The Structural Determination of Endohedral Metallofullerene Gd@C_{82} by XANES

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Supporting Information

Experimental procedures

(1) Sample preparation

Soot containing Gd@C_{82} metallofullerenes was produced by the direct current arc method (140A .40V) in a 600 torr of He atmosphere. A graphite rod filled with an atomic ratio of Gd/C = 0.1 was used as the anode for arc burning. The raw soot was collected and extracted in a high pressure autoclave with N, N-dimethylformamide (DMF) at its boiling point for 10 hrs. Afterwards, the solution was filtrated, then the DMF was evaporated in a vacuum and a black powder was obtained. The soluble fraction was redissolved in toluene and the isolation and purification was achieved by two-stage high performance liquid chromatography (HPLC) with a Buckyprep column and a Buckyclutcher column. Judging from the HPLC profiles and TOF mass spectrometry, the purity of the collected Gd@C_{82} was estimated to be more than 95%.

(2) XANES Test

The Gd L_{III}-edge XANES spectrum of Gd@C_{82} was recorded in transmission mode at the XAFS station (Beamline 1W1B) of the Beijing Synchrotron Radiation Facility (BSRF) using a Si (111) double crystal monochromator. The storage ring was working at the energy of 2.2 GeV with an electron current decreasing from 120 mA to 80 mA within approximately 12 hours. The incident and output beam intensities were monitored and recorded using two ionization chambers supplied by a continuous flow of nitrogen gas. To suppress the unwanted harmonics we detuned the monochromator crystals by 40%. The sample was encapsulated in a hole 1.5 mm of diameter at the center of a pure aluminum holder. Experiments were performed in vacuum (~3×10^{-3} torr.).

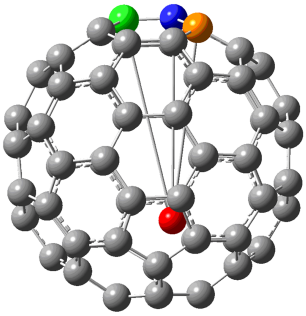
Details for Gaussian calculation

(1) Summary for Gaussian calculations shown in Figure 1

Conformation (multiplicity =7)	Relative energy (kcal/mol)	Relative energy including zero point energy correction (kcal/mol)	Imaginary frequency (cm^{-1})
(a) *C_2-bond*	54.5	54.5	-77.99i -62.42i
(b) *C_2-hexagon*	0	0	0
(c) *CC-hexagon*	1.0	0.8	-14.19i
(d) *C-pentagon*	6.9	6.4	-41.74i

(2) The 26 points on the potential energy surface are optimized as following:

During the optimization, the position of the gadolinium and the angle between blue, green colored carbons and gadolinium, the dihedral angle between orange, blue, green colored carbons and gadolinium are fixed to prevent C_{82} from rotating around the C_2 axis. The orange, blue and green colored carbons are located near the C-C bond on the C_2 axis. We need only to calculate configurations in a quarter of the cage; Additional configurations are derived because of the C_{2v} symmetry of C_{82}.



(3) The energies of the two representative configurations with different spin multiplicity

Configuration & spin multiplicity	Energy (a.u.)	ΔE (kcal/mol)
(r1) M=5	-3235.71493617	132.132
(r1) M=7	-3235.92550767	0
(r1) M=9	-3235.92554162	-0.021
(r1) M=11	-3235.87339740	32.699
(r25) M=5	-3235.86692487	36.760
(r25) M=7	-3235.92026014	3.293
(r25) M=9	-3235.92034397	3.240
(r25) M=11	-3235.87206700	33.534

(4) The relative energies of two representative configurations with different basis sets, the spin multiplicity is set to 7.

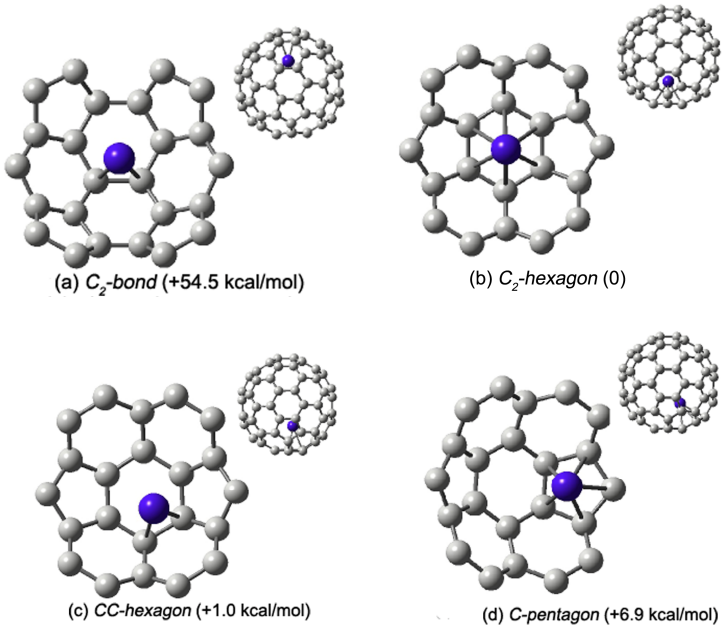
Conformation	ΔE (kcal/mol)	
	6-31G	6-31G*
(r1)	0	0
(r25)	3.293	3.373

(5) Relative energies and the positions of Gd in different conformations, the column *r* reports the displacement from (r1) position.

