Electronic Supplementary Material (ESI) for Nanoscale.

$Sc_{20}C_{60}$: A Volleyballene

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Section I. One of the tracks of the energy minimization for *Volleyballene* $Sc_{20}C_{60}$

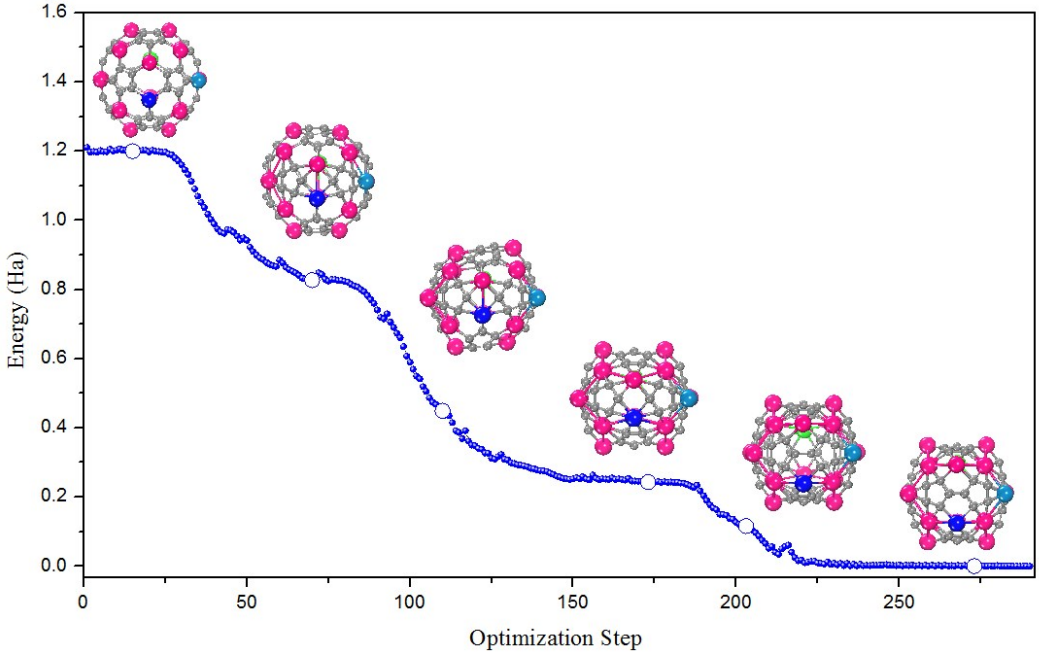


Figure S1. One of the energy minimization tracks for *Volleyballene* $Sc_{20}C_{60}$ based on DFT calculations at the GGA-BLYP level. The inserted configurations correspond to the highlighted steps. Here, the convergence thresholds were set to 10^{-4} hartree on the total energy, 0.02 hartree/Å for the force, 0.05 Å for the displacement, and 10^{-4} hartree for the energy change. During the course of energy minimization, the configuration, starting from the initial configuration, evolved step-by-step into the *Volleyballene* $Sc_{20}C_{60}$. The first highlighted structure lies on the first plateau of the energy curve and corresponds closely to the initial structure. It may be viewed as consisting of twelve Sc_5C_5 subunits with each Sc atom joining three Sc_5C_5 subunits together. One C-pentagon is surrounded by five Sc atoms to give the Sc_5C_5 subunit. The second highlighted structure lies on the second step of the energy curve. One Sc_5C_5 subunit has now clearly enlarged, leading to one neighboring C-pentagon being distorted out of its Sc_5C_5 plane. Next, the third highlighted structure corresponds to a configuration in which two Sc_8C_{10} subunits have formed. The fourth structure lies on the third energy plateau where four Sc_8C_{10} subunits have formed. The fifth structure corresponds to a configuration in which the fifth Sc_8C_{10} subunit has formed. Finally, with the sixth configuration, lying on the last step of the energy curve, all six of the Sc_8C_{10} subunits have formed and eventually evolved into the configuration of *Volleyballene* $Sc_{20}C_{60}$. This process, with the successive formation of Sc_8C_{10} subunits, further verifies the stability of *Volleyballene* $Sc_{20}C_{60}$. The large balls, including the pink, the green, the light blue and the dark blue are Sc atoms, and the small balls (the grey) are C atoms.

