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for

Oxidation states of infrequent I and common III for gallium: tunable via medium-sized C_{60} and small-sized C_{28} fullerenes

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Contents

I. Relative energy of partial important C_{60}^{m-} (m = 1 - 3) isomers on AM1 method in Table S1.

Table S1 Relative energy (ΔE, in kcal·mol^{-1}) of C_{60}^{m-} (m = 1 - 3) isomers on AM1.

Isomer	PA	C_{60}^{-}	C_{60}^{2-}	C_{60}^{3-}
I_h(1812)-C_{60}	0	0.0	0.0	0.0
C_{2v}(1809)-C_{60}	2	21.5	16.4	19.3
C_2(1789)-C_{60}	3	33.3	31.1	30.2
D_3(1803)-C_{60}	3	38.7	45.0	29.8
C_s(1804)-C_{60}	3	50.2	41.5	31.4

II. Relative energy and gap of Ga@C_{60} isomers on B3LYP/6-31G*~Lanl2dz in Table S2.

Table S2 Relative energy (*ΔE*), *gap* from *β* orbitals, and spin contamination ($\hat{S}^2$) of Ga@C_{60} isomers, in which different numbers of Ga position for Ga@I_h(1812)-C_{60} correspond to the numbers of metal position in Fig. S4.

Isomer	PA	Ga Position	Spin state	*ΔE*(kcal·mol^{-1})	*ΔE*(kJ·mol^{-1})	*gap*(eV)	$\hat{S}^2$
Ga@I_h(1812)-C_{60}	0	5	Doublet	0.00	0	2.57	0.76
		5	Quartet	38.57	161	0.92	3.76
		6	Doublet	0.02	0	2.57	0.76
		1	Doublet	0.02	0	2.57	0.76
		3	Doublet	0.04	0	2.59	0.76
		2	Doublet	0.04	0	2.56	0.76
		4	Doublet	0.07	0	2.56	0.76
Ga@C_{2v}(1809)-C_{60}	2	/	Doublet	24.43	102	1.78	0.76
		/	Quartet	56.19	235	1.03	3.76
Ga@C_2(1789)-C_{60}	3	/	Doublet	46.52	195	1.12	0.78
Ga@C_s(1804)-C_{60}	3	/	Doublet	44.10	185	1.90	0.76
Ga@D_3(1803)-C_{60}	3	/	Doublet	46.36	194	1.89	0.76

III. Relative energy of doublet Ga@C_{60} isomers on B3LYP/6-31G*, B3LYP/6-31G*~SDD, PBE0/6-31G*~SDD, and BP86/6-31G*~SDD in Table S3.

Table S3 Relative energy (*ΔE*, in kcal·mol^{-1}) of doublet Ga@C_{60} isomers on B3LYP/6-31G*, B3LYP/6-31G*~SDD, PBE0/6-31G*~SDD, and BP86/6-31G*~SDD.

Isomer	Spin state	B3LYP/6-31G*	BP86/6-31G* ~SDD	B3LYP/6-31G* ~SDD	PBE0/6-31G* ~SDD
Ga@I_h(1812)-C_{60}	Doublet	0.0	0.0	0.0	0.0
Ga@C_{2v}(1809)-C_{60}	Doublet	18.8	22.9	24.4	5.5
Ga@C_s(1804)-C_{60}	Doublet	38.2	61.1	63.6	44.7
Ga@D_3(1803)-C_{60}	Doublet	39.2	42.8	46.5	28.2
Ga@C_2(1789)-C_{60}	Doublet	41.2	42.9	46.5	46.7

Note: Except for 6-31G* basis set is for all of Ga and C atoms on B3LYP/6-31G*, 6-31G* basis set is only for C atoms and SDD basis set is for Ga atoms on B3LYP/6-31G*~SDD, PBE0/6-31G*~SDD, and BP86/6-31G*~SDD.

IV. Geometry of optimized Ga@C_{2v}(1809)-C_{60} on B3LYP/6-31G*~Lanl2dz in Fig. S1.

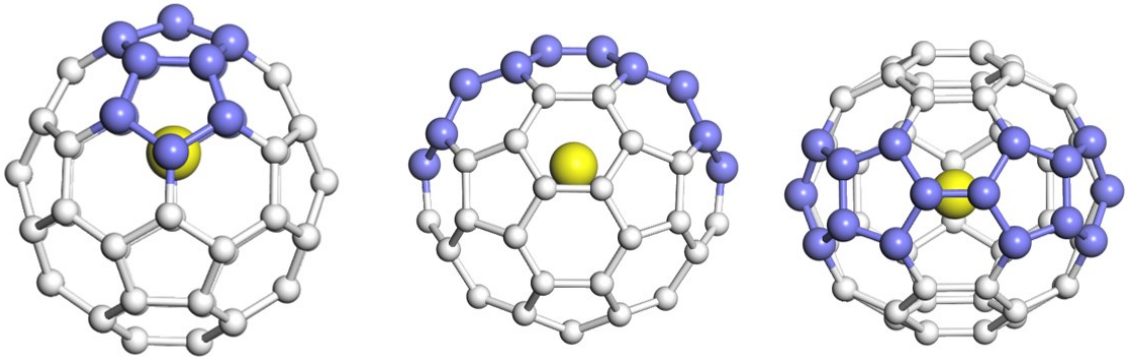


Fig. S1. Geometry from three perpendicular angles for optimized Ga@C_{2v}(1809)-C_{60}. (The C of PA fragment and Ga is marked in violet and yellow, respectively.)

