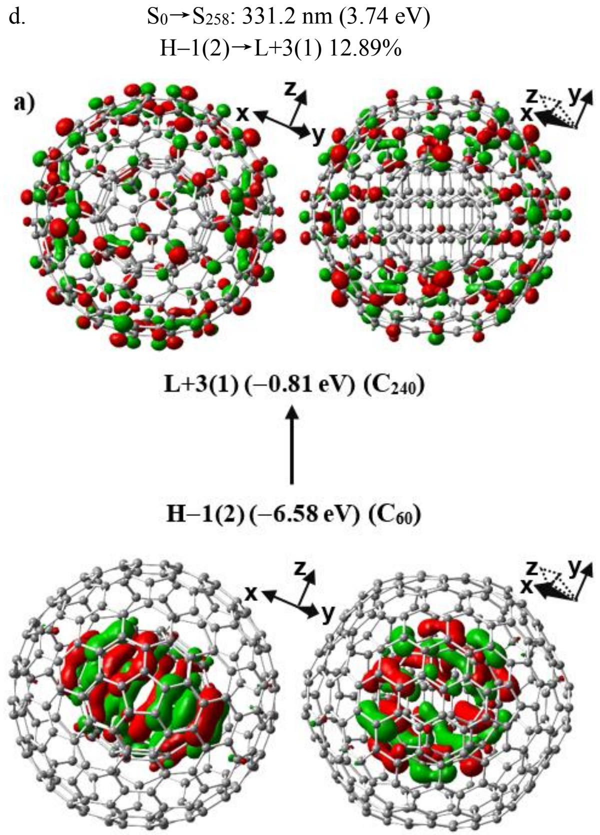
$S_0 \rightarrow S_{199}$: 347.3 nm (3.57 eV)





$S_0 \rightarrow S_{200}$: 347.3 nm (3.57 eV)
H(3)→L+3(3) 17.65%
H(1)→L+3(2) 16.17%
a)
b)
L+3(3) (−0.81 eV) (C_{240})
L+3(2) (−0.81 eV) (C_{240})
H(3) (−6.30 eV) [C_{240}+C_{60}(minor)]
H(1) (−6.30 eV) [C_{240}+C_{60}(minor)]

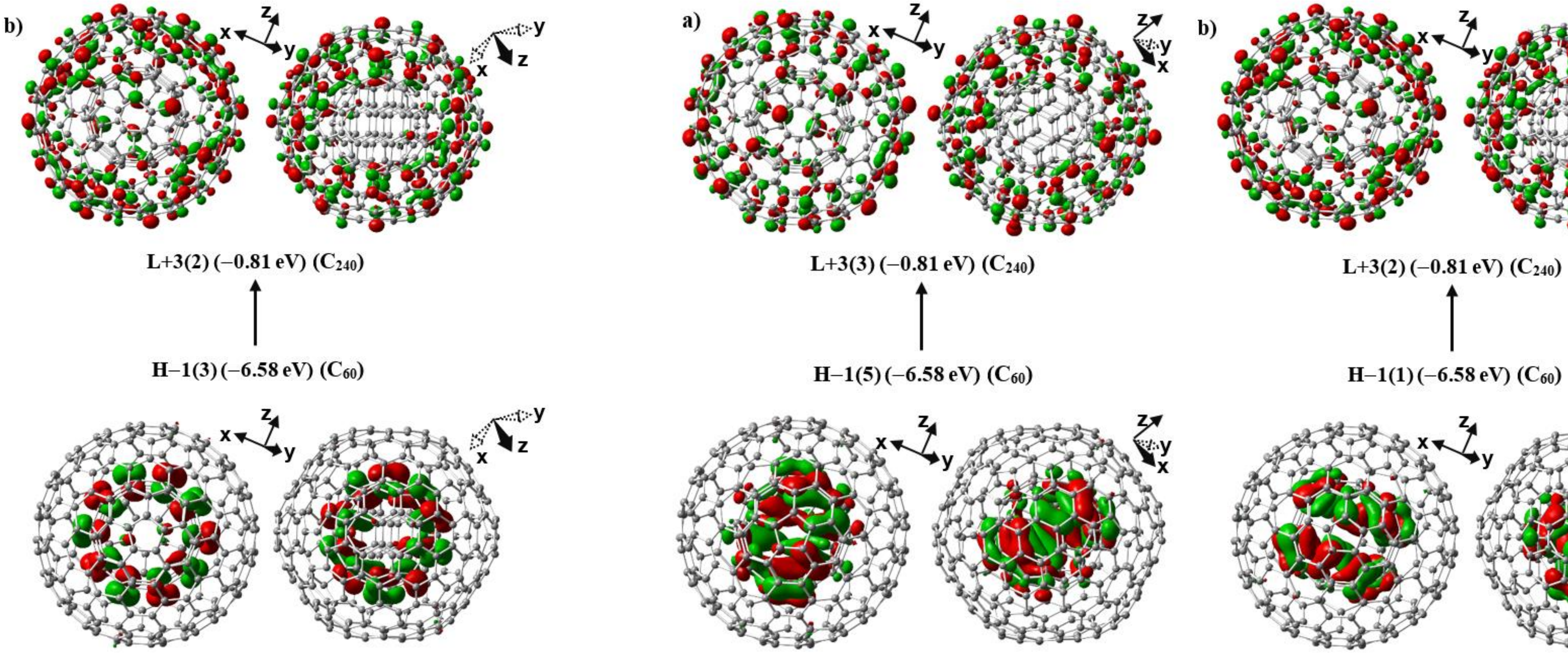
d.

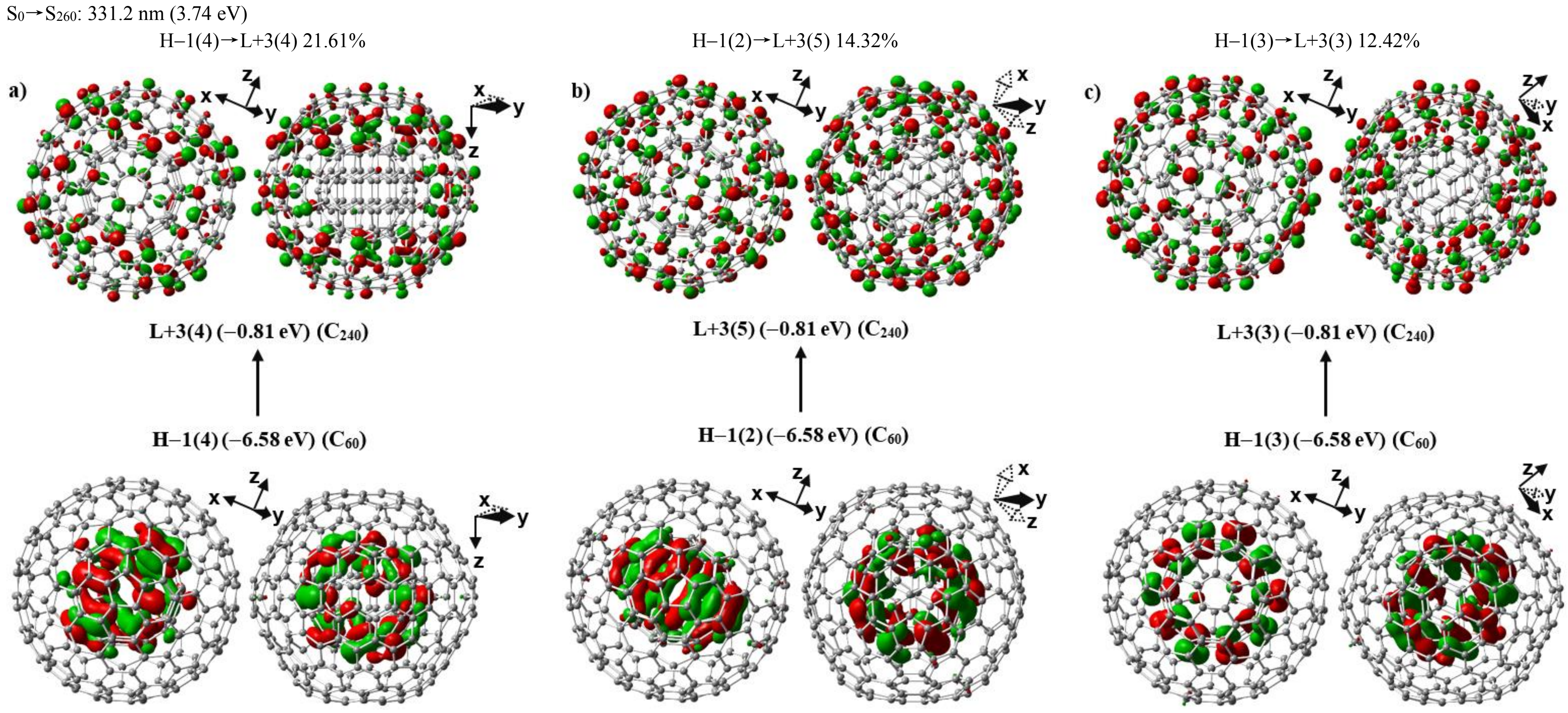


$S_0 \rightarrow S_{258}$: 331.2 nm (3.74 eV)
H−1(2)→L+3(1) 12.89%
a)
L+3(1) (−0.81 eV) (C_{240})
H−1(2) (−6.58 eV) (C_{60})

$S_0 \rightarrow S_{259}$: 331.2 nm (3.74 eV)

H−1(3)→L+3(2) 10.40% H−1(5)→L+3(3) 12.56% H−1(1)→L+3(2) 10.75%




S0→S260: 331.2 nm (3.74 eV)
H−1(4)→L+3(4) 21.61%
H−1(2)→L+3(5) 14.32%
H−1(3)→L+3(3) 12.42%
a)
b)
c)
x
y
z
L+3(4) (−0.81 eV) (C240)
L+3(5) (−0.81 eV) (C240)
L+3(3) (−0.81 eV) (C240)
H−1(4) (−6.58 eV) (C60)
H−1(2) (−6.58 eV) (C60)
H−1(3) (−6.58 eV) (C60)

e. 6_A—Corresponding to the transition at 3.29 eV (376.3 nm) in C_{60}.

$S_0 \rightarrow S_{285}$: 326.6 nm (3.80 eV)

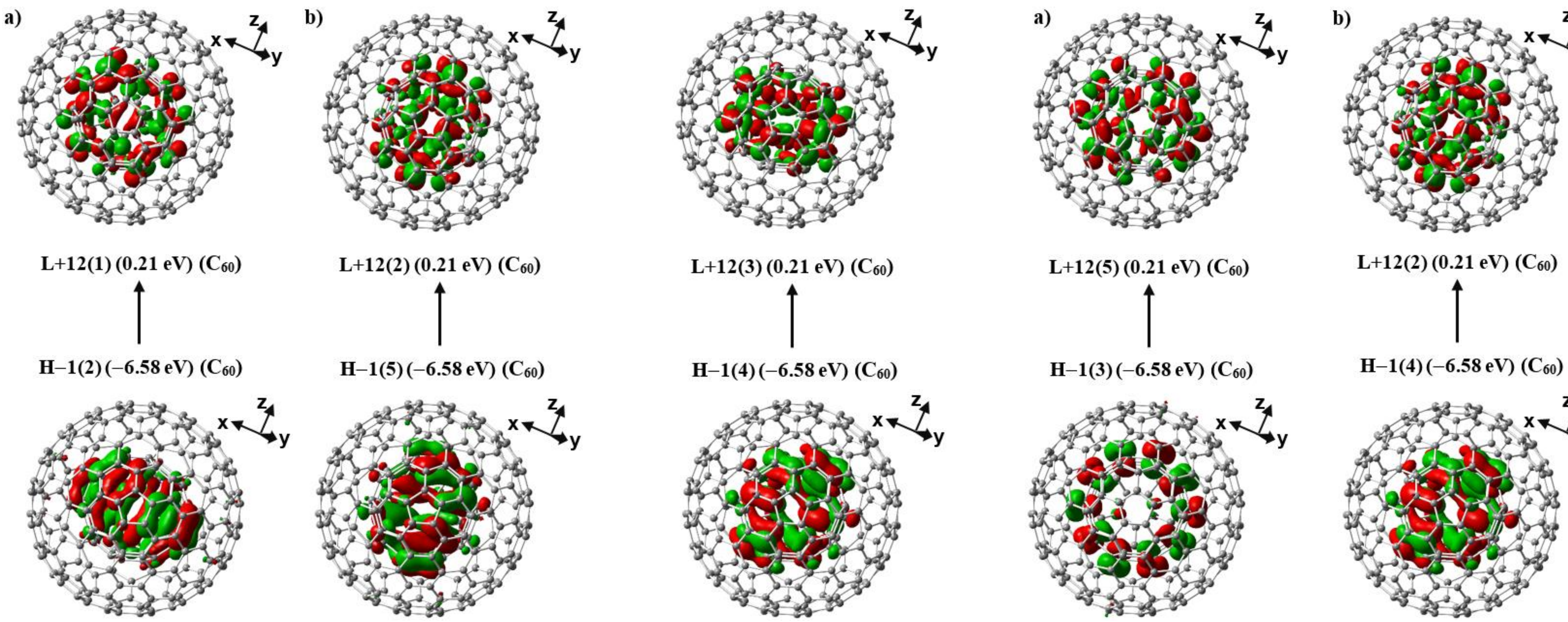
H−1(2)→L+12(1) 15.25% H−1(5)→L+12(2) 14.71%

$S_0 \rightarrow S_{286}$: 326.6 nm (3.80 eV)

H−1(4)→L+12(3) 14.17%

$S_0 \rightarrow S_{287}$: 326.6 nm (3.80 eV)

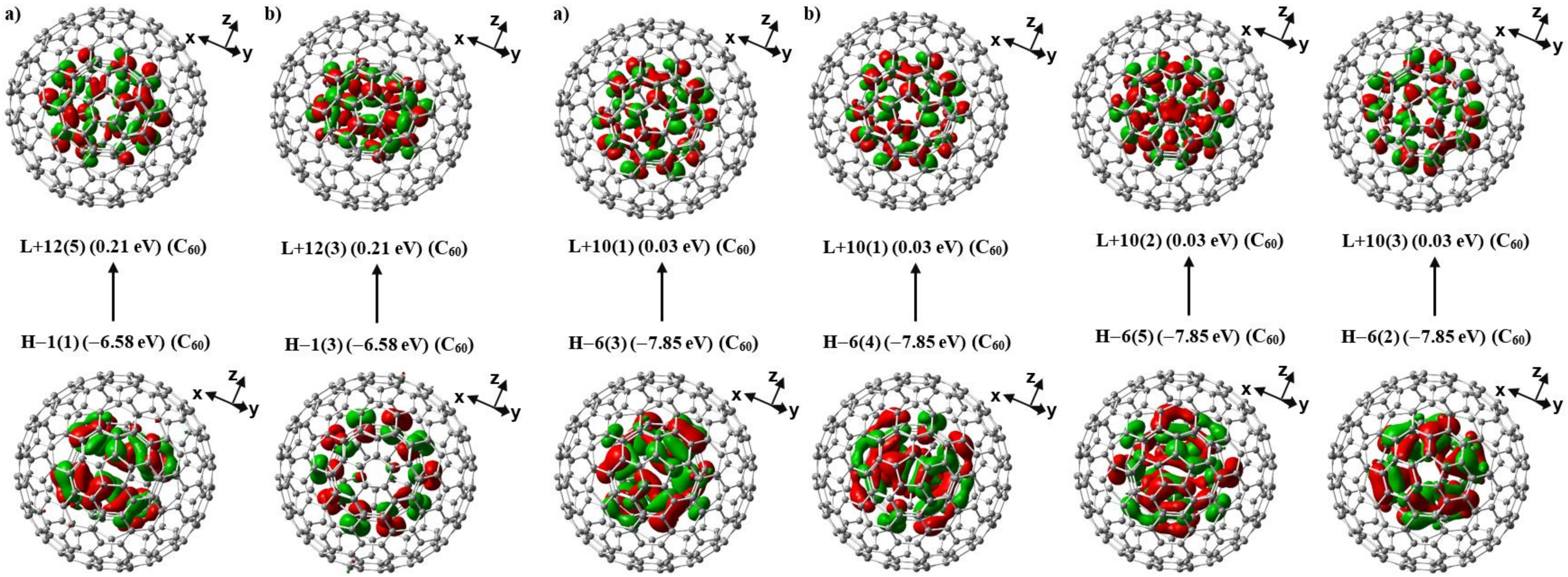
H−1(3)→L+12(5) 11.53% H−1(4)→L+12(2) 10.99%



f. 6_B—Corresponding to the transition at 5.26 eV (235.5 nm) in C_{60}.

$S_0 \rightarrow S_{288}$: 326.6 nm (3.80 eV) | $S_0 \rightarrow S_{1002}$: 247.1 nm (5.02 eV) | $S_0 \rightarrow S_{1003}$: 247.1 nm (5.02 eV) | $S_0 \rightarrow S_{1004}$: 247.1 nm (5.02 eV)

H−1(1)→L+12(5) 18.28% | H−1(3)→L+12(3) 13.70% | H−6(3)→L+10(1) 10.99% | H−6(4)→L+10(1) 10.21% | H−6(5)→L+10(2) 14.55% | H−6(2)→L+10(3) 15.82%



g. 6c—Corresponding to the transition at 5.57 eV (222.7 nm) in C_{60}.

$S_0 \rightarrow S_{1263}$: 230.4 nm (5.38 eV)

H−7(4)→L+10(2) 12.95% H−7(2)→L+10(1) 12.94%

$S_0 \rightarrow S_{1264}$: 230.4 nm (5.38 eV)

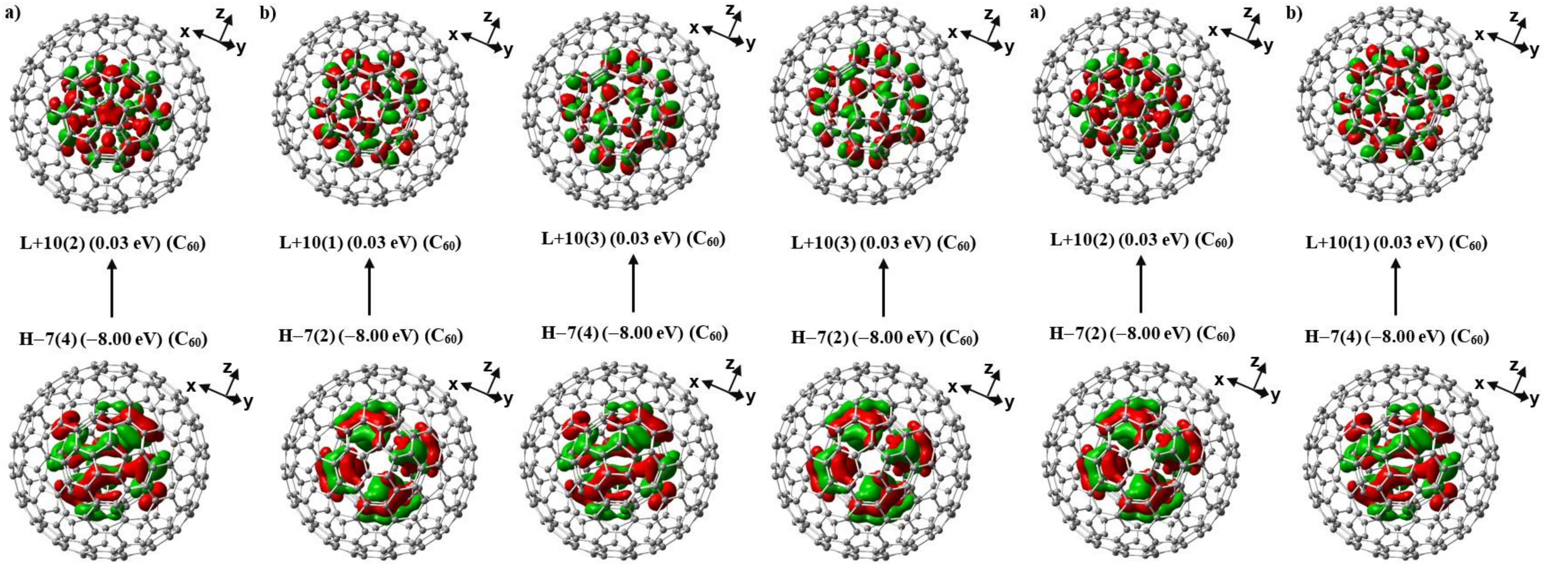
H−7(4)→L+10(3) 12.18%

$S_0 \rightarrow S_{1265}$: 230.4 nm (5.38 eV)

H−7(2)→L+10(3) 12.18%

$S_0 \rightarrow S_{1266}$: 230.4 nm (5.38 eV)

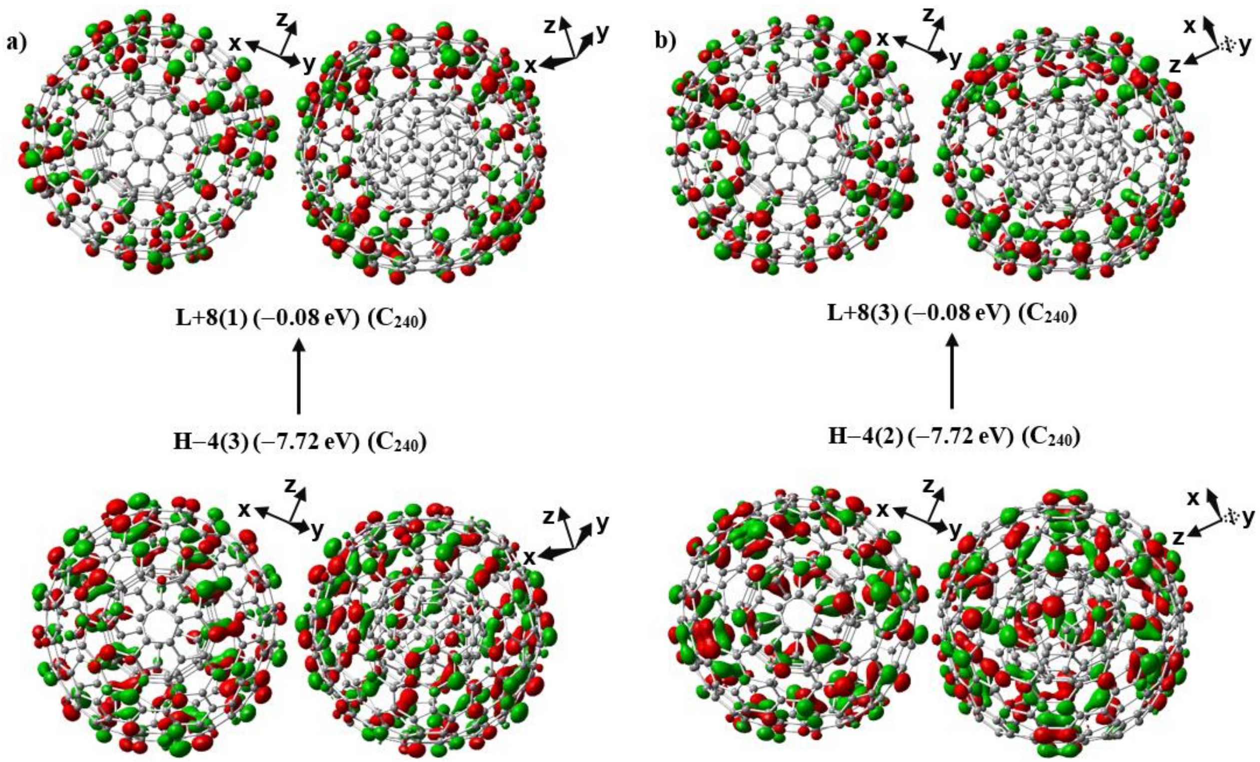
H−7(2)→L+10(2) 12.95% H−7(4)→L+10(1) 12.94%



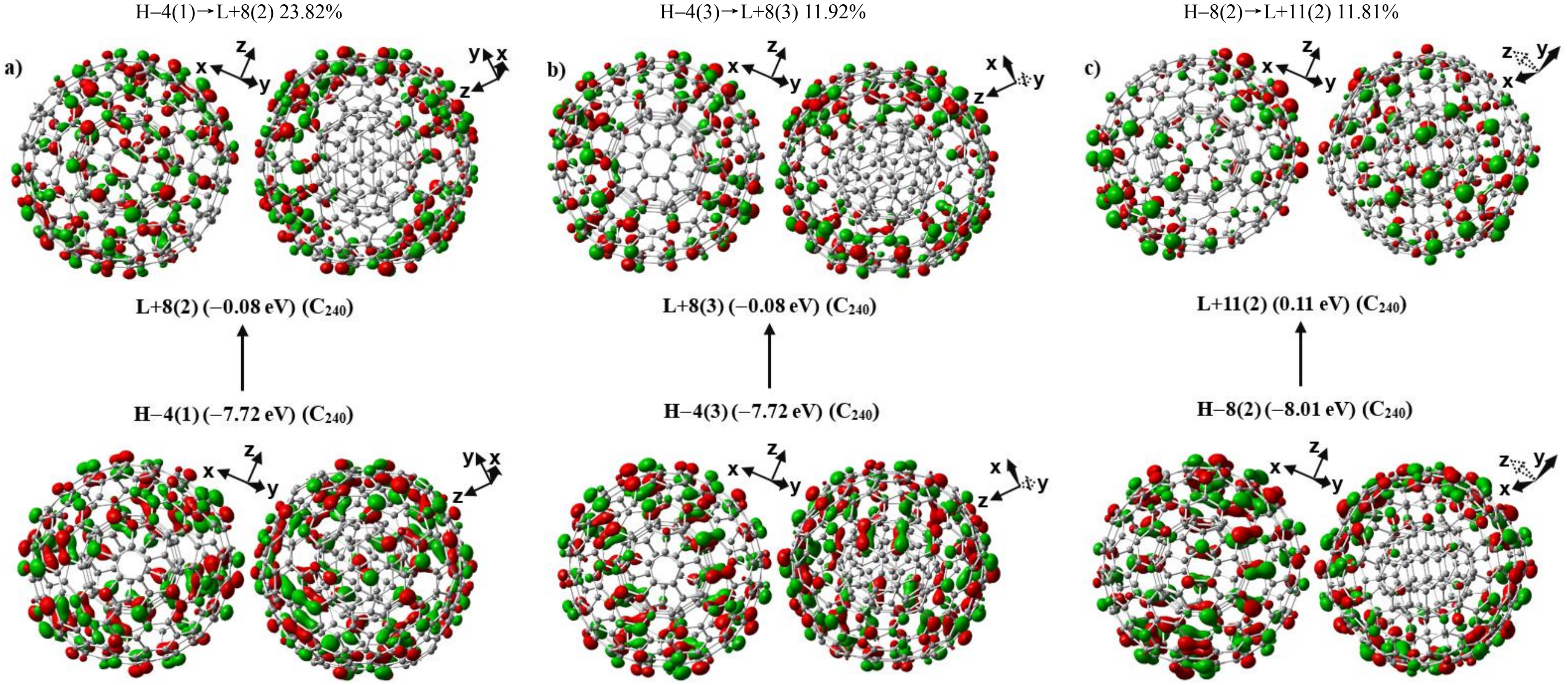
h. 2_A—Corresponding to the transition at 6.08 eV (203.8 nm) in C_{240}.