Section II. Vibrational frequency analysis

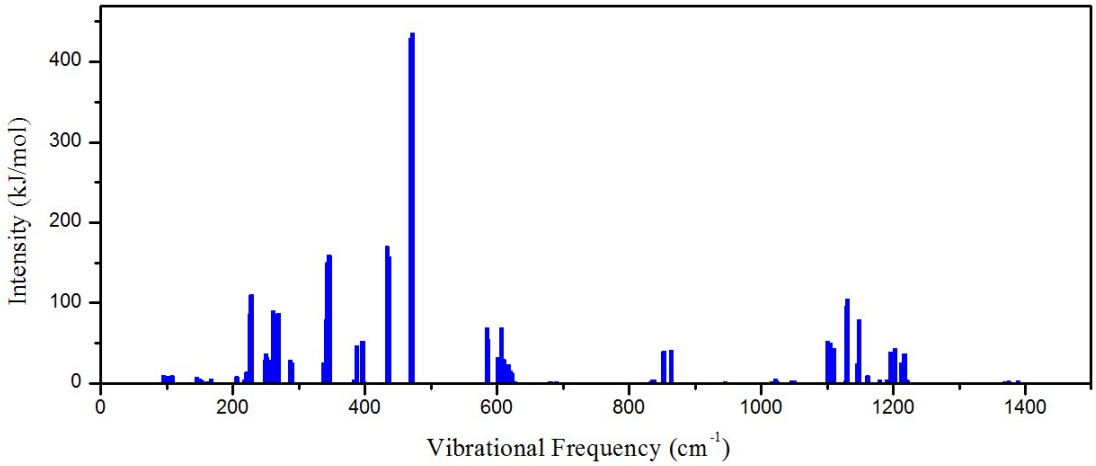


Figure S2. The vibrational frequency analysis for the *Volleyballene* $Sc_{20}C_{60}$. There were no imaginary frequencies and the two highest intensity frequencies were found to be 468.9 and 472.3 cm^{-1}.

Section III. Raman spectrum data

Table S1. The calculated frequencies for the *Volleyballene* $Sc_{20}C_{60}$ including Raman activities and intensities at a temperature of 300 K with incident light of wavelength 488.00 nm. Lorentzian smearing of 20.00 cm^{-1} was used. This Raman spectrum is presented as Figure 5 in the text.

Frequency (cm^{-1})	Raman activity(Å^4)	Raman intensity	Frequency (cm^{-1})	Raman activity(Å^4)	Raman intensity
80.1	41.62	171.109	528.8	0.000	0.000
83.6	45.082	171.371	530.4	0.136	0.027
84.9	45.972	169.894	531.2	0.000	0.000
94.5	0.008	0.023	571.7	130.865	23.313
96.6	41.065	120.038	585.0	0.001	0.000
99.6	40.451	111.904	585.8	0.005	0.001
100.9	0.026	0.070	585.9	0.003	0.001
108.0	0.003	0.007	590.7	19.242	3.285
112.4	7.859	17.513	592.7	25.766	4.380
113.2	0.297	0.653	600.9	0.101	0.017
113.8	5.777	12.594	603.3	7.378	1.226
117.6	0.001	0.001	606.7	0.398	0.066
120.5	0.002	0.004	607.0	0.020	0.003
121.0	0.000	0.001	609.3	11.008	1.806
123.1	3.313	6.286	610.3	0.003	0.000
123.3	0.017	0.033	612.2	2.479	0.404
124.1	0.000	0.000	613.0	0.002	0.000
133.6	0.217	0.357	613.9	0.002	0.000
144.2	0.221	0.319	615.9	11.411	1.846
145.3	0.002	0.003	617.6	0.144	0.023
146.4	2.215	3.110	617.8	2.295	0.370
146.9	0.001	0.001	620.4	0.028	0.005
150.0	0.002	0.003	621.7	10.29	1.645
151.6	0.596	0.788	622.5	0.006	0.001
153.4	0.000	0.001	623.2	0.120	0.019
158.4	0.001	0.001	627.3	1.356	0.214
161.0	0.002	0.002	627.8	7.402	1.168
165.5	59.328	67.589	680.0	0.158	0.023
167.4	0.003	0.003	682.0	0.146	0.021
171.0	33.87	36.521	688.3	0.007	0.001
171.0	6.724	7.250	688.6	0.007	0.001
172.9	21.15	22.387	688.7	0.006	0.001
179.9	0.002	0.002	689.5	0.003	0.000
189.8	127.314	115.393	820.8	0.000	0.000
195.5	2.997	2.588	821.5	0.296	0.033