V. Statistical thermodynamic analysis of Ga@C_{60} isomers on B3LYP/6-31G*~Lanl2dz in Fig. S2.

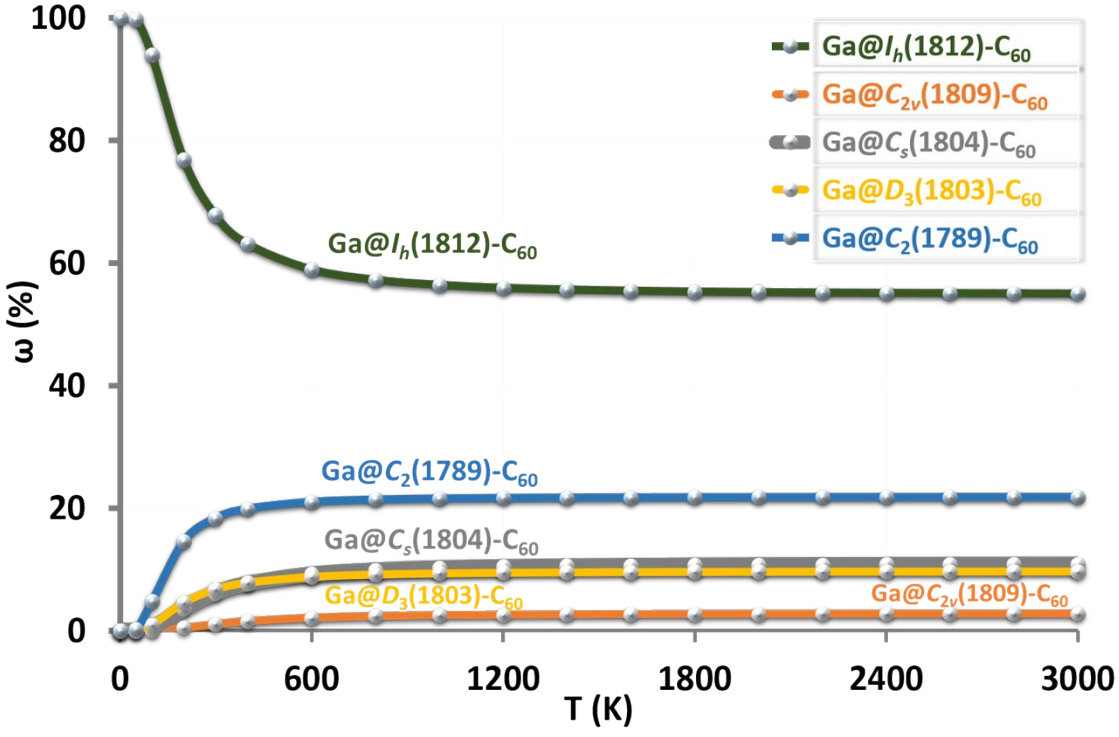


Fig. S2. Statistical thermodynamic analysis of Ga@C_{60} isomers on B3LYP/6-31G*~Lanl2dz.

VI. Schematic electronic structure analysis on $Ga^{m+}@C_{2n}^{m-}$ (n = 14, 18, 22, 25, 30, and 35; m = 0 - 3) in Fig. S3.

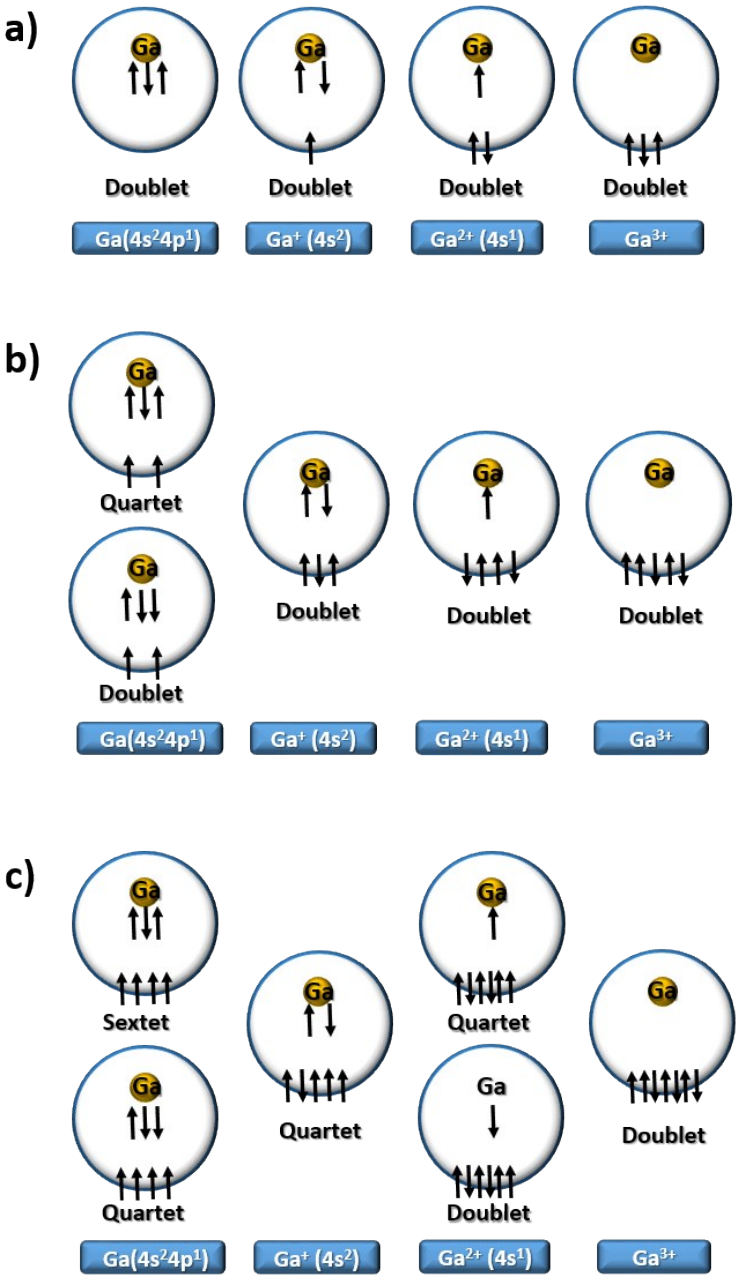


Fig. S3. Schematic electronic structure analysis of a) Ga@D_{2d}(14)-C_{36}, Ga@D_2(75)-C_{44}, Ga@D_2(89)-C_{44}, Ga@D_{5h}(271)-C_{50}, **Ga@I_h(1812)-C_{60}**, and Ga@D_{5h}(8149)-C_{70} (the ground states are singlet for the corresponding empty cages on B3LYP/6-31G*), b) Ga@D_{6h}(15)-C_{36} (the ground state is triplet for D_{6h}(15)-C_{36} on B3LYP/6-31G*), and c) Ga@T_d(2)-C_{28} (the ground state is quintet for T_d(2)-C_{28} on B3LYP/6-31G*).

