Supporting Information

Theoretical studies on the structural and spectra properties of two specific C_{54} isomers and the chlorinated species $C_{54}Cl_8$

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1. Optimized coordinates of C_{2v}-$^{\#540}C_{54}$ in gas phase:

Table S1. Coordinates of optimized structure of C_{2v}-$^{\#540}C_{54}$ in gas phase at the B3LYP/6-311++G(3*df*, 3*pd*)//B3LYP/6-31G** level.

Atoms	Coordinates		
	X	Y	Z
C	-2.869744	1.178079	0.887917
C	-2.307159	-1.169837	-1.902842
C	-2.869744	-1.178079	0.887917
C	1.144310	-3.243357	-1.431908
C	-2.451556	2.358915	0.290239
C	-1.219963	-0.732334	-2.725394
C	-2.256245	0.725723	2.126982
C	0.000000	-2.806553	-2.180415
C	-2.256245	-0.725723	2.126982
C	0.000000	-1.489228	-2.780121
C	-1.144310	-3.243357	-1.431908
C	-2.451556	-2.358915	0.290239
C	-2.903048	0.000000	-1.295344
C	-0.731580	-2.674207	2.032572
C	-1.170277	1.435496	2.652994
C	-2.207173	-2.378186	-1.171962
C	-1.433113	3.182351	0.922993
C	-1.219963	0.732334	-2.725394
C	2.207173	-2.378186	-1.171962
C	-3.163308	0.000000	0.079359
C	0.687147	-3.804375	-0.141409
C	-2.307159	1.169837	-1.902842
C	-0.687147	-3.804375	-0.141409
C	-1.170277	-1.435496	2.652994
C	-1.433113	-3.182351	0.922993
C	0.000000	0.697570	3.096158
C	0.731580	-2.674207	2.032572
C	2.869744	-1.178079	0.887917
C	2.307159	1.169837	-1.902842
C	2.869744	1.178079	0.887917
C	-1.144310	3.243357	-1.431908
C	2.451556	-2.358915	0.290239
C	1.219963	0.732334	-2.725394
C	2.256245	-0.725723	2.126982
C	0.000000	2.806553	-2.180415
C	2.256245	0.725723	2.126982

C	0.000000	1.489228	-2.780121
C	1.144310	3.243357	-1.431908
C	2.451556	2.358915	0.290239
C	2.903048	0.000000	-1.295344
C	0.731580	2.674207	2.032572
C	1.170277	-1.435496	2.652994
C	2.207173	2.378186	-1.171962
C	1.433113	-3.182351	0.922993
C	1.219963	-0.732334	-2.725394
C	-2.207173	2.378186	-1.171962
C	3.163308	0.000000	0.079359
C	-0.687147	3.804375	-0.141409
C	2.307159	-1.169837	-1.902842
C	0.687147	3.804375	-0.141409
C	1.170277	1.435496	2.652994
C	1.433113	3.182351	0.922993
C	0.000000	-0.697570	3.096158
C	-0.731580	2.674207	2.032572

2. Optimized coordinates of C_s-$^{\#369}C_{54}$ in gas phase:

Table S2. Coordinates of optimized structure of optimized coordinates of C_s-$^{\#369}C_{54}$ in gas phase at the B3LYP/6-311++G(3*df*, 3*pd*)//B3LYP/6-31G** level.

Atoms	Coordinates

	X	Y	Z
C	-2.302810	-1.968590	1.183532
C	-1.525322	-1.954323	2.337787
C	-1.319073	-0.684758	3.043089
C	0.053636	-0.641493	3.425220
C	0.861546	0.468579	3.119078
C	2.016513	-0.046511	2.373437
C	2.543388	0.673106	1.275508
C	2.840272	-0.042667	0.000000
C	2.543388	0.673106	-1.275508
C	2.016513	-0.046511	-2.373437
C	0.861546	0.468579	-3.119078
C	0.053636	-0.641493	-3.425220
C	-1.319073	-0.684758	-3.043089
C	-1.525322	-1.954323	-2.337787
C	-2.302810	-1.968590	-1.183532
C	-1.888511	-2.733570	0.000000
C	-2.959906	-0.756065	0.721396
C	-2.959906	-0.756065	-0.721396
C	-2.786967	0.452101	-1.417460
C	-1.901009	0.497647	-2.564589
C	-1.153188	1.741699	-2.526299
C	0.264558	1.719409	-2.753185
C	1.086408	2.597204	-1.986551
C	2.206037	2.061100	-1.224216
C	2.311256	2.813592	0.000000
C	2.206037	2.061100	1.224216
C	1.086408	2.597204	1.986551
C	0.264558	1.719409	2.753185
C	-1.153188	1.741699	2.526299
C	-1.901009	0.497647	2.564589
C	-2.786967	0.452101	1.417460
C	-2.636039	1.692346	0.697323
C	-2.636039	1.692346	-0.697323
C	-1.679091	2.529883	-1.428758
C	-0.882078	3.441665	-0.741088
C	0.494652	3.584068	-1.141448
C	1.326336	3.828671	0.000000