197.6	1.684	1.428	824.6	0.249	0.028
198.2	3.942	3.327	825.9	0.001	0.000
200.8	5.576	4.607	826.4	0.496	0.055
203.7	0.085	0.068	828.5	0.000	0.000
204.5	8.805	7.062	831.9	0.004	0.000
205.2	24.684	19.687	832.8	6.942	0.768
206.1	0.056	0.045	835.1	0.003	0.000
217.6	0.001	0.000	836.4	6.402	0.704
218.4	0.000	0.000	837.7	0.004	0.000
220.4	0.001	0.000	839.0	6.153	0.674
222.7	3.412	2.384	850.9	7.847	0.845
223.7	6.698	4.647	852.0	0.022	0.002
226.4	0.004	0.003	852.4	8.420	0.904
226.6	0.001	0.001	853.4	0.009	0.001
227.8	0.000	0.000	863.3	8.171	0.864
230.4	7.464	4.940	864.0	0.148	0.016
237.9	1.052	0.662	942.9	9.704	0.920
239.7	1.103	0.686	944.5	0.001	0.000
243.6	5.337	3.234	946.4	0.009	0.001
245.0	2.161	1.298	947.3	18.537	1.746
248.7	0.133	0.078	952.1	3.014	0.282
248.9	2.333	1.367	953.3	14.158	1.323
250.2	0.002	0.001	1015.8	0.664	0.057
251.6	0.002	0.001	1016.2	0.018	0.002
256.2	0.000	0.000	1018.8	0.021	0.002
259.6	0.001	0.001	1019.7	0.680	0.058
261.2	0.000	0.000	1020.8	24.261	2.083
263.4	0.001	0.000	1021.6	0.130	0.011
268.4	0.472	0.246	1024.0	0.058	0.005
268.6	0.029	0.015	1024.6	22.333	1.908
269.7	3.147	1.627	1045.6	0.889	0.074
269.9	20.344	10.507	1046.0	0.001	0.000
273.7	347.859	175.825	1050.0	0.001	0.000
278.0	0.003	0.002	1050.4	15.588	1.291
280.1	0.001	0.001	1099.7	2.496	0.195
283.2	7.337	3.520	1100.5	0.002	0.000
286.6	0.002	0.001	1103.6	4.099	0.319
286.7	1.290	0.607	1104.4	0.007	0.001
287.5	0.018	0.008	1108.5	1.818	0.141
288.1	10.643	4.974	1110.1	0.431	0.033
288.7	1.999	0.931	1127.7	5.594	0.424
289.6	0.004	0.002	1128.8	3.490	0.264