VII. Different positions of Ga inside I_h(1812)-C_{60} in Fig. S4.

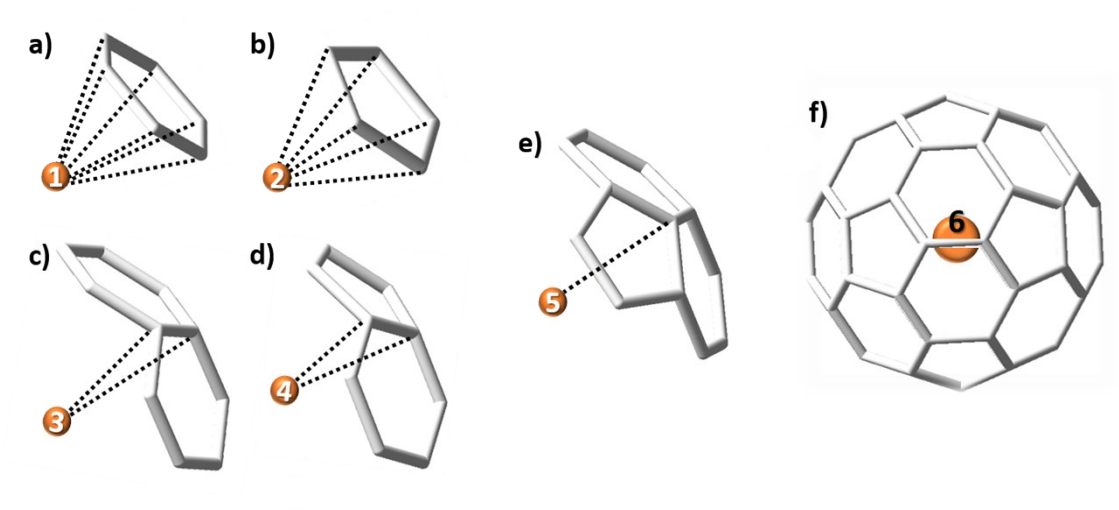


Fig. S4. Schematic diagram of different Ga positions inside I_h(1812)-C_{60}. (a) the center of hexagon, (b) the center of pentagon, (c) the center of the bond between two hexagons, (d) the center of the bond between hexagon and pentagon, (e) the vertex between one pentagon and two hexagons, and (f) the center of cage.

VIII. The RMSD of Ga@I_h(1812)-C_{60} and F-functionalized Ga@I_h(1812)-C_{60} in Fig. S5.

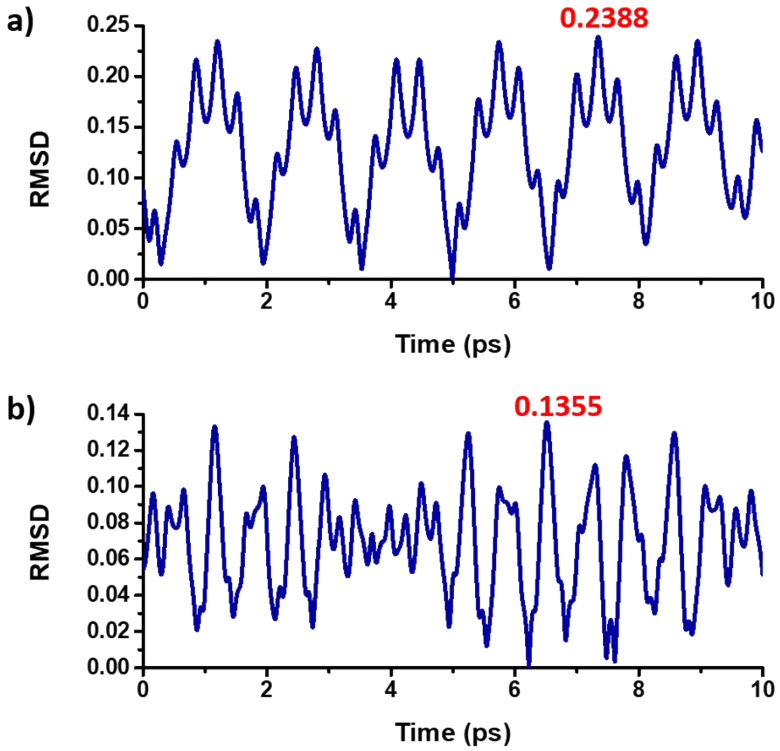


Fig. S5. The RMSD of a) Ga@I_h(1812)-C_{60} and b) F-functionalized Ga@I_h(1812)-C_{60}. (The minimum RMSD value are 0, and the maximum RMSD value are given in red.)

IX. Natural electron populations of Ga atoms for energetically optimal Ga@C_{2n} (2n = 28, 36, 44, 50, 60, and 70) with their ground states and Al atoms for doublet Al@C_{2n} (2n = 28 and 60) on different theoretical levels in Table S4 – S5.

Table S4 Natural electron populations of Ga for doublet Ga@C_{2n} (2n = 28, 36, 44, 50, 60, and 70) and Al for doublet Al@C_{2n} (2n = 28 and 60) on B3LYP/6-311G(d,p)~Lanl2dz.

Isomer	α-orbital population	β-orbital population
Ga@T_d(2)-C_{28}	$4s^{0.26}4p^{0.04}5p^{0.36}$	$4s^{0.29}4p^{0.04}5p^{0.36}$
Al@T_d(2)-C_{28}	$3s^{0.06}3p^{0.04}4s^{0.09}4p^{0.33}$	$3s^{0.04}3p^{0.04}4s^{0.07}4p^{0.33}$
Ga@D_{6h}(15)-C_{36}	$4s^{0.98}4p^{0.24}5p^{0.10}$	$4s^{0.98}4p^{0.24}5p^{0.10}$
Ga@D_{2d}(14)-C_{36}	$4s^{0.98}4p^{0.13}5p^{0.22}$	$4s^{0.99}4p^{0.13}5p^{0.22}$
Ga@D_2(75)-C_{44}	$4s^{0.99}4p^{0.16}5p^{0.07}$	$4s^{0.99}4p^{0.16}5p^{0.07}$
Ga@D_2(89)-C_{44}	$4s^{0.99}4p^{0.16}5p^{0.07}$	$4s^{0.99}4p^{0.16}5p^{0.07}$
Ga@D_{5h}(271)-C_{50}	$4s^{1.00}4p^{0.14}5p^{0.02}$	$4s^{0.99}4p^{0.14}5p^{0.02}$
Ga@I_h(1812)-C_{60}	$4s^{0.99}4p^{0.09}5p^{0.02}$	$4s^{0.99}4p^{0.09}5p^{0.02}$
Al@I_h(1812)-C_{60}	$3s^{0.99}3p^{0.09}4p^{0.02}$	$3s^{0.99}3p^{0.09}4p^{0.02}$
Ga@D_{5h}(8149)-C_{70}	$4s^{0.99}4p^{0.07}5p^{0.02}$	$4s^{0.99}4p^{0.07}5p^{0.02}$

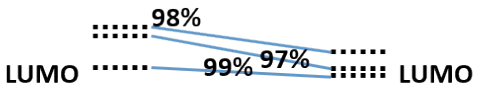
Table S5 Natural electron populations of Ga for doublet Ga@C_{2n} (2n = 28, 36, 44, 50, 60, and 70) on PBE0/6-311G(d,p)~SDD and B3LYP/6-31G*.