C	0.494652	3.584068	1.141448
C	-0.882078	3.441665	0.741088
C	-1.679091	2.529883	1.428758
C	-0.252719	-2.682827	2.338216
C	0.701538	-1.863248	2.984980
C	1.919121	-1.495748	2.342213
C	2.301323	-2.179518	1.182738
C	2.766521	-1.442040	0.000000
C	2.301323	-2.179518	-1.182738
C	1.919121	-1.495748	-2.342213
C	0.701538	-1.863248	-2.984980
C	-0.252719	-2.682827	-2.338216
C	0.151051	-3.416796	-1.192887
C	-0.709134	-3.463568	0.000000
C	0.151051	-3.416796	1.192887
C	1.475061	-3.249140	0.727707
C	1.475061	-3.249140	-0.727707

3. Optimized coordinates of C_2-$^{\#540}C_{54}Cl_8$ in gas phase:

Table S3. Coordinates of optimized structure of C_2-$^{\#540}C_{54}Cl_8$ in gas phase at the B3LYP/6-311++G(3*df*, 3*pd*)//B3LYP/6-31G** level.

Atoms	Coordinates		
	X	Y	Z

Cl	-2.145198	-0.491690	4.116715
Cl	-0.001344	5.884714	-0.326491
Cl	3.117677	3.896022	2.215149
Cl	2.997265	5.087215	-0.741967
C	-3.099253	-0.337726	-1.449922
C	-1.877473	1.727368	1.287475
C	-2.484562	1.924016	-1.472186
C	2.138980	2.969180	0.999897
C	-2.968067	-1.582472	-0.813762
C	-0.946625	1.039359	2.130790
C	-2.390788	-0.079481	-2.682020
C	0.748618	2.652203	1.511579
C	-2.008148	1.318170	-2.696437
C	0.390759	1.422764	2.156347
C	-0.189285	3.363382	0.803511
C	-1.739437	2.936625	-0.869682
C	-2.770409	0.760164	0.695205
C	-0.004264	2.766466	-2.554924
C	-1.511013	-1.060994	-3.161842
C	-1.479547	2.851166	0.565057
C	-2.197145	-2.627404	-1.414366
C	-1.472261	-0.378918	2.399638
C	2.785168	1.663859	0.610292
C	-3.085152	0.867107	-0.669468
C	1.877908	3.713573	-0.406267
C	-2.563899	-0.508200	1.321327
C	0.342832	4.095423	-0.399601
C	-0.748618	1.698471	-3.187111
C	-0.533165	3.448152	-1.480199
C	-0.185442	-0.673272	-3.610657
C	1.423292	2.351763	-2.525657
Cl	2.145198	0.491690	4.116715
Cl	0.001344	-5.884714	-0.326491
Cl	-3.117677	-3.896022	2.215149
Cl	-2.997265	-5.087215	-0.741967
C	3.099253	0.337726	-1.449922
C	1.877473	-1.727368	1.287475
C	2.484562	-1.924016	-1.472186

C	-2.138980	-2.969180	0.999897
C	2.968067	1.582472	-0.813762
C	0.946625	-1.039359	2.130790
C	2.390788	0.079481	-2.682020
C	-0.748618	-2.652203	1.511579
C	2.008148	-1.318170	-2.696437
C	-0.390759	-1.422764	2.156347
C	0.189285	-3.363382	0.803511
C	1.739437	-2.936625	-0.869682
C	2.770409	-0.760164	0.695205
C	0.004264	-2.766466	-2.554924
C	1.511013	1.060994	-3.161842
C	1.479547	-2.851166	0.565057
C	2.197145	2.627404	-1.414366
C	1.472261	0.378918	2.399638
C	-2.785168	-1.663859	0.610292
C	3.085152	-0.867107	-0.669468
C	-1.877908	-3.713573	-0.406267
C	2.563899	0.508200	1.321327
C	-0.342832	-4.095423	-0.399601
C	0.748618	-1.698471	-3.187111
C	0.533165	-3.448152	-1.480199
C	0.185442	0.673272	-3.610657
C	-1.423292	-2.351763	-2.525657

3. Optimized coordinates of C_2-$^{\#540}C_{54}Cl_8$ in the toluene solution:

Table S4. Coordinates of optimized structure of C_2-$^{\#540}C_{54}Cl_8$ in the toluene solution at the B3LYP/6-311++G(3*df*, 3*pd*)//B3LYP/6-31G(*d*, *p*) level.