293.0	8.617	3.925	1129.1	0.155	0.012
313.3	9.647	3.973	1130.2	0.023	0.002
314.6	8.298	3.397	1145.5	3.689	0.274
318.4	9.599	3.860	1148.2	1.382	0.102
324.8	5.408	2.111	1160.4	6.488	0.474
337.3	0.000	0.000	1160.5	21.428	1.566
339.6	0.000	0.000	1161.3	23.714	1.732
340.9	0.000	0.000	1161.4	0.474	0.035
343.2	0.003	0.001	1170.4	15.832	1.145
344.6	0.001	0.000	1170.8	13.742	0.993
346.0	0.000	0.000	1179.5	0.011	0.001
358.1	5.271	1.784	1181.5	35.34	2.525
359.7	5.682	1.911	1185.2	0.002	0.000
377.4	0.183	0.057	1186.1	14.15	1.006
381.0	0.000	0.000	1191.0	0.002	0.000
383.1	0.000	0.000	1193.2	124.342	8.776
384.4	0.211	0.065	1194.2	44.016	3.103
384.6	0.312	0.095	1196.2	0.035	0.002
387.5	0.003	0.001	1198.3	204.506	14.355
388.0	0.000	0.000	1201.4	0.006	0.000
395.8	0.000	0.000	1203.1	0.004	0.000
397.5	0.002	0.001	1208.1	40.375	2.805
398.2	0.116	0.034	1209.0	9.865	0.685
399.1	0.049	0.014	1212.5	0.004	0.000
401.6	0.063	0.018	1217.0	1.764	0.121
433.3	0.003	0.001	1217.6	488.91	33.631
435.0	0.973	0.250	1219.6	3.245	0.223
435.7	0.103	0.026	1221.3	0.062	0.004
435.8	0.051	0.013	1242.6	0.005	0.000
436.9	0.000	0.000	1243.3	0.746	0.050
437.5	2.533	0.646	1245.2	0.575	0.038
445.0	24.248	6.040	1245.7	0.034	0.002
447.3	28.573	7.067	1257.3	3.006	0.198
451.1	27.687	6.769	1258.8	2.963	0.195
468.9	0.000	0.000	1368.4	245.011	14.511
471.4	0.001	0.000	1369.2	282.612	16.725
472.3	0.001	0.000	1375.1	108.078	6.361
524.3	0.000	0.000	1375.4	335.574	19.743
525.8	0.032	0.006	1389.3	30.951	1.797
527.8	0.025	0.005	1389.5	406.381	23.595

Section IV. Relative stability

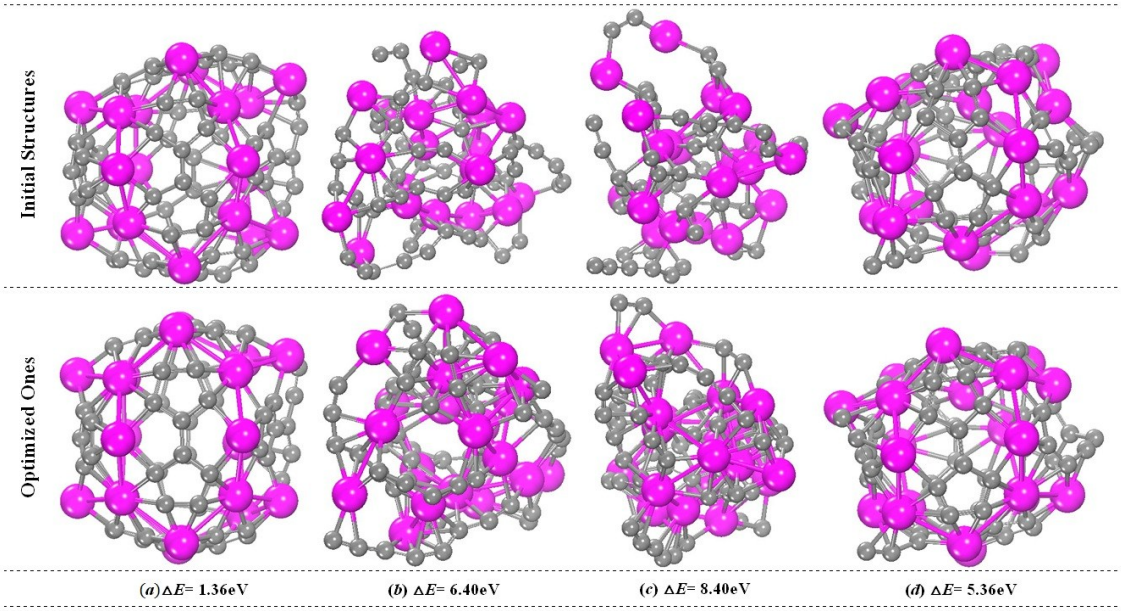


Figure S3. The initial and optimized configurations of $Sc_{20}C_{60}$ clusters selected randomly from the NVE dynamic simulations with temperatures of 4000 and 5000 K. (*a*), (*b*), (*c*), and (*d*) correspond to the 2001*th* step of NVE-4000K, the 463*th*, 1010*th*, and 1038*th* steps of NVE-5000K, respectively. Beneath each isomer is listed the relative energy (ΔE) with respect to the *Volleyballene*.