	[a]PBE0/6-311G(d,p)~SDD		[b]B3LYP/6-31G*	
Isomer	α-orbital population	β-orbital population	α-orbital population	β-orbital population
Ga@T_d(2)-C_{28}	$4s^{0.24}4p^{0.04}5s^{0.03}5p^{0.28}$	$4s^{0.37}4p^{0.04}5s^{0.03}5p^{0.28}$	$4s^{0.25}4p^{0.38}4d^{0.01}5s^{0.03}8s^{0.15}$	$4s^{0.30}4p^{0.38}4d^{0.01}5s^{0.03}8s^{0.15}$
Ga@D_{6h}(15)-C_{36}	$4s^{0.98}4p^{0.22}5p^{0.10}$	$4s^{0.99}4p^{0.22}5p^{0.10}$	$4s^{0.99}4p^{0.31}4d^{0.01}5s^{0.01}5p^{0.02}$	$4s^{0.99}4p^{0.31}4d^{0.01}5s^{0.01}5p^{0.02}$
Ga@D_{2d}(14)-C_{36}	$4s^{0.98}4p^{0.32}5p^{0.02}$	$4s^{0.99}4p^{0.32}5p^{0.02}$	$4s^{0.99}4p^{0.31}4d^{0.01}5s^{0.01}5p^{0.02}$	$4s^{0.99}4p^{0.31}4d^{0.01}5s^{0.01}5p^{0.02}$
Ga@D_2(75)-C_{44}	$4s^{0.99}4p^{0.18}5p^{0.07}$	$4s^{0.99}4p^{0.18}5p^{0.07}$	$4s^{1.00}4p^{0.20}5s^{0.01}5p^{0.02}$	$4s^{0.99}4p^{0.20}5s^{0.01}5p^{0.02}$
Ga@D_2(89)-C_{44}	$4s^{0.99}4p^{0.23}5p^{0.02}$	$4s^{0.99}4p^{0.23}5p^{0.02}$	$4s^{1.00}4p^{0.19}5s^{0.01}5p^{0.02}$	$4s^{1.00}4p^{0.19}5s^{0.01}5p^{0.02}$
Ga@D_{5h}(271)-C_{50}	$4s^{0.99}4p^{0.16}5p^{0.02}$	$4s^{0.99}4p^{0.16}5p^{0.02}$	$4s^{1.00}4p^{0.13}5p^{0.02}6s^{0.01}$	$4s^{1.00}4p^{0.13}5p^{0.02}6s^{0.01}$
Ga@I_h(1812)-C_{60}	$4s^{0.99}4p^{0.10}5p^{0.02}$	$4s^{0.99}4p^{0.10}5p^{0.02}$	$4s^{0.99}4p^{0.09}5s^{0.01}5p^{0.01}$	$4s^{0.99}4p^{0.09}5s^{0.01}5p^{0.01}$
Ga@D_{5h}(8149)-C_{70}	$4s^{0.99}4p^{0.07}5p^{0.02}$	$4s^{0.99}4p^{0.07}5p^{0.02}$	$4s^{0.99}4p^{0.08}5p^{0.02}$	$4s^{0.99}4p^{0.08}5p^{0.02}$

[a]6-311G(d,p) basis set is for C atoms, and SDD basis set is for Ga atoms on PBE0/6-311G(d,p)~SDD.

[b]6-31G* basis set is for all of Ga and C atoms on B3LYP/6-31G*.

X. Interplay diagram from β orbitals of C_{60}, Ga, and Ga@I_h(1812)-C_{60} in Fig. S6.



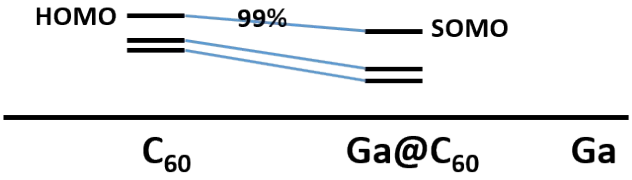


Fig. S6. Interplay diagram from β orbitals of C_{60}, Ga, and Ga@I_h(1812)-C_{60}.

XI. Spin density map for doublet Ga@I_h(1812)-C_{60} on B3LYP/6-31G*~Lanl2dz in Fig. S7.

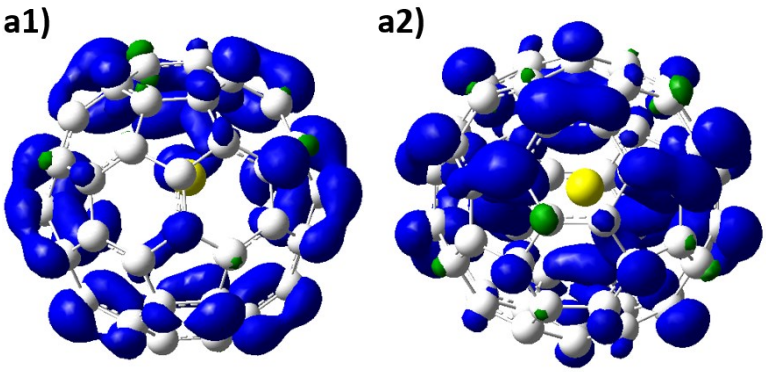
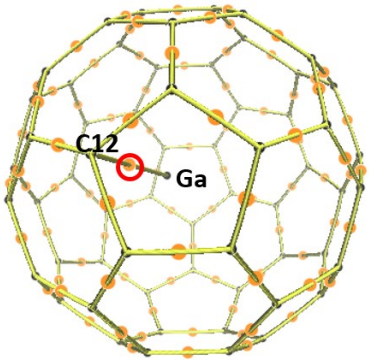


Fig. S7. a1) side view and a2) top view of spin density map of doublet Ga@I_h(1812)-C_{60}. (Isovalue = 0.001)

XII. The topology result of BCPs for Ga@I_h(1812)-C_{60}, and parameters related to the especial BCP in Fig. S8.



MBO = 0.03
WBO = 0.07
ρ_{BCP} = 0.0185
$\nabla^2\rho_{BCP}$ = 0.0460
H_{BCP} = -0.0003
$|V_{BCP}|/G_{BCP}$ = 1.0286

Fig. S8. BCPs and bond paths in Ga@I_h(1812)-C_{60}. Black balls, orange balls, and yellow sticks represent atoms, BCPs, and BCP paths, respectively. The especial BCP is enclosed by red circle for Ga-C12 in Ga@I_h(1812)-C_{60}. (MBO is Mayer bond order,

WBO is Wiberg bond order, ρ_{BCP} is the density of all electrons, $\nabla^2\rho_{BCP}$ is the Laplacian of the electron density, H_{BCP} is the energy density, $|V_{BCP}|/G_{BCP}$ is the potential energy density to the Lagrangian kinetic energy.)