Atoms	Coordinates		
	X	Y	Z
C	-3.098926	-0.336387	-1.449615

C	-1.877659	1.728564	1.286996
C	-2.483584	1.924492	-1.471468
C	2.137855	2.966138	0.996921
C	-2.969104	-1.581184	-0.814305
C	-0.946654	1.040940	2.129889
C	-2.390210	-0.078562	-2.681265
C	0.749056	2.654358	1.513580
C	-2.006928	1.318511	-2.695170
C	0.390689	1.424141	2.156991
C	-0.189391	3.364980	0.804718
C	-1.738416	2.936862	-0.869388
C	-2.770906	0.761859	0.695383
C	-0.002874	2.765579	-2.554490
C	-1.510804	-1.059971	-3.161114
C	-1.478949	2.851955	0.564848
C	-2.199644	-2.626500	-1.416190
C	-1.469554	-0.378312	2.393754
C	2.785802	1.662242	0.609564
C	-3.085103	0.868341	-0.669148
C	1.877659	3.710628	-0.407376
C	-2.563962	-0.506751	1.320777
C	0.343673	4.091761	-0.400449
C	-0.747652	1.698068	-3.185858
C	-0.532678	3.447752	-1.480730
C	-0.185534	-0.672993	-3.610615
C	1.424072	2.350833	-2.525960
C	3.098926	0.336387	-1.449615
C	1.877659	-1.728564	1.286996
C	2.483584	-1.924492	-1.471468
C	-2.137855	-2.966138	0.996921
C	2.969104	1.581184	-0.814305
C	0.946654	-1.040940	2.129889
C	2.390210	0.078562	-2.681265
C	-0.749056	-2.654358	1.513580
C	2.006928	-1.318511	-2.695170
C	-0.390689	-1.424141	2.156991
C	0.189391	-3.364980	0.804718
C	1.738416	-2.936862	-0.869388

C	2.770906	-0.761859	0.695383
C	0.002874	-2.765579	-2.554490
C	1.510804	1.059971	-3.161114
C	1.478949	-2.851955	0.564848
C	2.199644	2.626500	-1.416190
C	1.469554	0.378312	2.393754
C	-2.785802	-1.662242	0.609564
C	3.085103	-0.868341	-0.669148
C	-1.877659	-3.710628	-0.407376
C	2.563962	0.506751	1.320777
C	-0.343673	-4.091761	-0.400449
C	0.747652	-1.698068	-3.185858
C	0.532678	-3.447752	-1.480730
C	0.185534	0.672993	-3.610615
C	-1.424072	-2.350833	-2.525960
Cl	-2.144485	-0.490469	4.123216
Cl	0.000790	5.889551	-0.329962
Cl	3.126521	3.899616	2.213126
Cl	2.999692	5.091342	-0.740596
Cl	2.144485	0.490469	4.123216
Cl	-0.000790	-5.889551	-0.329962
Cl	l-3.126521	-3.899616	2.213126
Cl	-2.999692	-5.091342	-0.740596

4. Optimized coordinates of C_s-$^{\#369}C_{54}Cl_8$ in gas phase:

Table S5. Coordinates of optimized structure of C_s-$^{\#369}C_{54}Cl_8$ in gas phase at the B3LYP/6-311++G (3*df*, 3*pd*)//B3LYP/6-31G** level.

Atoms	Coordinate		
	X	Y	Z
C	-2.897656	-2.020166	1.169798
C	-2.071095	-2.033579	2.298012