$S_0 \rightarrow S_{1866}$: 200.3 nm (6.19 eV)

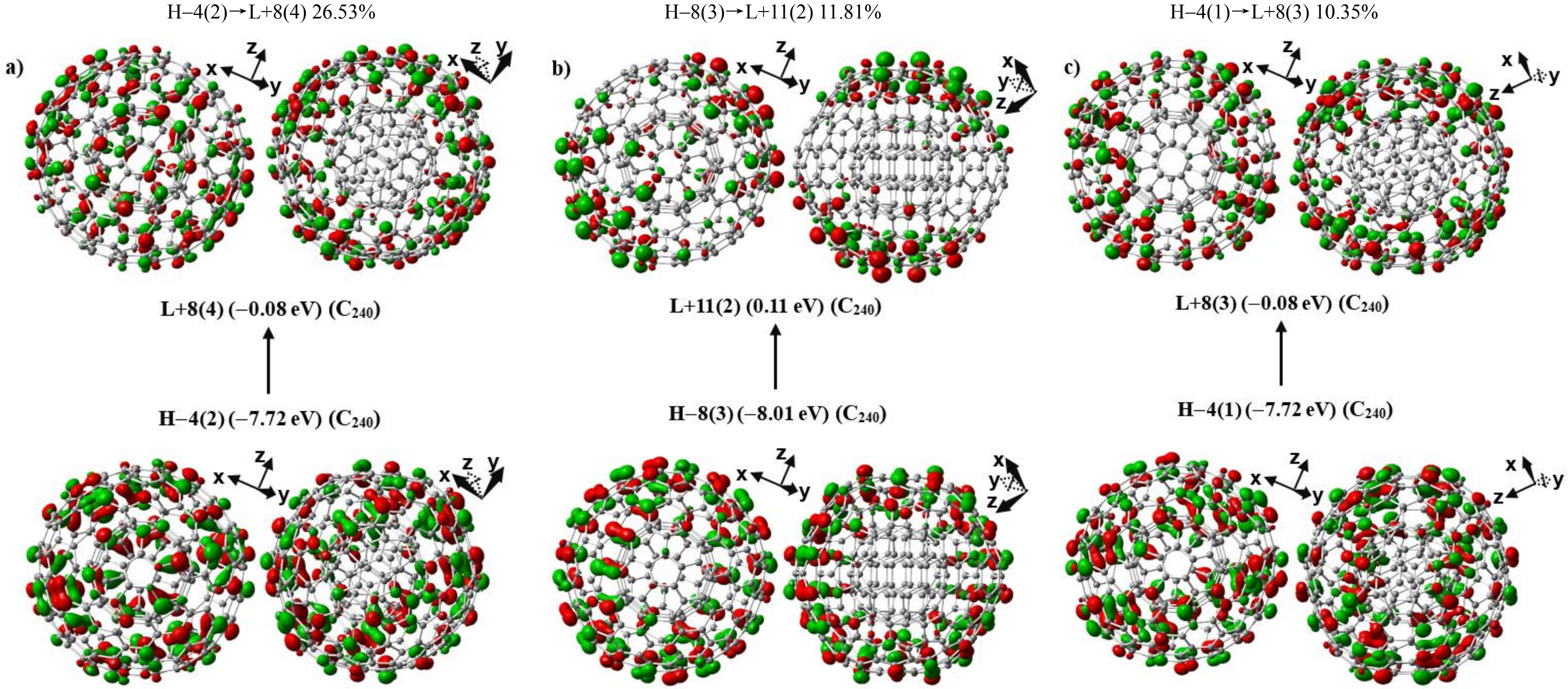
H−4(3)→L+8(1) 30.02% H−4(2)→L+8(3) 11.79%



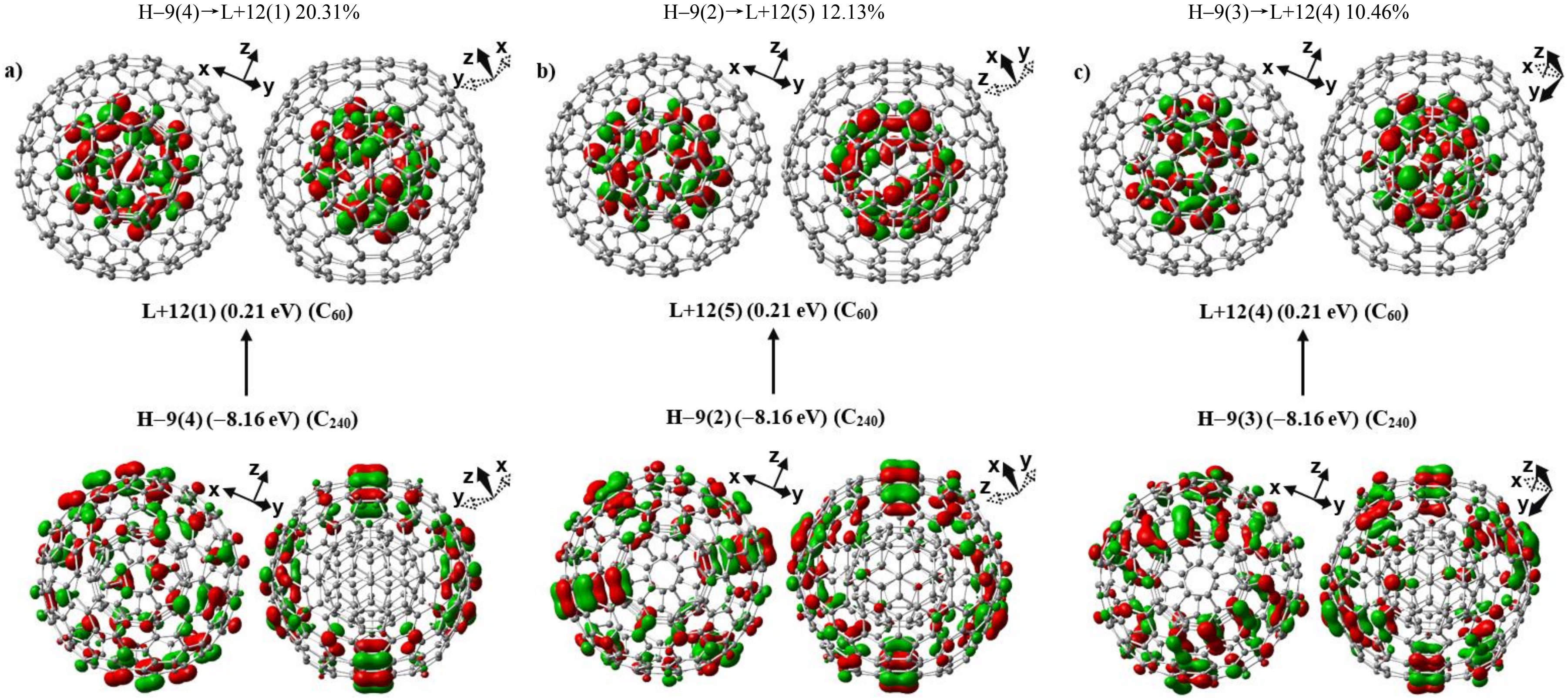
$S_0 \rightarrow S_{1867}$: 200.3 nm (6.19 eV)



$S_0 \rightarrow S_{1868}$: 200.3 nm (6.19 eV)

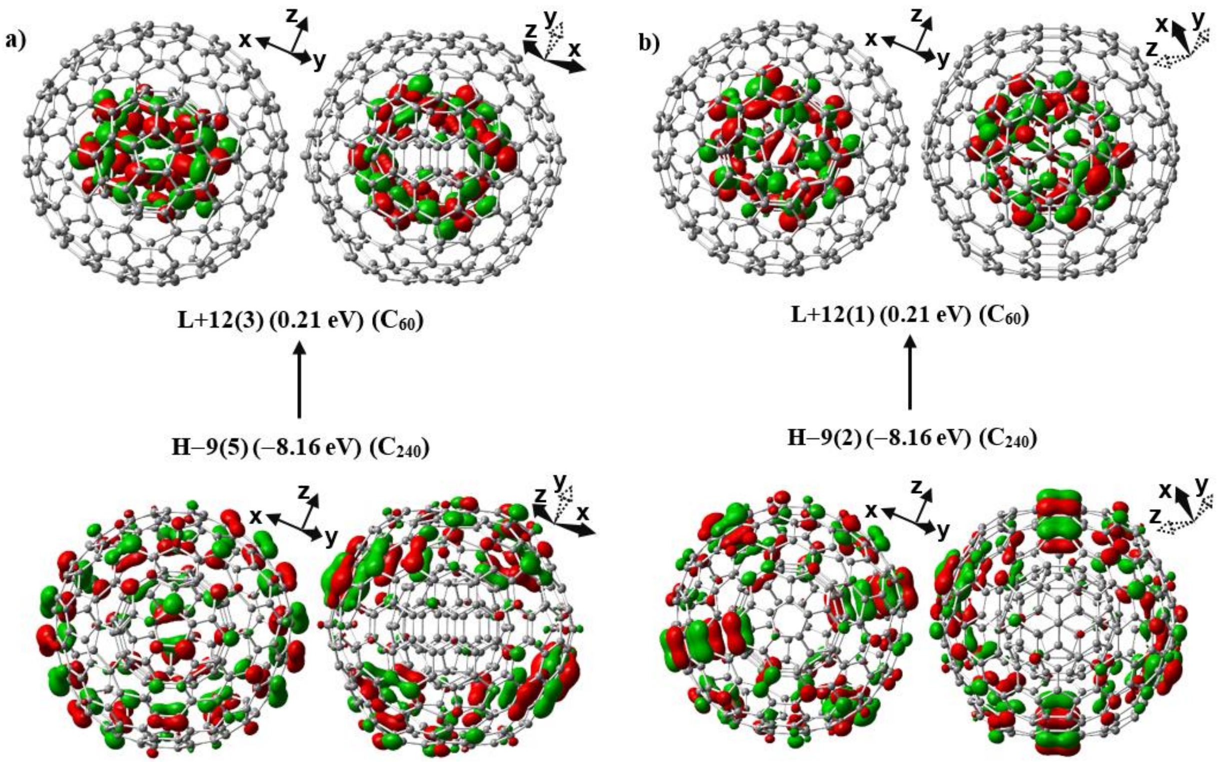


i. $S_0 \rightarrow S_{1971}$: 192.1 nm (6.45 eV)



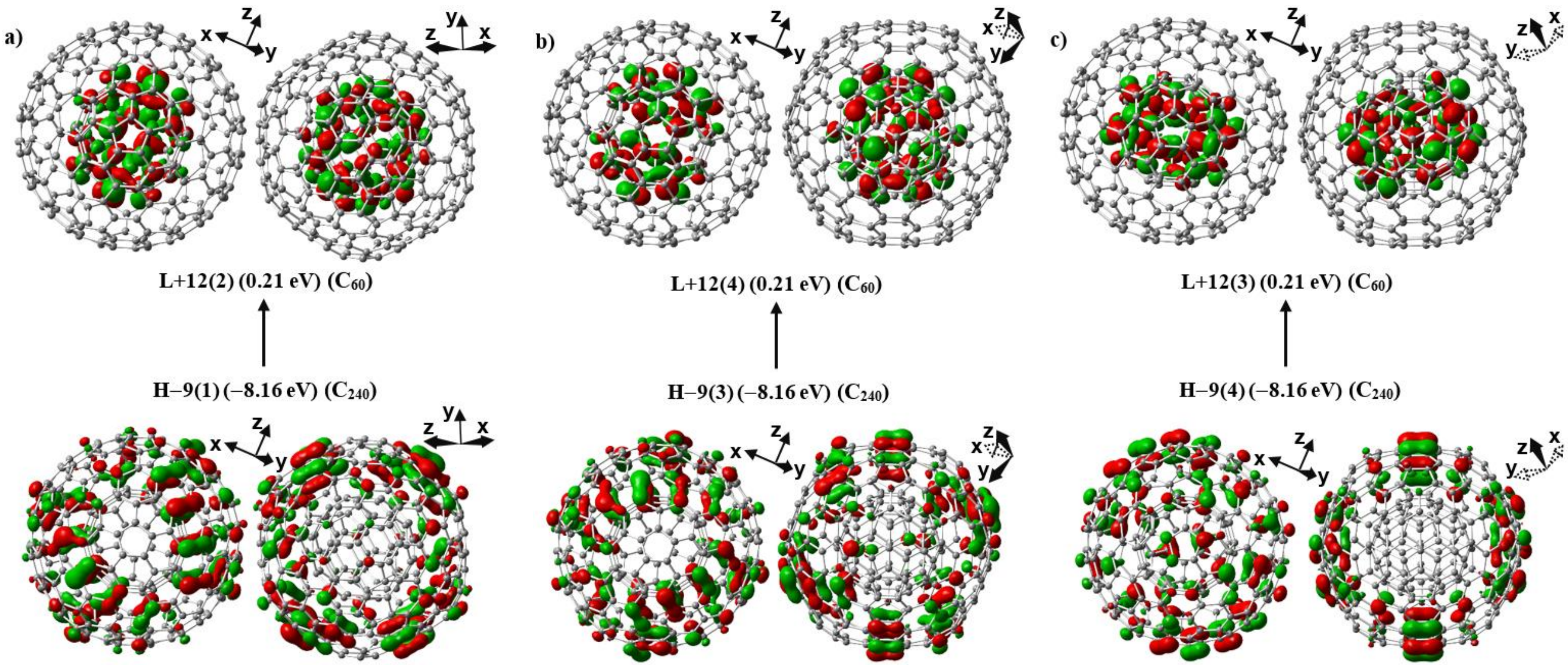
$S_0 \rightarrow S_{1972}$: 192.1 nm (6.45 eV)

H−9(5)→L+12(3) 28.90% H−9(2)→L+12(1) 21.68%



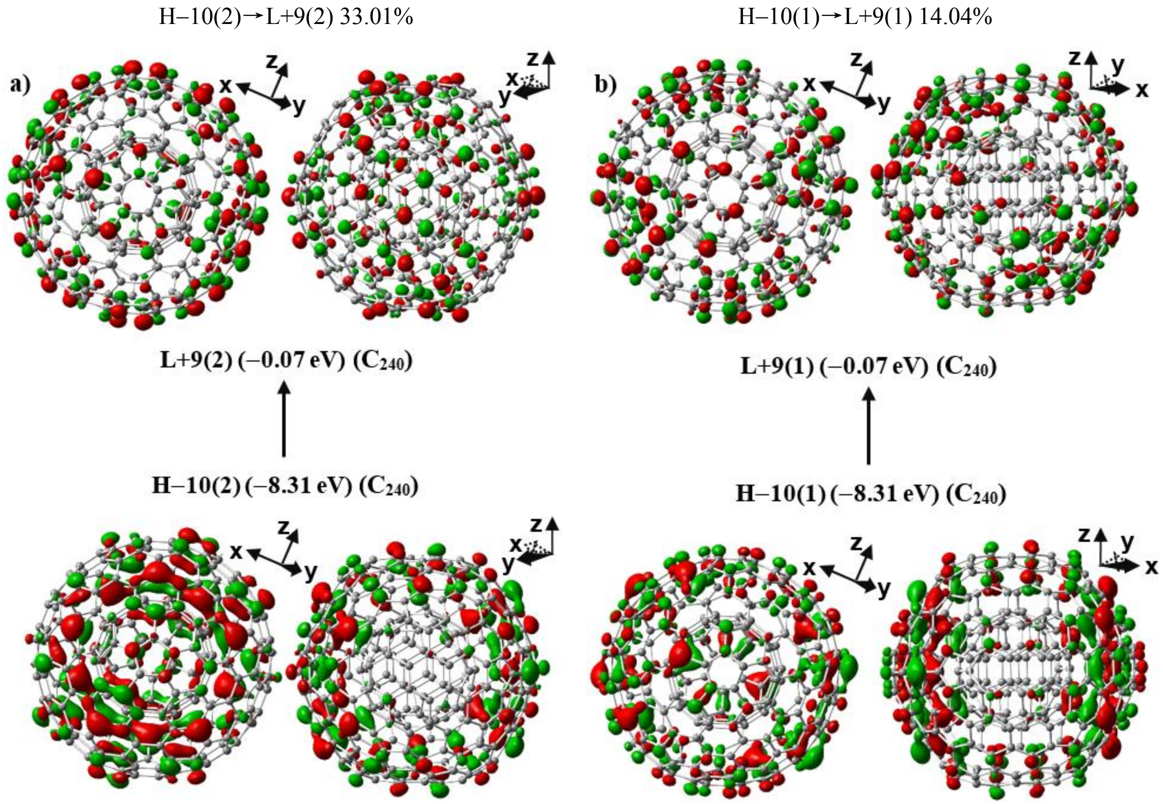
$S_0 \rightarrow S_{1973}$: 192.1 nm (6.45 eV)

H−9(1)→L+12(2) 27.08%　　H−9(3)→L+12(4) 19.32%　　H−9(4)→L+12(3) 10.37%



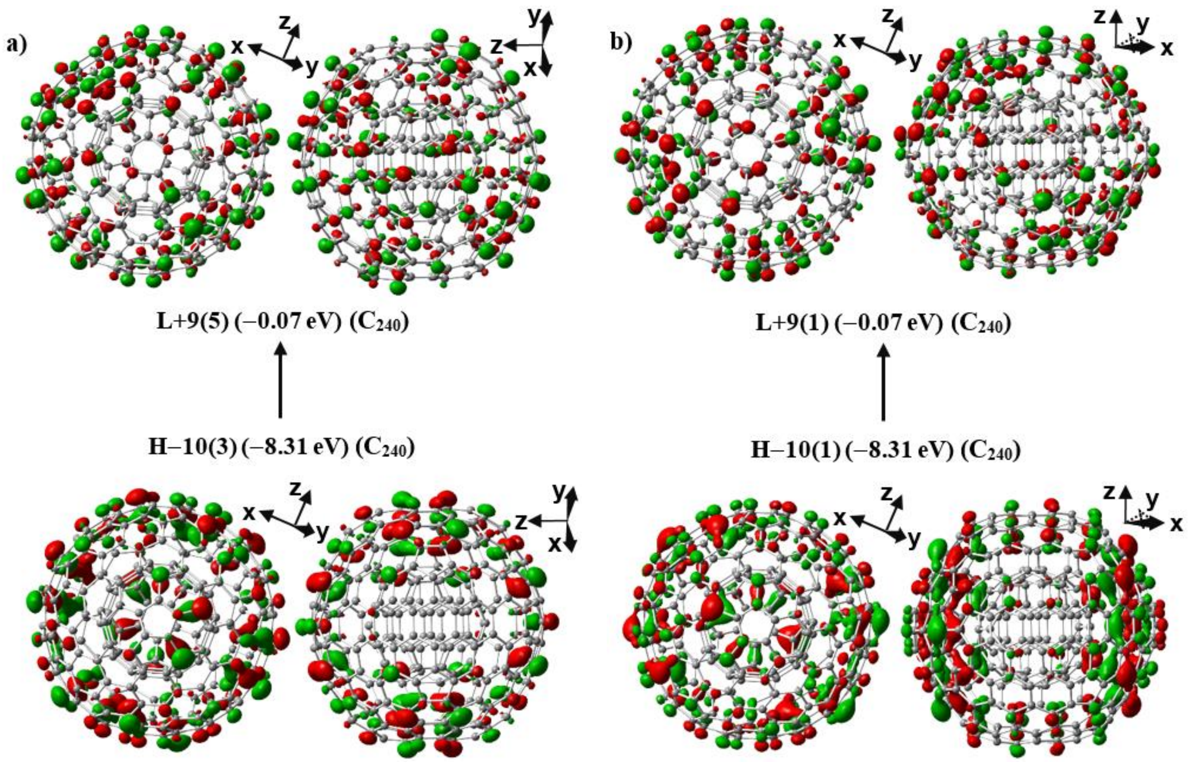
j. 2_B—Corresponding to the transition at 6.61 eV (187.5 nm) in C_{240}.

$S_0 \rightarrow S_{2031}$: 190.0 nm (6.53 eV)



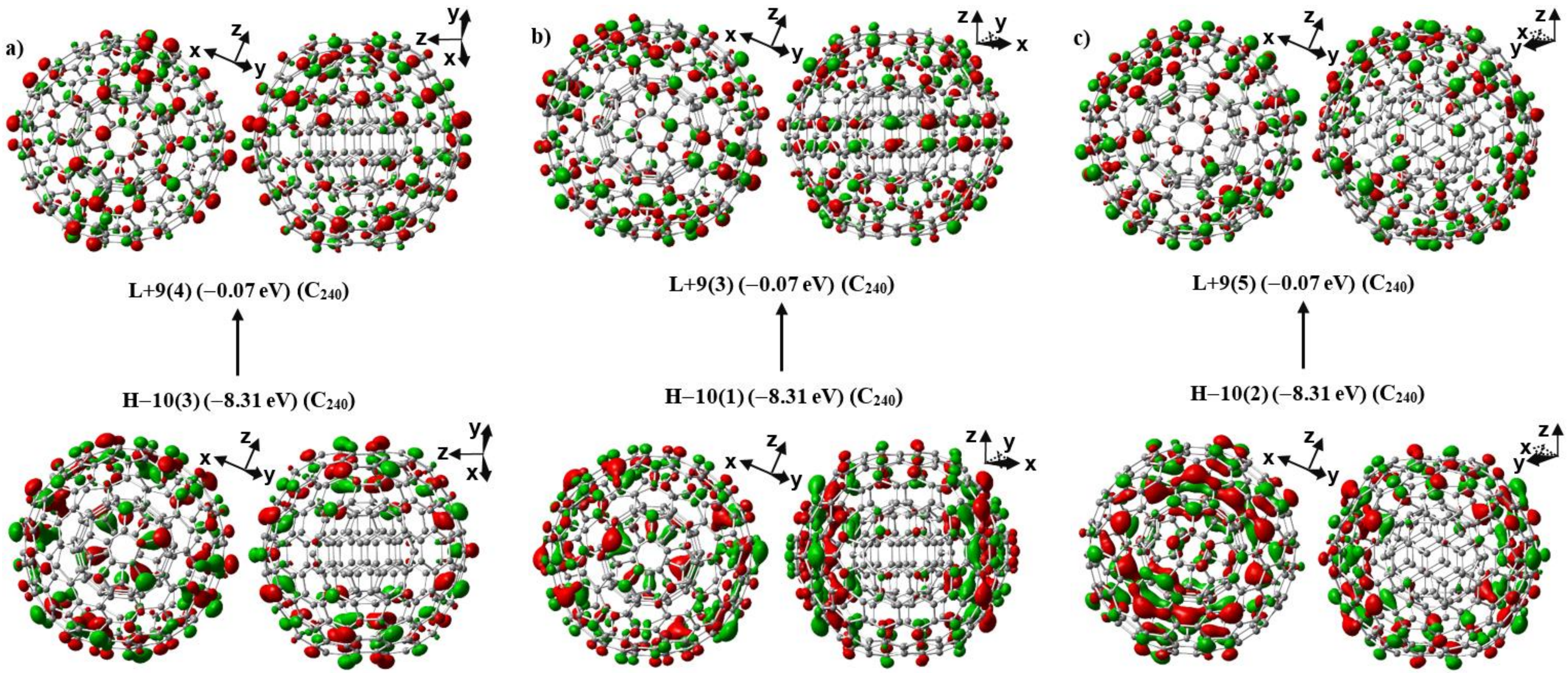
$S_0 \rightarrow S_{2032}$: 190.0 nm (6.53 eV)

H−10(3)→L+9(5) 31.12%　　　　H−10(1)→L+9(1) 26.95%



$S_0 \rightarrow S_{2033}$: 190.0 nm (6.53 eV)

H−10(3)→L+9(4) 27.69%   H−10(1)→L+9(3) 21.66%   H−10(2)→L+9(5) 12.82%



k.