Conformation	**Gd (Å)**				***E* (a.u.)**	**Δ*E***
(multiplicity =7)	***X***	***y***	***z***	***r***		**(kcal/mol)**
(r1)	0.00000000	0.00000000	1.81377200	0.00000000	-3235.92550767	0
(r2)	0.09075758	-0.09290495	1.80886340	0.12997062	-3235.92535761	0.094
(r3)	0.20102226	-0.20896937	1.78925151	0.29099725	-3235.92495059	0.350
(r4)	0.30239709	-0.27682391	1.76564047	0.41278581	-3235.92468051	0.519
(r5)	0.38969963	-0.32787239	1.74027309	0.51455631	-3235.92448937	0.639
(r6)	0.48433351	-0.37825249	1.70717185	0.62371266	-3235.92429015	0.764
(r7)	0.59519733	-0.43497761	1.66066341	0.75293268	-3235.92414429	0.856
(r8)	0.61784535	-0.44007577	1.65079871	0.77586072	-3235.92384835	1.041
(r9)	0.68036638	-0.49531384	1.61538792	0.86463313	-3235.92381749	1.061
(r10)	0.75032083	-0.57222754	1.56530243	0.97578831	-3235.92293578	1.614
(r11)	0.06292687	-0.24342173	1.79591507	0.25205714	-3235.92498150	0.330
(r12)	0.14840875	-0.06245647	1.80650447	0.16117936	-3235.92504126	0.293
(r13)	0.11534446	-0.32606064	1.78047619	0.34746006	-3235.92434782	0.728
(r14)	0.23093147	-0.41110619	1.75214594	0.47553697	-3235.92328158	1.397
(r15)	0.20263941	-0.39466696	1.75954717	0.44695086	-3235.92348924	1.267
(r16)	0.52227103	0.34019472	1.70295408	0.63307195	-3235.92415890	0.846
(r17)	0.70243770	-0.00603166	1.66901404	0.71722379	-3235.92314302	1.484
(r18)	0.38724946	-0.18903785	1.75860544	0.43444309	-3235.92383116	1.052
(r19)	0.05441093	-0.00776878	1.81302739	0.05496779	-3235.92546798	0.025
(r20)	0.09532468	-0.03099525	1.81116743	0.10027105	-3235.92536785	0.088
(r21)	0.13533129	-0.04948985	1.80793546	0.14421466	-3235.92519364	0.197
(r22)	0.16238858	-0.07307608	1.80486684	0.17829601	-3235.92494398	0.354
(r23)	0.22587816	-0.10853578	1.79528427	0.25128222	-3235.92463686	0.546
(r24)	0.28798776	-0.13659190	1.78380025	0.32014466	-3235.92430578	0.754
(r25)	0.84542966	-0.70640566	1.47114699	1.15375568	-3235.92026014	3.293
(r26)	0.89923385	-0.97631591	1.30420471	1.42178518	-3235.91364559	7.444

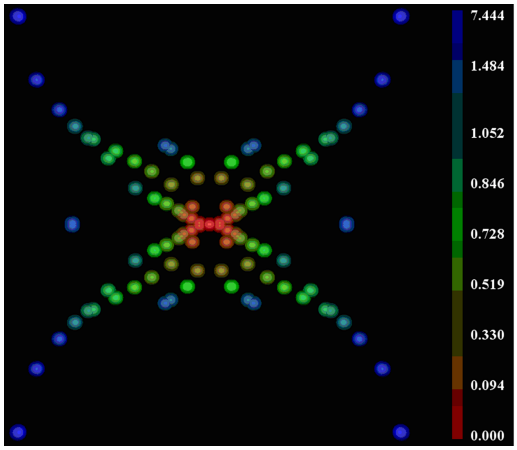
Details for Figure 1

The four proposed $Gd@C_{82}$ structures available in the literature (The numbers in the parenthesis are the relative energy with respect to the optimized structure.)

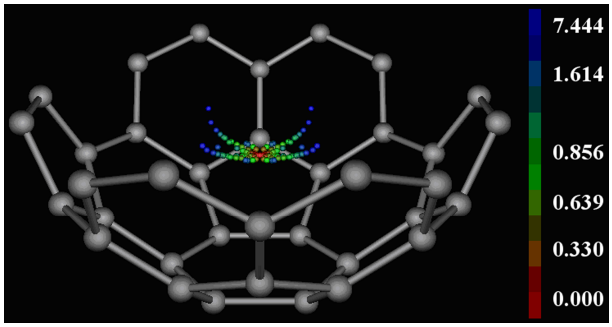


Details for Figure 2

(a) The potential energy surface in the vicinity of *C_2-hexagon* structure. (the energy units is kcal/mol)



(b) The potential energy surface in the vicinity of *C_2-hexagon* structure with details of the fullerene cage. (the energy units is kcal/mol)



Details for Figure 3

Comparison of the experimental XANES and the spectra obtained from the 26 configurations on the potential energy surface