Section V. *Ab* initio molecular dynamics

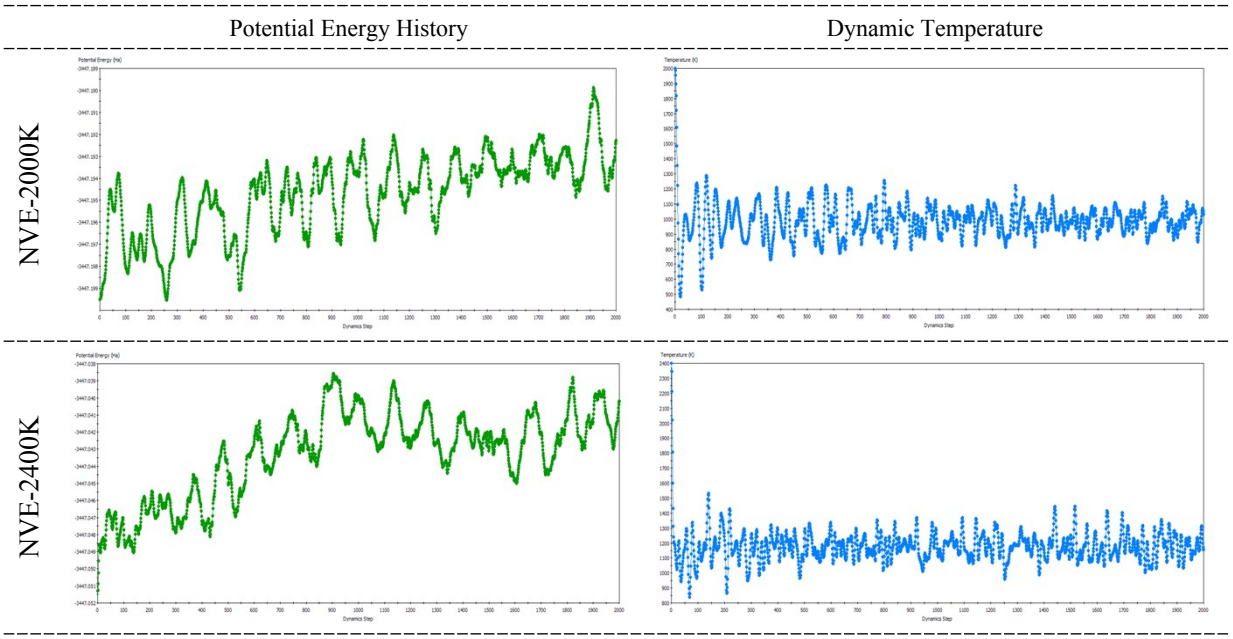


Figure S4. Results of *ab* initio molecular dynamics simulations with NVE ensembles at initial temperatures of 2000 K and 2400 K, including the dynamic potential energy history and the temperature history *vs* the dynamic step for the $Sc_{20}C_{60}$ *Volleyballene*. The corresponding animations are attached.