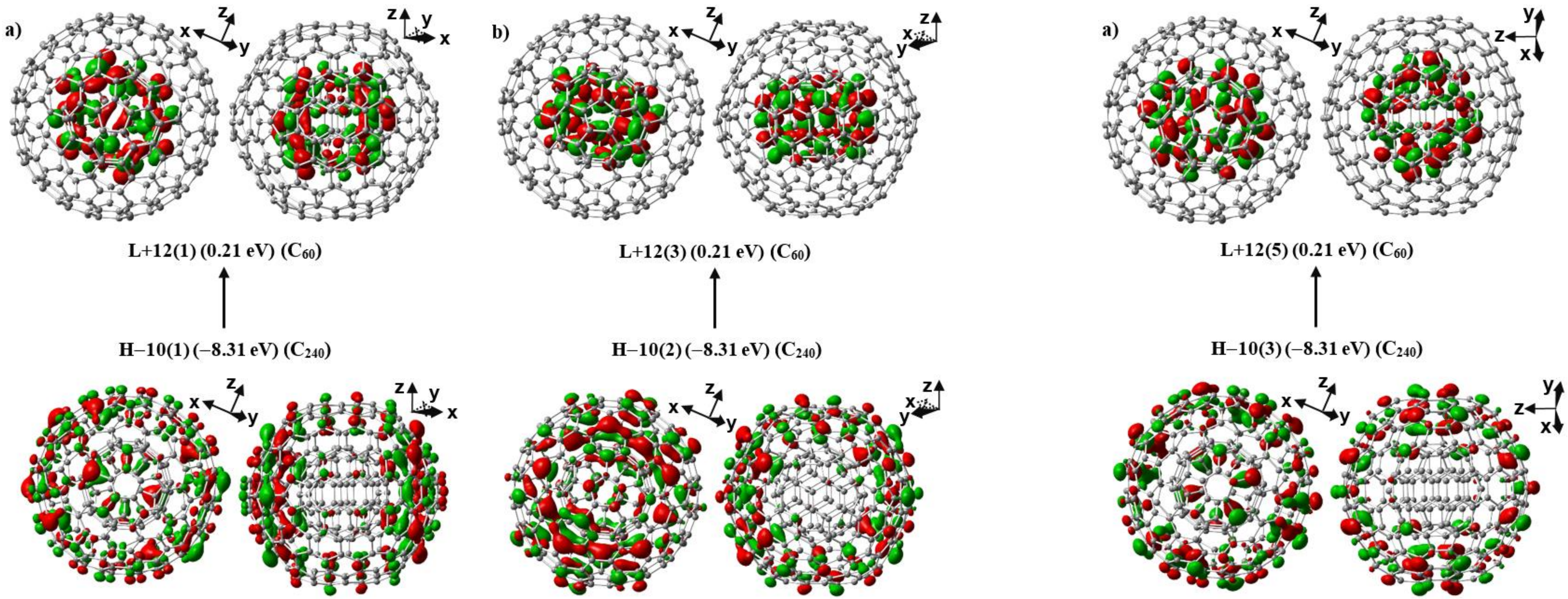
$S_0 \rightarrow S_{2061}$: 187.8 nm (6.60 eV)

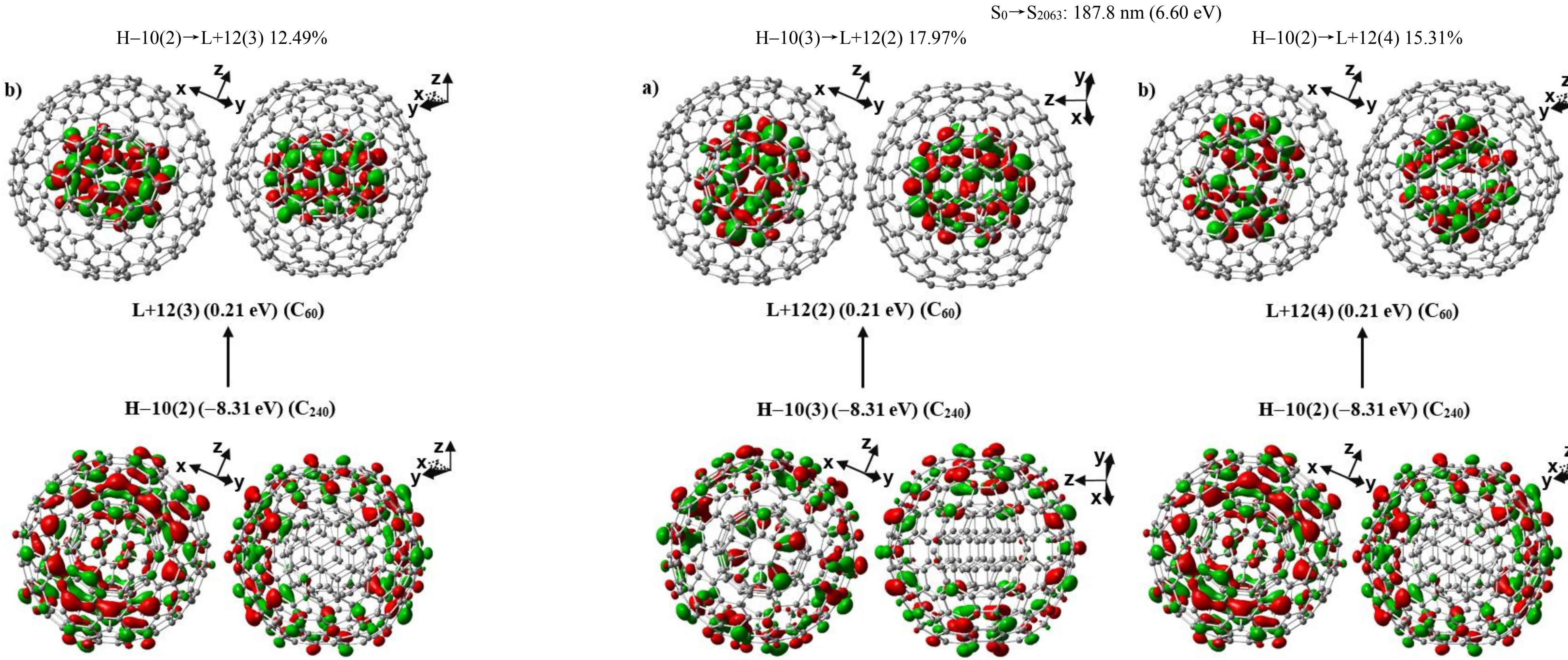
H−10(1)→L+12(1) 18.65%

H−10(2)→L+12(3) 12.75%

$S_0 \rightarrow S_{2062}$: 187.8 nm (6.60 eV)

H−10(3)→L+12(5) 22.57%



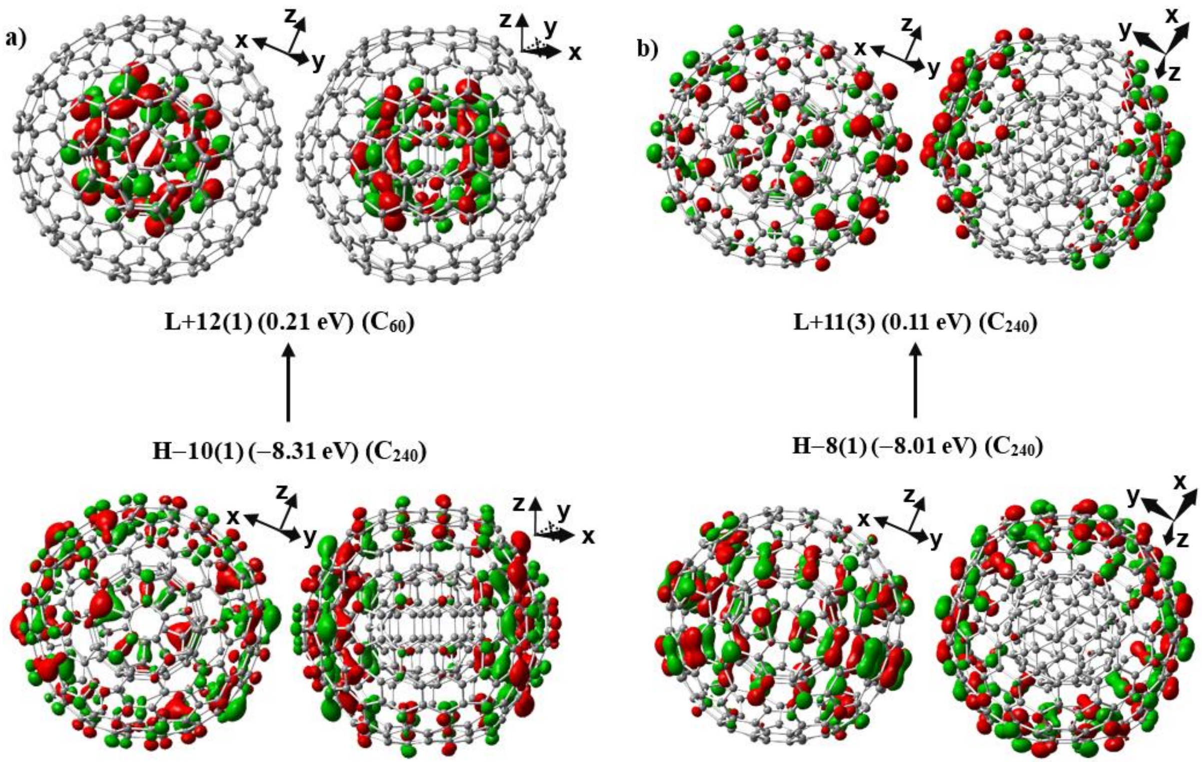


S0→S2063: 187.8 nm (6.60 eV)
H−10(2)→L+12(3) 12.49%
H−10(3)→L+12(2) 17.97%
H−10(2)→L+12(4) 15.31%
b)
a)
b)
L+12(3) (0.21 eV) (C60)
L+12(2) (0.21 eV) (C60)
L+12(4) (0.21 eV) (C60)
H−10(2) (−8.31 eV) (C240)
H−10(3) (−8.31 eV) (C240)
H−10(2) (−8.31 eV) (C240)
x
y
z

l. $S_0 \rightarrow S_{2071}$: 187.2 nm (6.62 eV)

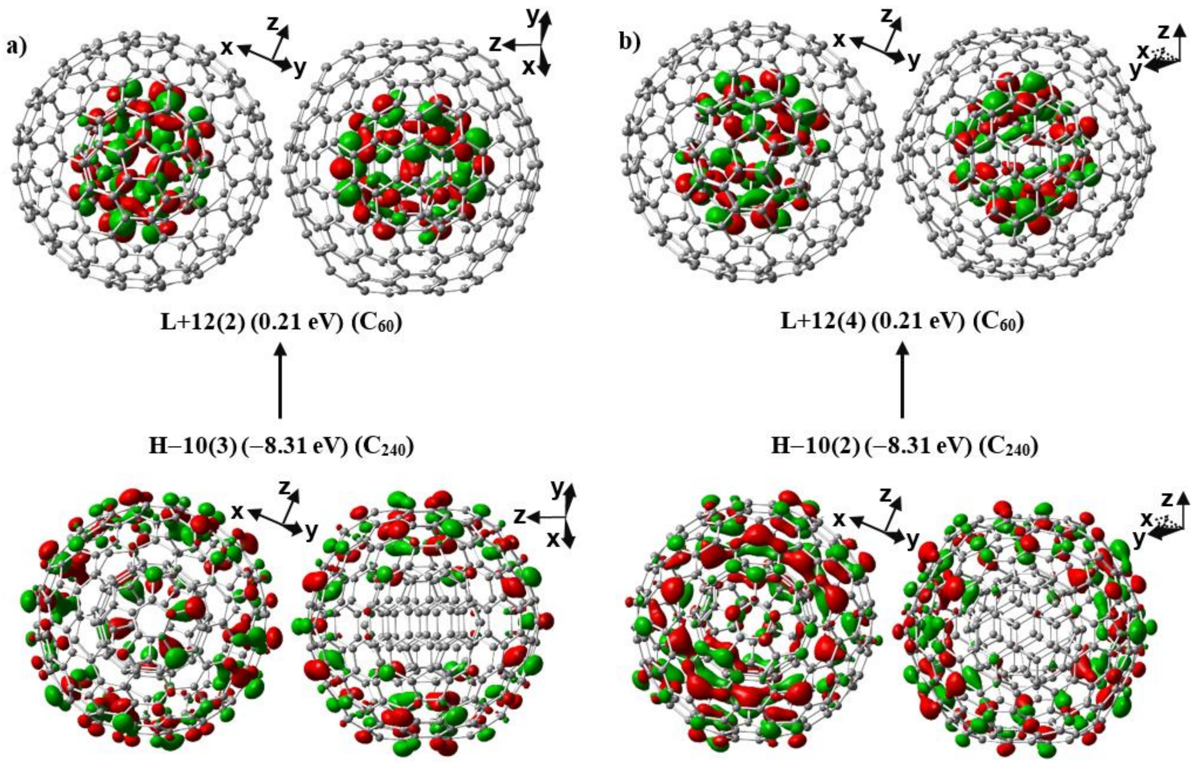
H−10(1)→L+12(1) 15.43%

H−8(1)→L+11(3) 10.31%



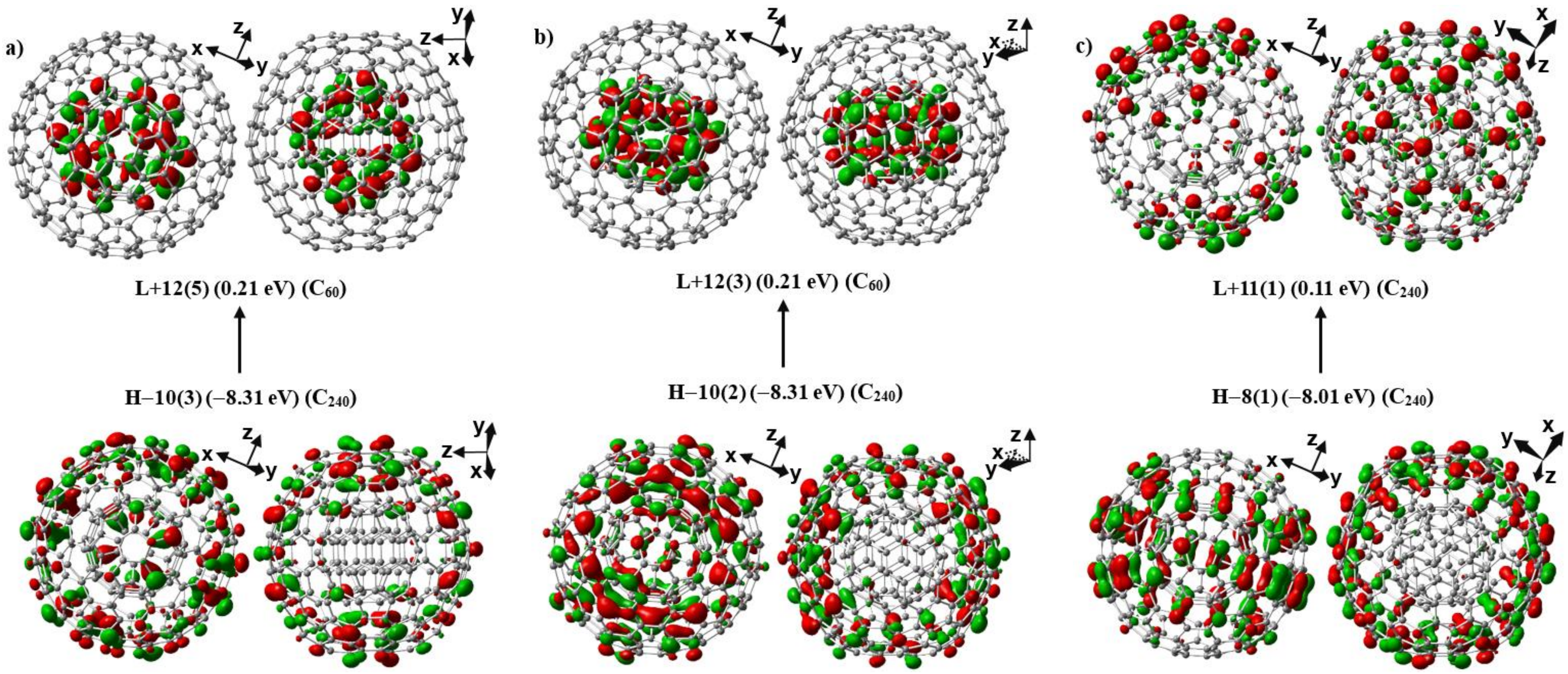
$S_0 \rightarrow S_{2072}$: 187.2 nm (6.62 eV)

H−10(3)→L+12(2) 11.77%   H−10(2)→L+12(4) 10.03%



$S_0 \rightarrow S_{2073}$: 187.2 nm (6.62 eV)

H−10(3)→L+12(5) 14.09% H−10(2)→L+12(3) 12.07% H−8(1)→L+11(1) 10.31%



m. The strongest oscillator strength: 2_C—Corresponding to the transition at 6.63 eV (187.1 nm) in C_{240}.

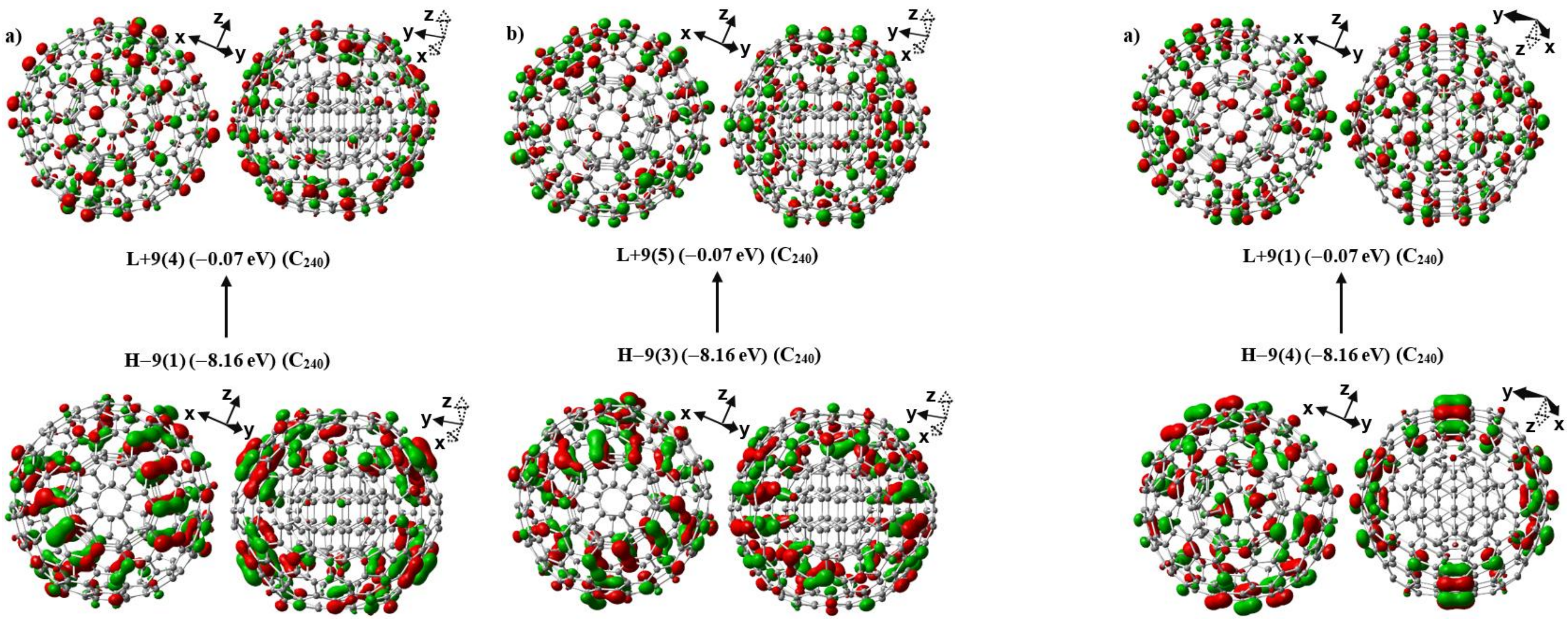
$S_0 \rightarrow S_{2084}$: 186.5 nm (6.65 eV)

H−9(1)→L+9(4) 23.97%

H−9(3)→L+9(5) 14.64%

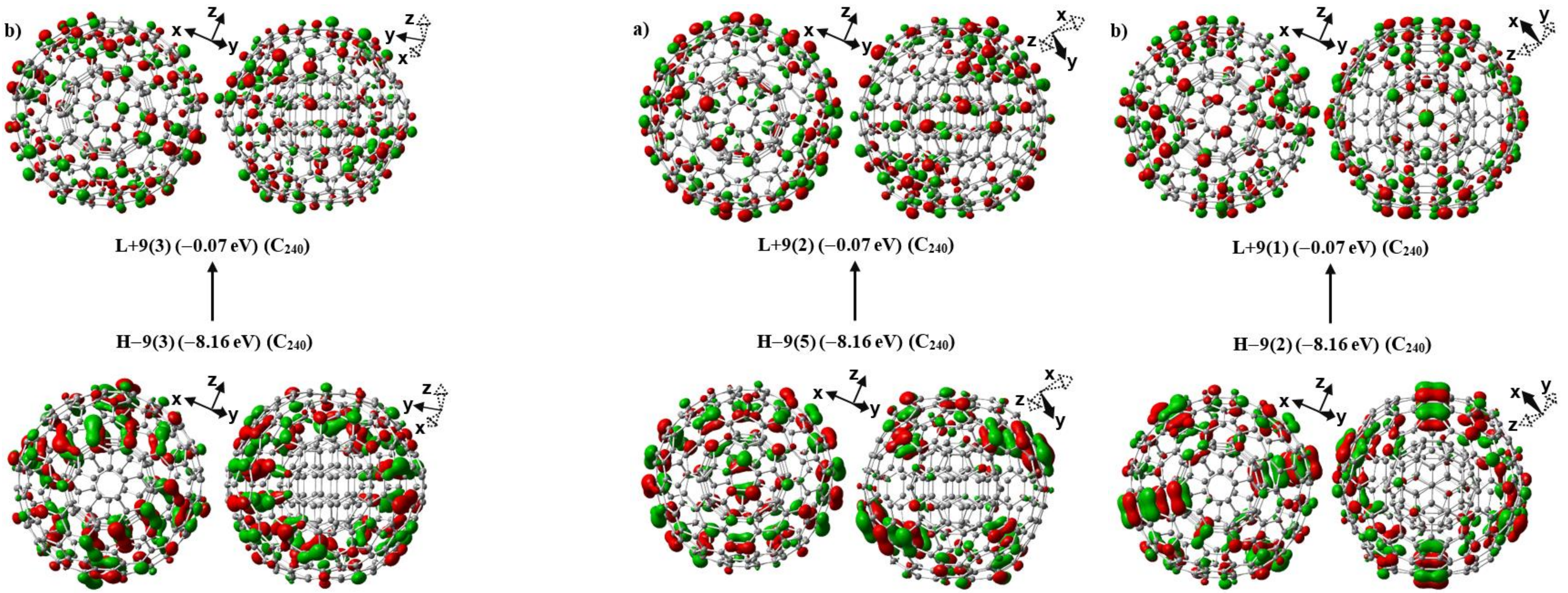
$S_0 \rightarrow S_{2085}$: 186.4 nm (6.65 eV)

H−9(4)→L+9(1) 15.45%



$S_0 \rightarrow S_{2086}$: 186.4 nm (6.65 eV)

H−9(3)→L+9(3) 11.61%　　H−9(5)→L+9(2) 22.30%　　H−9(2)→L+9(1) 14.01%



4) C_{540} (1850) (Isosurface value=0.02) [HOMO−6, HOMO, LUMO+2, LUMO+3, and LUMO+8 are five-fold degenerate. HOMO−7, HOMO−5, LUMO, LUMO+1, and LUMO+4 are three-fold degenerate. HOMO−2 is four-fold degenerate.]