XIII. ELF map between two C atoms closest to Ga and Ga for Ga@I_h(1812)-C_{60} in Fig. S9.

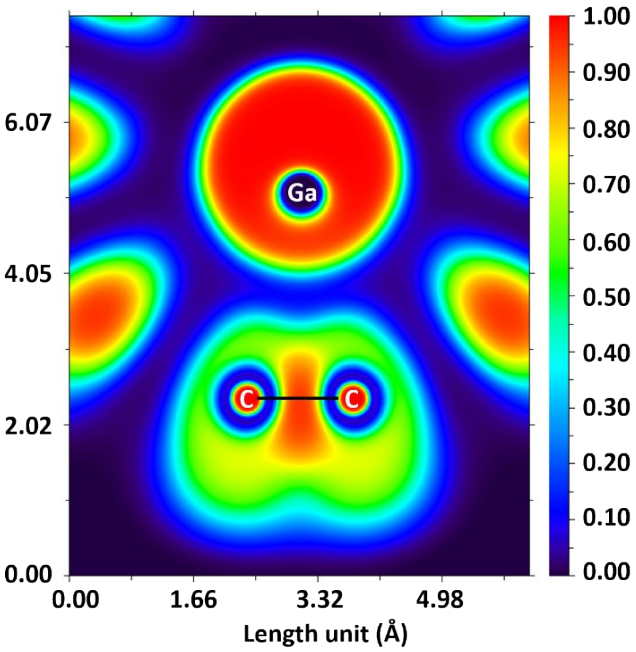


Fig. S9. The ELF map between Ga and two C atoms closest to Ga of Ga@I_h(1812)-C_{60}.

XIV. H-functionalized Ga@I_h(1812)-C_{60} with different reaction sites of H on B3LYP/6-31G*~Lanl2dz in Fig. S10.

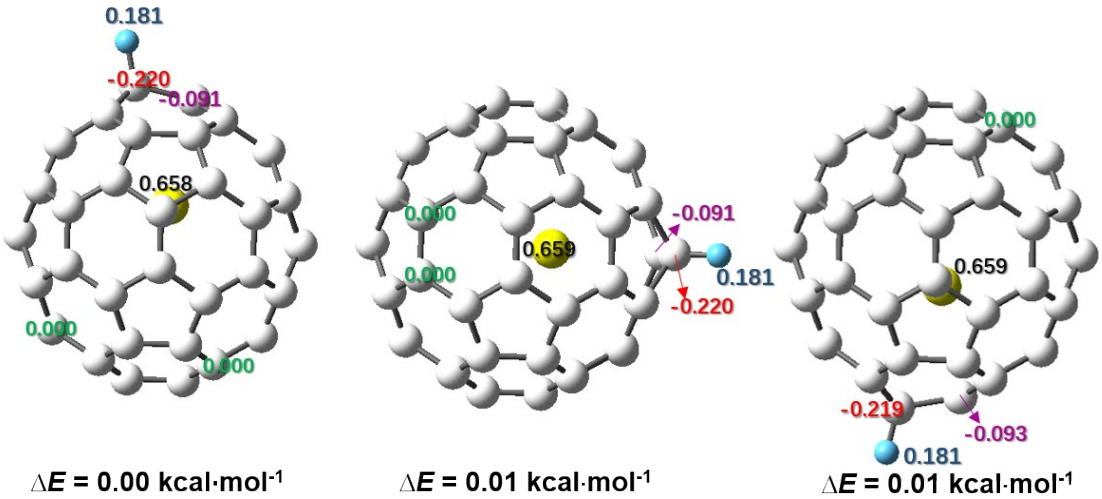


Fig. S10. The relative energy (ΔE) and Mulliken charge for Ga@I_h(1812)-C_{60} with three different reaction sites of H. (The Mulliken charge is marked in black for Ga, the Mulliken charge is marked in blue for H, the Mulliken charge is marked in red for C bonded by H, the Mulliken charge is marked in purple for C of the second negative

charge, and the Mulliken charge is marked in green for C of the least negative charge.)

XV. Optimized geometries of Ga@I_h(1812)-C_{60} with different functionalized groups on the same reaction site in Fig. S11.