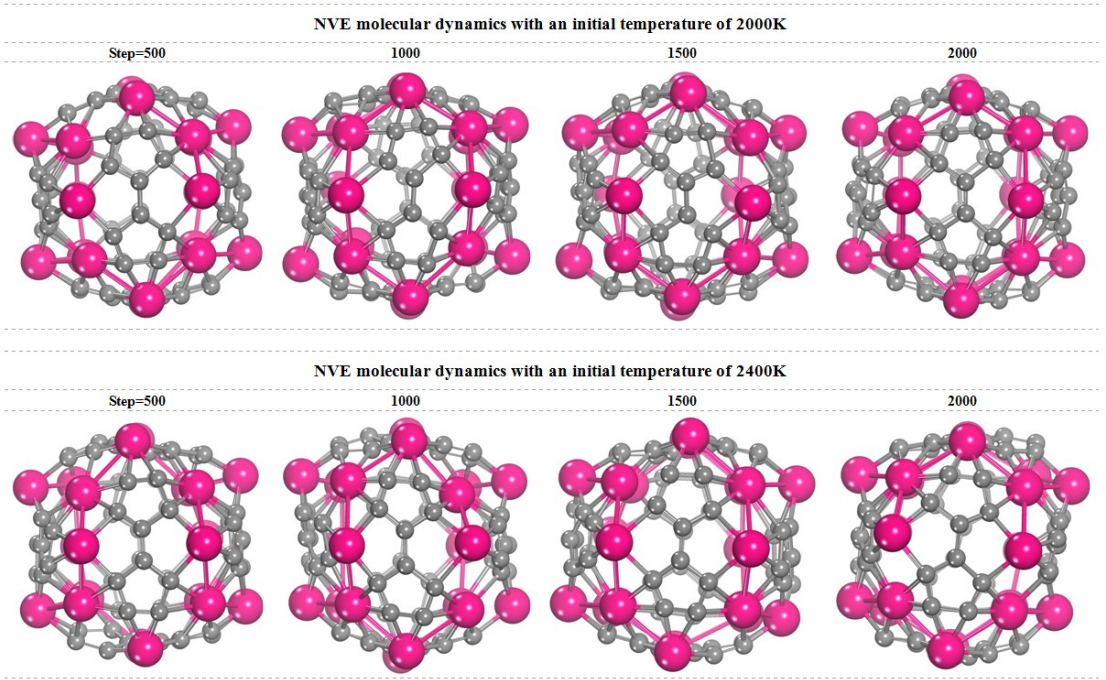


Figure S5. Selected typical frames at the 500*th*, 1000*th*, 1500*th*, and 2000*th* step from the NVE molecular dynamics simulations with initial temperatures of 2000 K and 2400 K.

Section VI. Comparison of calculated results based on three levels of optimization