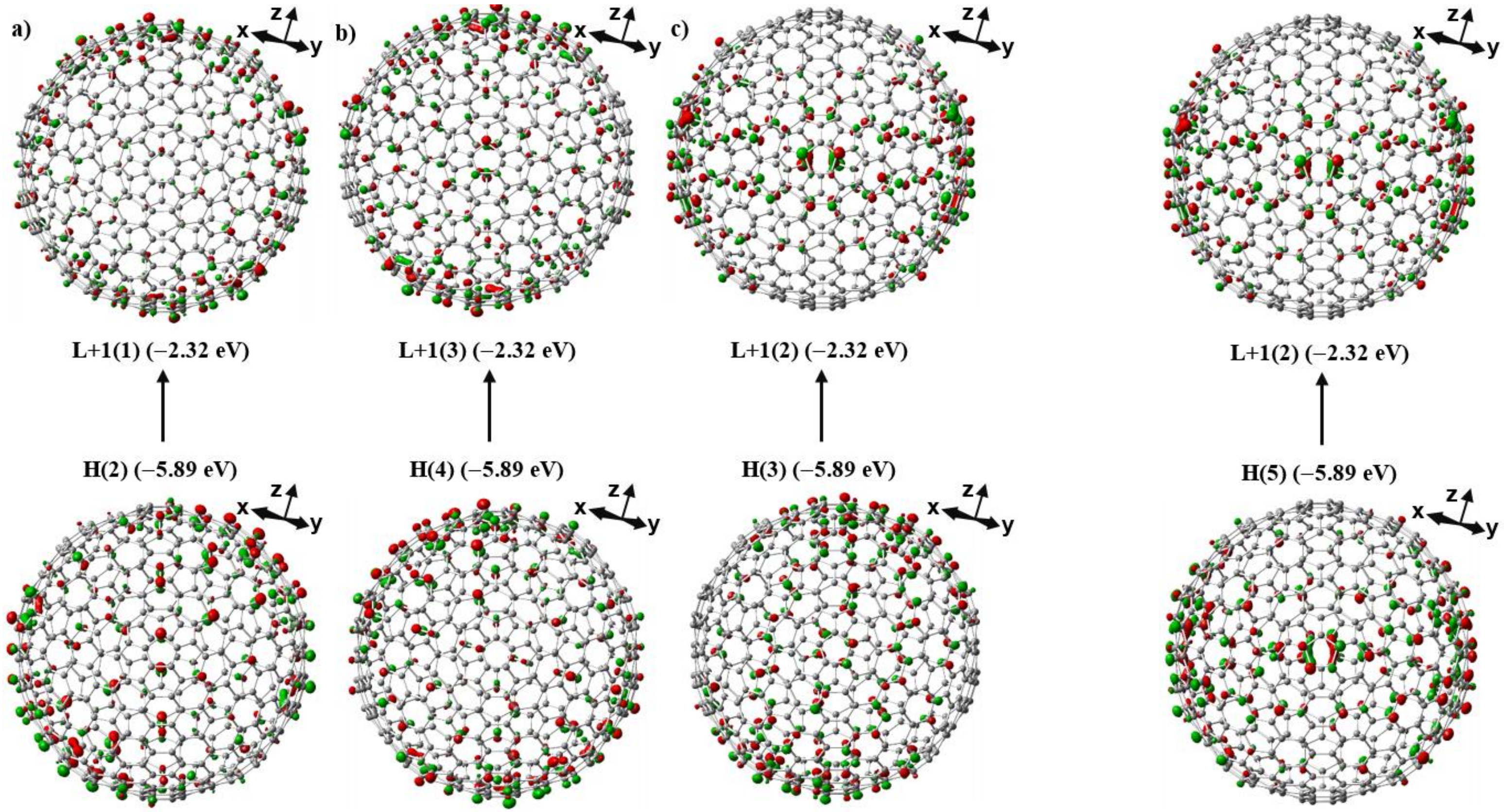
a. The lowest electronic excitation:

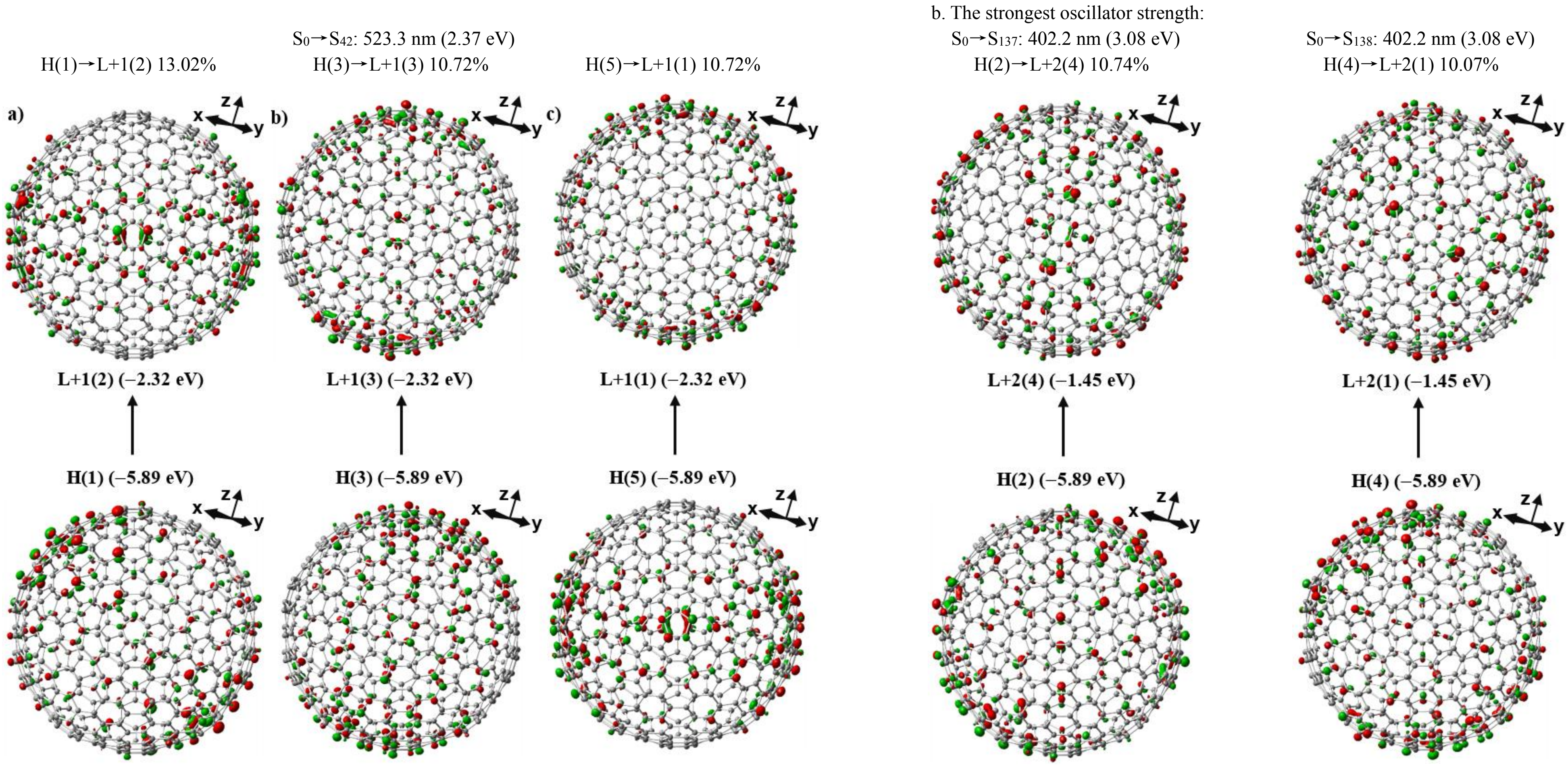
$S_0 \rightarrow S_{40}$: 523.3 nm (2.37 eV)

H(2)→L+1(1) 21.64% H(4)→L+1(3) 13.84% H(3)→L+1(2) 10.83%

$S_0 \rightarrow S_{41}$: 523.3 nm (2.37 eV)

H(5)→L+1(2) 10.83%



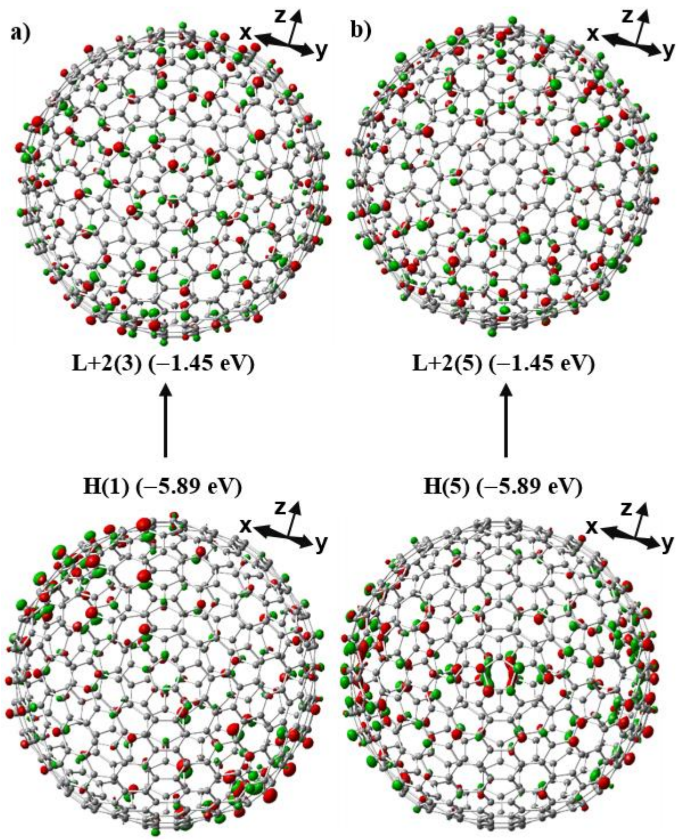


b. The strongest oscillator strength:
S0→S42: 523.3 nm (2.37 eV)
H(1)→L+1(2) 13.02%
H(3)→L+1(3) 10.72%
H(5)→L+1(1) 10.72%
S0→S137: 402.2 nm (3.08 eV)
H(2)→L+2(4) 10.74%
S0→S138: 402.2 nm (3.08 eV)
H(4)→L+2(1) 10.07%
a)
b)
c)
x
y
z
L+1(2) (−2.32 eV)
L+1(3) (−2.32 eV)
L+1(1) (−2.32 eV)
L+2(4) (−1.45 eV)
L+2(1) (−1.45 eV)
H(1) (−5.89 eV)
H(3) (−5.89 eV)
H(5) (−5.89 eV)
H(2) (−5.89 eV)
H(4) (−5.89 eV)

c. 5_A—Corresponding to the transition at 3.98 eV (311.9 nm) in $C_{60}@C_{240}@C_{540}$.

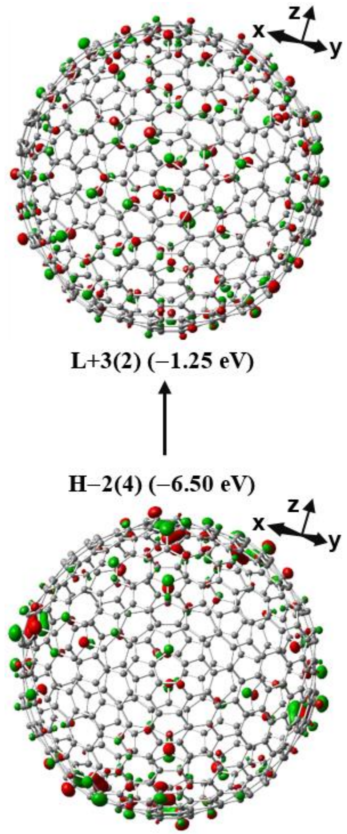
$S_0 \rightarrow S_{139}$: 402.2 nm (3.08 eV)

H(1)→L+2(3) 12.54%　　H(5)→L+2(5) 11.70%



$S_0 \rightarrow S_{387}$: 319.4 nm (3.88 eV) (NO)　　$S_0 \rightarrow S_{388}$: 319.4 nm (3.88 eV)　　$S_0 \rightarrow S_{389}$: 319.4 nm (3.88 eV) (NO)

H−2(4)→L+3(2) 10.05 %



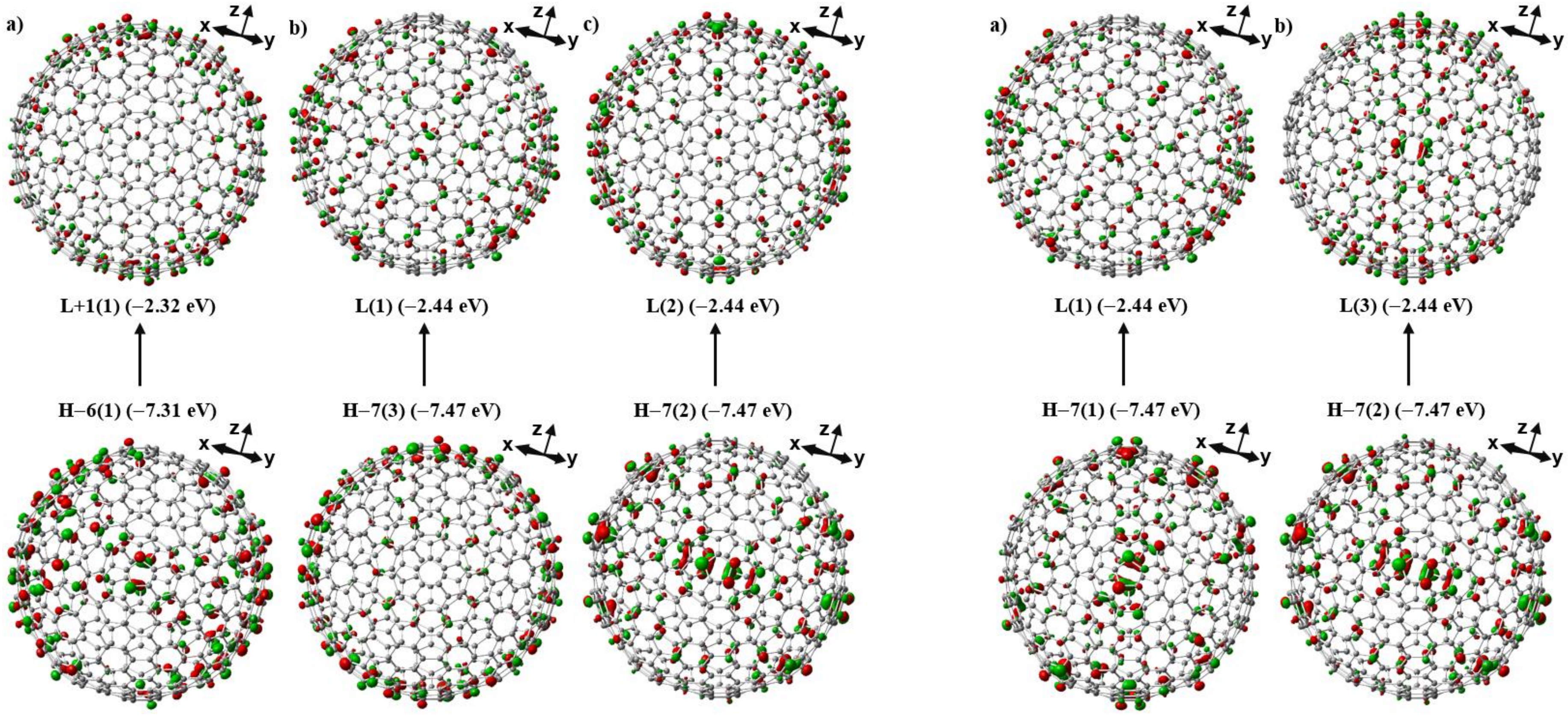
d.

$S_0 \rightarrow S_{430}$: 313.8 nm (3.95 eV)

H−6(1)→L+1(1) 12.02% H−7(3)→L(1) 11.54% H−7(2)→L(2) 11.43%

$S_0 \rightarrow S_{431}$: 313.8 nm (3.95 eV)

H−7(1)→L(1) 11.54% H−7(2)→L(3) 11.43%

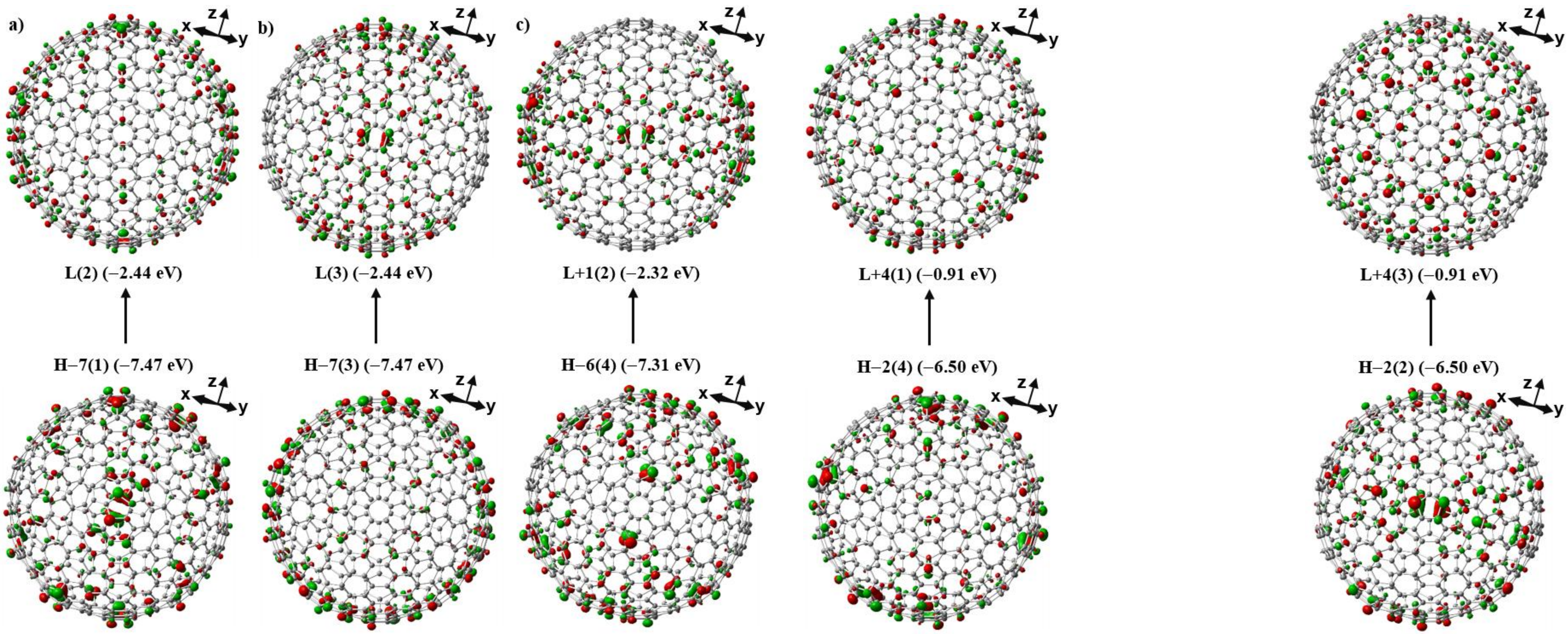


e. 5_B—Corresponding to the transition at 4.33 eV (286.4 nm) in $C_{60}@C_{240}@C_{540}$.

$S_0 \rightarrow S_{432}$: 313.8 nm (3.95 eV)

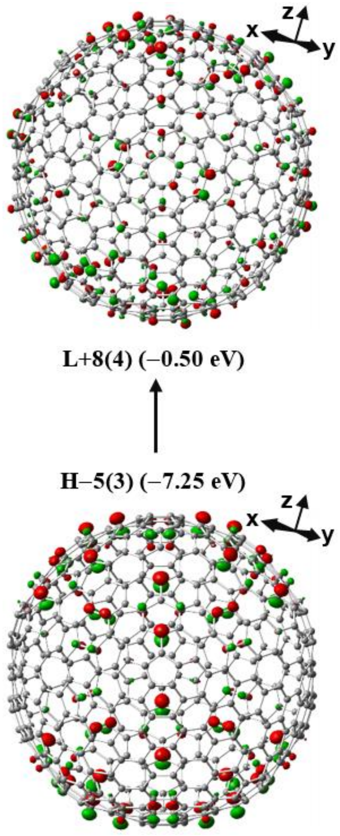
$S_0 \rightarrow S_{730}$: 276.2 nm (4.49 eV) $S_0 \rightarrow S_{731}$: 276.2 nm (4.49 eV) (NO) $S_0 \rightarrow S_{732}$: 276.2 nm (4.49 eV)

H−7(1)→L(2) 11.84% H−7(3)→L(3) 11.84% H−6(4)→L+1(2) 10.62% H−2(4)→L+4(1) 12.49% H−2(2)→L+4(3) 14.31%

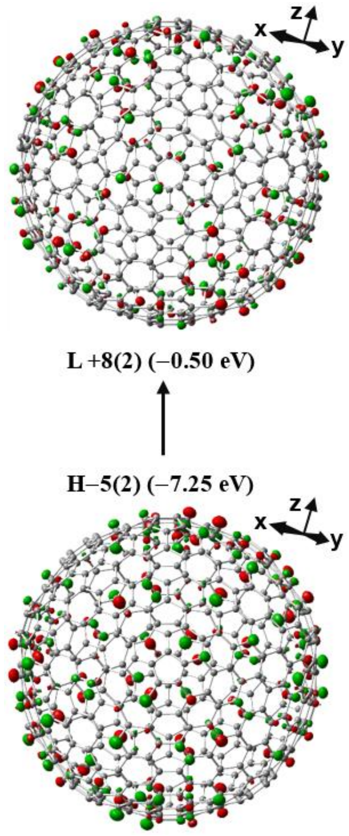


f. $S_0 \rightarrow S_{1331}$: 227.3 nm (5.45 eV) (NO)