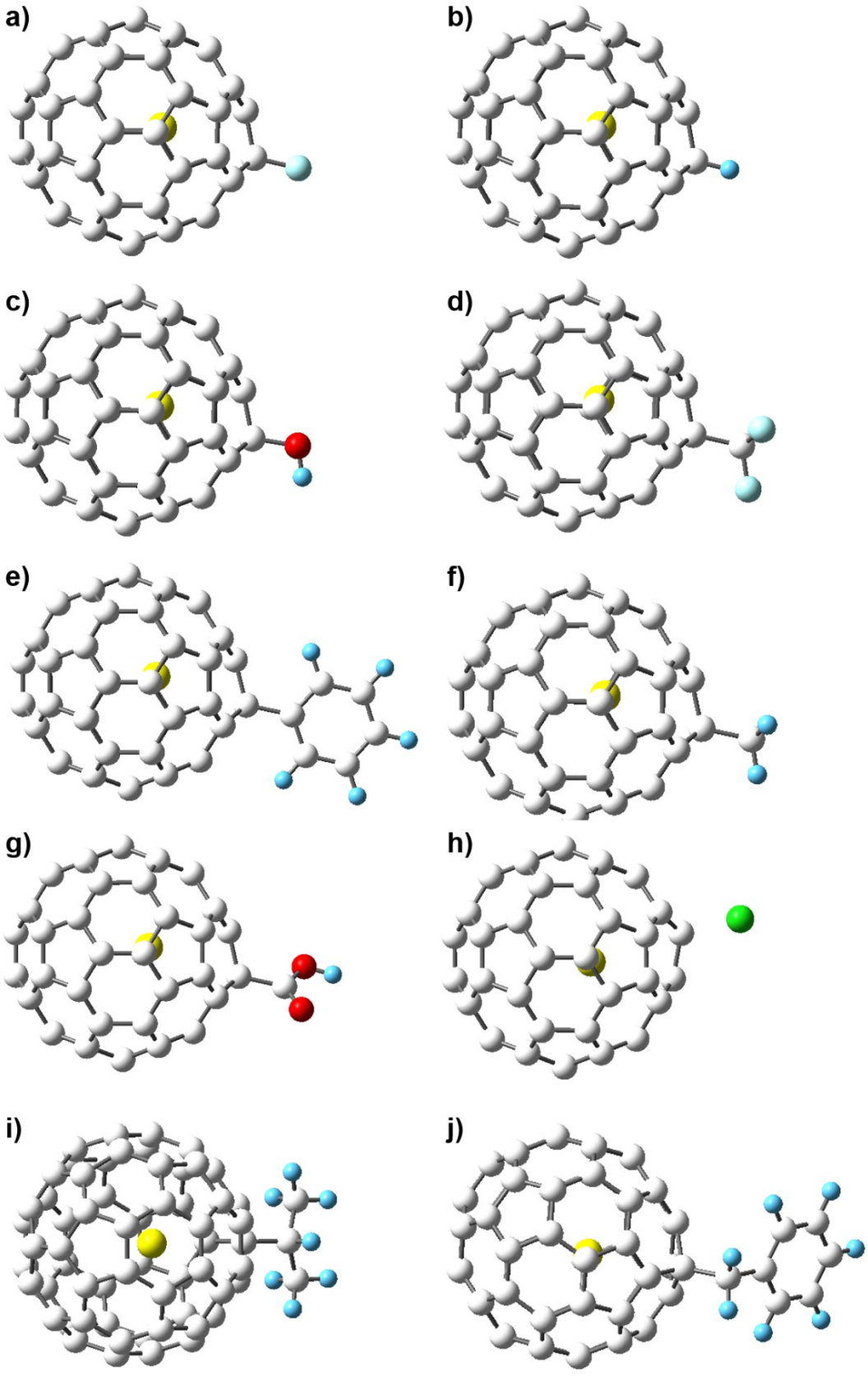


Fig. S11. Optimized geometries of Ga@I_h(1812)-C_{60} with different functionalized radicals a) F, b) H, c) OH, d) CF_3, e) C_6H_5, f) CH_3, g) COOH, h) Cl, i) $CH(CH_3)_2$, and j) $CH_2C_6H_5$ on the same reaction site.

XVI. The *ΔG*, Mulliken charge of Ga, and Mulliken charge of cage for Ga@I_h(1812)-C_{60} using different functionalized radicals with and without toluene solvent on B3LYP/6-31G*~Lanl2dz in Table S6.

Table S6 The *ΔG* (kcal·mol^{-1}), Mulliken charge of Ga, and Mulliken charge of cage for Ga@I_h(1812)-C_{60} using different functionalized groups with and without toluene solvent.

Radical	Without sovlent			With toluene solvent		
	ΔG	Mulliken charge of Ga	Mulliken charge of cage	*ΔG*	Mulliken charge of Ga	Mulliken charge of cage
/	/	0.740	-0.740	/	0.740	-0.740
H	-48.8	0.658	-0.839	-49.1	0.658	-0.847
CF_3	-38.4	0.661	-0.755	-38.5	0.662	-0.747
$CH_2C_6H_5$	-15.2	0.656	-0.697	-15.1	0.656	-0.702
Cl	-28.3	0.655	-0.535	-29.3	0.657	-0.457
F	-63.5	0.657	-0.303	-63.9	0.660	-0.295
CH_3	-31.2	0.659	-0.699	-31.3	0.658	-0.705
C_6H_5	-36.3	0.655	-0.777	-36.4	0.656	-0.775
OH	-39.7	0.656	-0.421	-39.6	0.657	-0.417
COOH	-29.1	0.660	-0.688	-28.8	0.660	-0.687
CH_3CHCH_3	-21.0	0.659	-0.717	-21.2	0.658	-0.722

XVII. Natural electron populations of Ga and F atoms for F-functionalized Ga@I_h(1812)-C_{60} on different calculation levels in Table S7.

Table S7 Natural electron populations of Ga and F for F-functionalized Ga@I_h(1812)-C_{60} on B3LYP/6-311G(d,p)~Lanl2dz, PBE0/6-311G(d,p)~SDD, and B3LYP/6-31G*.

Atom	B3LYP/6-311G(d,p)~Lanl2dz	PBE0/6-311G(d,p)~SDD	B3LYP/6-31G*
Ga	$4s^{1.97}4p^{0.21}5p^{0.05}$	$4s^{1.98}4p^{0.22}5p^{0.06}$	$4s^{1.98}4p^{0.22}5s^{0.01}5p^{0.05}$
F	$2s^{1.84}2p^{5.55}$	$2s^{1.84}2p^{5.54}$	$2s^{1.84}2p^{5.53}$

XVIII. The geometries of energetically optimal Ga@C_{2n} (2n = 28, 36, 44, 50, 60, and 70) isomers on B3LYP/6-311G*~Lanl2dz in Fig. S12.