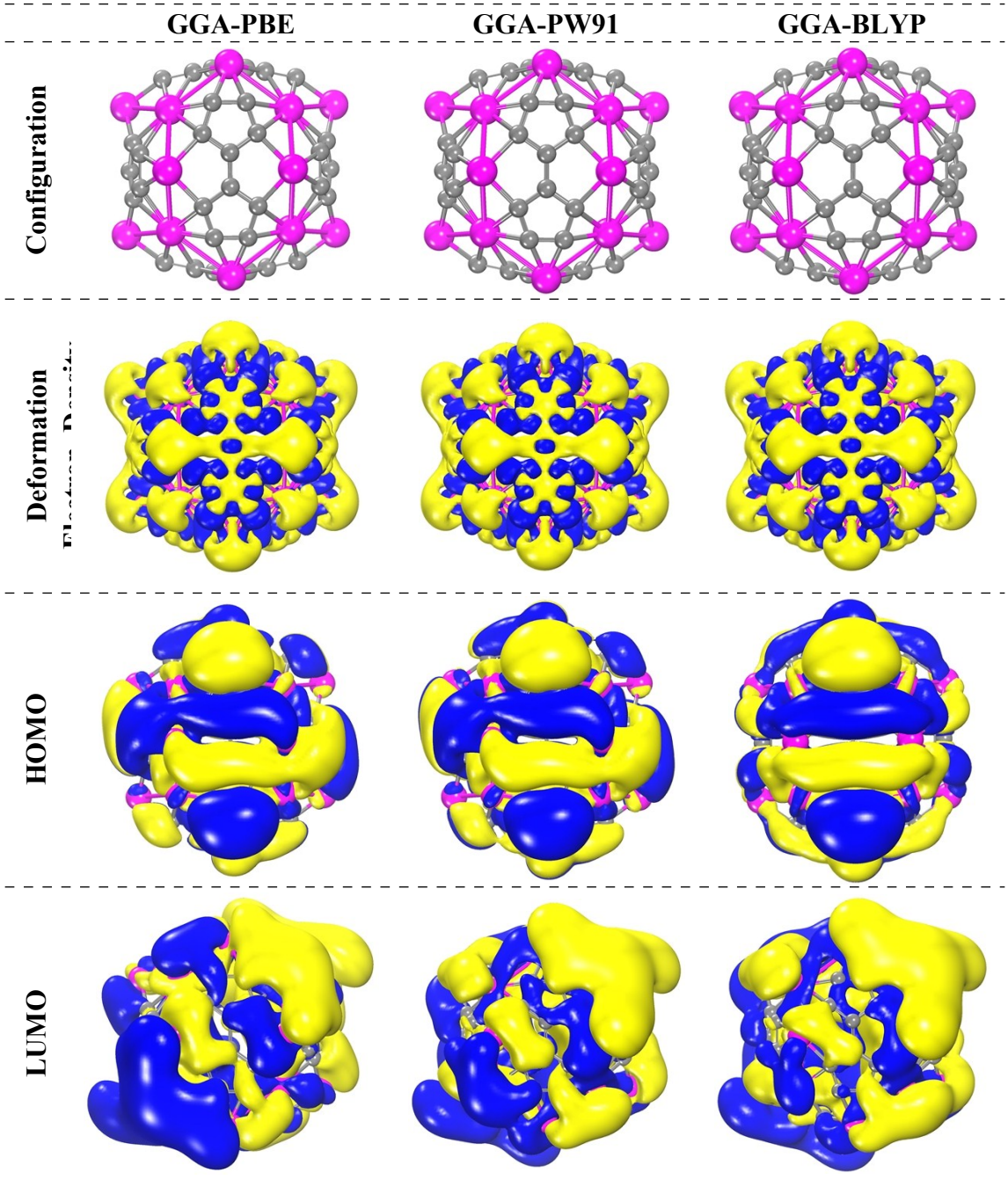
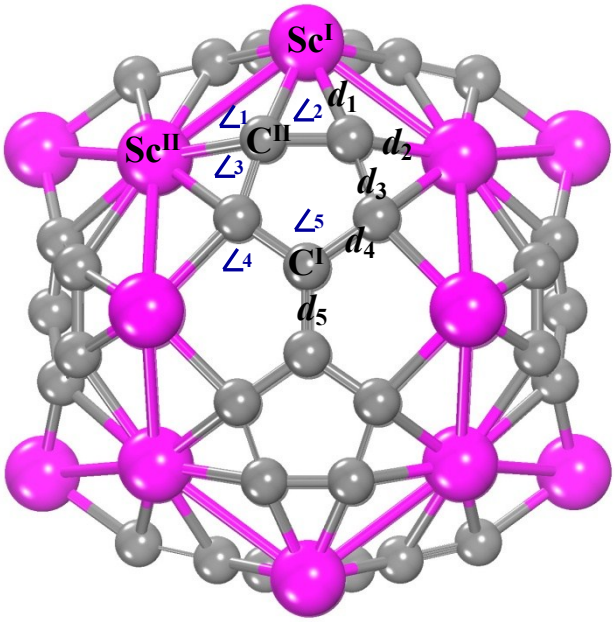


Figure S6. Calculated results for the configuration, deformation electron density, HOMO and LUMO orbitals based on the GGA-PBE, GGA-PW91, and GGA-BLYP levels of optimization. The isosurfaces for the deformation electron density are set to be 0.03 e/A^3, for the others they are taken to be 0.005 e/A^3. The three configurations obtained after the energy minimizations at the three different levels listed above are quite similar. They also have similar bonding characters. The three HOMO or LUMO orbitals are also similar. In particular, the two HOMO orbitals obtained at the GGA-PBE and GGA-PW91 levels have nearly identical characteristics and the two LUMO orbitals obtained at the GGA- PW91 and GGA-BLYP levels have very similar characteristics.