$S_0 \rightarrow S_{1332}$: 227.3 nm (5.45 eV)
H−5(3)→L+8(4) 11.81%



$S_0 \rightarrow S_{1333}$: 227.3 nm (5.45 eV)
H−5(2)→L +8(2) 13.15%

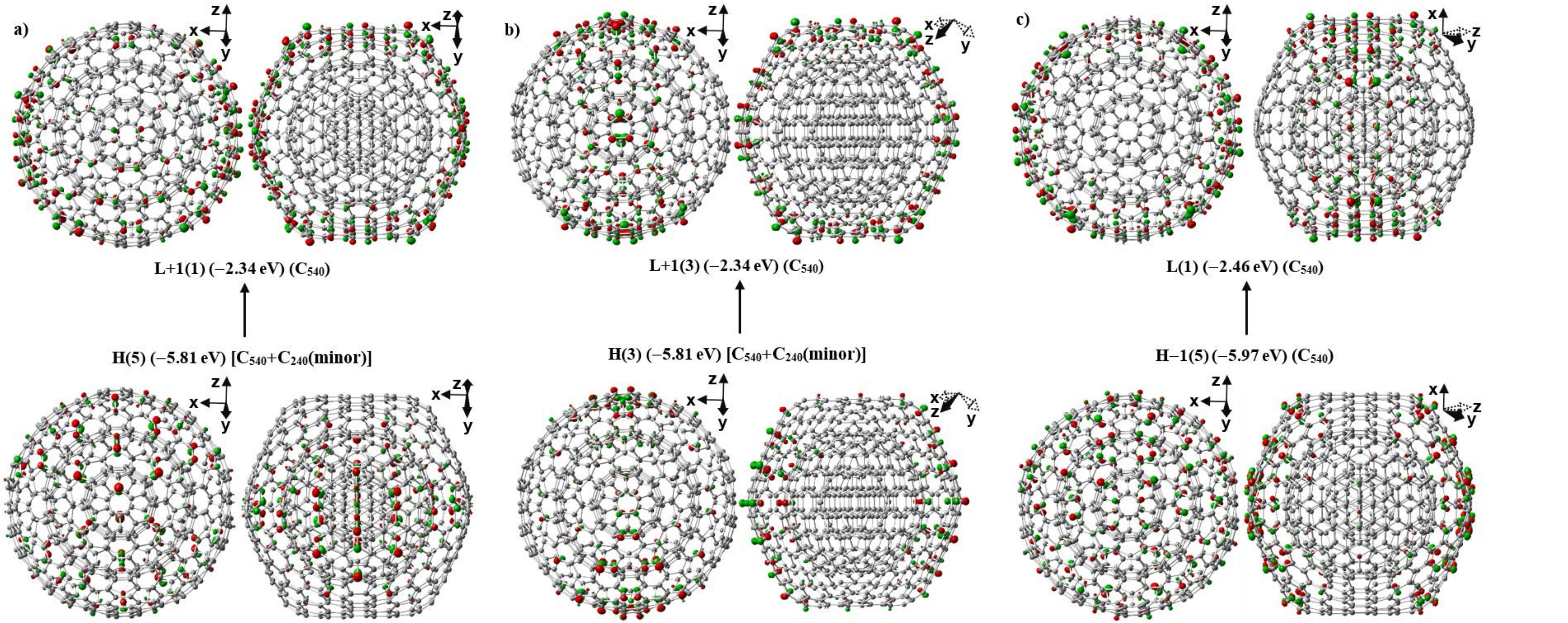


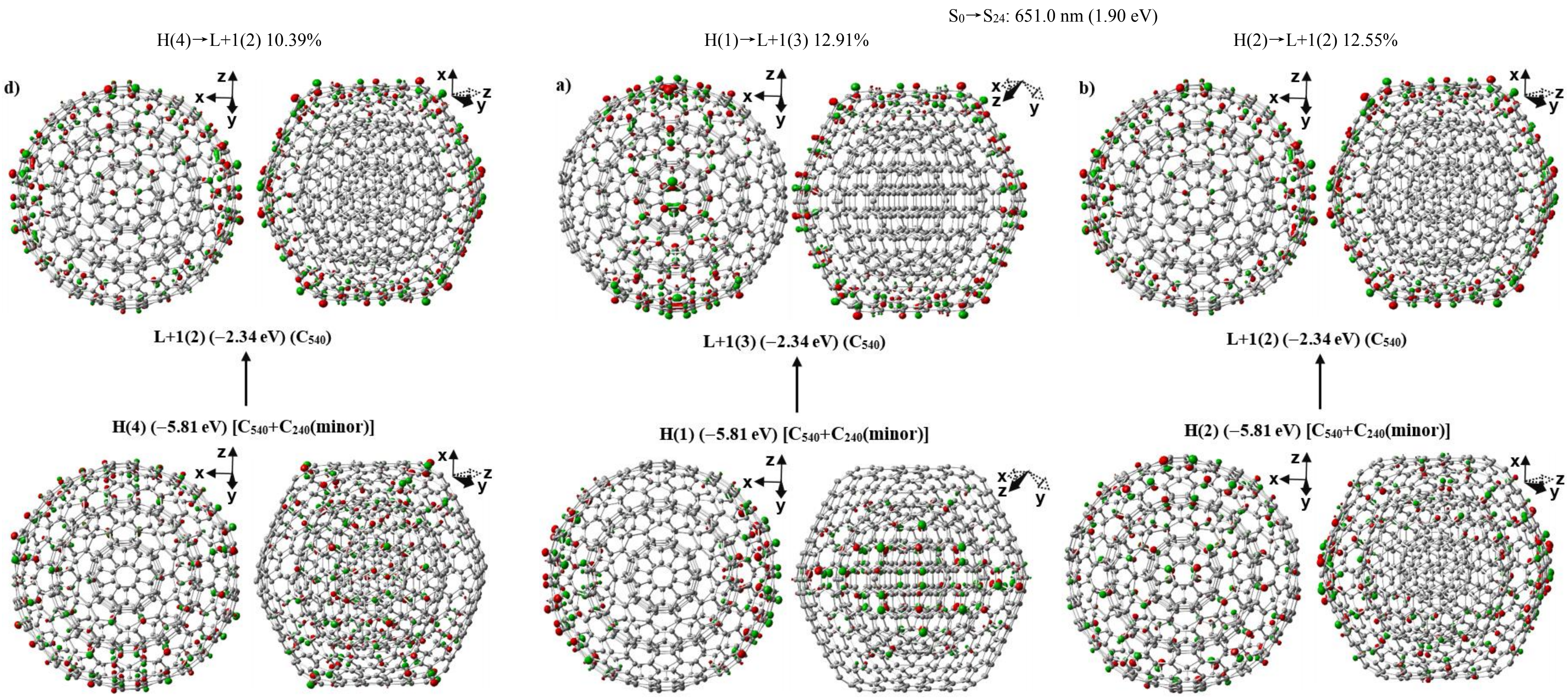
5) $C_{60}@C_{240}@C_{540}$ (1057) (Isosurface value=0.02) [HOMO−4, HOMO−3, HOMO-1, HOMO, and LUMO+5 are five-fold degenerate. LUMO, LUMO+1, LUMO+3, LUMO+6, and LUMO+8 are three-fold degenerate. HOMO−5 is four-fold degenerate.]

a. The lowest electronic excitation:

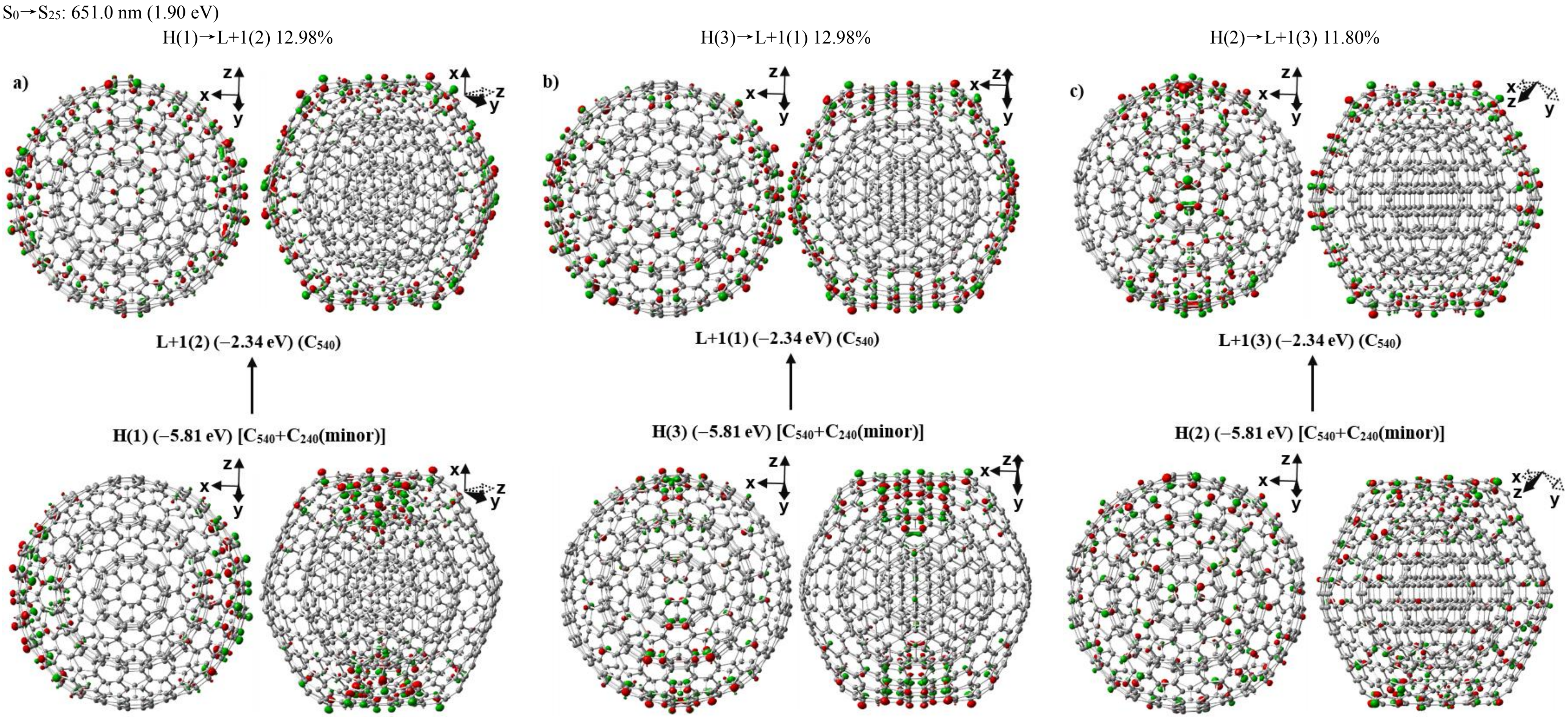
$S_0 \rightarrow S_{23}$: 651.0 nm (1.90 eV)

H(5)→L+1(1) 14.51% H(3)→L+1(3) 12.91% H−1(5)→L(1) 10.93%





S0→S24: 651.0 nm (1.90 eV)
H(4)→L+1(2) 10.39%
H(1)→L+1(3) 12.91%
H(2)→L+1(2) 12.55%
d)
a)
b)
L+1(2) (−2.34 eV) (C540)
L+1(3) (−2.34 eV) (C540)
L+1(2) (−2.34 eV) (C540)
H(4) (−5.81 eV) [C540+C240(minor)]
H(1) (−5.81 eV) [C540+C240(minor)]
H(2) (−5.81 eV) [C540+C240(minor)]

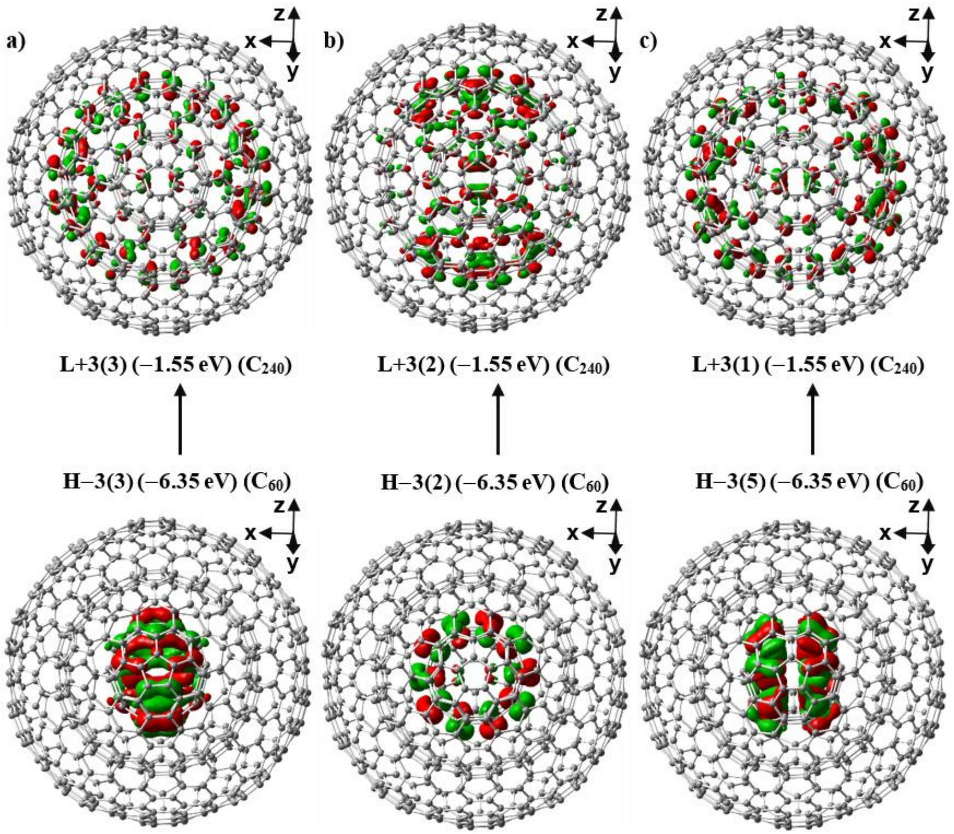


S0→S25: 651.0 nm (1.90 eV)
H(1)→L+1(2) 12.98%
H(3)→L+1(1) 12.98%
H(2)→L+1(3) 11.80%
a)
b)
c)
L+1(2) (−2.34 eV) (C540)
L+1(1) (−2.34 eV) (C540)
L+1(3) (−2.34 eV) (C540)
H(1) (−5.81 eV) [C540+C240(minor)]
H(3) (−5.81 eV) [C540+C240(minor)]
H(2) (−5.81 eV) [C540+C240(minor)]

b. 6@2—Corresponding to the transition at 2.88 eV (430.0 nm) in $C_{60}@C_{240}$.

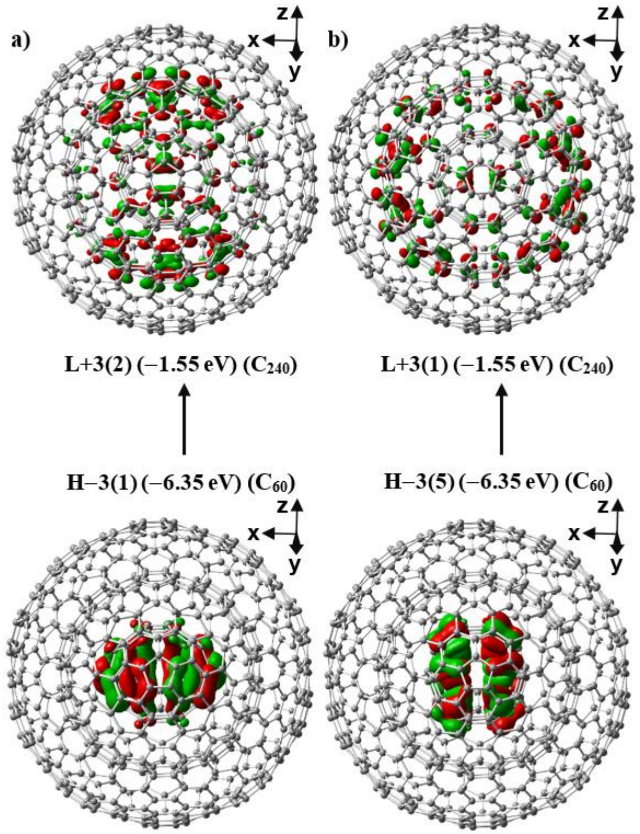
$S_0 \rightarrow S_{273}$: 429.0 nm (2.89 eV)

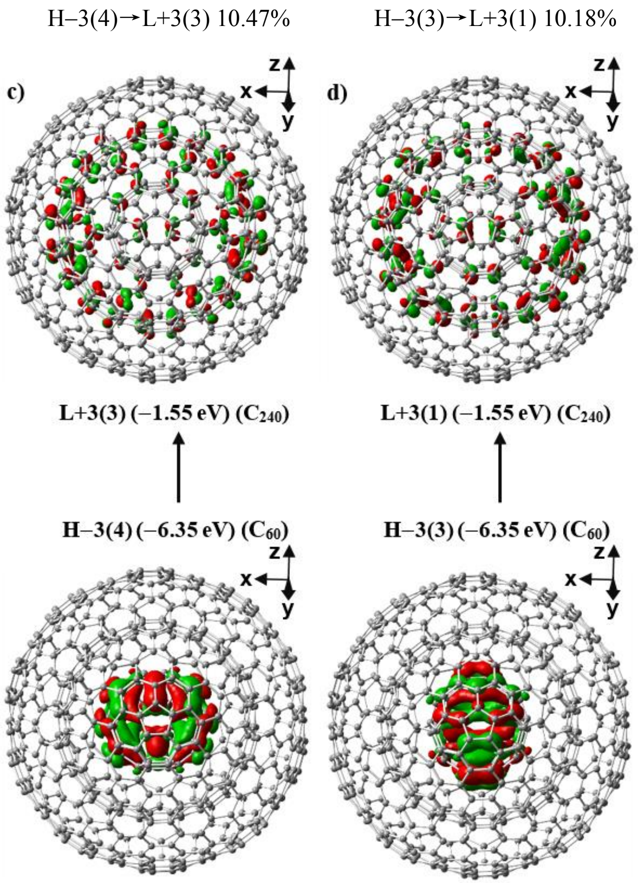
H−3(3)→L+3(3) 22.44% H−3(2)→L+3(2) 18.75% H−3(5)→L+3(1) 12.50%

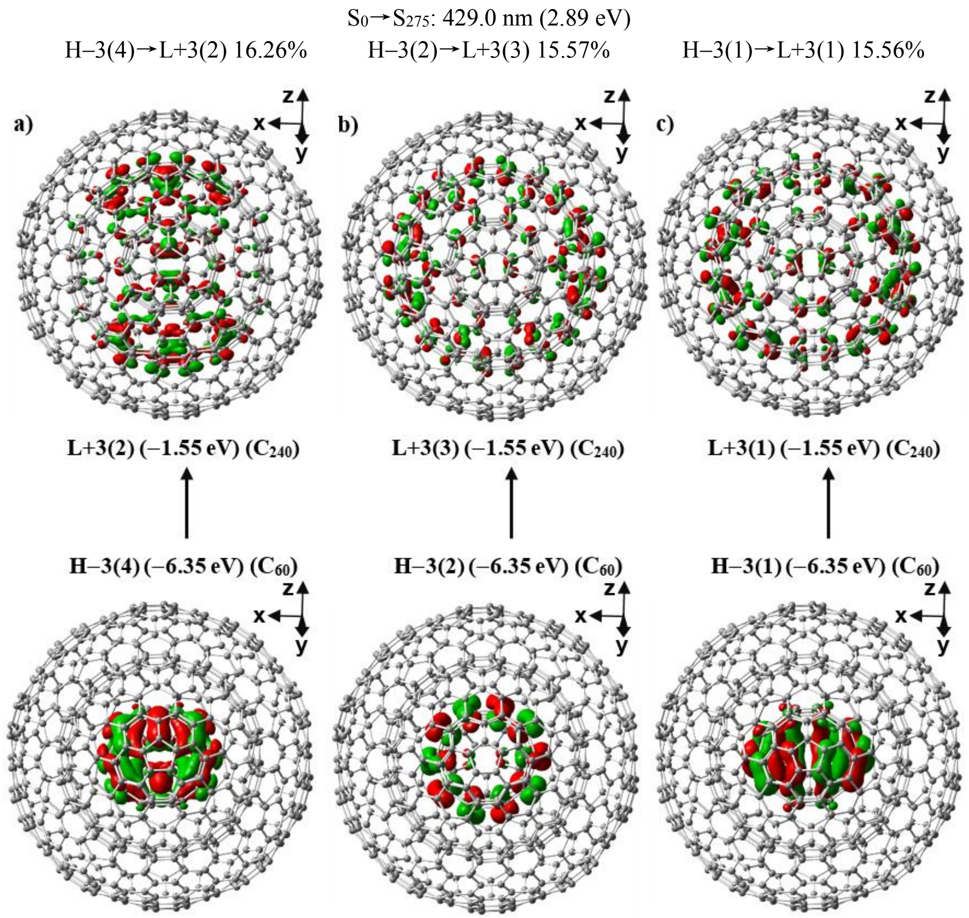


$S_0 \rightarrow S_{274}$: 429.0 nm (2.89 eV)

H−3(1)→L+3(2) 18.74% H−3(5)→L+3(1) 10.88%

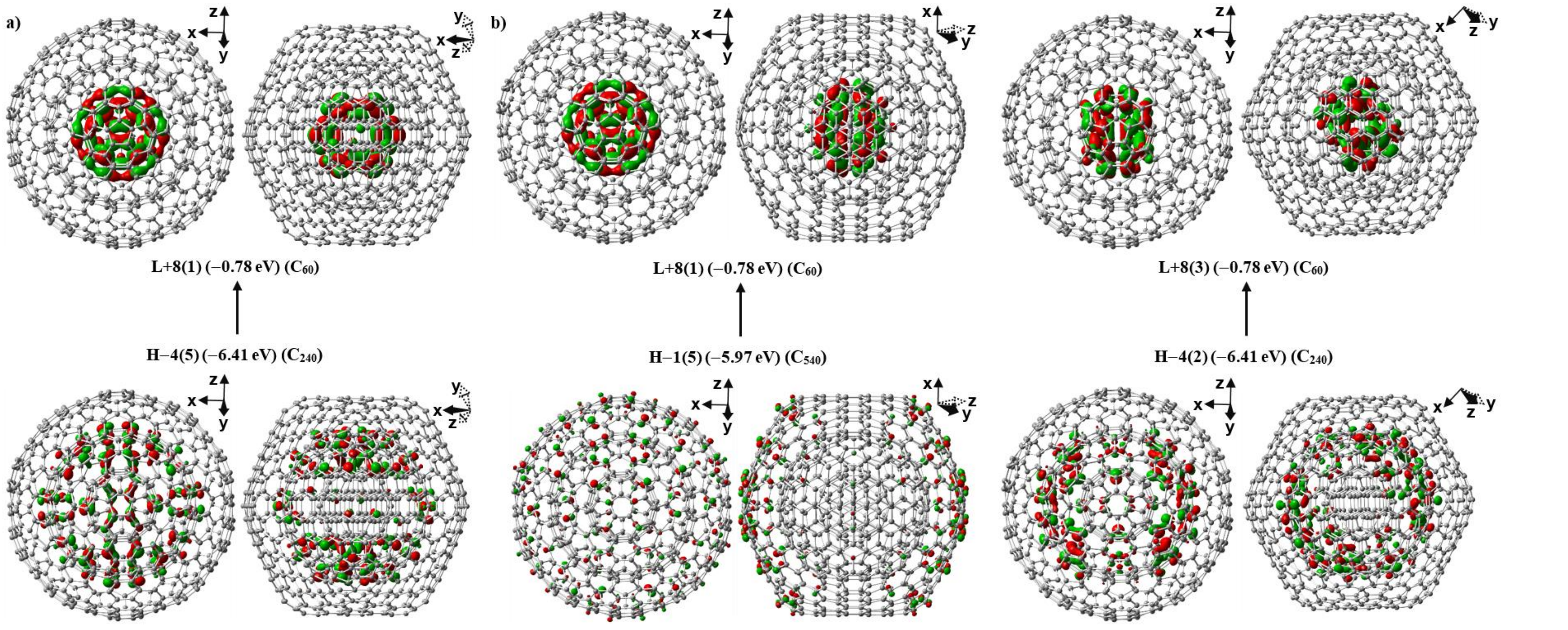



H–3(4)→L+3(3) 10.47%
H–3(3)→L+3(1) 10.18%
c)
d)
L+3(3) (–1.55 eV) (C_{240})
L+3(1) (–1.55 eV) (C_{240})
H–3(4) (–6.35 eV) (C_{60})
H–3(3) (–6.35 eV) (C_{60})


$S_0 \rightarrow S_{275}$: 429.0 nm (2.89 eV)
H–3(4)→L+3(2) 16.26%
H–3(2)→L+3(3) 15.57%
H–3(1)→L+3(1) 15.56%
a)
b)
c)
L+3(2) (–1.55 eV) (C_{240})
L+3(3) (–1.55 eV) (C_{240})
L+3(1) (–1.55 eV) (C_{240})
H–3(4) (–6.35 eV) (C_{60})
H–3(2) (–6.35 eV) (C_{60})
H–3(1) (–6.35 eV) (C_{60})

c. $S_0 \rightarrow S_{559}$: 354.7 nm (3.50 eV) $S_0 \rightarrow S_{560}$: 354.7 nm (3.50 eV) $S_0 \rightarrow S_{561}$: 354.7 nm (3.50 eV) (NO)

H−4(5)→L+8(1) 12.19% H−1(5)→L+8(1) 11.48% H−4(2)→L+8(3) 10.04%

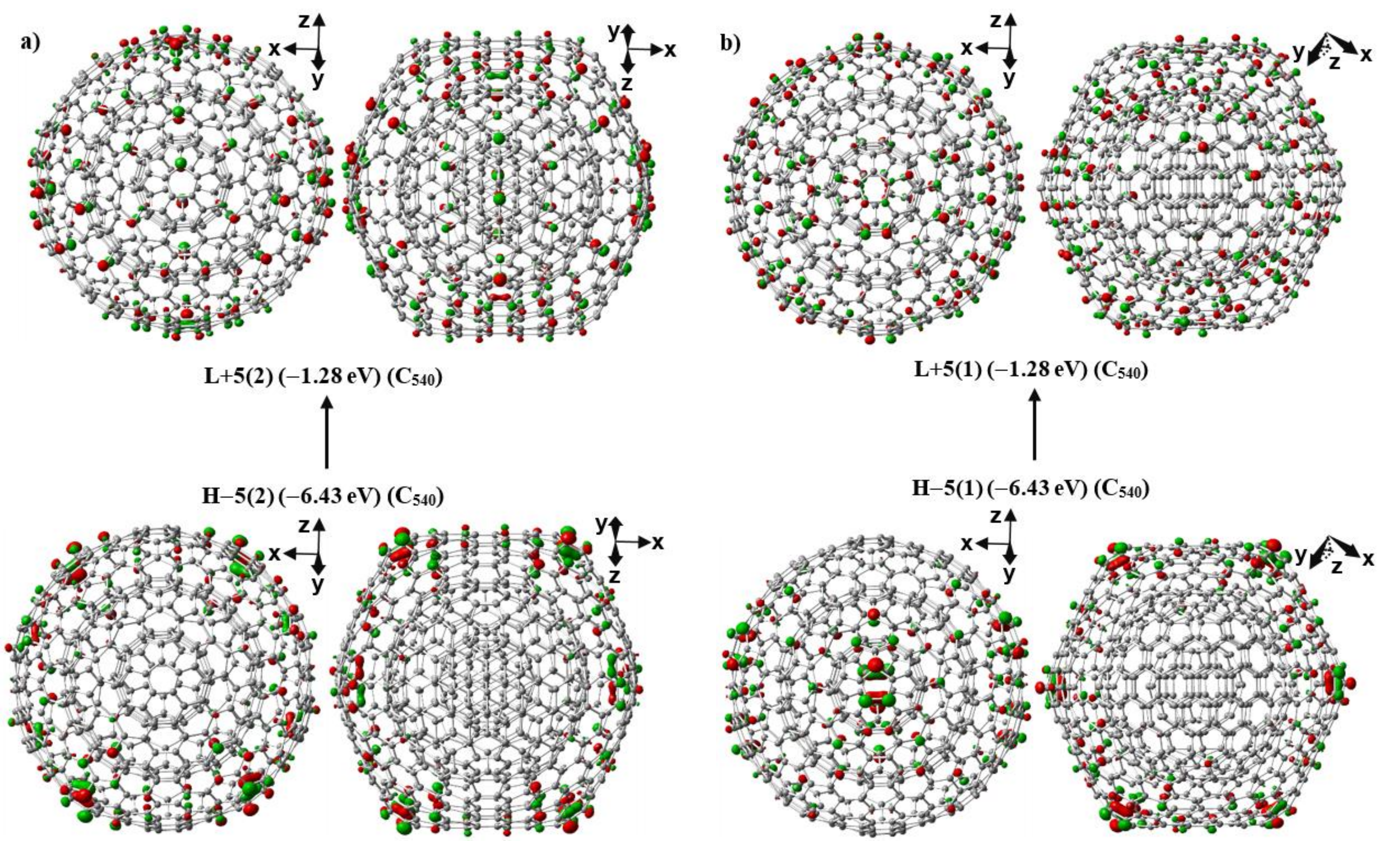


d. The strongest oscillator strength: 5_A—Corresponding to the transition at 3.86 eV (321.0 nm) in C_{540}.