C	-1.841162	-0.788041	3.035981
C	-0.494002	-0.785699	3.442541
C	0.324590	0.298687	3.093548
C	1.453025	-0.245216	2.328096
C	1.978665	0.480267	1.244608
C	2.246505	-0.221147	0.000000
C	1.978665	0.480267	-1.244608
C	1.453025	-0.245216	-2.328096
C	0.324590	0.298687	-3.093548
C	-0.494002	-0.785699	-3.442541
C	-1.841162	-0.788041	-3.035981
C	-2.071095	-2.033579	-2.298012
C	-2.897656	-2.020166	-1.169798
C	-2.509329	-2.763344	0.000000
C	-3.523029	-0.779327	0.729606
C	-3.523029	-0.779327	-0.729606
C	-3.313623	0.404573	-1.429907
C	-2.427406	0.418618	-2.592436
C	-1.651887	1.616541	-2.538911
C	-0.244507	1.552692	-2.725471
C	0.585917	2.409345	-1.902386
C	1.633477	1.884186	-1.194565
C	1.995515	2.718719	0.000000
C	1.633477	1.884186	1.194565
C	0.585917	2.409345	1.902386
C	-0.244507	1.552692	2.725471
C	-1.651887	1.616541	2.538911
C	-2.427406	0.418618	2.592436
C	-3.313623	0.404573	1.429907
C	-3.119704	1.643265	0.706384
C	-3.119704	1.643265	-0.706384
C	-2.150100	2.422032	-1.406052
C	-1.302320	3.277267	-0.702159
C	0.043055	3.664349	-1.268656
C	0.975002	3.937266	0.000000
C	0.043055	3.664349	1.268656
C	-1.302320	3.277267	0.702159
C	-2.150100	2.422032	1.406052

C	-0.859658	-2.812717	2.295476
C	0.177963	-2.117902	3.165230
C	1.345635	-1.670929	2.298554
C	1.689168	-2.355838	1.164365
C	2.108668	-1.641000	0.000000
C	1.689168	-2.355838	-1.164365
C	1.345635	-1.670929	-2.298554
C	0.177963	-2.117902	-3.165230
C	-0.859658	-2.812717	-2.295476
C	-0.478588	-3.510352	-1.173702
C	-1.295298	-3.483117	0.000000
C	-0.478588	-3.510352	1.173702
C	0.996389	-3.667097	0.798048
C	0.996389	-3.667097	-0.798048
Cl	-0.104292	5.021349	2.478994
Cl	3.774757	3.130009	0.000000
Cl	-0.104292	5.021349	-2.478994
Cl	0.652558	-3.038812	4.670313
Cl	1.767526	-5.097686	1.591295
Cl	1.748710	5.529479	0.000000
Cl	1.767526	-5.097686	-1.591295
Cl	0.652558	-3.038812	-4.670313

5. The relative energies of singlet and triplet state of C_{54} systems:

Table S6. The relative energies (kcal/mol) of singlet and triplet state of two C_{54} isomers and the corresponding chlorides C_2-$^{\#540}C_{54}Cl_8$ and C_s-$^{\#369}C_{54}Cl_8$ at the B3LYP/6-311++G(3df, 3pd) level.

Molecule	Relative energies
C_{2v}-$^{\#540}C_{54}$ (singlet)	0.00

C_{2v}-$^{\#540}C_{54}$ (triplet)	2.90
C_s-$^{\#369}C_{54}$ (singlet)	0.00
C_s-$^{\#369}C_{54}$ (triplet)	15.96
C_2-$^{\#540}C_{54}Cl_8$ (singlet)	0.00
C_2-$^{\#540}C_{54}Cl_8$ (triplet)	49.12
C_s-$^{\#369}C_{54}Cl_8$ (singlet)	0.00
C_s-$^{\#369}C_{54}Cl_8$ (triplet)	26.52