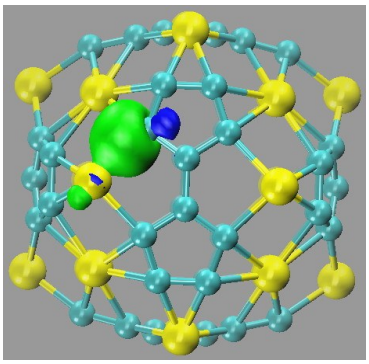
Section VII. Bond lengths and bond angles



Bond length	Sc^I-C^{II}	2.171	d_1
	Sc^{II}-C^{II}	2.325	d_2
	C^{II}-C^{II}	1.445	d_3
	C^I-C^{II}	1.446	d_4
	C^I-C^I	1.463	d_5
Bond angle (°)	Sc^I-C^{II}-Sc^{II}	91.478	∠1
	Sc^I-C^{II}-C^{II}	69.890	∠2
	Sc^{II}-C^{II}-C^{II}	98.909	∠3
	Sc^I-C^{II}-C^I	72.101	∠4
	C^{II}-C^I-C^{II}	109.771	∠5

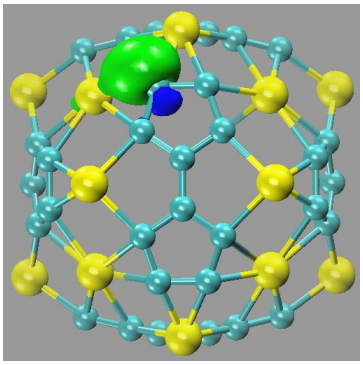
Figure S7. Some typical bond lengths and bond angles of Sc^I/Sc^{II} and C^I/C^{II} for the $Sc_{20}C_{60}$ *Volleyballene*.

Section VIII. Natural bond orbitals



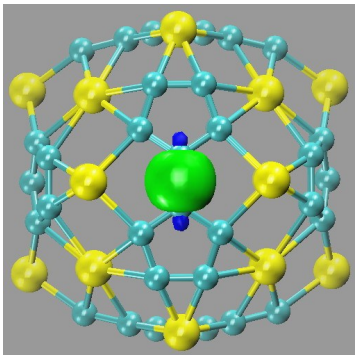
BD: Sc^{I}-C^{II}

$\sigma_1=0.360(sp^{1.76}d^{5.38})_{Sc}+0.933(sp^{1.75})_C$



BD: Sc^{II}-C^{II}

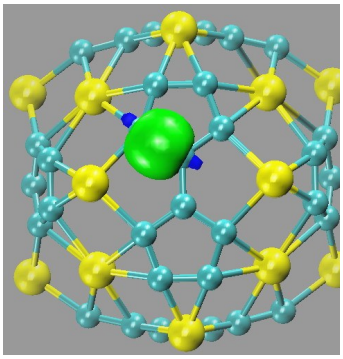
$\sigma_2=0.314(sp^{2.38}d^{4.73})_{Sc}+0.949(sp^{1.99})_C$



BD: C^{I}-C^{I}

$\sigma_3=0.707(sp^{2.07})_C$

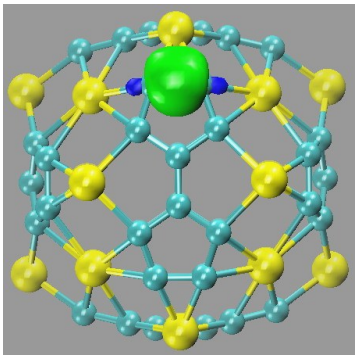
$+0.707(sp^{2.07})_C$



BD: C^{I}-C^{II}

$\sigma_4=0.711(sp^{1.98})_C$

$+0.703(sp^{2.10})_C$



BD: C^{II}-C^{II}

$\sigma_5=0.706(sp^{2.14})_C$

$+0.709(sp^{1.95})_C$

Figure S8. Some typical natural bond orbitals for the $Sc_{20}C_{60}$ *Volleyballene*. Below each configurations, the first lines list the bond types (BD for 2-center bond) and the next lines summarize the natural atomic hybrids of this natural bond orbital. The results indicate that Sc-C bond are mainly composed *sp-d* of Sc and *sp* hybrid of C. For C^{I} and C^{II}, both are characterized by sp^2 hybridization.