$S_0 \rightarrow S_{844}$: 311.9 nm (3.98 eV)

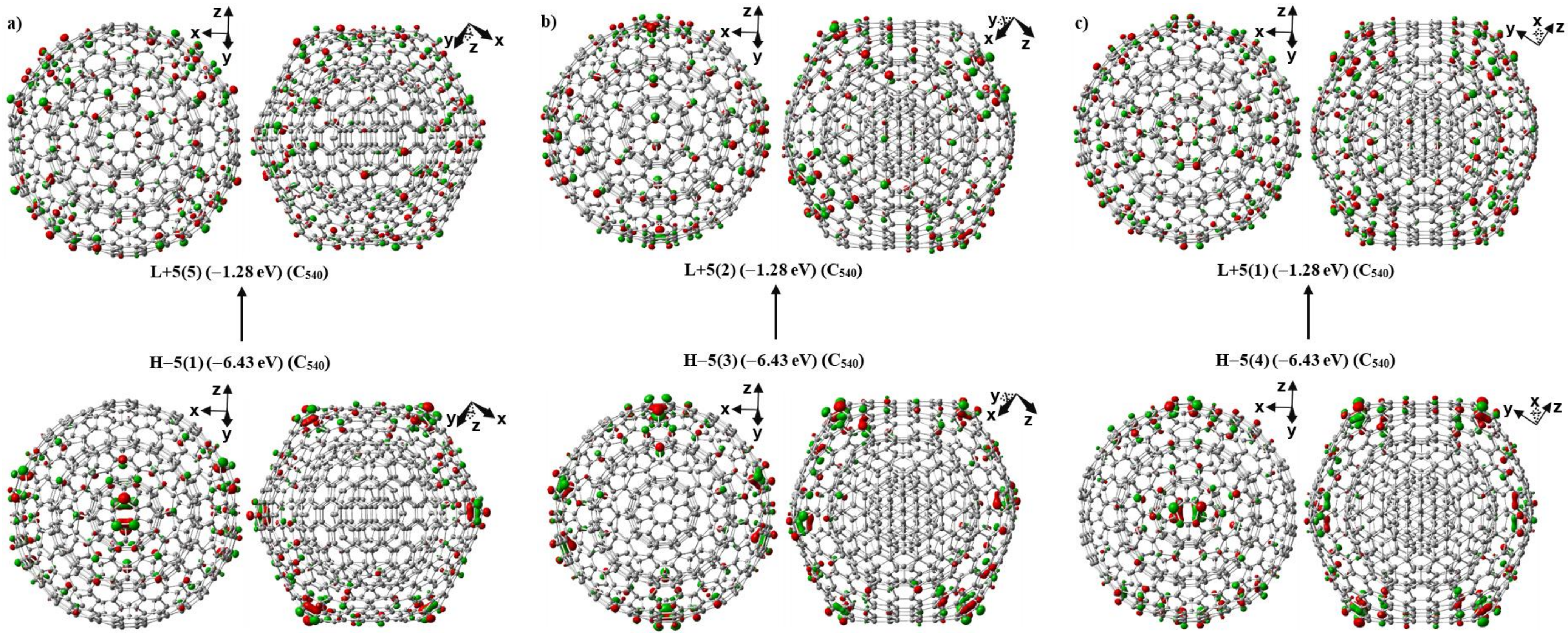
H−5(2)→L+5(2) 18.87%

H−5(1)→L+5(1) 16.36%

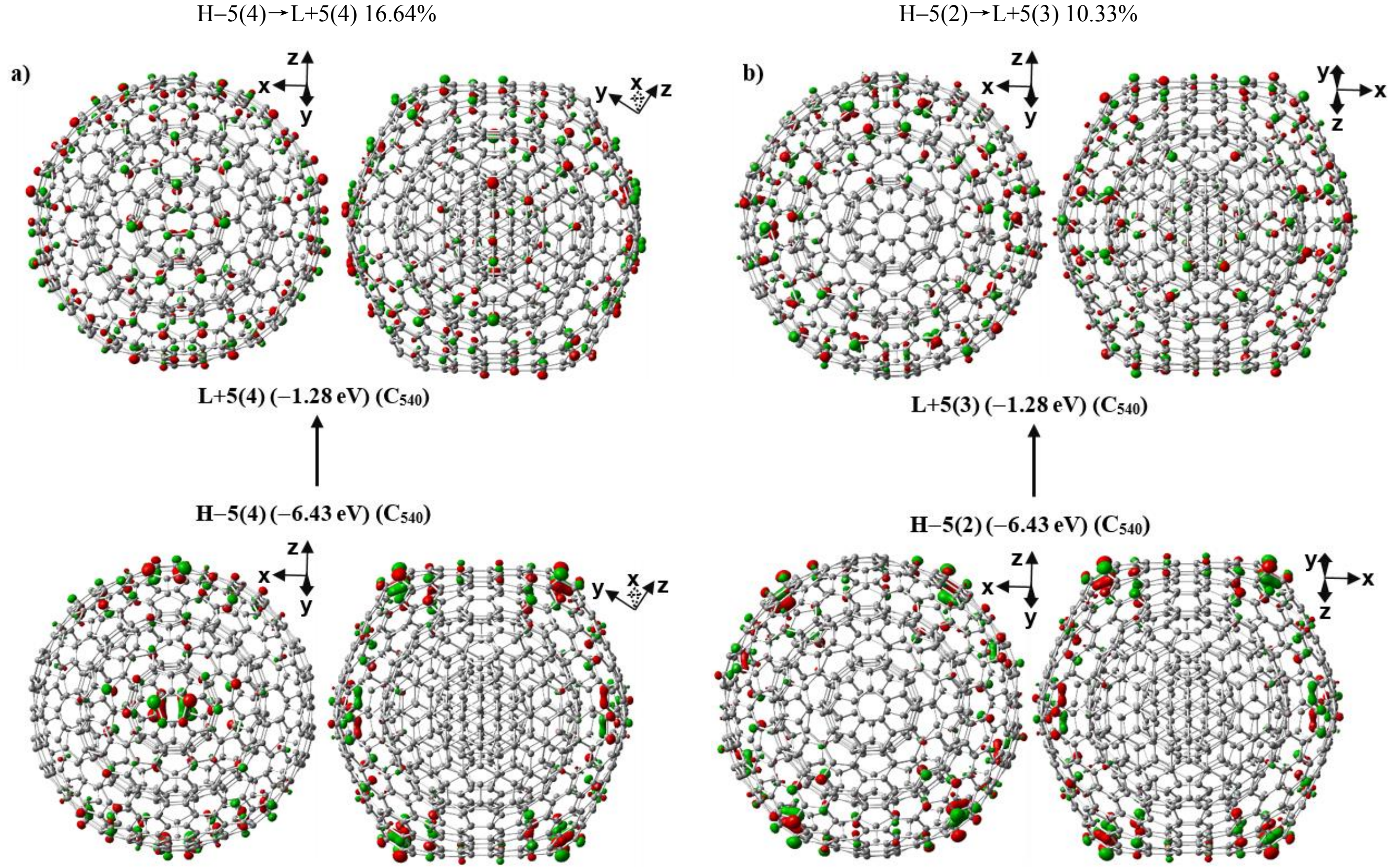


$S_0 \rightarrow S_{845}$: 311.9 nm (3.98 eV)

H−5(1)→L+5(5) 15.65%　　H−5(3)→L+5(2) 10.95%　　H−5(4)→L+5(1) 10.68%



$S_0 \rightarrow S_{846}$: 311.9 nm (3.98 eV)



e.

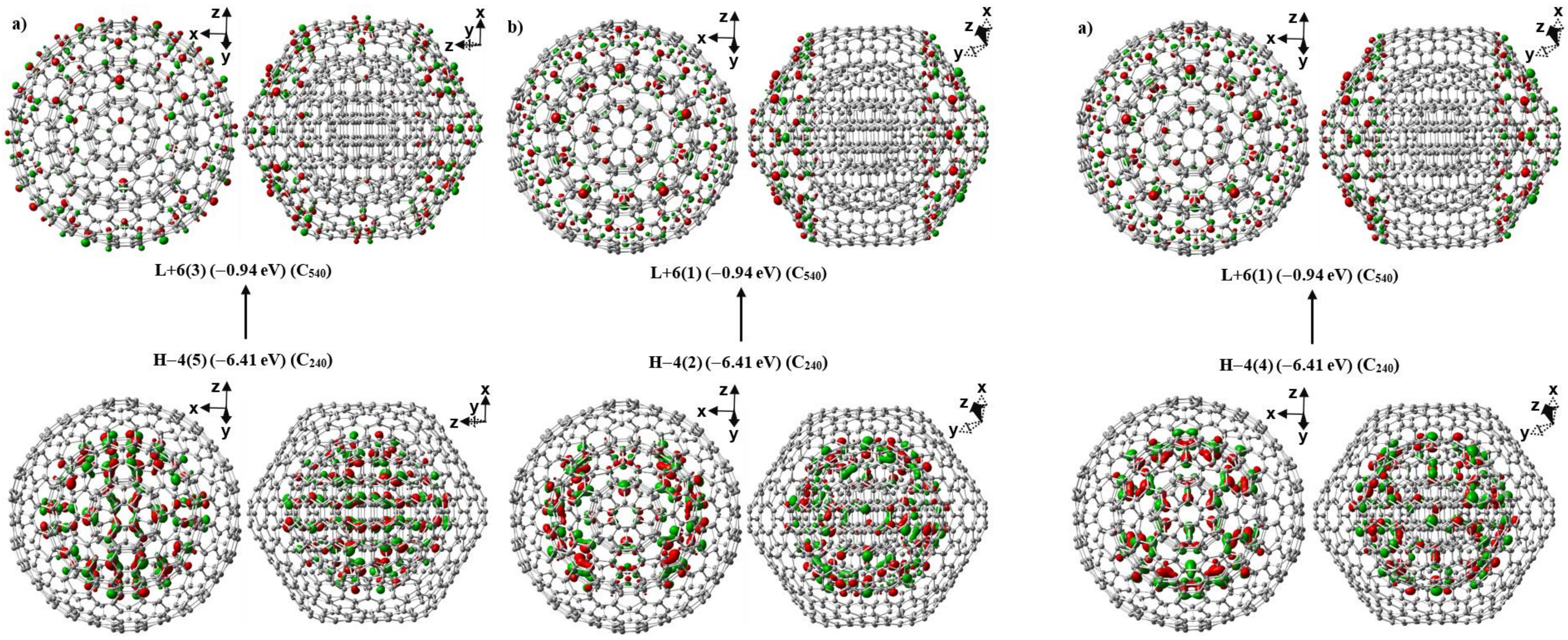
$S_0 \rightarrow S_{926}$: 297.8 nm (4.16 eV)

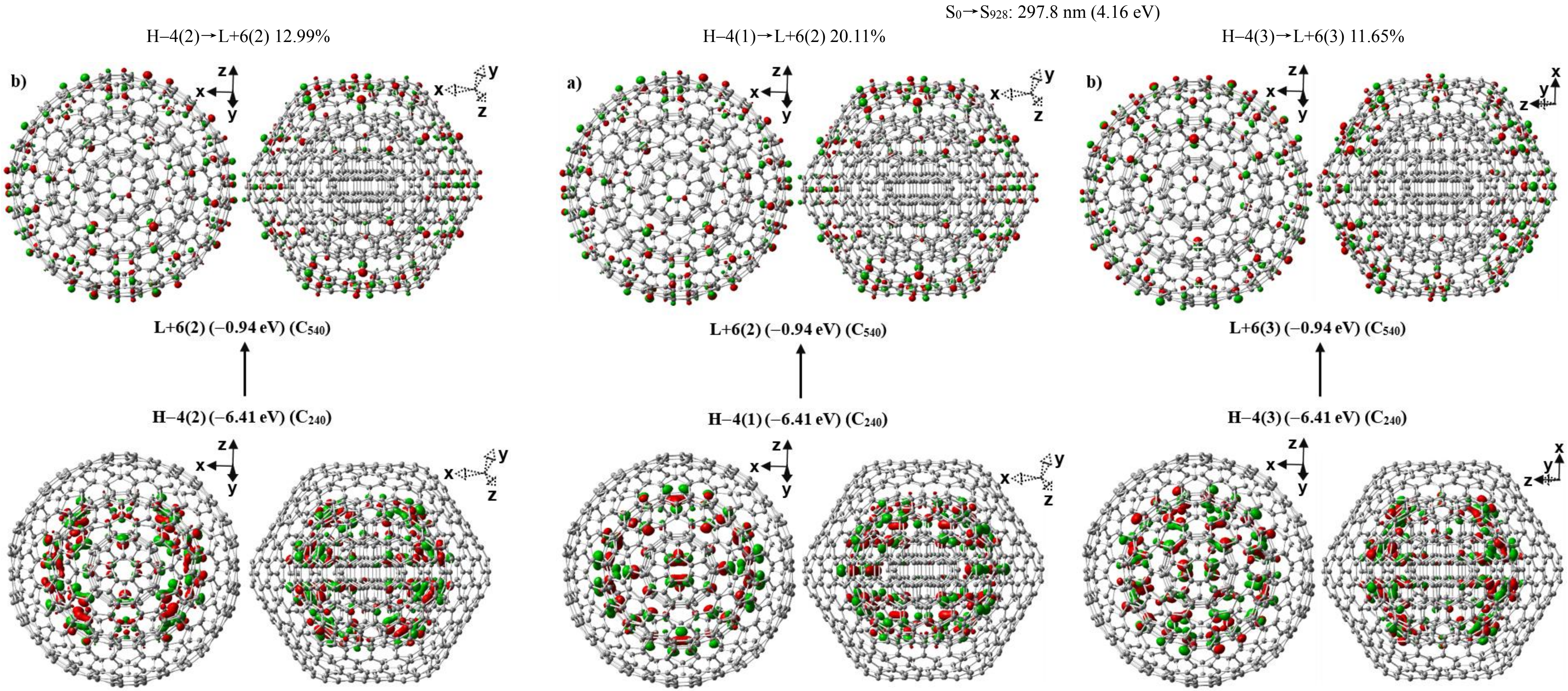
H−4(5)→L+6(3) 17.94%

H−4(2)→L+6(1) 11.25%

$S_0 \rightarrow S_{927}$: 297.8 nm (4.16 eV)

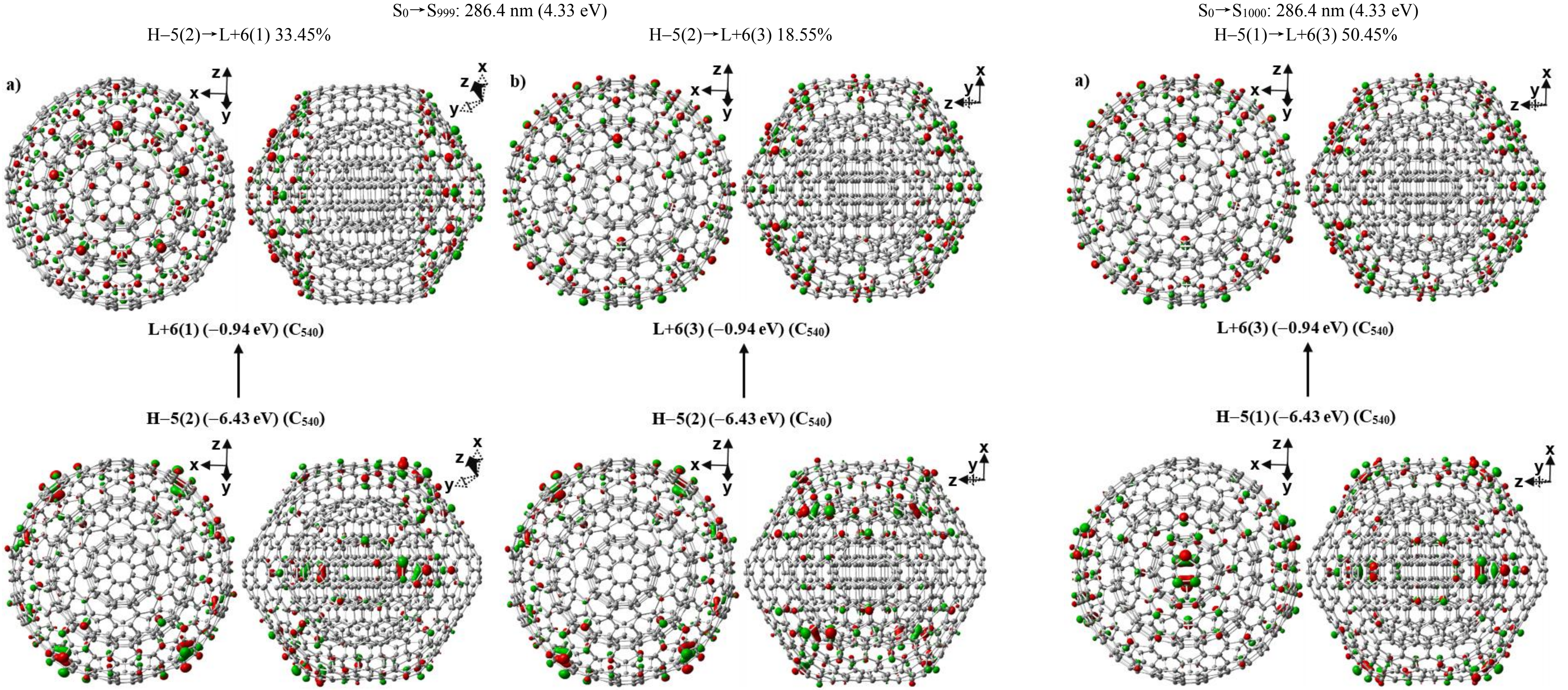
H−4(4)→L+6(1) 22.48%



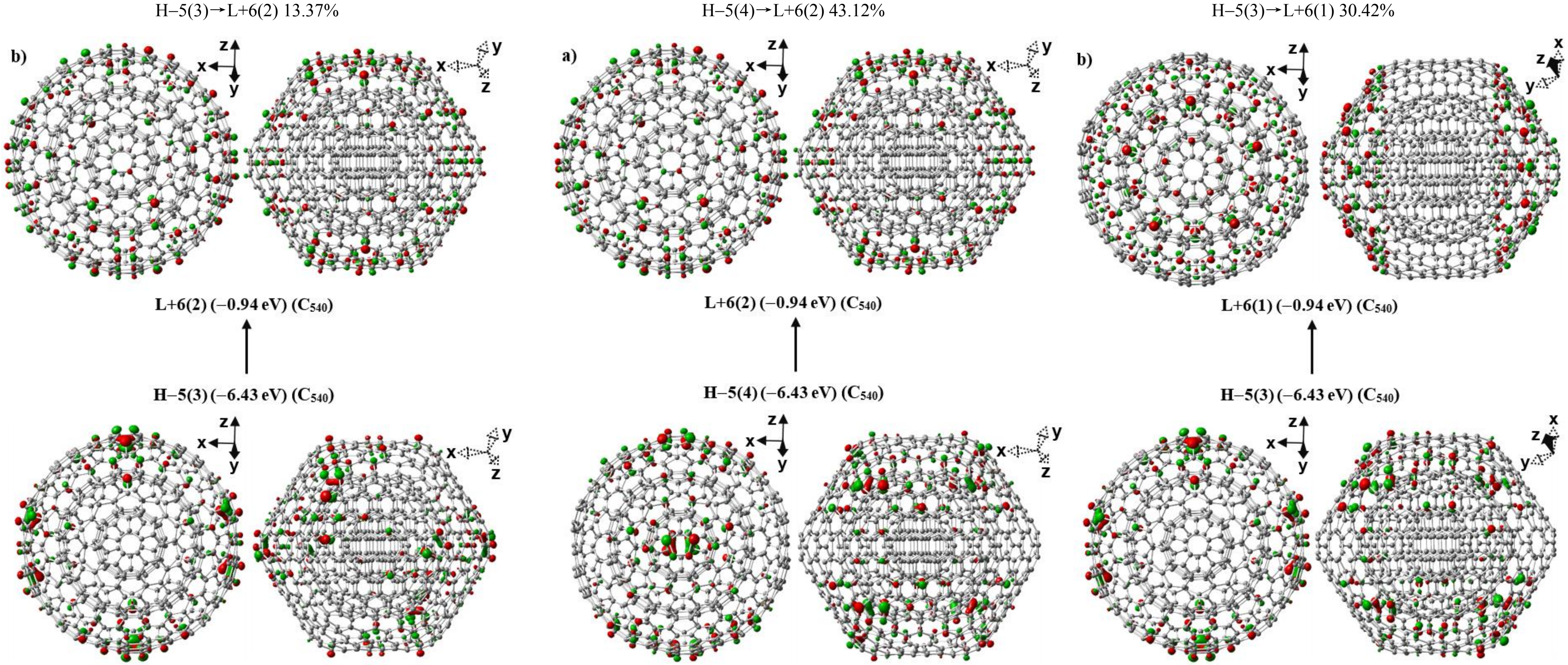


S0→S928: 297.8 nm (4.16 eV)
H−4(2)→L+6(2) 12.99%
H−4(1)→L+6(2) 20.11%
H−4(3)→L+6(3) 11.65%
b)
a)
b)
L+6(2) (−0.94 eV) (C540)
L+6(2) (−0.94 eV) (C540)
L+6(3) (−0.94 eV) (C540)
H−4(2) (−6.41 eV) (C240)
H−4(1) (−6.41 eV) (C240)
H−4(3) (−6.41 eV) (C240)

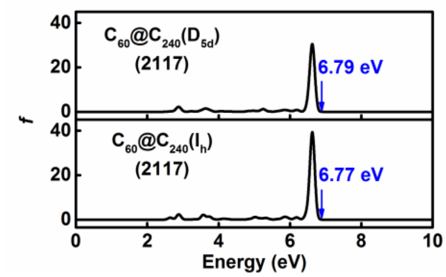
f. 5_B—Corresponding to the transition at 4.49 eV (276.2 nm) in C_{540}.



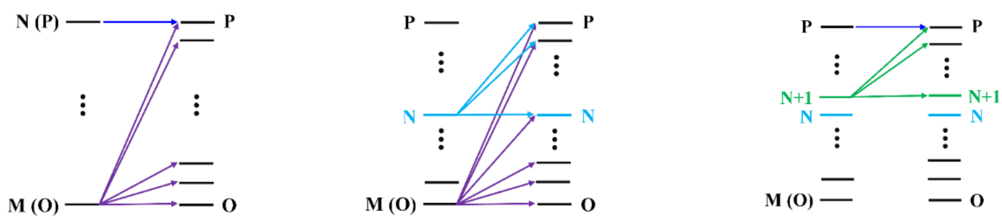
S$_0$→S$_{1001}$: 286.4 nm (4.33 eV)



8. **Fig. S6** Electronic spectra of $C_{60}@C_{240}$ (I_h) and $C_{60}@C_{240}$ (D_{5d}) with 2117 (46×46) configurations. f is the oscillator strength. The numbers are the predicted highest electron transition energies.