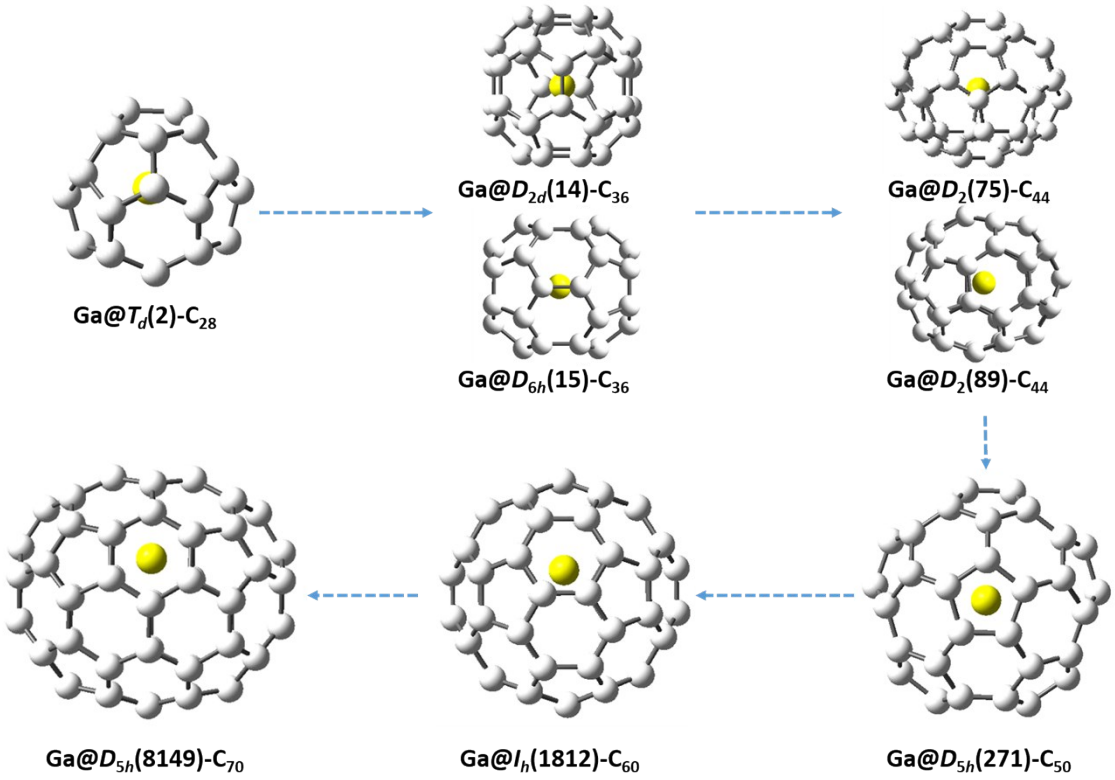


Fig. S12. The geometries of energetically optimal Ga@C_{2n} (2n = 28, 36, 44, 50, 60, and 70) isomers.

XIX. Relative energy of partial important C_{2n}^{m-} (m = 1 - 3) isomers on AM1 method and their corresponding optimized Ga@C_{2n} isomers on B3LYP/6-31G*~Lanl2dz in Table S8 - S13.

Table S8 Relative energy (kcal·mol^{-1}) of C_{28}^{m-} (m = 1 - 3) isomers and their corresponding Ga@C_{28} isomers.

Isomer	Spin state	Ga@C_{28}	C_{28}^{-}	C_{28}^{2-}	C_{28}^{3-}
T_d(2)-C_{28}	Doublet	**0**	**0**	**0**	**0**
	Quartet	16.0	/	/	/
D_2(1)-C_{28}	Doublet	26.7	50.2	24.7	37.8

Table S9 Relative energy (kcal·mol^{-1}) of C_{36}^{m-} (m = 1 - 3) isomers and their corresponding Ga@C_{36} isomers.

Isomer	Spin state	Ga@C_{36}	C_{36}^{-}	C_{36}^{2-}	C_{36}^{3-}
D_{2d}(14)-C_{36}	Doublet	0.2	16.8	5.5	7.3
	Quartet	**0.0**	/	/	/
D_{6h}(15)-C_{36}	Doublet	0.5	**0.0**	**0.0**	**0.0**
	Quartet	8.4	/	/	/
C_2(12)-C_{36}	Doublet	4.5	22.2	2.1	17.9

C_{2v}(9)-C_{36}	Doublet	7.1	13.0	12.5	17.4
C_2(11)-C_{36}	Doublet	14.9	30.7	4.2	14.7
C_s(8)-C_{36}	Doublet	30.3	44.5	26.3	22.5

Note: Although the relative energy of doublet Ga@D_{2d}(14)-C_{36} is 0.2 kcal·mol^{-1} greater than that of quartet Ga@D_{2d}(14)-C_{36}, doublet and quartet Ga@D_{2d}(14)-C_{36} were nearly isoenergetic. For the isoenergetic doublet and quartet Ga@D_{2d}(14)-C_{36}, the ground state preferred doublet to quartet for Ga@D_{2d}(14)-C_{36} from the chemical viewpoint.

Table S10 Relative energy (kcal·mol^{-1}) of C_{44}^{m-} (m = 1 - 3) isomers and their corresponding Ga@C_{44} isomers.

Isomer	Spin state	Ga@C_{44}	C_{44}^{-}	C_{44}^{2-}	C_{44}^{3-}
D_2(75)-C_{44}	Doublet	**0.0**	**0.0**	**0.0**	**0.0**
	Quartet	24.6	/	/	/
D_2(89)-C_{44}	Doublet	0.5	2.6	**0.0**	0.6
	Quartet	23.1	/	/	/
C_1(88)-C_{44}	Doublet	26.9	12.7	17.3	15.9
C_1(69)-C_{44}	Doublet	15.7	13.6	9.5	12.0
C_1(52)-C_{44}	Doublet	19.7	15.2	12.1	11.5
C_2(87)- C_{44}	Doublet	32.2	15.3	20.6	12.0
C_1(78)-C_{44}	Doublet	28.0	15.5	17.3	12.5
C_1(77)-C_{44}	Doublet	25.2	17.0	16.4	13.4
D_{3h}(72)-C_{44}	Doublet	11.7	22.5	0.6	15.2
C_1(67)-C_{44}	Doublet	50.3	25.6	44.4	30.5
C_1(57)-C_{44}	Doublet	47.3	29.5	37.5	27.1
C_{2v}(55)-C_{44}	Doublet	22.4	41.7	8.4	18.9

Table S11 Relative energy (kcal·mol^{-1}) of C_{50}^{m-} (m = 1 - 3) isomers and their corresponding Ga@C_{50} isomers.

Isomer	Spin state	Ga@C_{50}	C_{50}^{-}	C_{50}^{2-}	C_{50}^{3-}
D_{5h}(271)-C_{50}	Doublet	**0.0**	1.3	**0.0**	**0.0**
	Quartet	27.7	/	/	/
D_3(270)-C_{50}	Doublet	6.2	12.7	4.3	18.8
C_s(266)-C_{50}	Doublet	9.2	**0.0**	7.8	9.0
C_2(263)-C_{50}	Doublet	11.5	19.0	7.5	25.6
C_s(264)-C_{50}	Doublet	14.3	14.9	9.4	25.4
C_2(260)-C_{50}	Doublet	22.2	19.6	19.0	28.9
C_s(262)-C_{50}	Doublet	26.9	16.4	29.0	34.5
C_2(265)-C_{50}	Doublet	32.6	20.2	35.4	25.4

C_1(268)-C_{50}	Doublet	34.7	22.8	40.1	38.4
C_1(248)-C_{50}	Doublet	39.4	22.2	37.9	32.6

Table S12 Relative energy (kcal·mol^{-1}) of C_{70}^{m-} (m = 1 - 3) isomers and their corresponding Ga@C_{70} isomers.