6. UV-Vis absorption spectrum of C_2-$^{\#540}C_{54}Cl_8$ simulated by using functionals with different HF%.

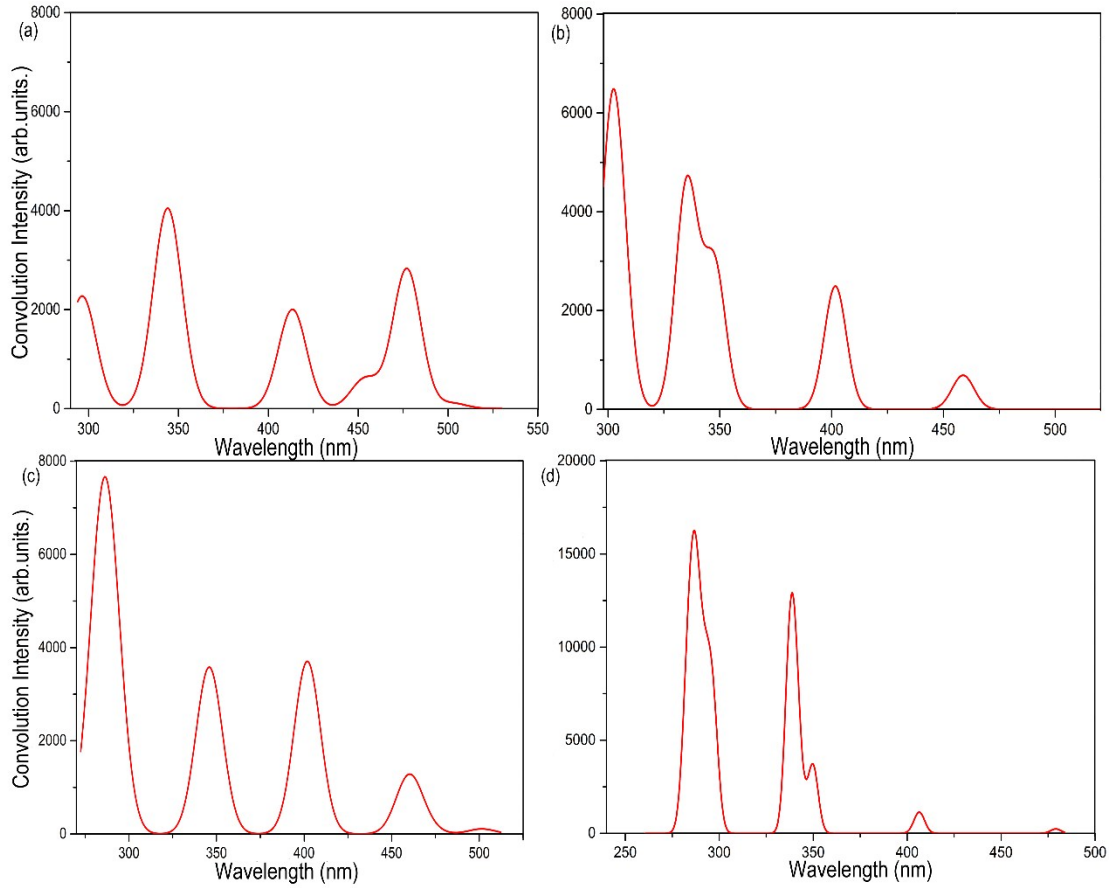

Fig. S1. The calculated UV-vis absorption spectrum of C_2-$^{\#540}C_{54}Cl_8$ with (a) TPSSh (10% HF), (b) O3LYP (11.61% HF), (c) B3LYP (20% HF) and (d) PBE0 (25% HF) functionals.

7. The consideration of dispersive interaction.

Considering the dispersive interaction in the functional, we used wB97XD and

B3LYP to simulate the optimization of structure and energy of chlorides respectively, and the results are listed in Table S7. As shown in the table, the difference of calculations between the average bond length of R_{cc} and $R_{C\text{-}Cl}$ obtained by the two functional is not large, and the relative energy is almost the same. From the data, we think the average distance between chlorine and chlorine is also negligible. All in all, the potential pitfall of the optimization process is that the hybrid density functional method (B3LYP) is difficult to describe the weak interaction. But according to our calculations, the little effects on the systems of the present work can be reasonably neglected.

Table S7. Statistics over bond lengths and distance of ***Cl…Cl*** (Å), total energies of two C_{54} chlorinated species (a.u.), relative energies (kcal/mol) of two C_{54} chlorinated species as well as the sum of Mulliken charges on all carbon atoms (ρ^c) for the two chlorinated fullerenes.

Molecular	C_2-$^{\#540}C_{54}Cl_8$		C_s-$^{\#369}C_{54}Cl_8$	
Fuctional	wB97XD	B3LYP	wB97XD	B3LYP
Average R_{cc}	1.447	1.452	1.447	1.452
Shortest $R_{C\text{-}Cl}$	1.785	1.804	1.758	1.770
Longest $R_{C\text{-}Cl}$	1.816	1.848	1.780	1.827
Average $R_{C\text{-}Cl}$	1.798	1.822	1.791	1.815
Average distance of *Cl…Cl*	7.467	7.518	7.398	7.649
ρ^c	7.072	6.859	8.119	7.587
Total Energy	-5739.121519	-5739.865674	-5739.135691	-5739.880925
Relative Energy	0.00	0.00	9.57	9.57

8. The details of calculations:

At the level of B3LYP/6-311+ G(d,p) B3LYP/6-311+ G(d,p), the two C_{54} isomers and the chlorine derivatives $C_{54}Cl_8$ have been optimized, using Gaussian 09 program with eight-cores CPU (Intel Xeon X5450, 3.0GHz) and 6000MB memory. Table S8 lists the total CPU time.

Table S8. The total CPU times (hour) for the optimization and single point calculations of the two C_{54} isomers and the corresponding chlorides $C_{54}Cl_8$.

Molecule	CPU time(h)
C_{2v}-$^{\#540}C_{54}$	53.0
C_s-$^{\#369}C_{54}$	87.1
C_2-$^{\#540}C_{54}Cl_8$	123.0
C_s-$^{\#369}C_{54}Cl_8$	132.1