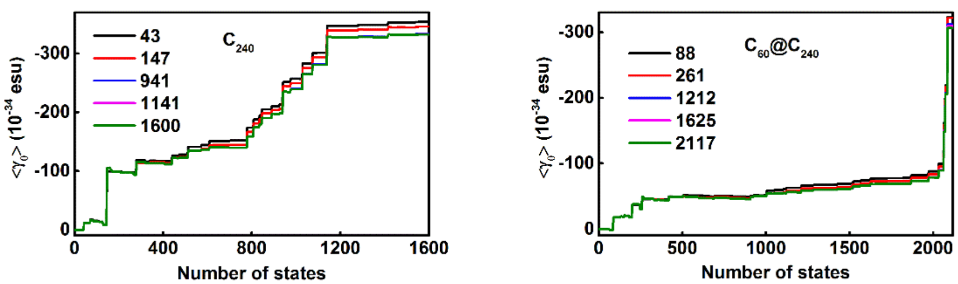


9. **Fig. S7** The truncation scheme of excited states which is tested with the <γ_0> of C_{240} and $C_{60}@C_{240}$.



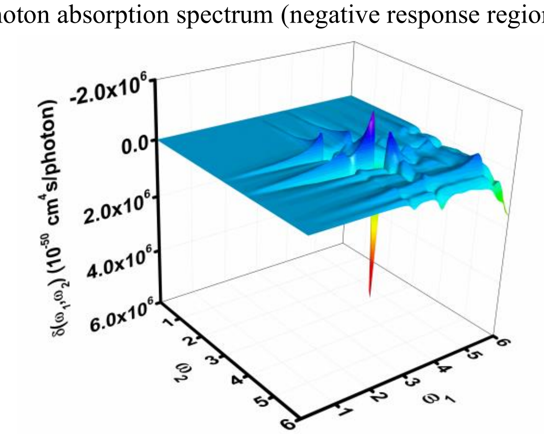
Full CIS [(M, P)→(O, P)] Truncated CIS [(M, N)→(O, P)] Missed CIS [(N+1, P)→(N+1, P)]

a) The truncation scheme of excited states, where O ≥ M and P ≥ N.



b) The truncation scheme in a) is tested with the <γ_0> of C_{240} and $C_{60}@C_{240}$. The truncated upper starting excited state is the 42th, 146th, 940th, and 1140th excited state for C_{240}, respectively. The truncated upper starting excited state is the 87th, 260th, 1211th, and 1624th excited state for $C_{60}@C_{240}$, respectively.

10. **Fig. S8** Two-dimensional two-photon absorption spectrum (negative response region) of C_{240}.

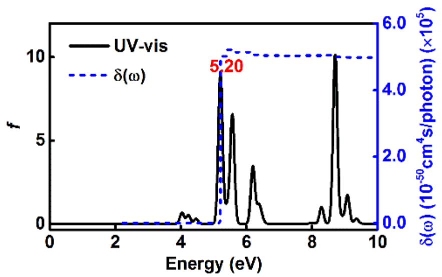


11. **Table S3** The strong response and corresponding major electronic excitation contribution of dynamic third-order nonlinear optic process for C_{60} (931).

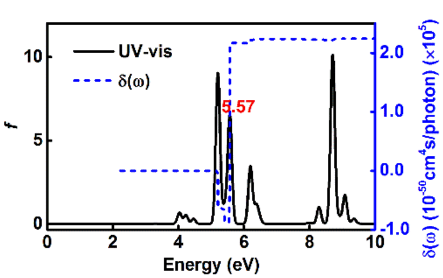
Processes	External Field/eV (λ/nm)	Responses	Major Electronic Excitation Contribution
STPA δ(−w; w, −w, w)	5.20 (238.3)	497407	5.20 eV(238.3 nm) (501694)
	5.55 (223.4)	224667	5.57 eV(222.7 nm) (304389)
	5.05 (245.5)	−259395	5.20 eV(238.3 nm) (−96138); 5.57 eV(222.7 nm) (−96523)
DFWM γ(−w; w, −w, w)	5.15 (240.7)	9873	5.20 eV(238.3 nm) (5554); 5.57 eV(222.7 nm) (2668)
	5.65 (219.4)	−4011	5.57 eV(222.7 nm) (−4731)
THG γ(−3w; w, w, w)	5.20 (238.3)	780	5.20 eV(238.3 nm) (390); 5.57 eV(222.7 nm) (70)
	5.55 (223.4)	318	5.57 eV(222.7 nm) (239)
EFISH γ(−2w; w, w, 0)	5.35 (231.7)	612	5.20 eV(238.3 nm) (85); 5.47 eV(226.8 nm) (133); 5.59 eV(221.9 nm) (160)
	5.10 (243.1)	−294	5.57 eV(222.7 nm) (−104); 5.59 eV(221.9 nm) (−125)

12. **Fig. S9** The evolution of third-order nonlinear optic properties with electronic spectra for C_{60} (931) at specific external fields.

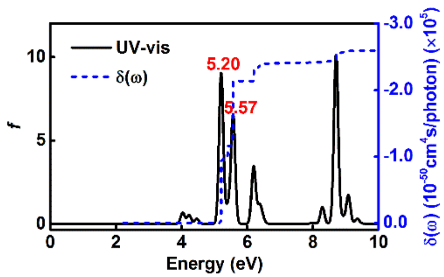
STPA: a) STPA-5.20 eV



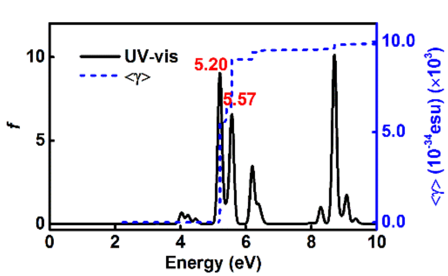
b) STPA-5.55 eV



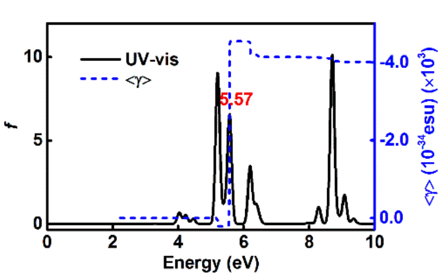
c) STPA-5.05 eV



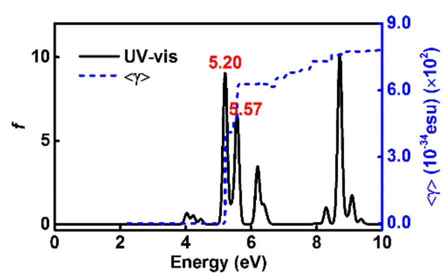
DFWM: a) DFWM-5.15 eV



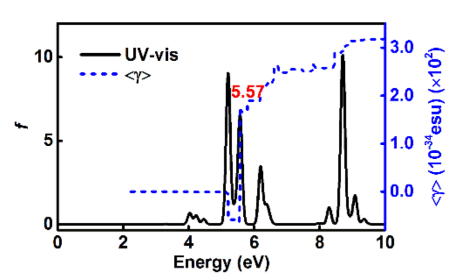
b) DFWM-5.65 eV



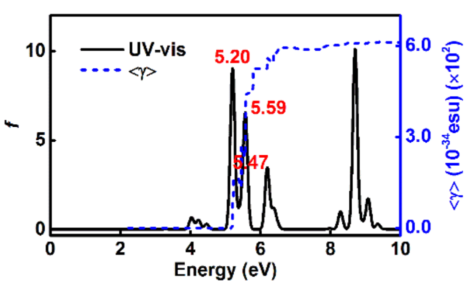
THG: a) THG-5.20 eV

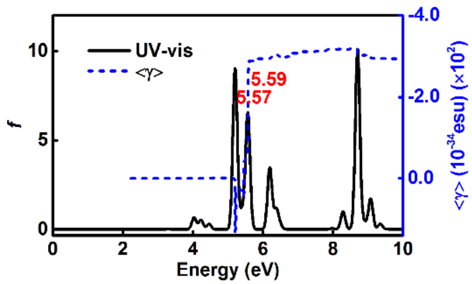


b) THG-5.55 eV



EFISH: a) EFISH-5.35 eV b) EFISH-5.10 eV



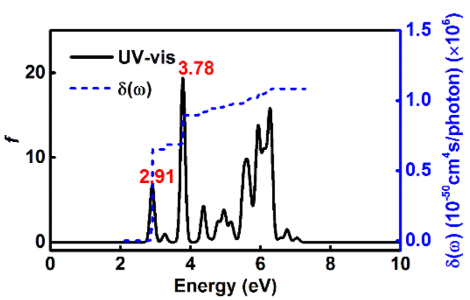


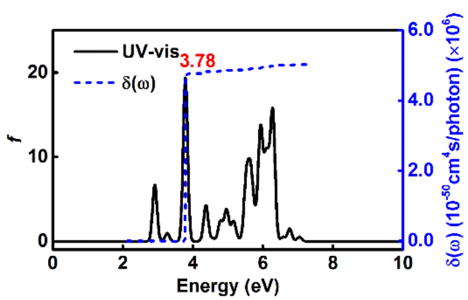
13. **Table S4** The strong response and corresponding major electronic excitation contribution of dynamic third-order nonlinear optic process for C_{240} (1600).

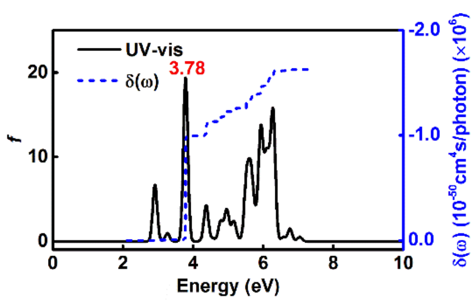
Processes	External Field/eV (λ/nm)	Responses	Major Electronic Excitation Contribution
STPA δ(−w; w, −w, w)	2.95 (420.3)	1086560	2.91 eV(425.8 nm) (652461); 3.78 eV(327.6 nm) (202104)
	3.80 (326.3)	5024070	3.78 eV(327.6 nm) (4731332)
	3.65 (339.7)	−1627150	3.78 eV(327.6 nm) (−980366)
DFWM γ(−w; w, −w, w)	2.90 (427.5)	66670	2.91 eV(425.8 nm) (24807); 3.78 eV(327.6 nm) (19667)
	3.75 (330.6)	124464	3.78 eV(327.6 nm) (89526)
	3.85 (322.0)	−106723	3.78 eV(327.6 nm) (−127152)
THG γ(−3w; w, w, w)	2.90 (427.5)	9593	2.91 eV(425.8 nm) (2849); 3.74 eV(331.6 nm) (2273); 4.49 eV(276.4 nm) (1197)
	3.80 (326.3)	11075	3.78 eV(327.6 nm) (5275)
EFISH γ(−2w; w, w, 0)	2.95 (420.3)	3752	2.91 eV(425.8 nm) (2430)
	3.85 (322.0)	4285	3.78 eV(327.6 nm) (3208); 3.85 eV(322.0 nm) (1397)
	3.70 (335.1)	−3962	3.78 eV(327.6 nm) (−1275); 3.85 eV(322.0 nm) (−737); 4.37 eV(283.7 nm) (−545)

14. **Fig. S10** The evolution of third-order nonlinear optic properties with electronic spectra for C_{240} (1600) at specific external fields.

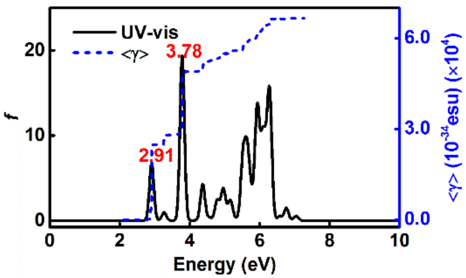
STPA: a) STPA-2.95 eV b) STPA-3.80 eV c) STPA-3.65 eV



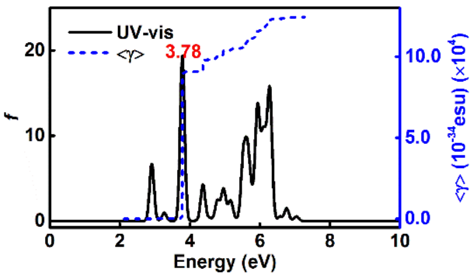




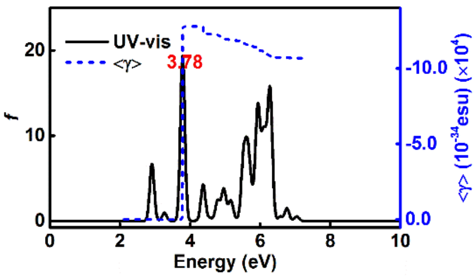
DFWM: a) DFWM-2.90 eV



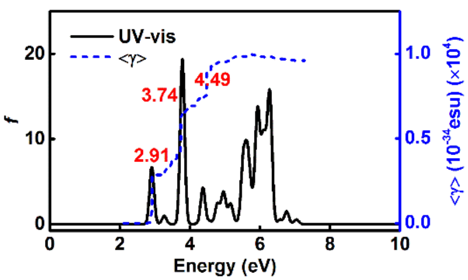
b) DFWM-3.75 eV



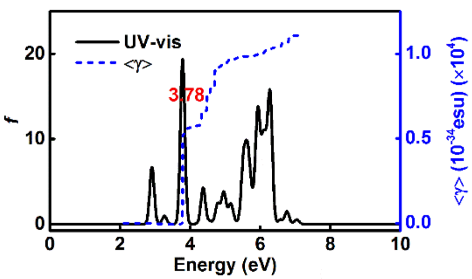
c) DFWM-3.85 eV



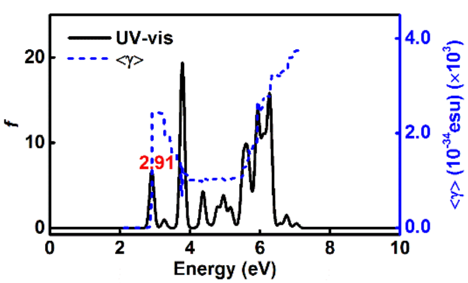
THG: a) THG-2.90 eV



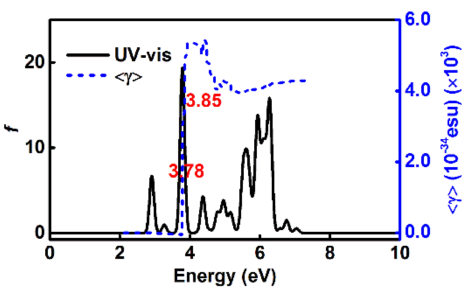
b) THG-3.80 eV



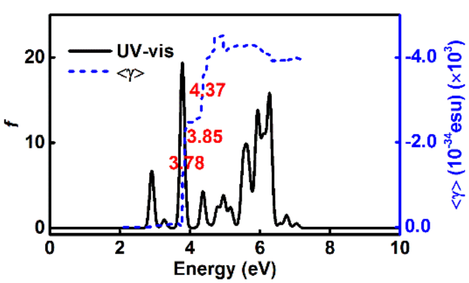
EFISH: a) EFISH-2.95 eV



b) EFISH-3.85 eV



c) EFISH-3.70 eV



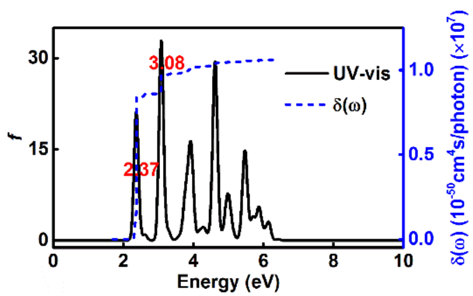
15. **Table S5** The strong response and corresponding major electronic excitation contribution of dynamic third-order nonlinear optic process for C_{540} (1850).

	External Field/eV (λ/nm)	Responses	Major Electronic Excitation Contribution
STPA δ(−w; w, −w, w)	2.40 (516.6)	10620200	2.37 eV(523.3 nm) (8432640); 3.08 eV(402.2 nm) (1123990)
	3.10 (399.9)	13386900	3.08 eV(402.2 nm) (12437710)
	3.90 (317.9)	2242480	3.95 eV(313.8 nm) (2282906)
	4.60 (269.5)	3804370	4.61 eV(269.1 nm) (2343120); 4.65 eV(226.4 nm) (1668320)
	2.25 (551.0)	−5155620	2.37 eV(523.3 nm) (−3012840); 3.08 eV(402.2 nm) (−1069630)
DFWM γ(−w; w, −w, w)	2.35 (527.6)	886669	2.37 eV(523.3 nm) (528872); 3.08 eV(402.2 nm) (184471)
	3.00 (413.3)	479717	3.08 eV(402.2 nm) (401490)
	3.75 (330.6)	50650	3.88 eV(319.4 nm) (15716); 3.95 eV(313.8 nm) (30054); 4.61 eV(269.1 nm) (8066)
	4.50 (275.5)	48850	4.61 eV(269.1 nm) (8763); 4.65 eV(226.4 nm) (18218)
	2.45 (506.0)	−472664	2.37 eV(523.3 nm) (−544957)
	3.15 (393.6)	−452904	3.08 eV(402.2 nm) (−554948)
THG γ(−3w; w, w, w)	2.35 (527.6)	102868	2.37 eV(523.3 nm) (40065); 2.97 eV(417.1 nm) (27121)
	3.10 (399.9)	52896	3.08 eV(402.2 nm) (27777)
	3.90 (317.9)	9184	3.88 eV(319.4 nm) (1858); 3.95 eV(313.8 nm) (4227); 4.61 eV(269.1 nm) (1437)
	4.60 (269.5)	4863	4.61 eV(269.1 nm) (3443); 4.65 eV(226.4 nm) (1956)
EFISH γ(−2w; w, w, 0)	2.40 (516.6)	29343	2.37 eV(523.3 nm) (31552);
	3.15 (393.6)	14953	3.08 eV(402.2 nm) (15255)
	4.00 (310.0)	9343	3.95 eV(313.8 nm) (5596)
	4.60 (269.5)	4481	4.61 eV(269.1 nm) (3144); 4.65 eV(226.4 nm) (1449)
	3.00 (413.3)	−14032	3.08 eV(402.2 nm) (−14578)

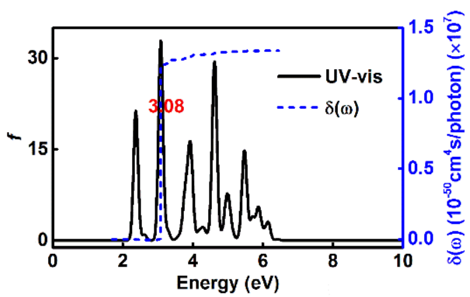
16. **Fig. S11** The evolution of third-order nonlinear optic properties with electronic spectra for C_{540} (1850) at specific external fields.

STPA:

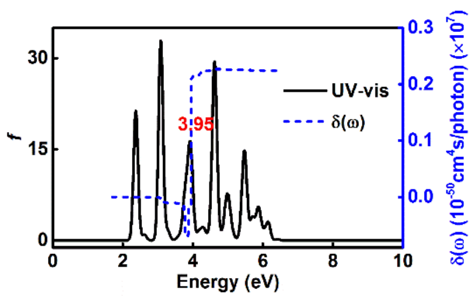
a) STPA-2.40 eV



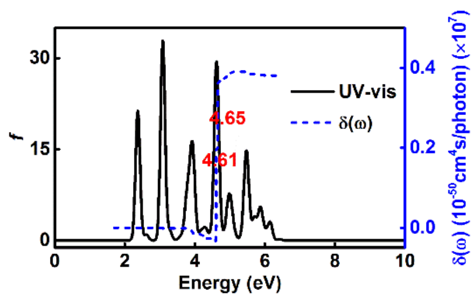
b) STPA-3.10 eV



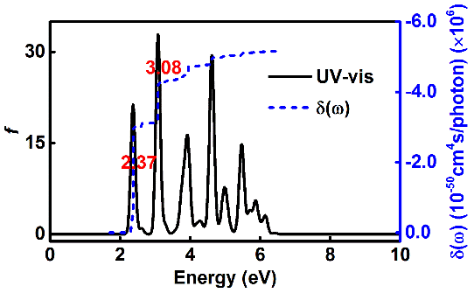
c) STPA-3.90 eV



d) STPA-4.60 eV

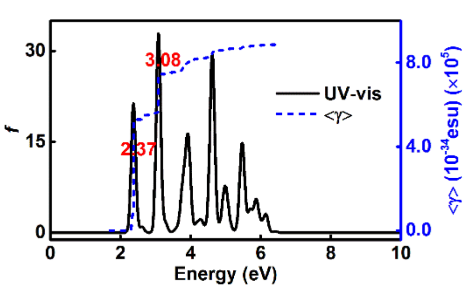


e) STPA-2.25 eV

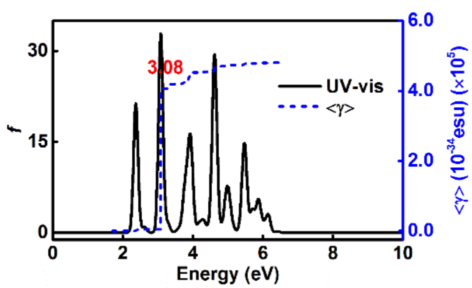


DFWM:

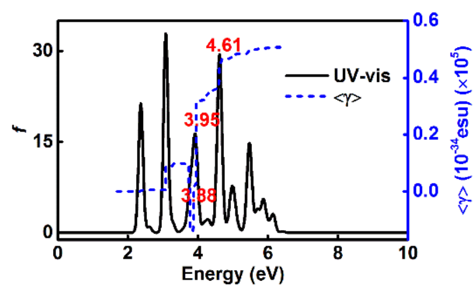
a) DFWM-2.35 eV



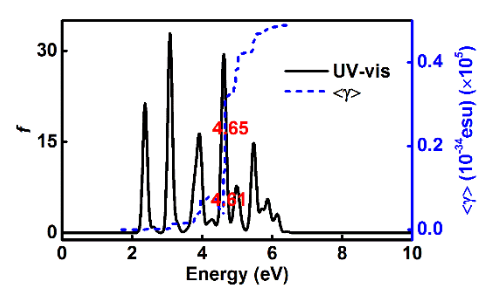
b) DFWM-3.00 eV



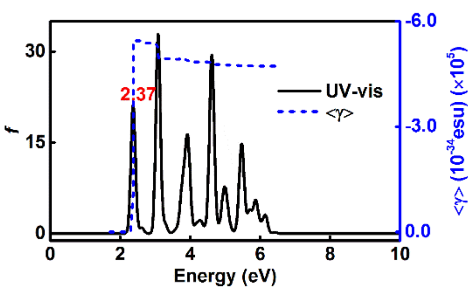
c) DFWM-3.75 eV



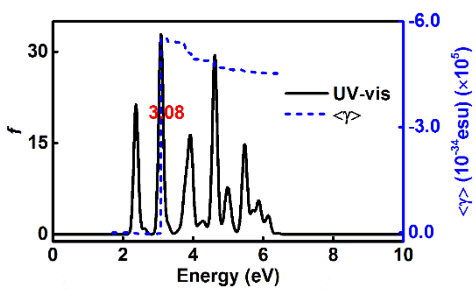
d) DFWM-4.50 eV



e) DFWM-2.45 eV

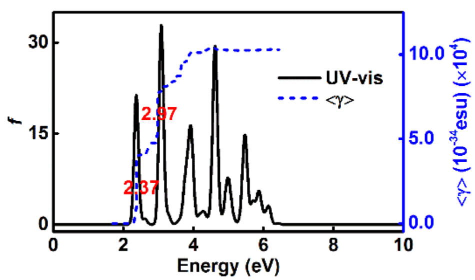


f) DFWM-3.15 eV

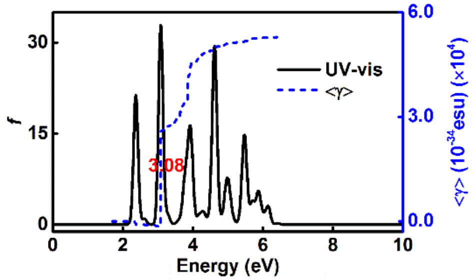


THG:

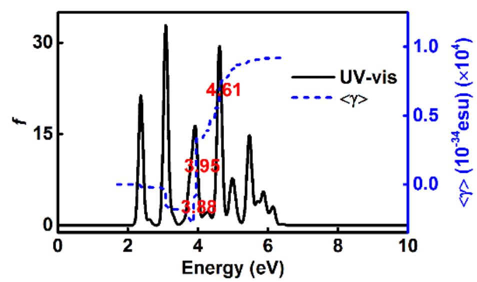
a) THG-2.35 eV



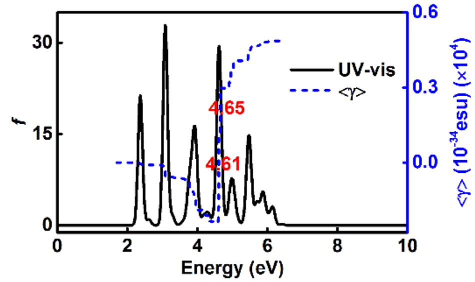
b) THG-3.10 eV



c) THG-3.90 eV

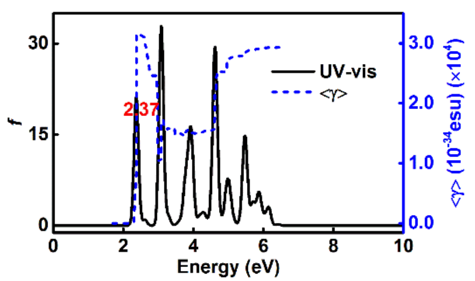


d) THG-4.60 eV

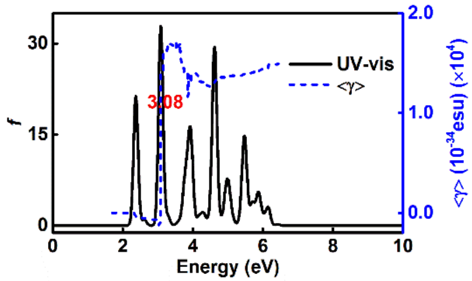


EFISH:

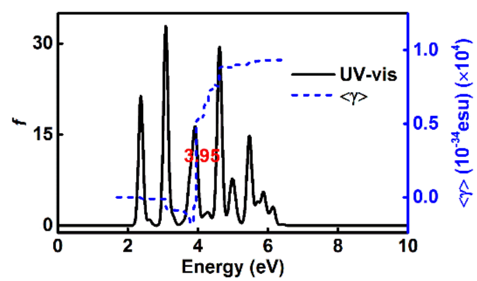
a) EFISH-2.40 eV



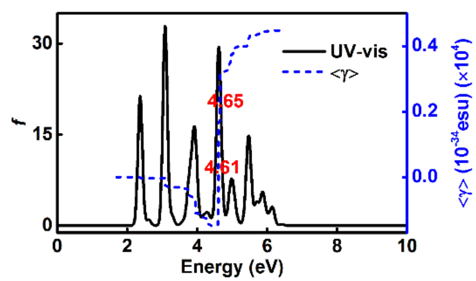
b) EFISH-3.15 eV



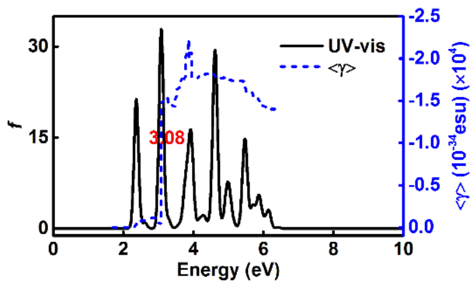
c) EFISH-4.00 eV



d) EFISH-4.60 eV



e) EFISH-3.00 eV



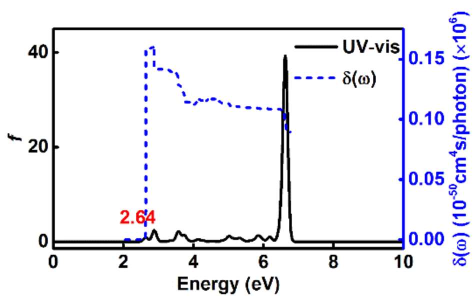
17. **Table S6** The strong response and corresponding major electronic excitation contribution of dynamic third-order nonlinear optic process for $C_{60}@C_{240}(I_h)$ (2117).