Isomer	Spin state	Ga@C_{70}	C_{70}^{-}	C_{70}^{2-}	C_{70}^{3-}
D_{5h}(8149)-C_{70}	Doublet	**0.0**	**0.0**	**0.0**	**0.0**
	Quartet	37.1	/	/	/
C_2(7892)-C_{70}	Doublet	33.4	16.1	24.4	24.8
C_2(7957)-C_{70}	Doublet	42.9	23.3	39.2	22.9
C_1(8005)-C_{70}	Doublet	37.3	25.9	35.2	29.0
C_s(8111)-C_{70}	Doublet	30.5	27.1	31.8	31.0
C_2(8064)-C_{70}	Doublet	33.7	27.4	26.2	24.3
C_1(7924)-C_{70}	Doublet	40.4	28.4	31.7	30.3
C_1(8042)-C_{70}	Doublet	38.1	28.6	28.1	34.9
C_s(8094)-C_{70}	Doublet	22.7	30.9	34.7	23.7
C_s(7960)-C_{70}	Doublet	40.4	30.9	35.2	25.3

Table S13 Relative energy (ΔE, in kcal·mol^{-1}) of Ga@C_{30} isomers on B3LYP/6-31G*~Lanl2dz and natural electron populations of energetically optimal isomer with the ground state on B3LYP/6-311G(d,p)~Lanl2dz.

Isomer	Spin state	ΔE	α-orbital population	β-orbital population
Ga@C_{2v}(3)-C_{30}	Doublet	0	$4s^{0.99}4p^{0.04}5p^{0.37}$	$4s^{0.14}4p^{0.03}5p^{0.37}$
	Quartet	20.6	/	/
Ga@C_{2v}(2)-C_{30}	Doublet	30.7	/	/
Ga@D_{5h}(1)-C_{30}	Doublet	69.0	/	/

Note: Ga@C_{30} as an example was focused to explore whether Ga (Ⅱ) could be realized. There was indeed two electrons transferred from Ga to C_{2v}(3)-C_{30} for doublet Ga@C_{2v}(3)-C_{30} according to the natural electron population on the B3LYP/6-311G(d,p)~Lanl2dz.

XX. Cartesian coordinate of Ga@I_h(1812)-C_{80}.

Ga@I_h(1812)-C_{80}

C	0.54450000	-3.50000000	0.23540000
C	0.18530000	-3.35980000	-1.11690000
C	1.07230000	-2.68380000	-2.03790000
C	0.25840000	-1.90860000	-2.96690000
C	0.69850000	-0.65950000	-3.40950000
C	-0.24710000	0.44130000	-3.51650000
C	0.44260000	1.65430000	-3.10710000

C	-0.23900000	2.63470000	-2.38290000
C	0.41630000	3.30740000	-1.26600000
C	-0.56740000	3.52600000	-0.23160000
C	-0.20630000	3.38380000	1.13240000
C	-1.09150000	2.70650000	2.05130000
C	-0.27290000	1.92480000	2.98400000
C	-0.71780000	0.66960000	3.42370000
C	0.23000000	-0.43380000	3.53350000
C	-0.46190000	-1.64390000	3.12310000
C	0.21670000	-2.61750000	2.38670000
C	-0.43860000	-3.28820000	1.27330000
C	1.81230000	-2.95990000	0.69920000
C	1.61430000	-2.41940000	2.03550000
C	2.28090000	-1.25700000	2.43000000
C	1.57420000	-0.23950000	3.19250000
C	2.03420000	1.06170000	2.73590000
C	1.12180000	2.12690000	2.63610000
C	1.16160000	3.01640000	1.48160000
C	2.10950000	2.80630000	0.47470000
C	1.73810000	2.95870000	-0.92940000
C	2.43990000	1.94650000	-1.68270000
C	1.81150000	1.29980000	-2.75990000
C	1.96920000	-0.12410000	-2.94900000
C	2.75280000	-0.87260000	-2.05200000
C	2.29610000	-2.16630000	-1.59310000
C	2.66890000	-2.30890000	-0.19060000
C	3.35860000	-1.09830000	0.21660000
C	3.17290000	-0.57980000	1.50210000
C	3.01850000	0.85160000	1.69330000
C	3.05850000	1.71100000	0.58250000
C	3.25090000	1.17040000	-0.75090000
C	3.39870000	-0.20630000	-0.93380000
C	-1.17850000	-2.99580000	-1.46430000
C	-1.13620000	-2.10760000	-2.61730000
C	-2.04750000	-1.05150000	-2.72400000
C	-1.59050000	0.24970000	-3.18410000
C	-2.30030000	1.26660000	-2.42410000
C	-1.63610000	2.43570000	-2.03480000
C	-1.83380000	2.97620000	-0.69530000
C	-2.69820000	2.32400000	0.19500000
C	-2.32510000	2.18100000	1.60570000
C	-2.78310000	0.89070000	2.06590000
C	-1.99390000	0.13510000	2.97070000
C	-1.83370000	-1.28680000	2.77550000

C	-2.46260000	-1.93280000	1.69520000
C	-1.75890000	-2.94100000	0.93850000
C	-2.13090000	-2.79260000	-0.46380000
C	-3.07900000	-1.69750000	-0.57320000
C	-3.03880000	-0.83890000	-1.68470000
C	-3.19570000	0.59000000	-1.49950000
C	-3.39110000	1.11460000	-0.21060000
C	-3.42920000	0.22270000	0.94230000
C	-3.27250000	-1.15530000	0.75990000
Ga	-0.34360000	0.50510000	0.38820000

XXI. The movement of Ga in I_h(1812)-C_{80} cage in S1.avi and the details for ab initio molecular dynamic calculation.

Calculation details about *ab Initio* molecular dynamics (AIMD):

Standard AIMD, in which a Verlet algorithm was used to integrate Newton's equations of motion, was performed under microcanonical (NVE) ensemble, with spin polarization obtained on PBE-style generalized gradient approximation (GGA)[1] via VASP program[2-4]. To ensure small enough intermolecular interaction, three-dimensional periodic boundary condition with the minimum intermolecular distance of 15 Å was used. The time step was two femto seconds. Temperature of 1000 K was considered during fullerene-formation temperature region. The default cut-off energy was used for the pseudopotentials (400 eV). Tetragonal lattices (25 Å) were utilized. An automatic k-points mesh (1×1×1) was generated with a Gamma-centered grid. Movie was made by Jmol.

XXII. The movement of Ga in F-functionalized I_h(1812)-C_{80} cage in S2.avi.

References:

1. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
2. G. Kresse, J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251.
3. G. Kresse, J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.
4. G. Kresse, J. Furthmüller, *Comp. Mater. Sci.*, 1996, **6**, 15.