Processes	External Field/eV (λ/nm)	Responses	Major Electronic Excitation Contribution
STPA δ(−w; w, −w, w)	2.65 (467.9)	88989	2.64 eV(469.1 nm) (159020)
	2.90 (427.5)	909033	2.88 eV(430.0 nm) (767055)
	3.60 (344.4)	421239	3.57 eV(347.3 nm) (234526); 3.74 eV(331.2 nm) (172549)
DFWM γ(−w; w, −w, w)	2.60 (476.9)	18047	2.64 eV(469.1 nm) (8008); 2.88 eV(430.0 nm) (6791)
	2.85 (435.0)	46287	2.88 eV(430.0 nm) (25825)
	3.55 (349.2)	16361	3.74 eV(331.2 nm) (7592); 6.60 eV(187.8 nm) (1665); 6.62 eV(187.2 nm) (1297); 6.65 eV(186.4 nm) (1952)
	2.95 (420.3)	−27272	2.88 eV(430.0 nm) (−35873)
THG γ(−3w; w, w, w)	2.65 (467.9)	3650	2.64 eV(469.1 nm) (747); 3.71 eV(334.1 nm) (635)
	2.90 (427.5)	7576	2.88 eV(430.0 nm) (2126); 3.71 eV(334.1 nm) (1080)
	3.55 (349.2)	2196	3.57 eV(347.3 nm) (679)
EFISH γ(−2w; w, w, 0)	2.90 (427.5)	2385	2.88 eV(430.0 nm) (3297)
	3.40 (364.6)	2825	3.57 eV(347.3 nm) (285); 6.60 eV(187.8 nm) (536); 6.62 eV(187.2 nm) (492); 6.65 eV(186.4 nm) (935)
	3.65 (339.7)	1343	3.71 eV(334.1 nm) (272); 3.91 eV(316.9 nm) (394); 6.65 eV(186.4 nm) (354)
	2.65 (467.9)	−2223	2.88 eV(430.0 nm) (−1892); 6.65 eV(186.4 nm) (−416)

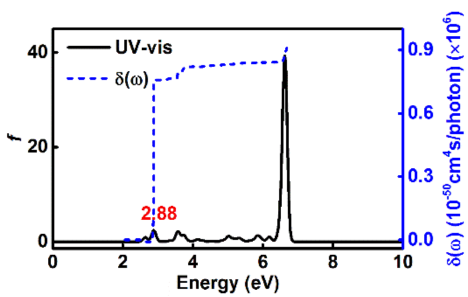
18. **Fig. S12** The evolution of third-order nonlinear optic properties with electronic spectra for $C_{60}@C_{240}(I_h)$ (2117) at specific external fields.

STPA:

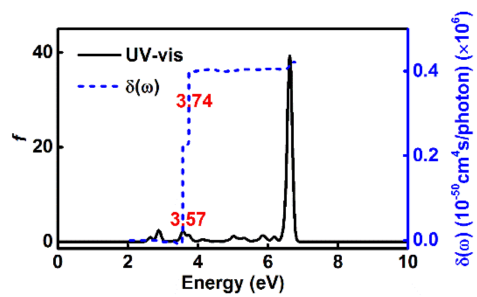
a) STPA-2.65 eV



b) STPA-2.90 eV

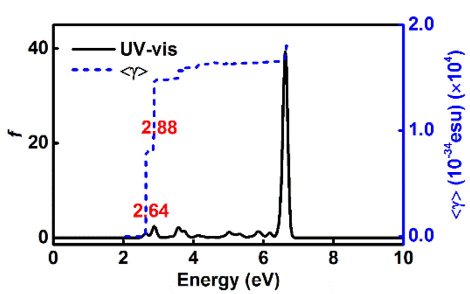


c) STPA-3.60 eV

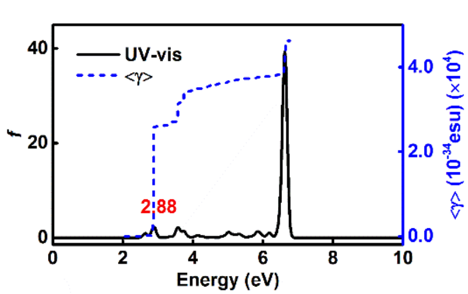


DFWM:

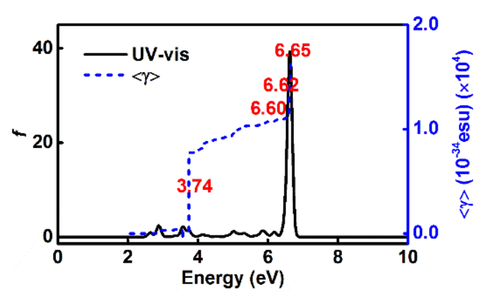
a) DFWM-2.60 eV



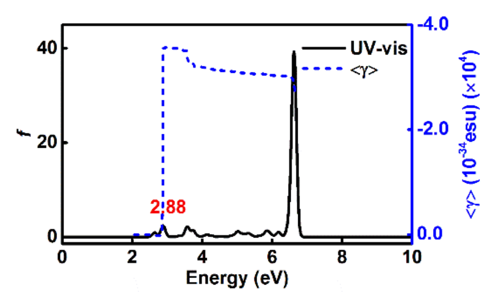
b) DFWM-2.85 eV



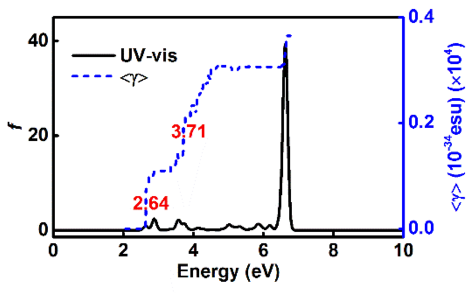
c) DFWM-3.55 eV



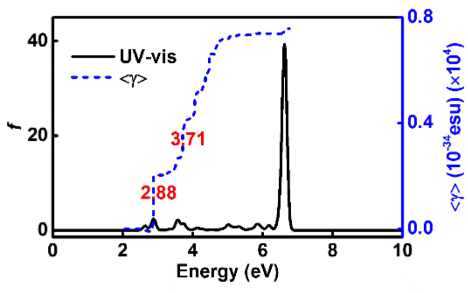
d) DFWM-2.95 eV



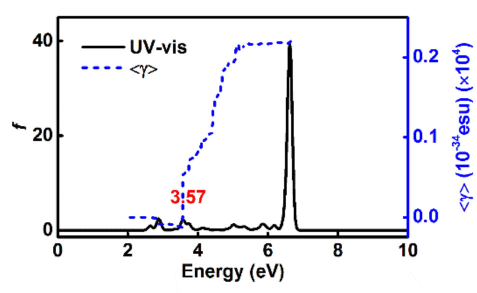
THG: a) THG-2.65 eV



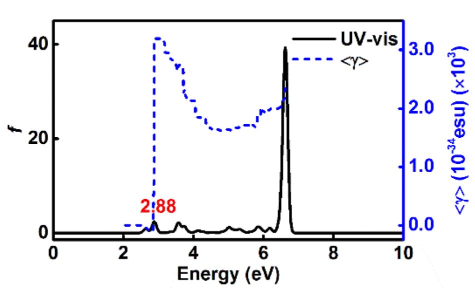
b) THG-2.90 eV



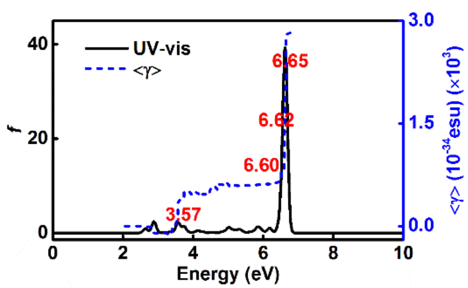
c) THG-3.55 eV



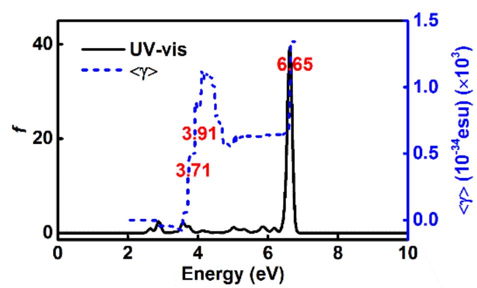
EFISH: a) EFISH-2.90 eV



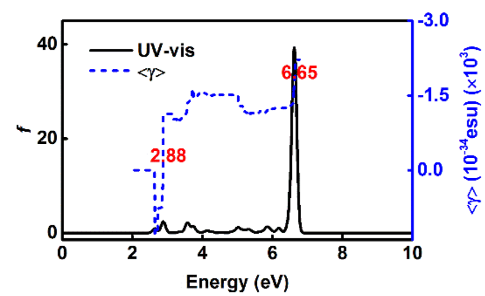
b) EFISH-3.40 eV



c) EFISH-3.65 eV



d) EFISH-2.65 eV



19. **Table S7** The strong response and corresponding major electronic excitation contribution of dynamic third-order nonlinear optic process for $C_{60}@C_{240}(I_h)@C_{540}$ (1057).

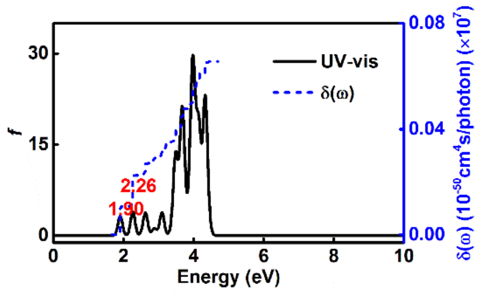
Processes	External Field/eV (λ/nm)	Responses	Major Electronic Excitation Contribution
STPA δ(−w; w, −w, w)	1.95 (635.8)	656197	1.90 eV(651.0 nm) (107909); 2.26 eV(547.3 nm) (116206)
	2.30 (539.1)	704106	2.26 eV(547.3 nm) (255872)
	3.70 (335.1)	5310810	3.66 eV(339.1 nm) (1165311); 3.72 eV(333.7 nm) (3346949); 3.98 eV(311.9 nm) (1337110)
	4.00 (310.0)	10787400	3.98 eV(311.9 nm) (5049800); 4.09 eV(303.3 nm) (3900620); 4.16 eV(297.8 nm) (3344300)
	4.50 (275.5)	−7206800	4.16 eV(297.8 nm) (−1251560); 4.33 eV(286.4 nm) (−4546350)
DFWM γ(−w; w, −w, w)	1.90 (652.5)	130017	1.90 eV(651.0 nm) (15782); 2.26 eV(547.3 nm) (24085); 3.98 eV(311.9 nm) (12865)
	2.25 (551.0)	82424	2.26 eV(547.3 nm) (7359); 2.63 eV(472.1 nm) (13811); 3.66 eV(339.1 nm) (8036); 3.98 eV(311.9 nm) (9655)
	3.45 (359.4)	226165	3.66 eV(339.1 nm) (88208); 3.72 eV(333.7 nm) (40645); 3.98 eV(311.9 nm) (39074)
	3.90 (317.9)	169832	4.09 eV(303.3 nm) (60975); 4.16 eV(297.8 nm) (77489); 4.33 eV(286.4 nm) (64026)
	4.35 (285.0)	−238711	4.33 eV(286.4 nm) (−222517)
THG γ(−3w; w, w, w)	1.90 (652.5)	31628	1.90 eV(651.0 nm) (3222); 2.83 eV(437.7 nm) (5096); 2.92 eV(425.2 nm) (7115); 3.22 eV(385.6 nm) (2976)
	2.25 (551.0)	14523	2.26 eV(547.3 nm) (3200); 2.92 eV(425.2 nm) (1187); 3.20 eV(387.2 nm) (2364); 3.30 eV(376.2 nm) (1068)

	3.70 (335.1)	21415	3.66 eV(339.1 nm) (3291); 3.72 eV(333.7 nm) (4935); 3.98 eV(311.9 nm) (8020)
	3.95 (313.9)	25613	3.98 eV(311.9 nm) (12671); 4.09 eV(303.3 nm) (5140); 4.16 eV(297.8 nm) (6099); 4.33 eV(286.4 nm) (4922)
	4.55(272.5)	–9427	3.98 eV(311.9 nm) (–1972); 4.16 eV(297.8 nm) (–1821); 4.33 eV(286.4 nm) (–3290)
EFISH $\gamma(-2w; w, w, 0)$	2.00 (619.9)	16217	2.01 eV (616.4 nm) (5741); 3.98 eV(311.9 nm) (5031)
	2.35 (527.6)	9775	2.30 eV(538.1 nm) (1265); 2.41 eV(514.5 nm) (984); 4.33 eV(286.4 nm) (2162)
	3.70 (335.1)	13340	3.66 eV(339.1 nm) (1926); 3.72 eV(333.7 nm) (2926); 3.98 eV(311.9 nm) (4916);
	3.95 (313.9)	15438	3.98 eV(311.9 nm) (7521); 4.09 eV(303.3 nm) (3088); 4.16 eV(297.8 nm) (3703); 4.33 eV(286.4 nm) (3083)
	4.55 (272.5)	–5781	3.98 eV(311.9 nm) (–1208); 4.16 eV(297.8 nm) (–1125); 4.33 eV(286.4 nm) (–2059)

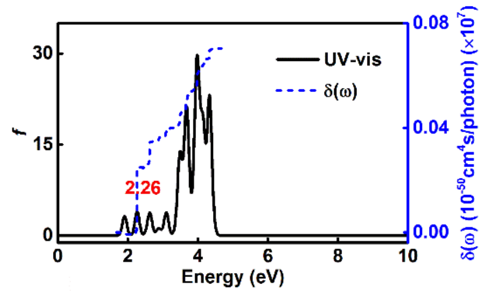
20. **Fig. S13** The evolution of third-order nonlinear optic properties with electronic spectra for C_{60}@$C_{240}(I_h)$@C_{540} (1057) at specific external fields.

STPA:

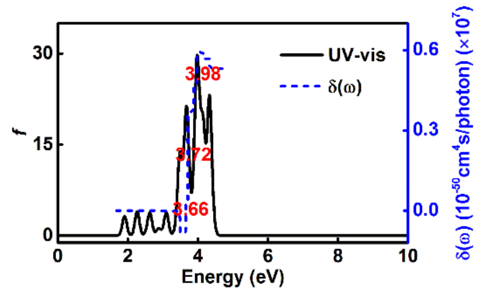
a) STPA-1.95 eV



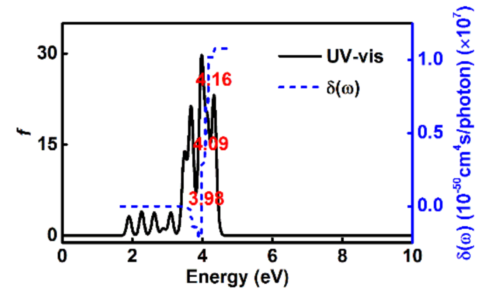
b) STPA-2.30 eV



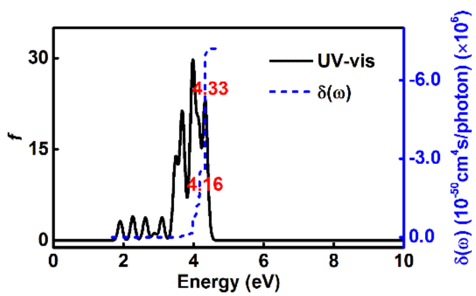
c) STPA-3.70 eV



d) STPA-4.00 eV

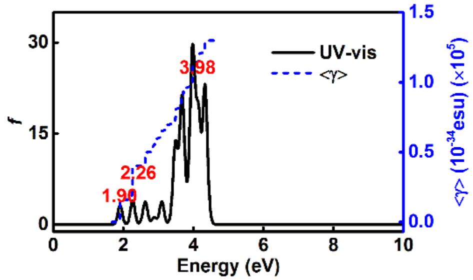


e) STPA-4.50 eV

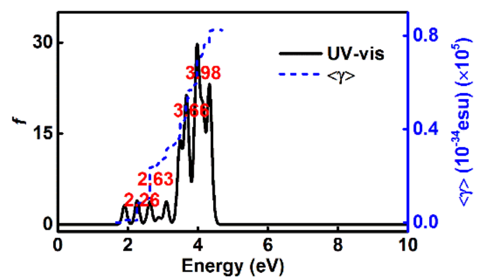


DFWM:

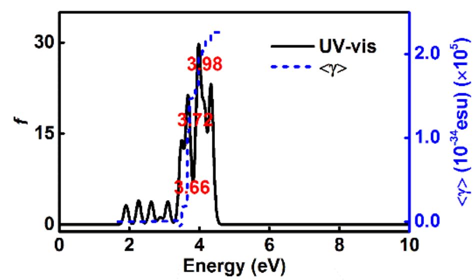
a) DFWM-1.90 eV



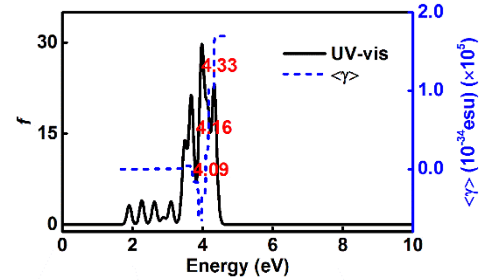
b) DFWM-2.25 eV



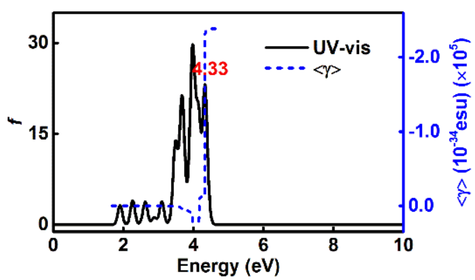
c) DFWM-3.45 eV



d) DFWM-3.90 eV

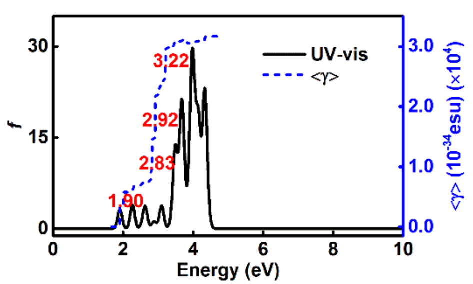


e) DFWM-4.35 eV

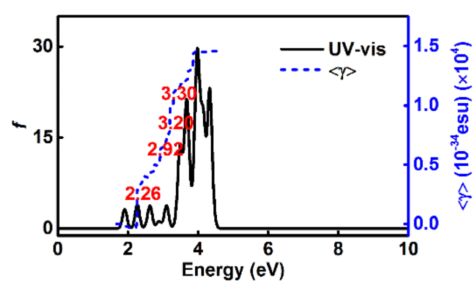


THG:

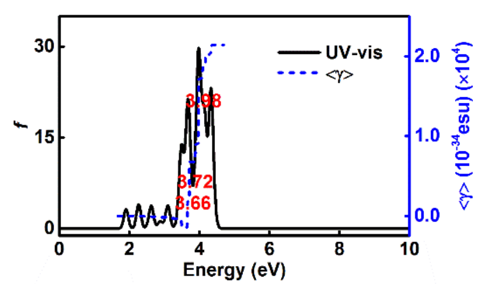
a) THG-1.90 eV



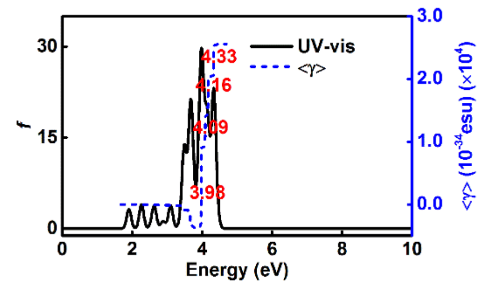
b) THG-2.25 eV



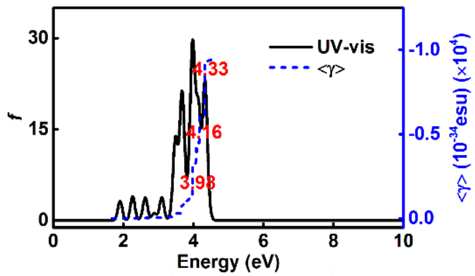
c) THG-3.70 eV



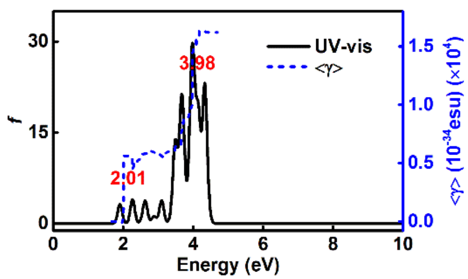
d) THG-3.95 eV



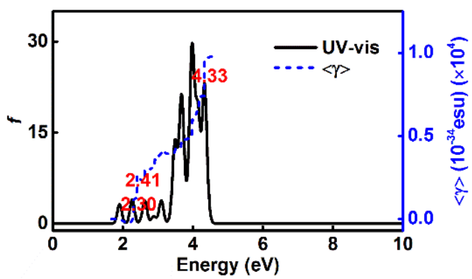
e) THG-4.55 eV



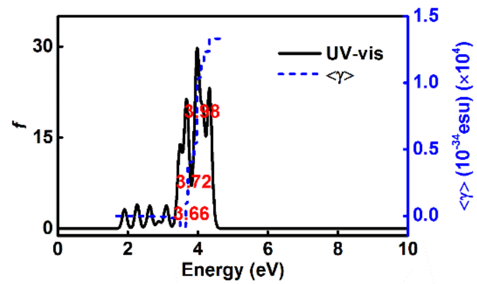
EFISH: a) EFISH-2.00 eV



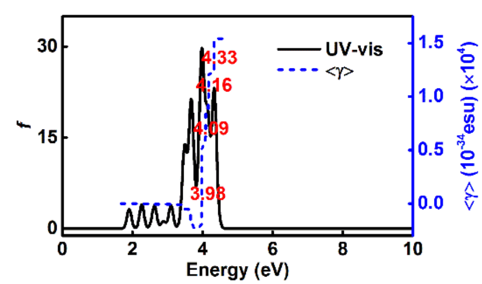
b) EFISH-2.35 eV



c) EFISH-3.70 eV



d) EFISH-3.95 eV



e) EFISH-4.55 eV