Closed Network Growth of Fullerenes – Supplementary Information

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Supplementary Figures

Supplementary Figure S1  |  Low-mass region after exposure of C₆₀ to carbon vapor.
Growth to larger fullerenes occurs exclusively from the desorbed fullerene after interaction with carbon vapor achieved by ablation of a C₆₀ coated graphite target. Smaller fullerenes are not produced by the growth processes of the higher fullerenes, nor are they produced directly from graphite because the helium pressure is lower than that required for direct fullerene formation from graphite. Note: the small peak at m/z 360 is the second harmonic of the C₆₀ cations (i.e., at twice the ICR frequency and thus apparently half the mass-to-charge ratio).
Supplementary Figure S2  |  Isolation and fragmentation of C$_{70}$ grown from C$_{60}$ after exposure to carbon vapor. a, SWIFT-isolated C$_{70}$. b, Fragmentation of C$_{70}$ formed by exposure of C$_{60}$ to carbon vapor, clearly showing successive neutral C$_2$ loss, the hallmark of fullerenes. “Calculated” distributions, here and throughout, are the calculated natural abundance isotopic distributions.
Supplementary Figure S3  |  FT-ICR mass spectrum produced after exposure of C₆₀ to highly ¹³C-enriched carbon vapor. Left inset: Mass scale expansion for C₆₀ after exposure to carbon vapor produced from ¹³C-enriched amorphous carbon. The isotopic distribution unequivocally shows that extensive atom exchange occurs. Right inset: The isotopic distribution of the C₆₀ starting material is dominated by ¹²C₆₀ before exposure to carbon vapor produced from amorphous ¹³C.
Supplementary Figure S4 | C_{62} to C_{74} species after exposure of C_{60} to $^{13}$C vapor. C_{62} is formed primarily by $^{13}$C ingestion into $^{12}$C_{60}, either by incorporation of two separate $^{13}$C atoms or via direct $^{13}$C_{2} insertion. The extent of pure $^{12}$C_{2} addition with regard to C_{62} formation corresponds to roughly 1% of the isotopic distribution, consistent with the proportion of $^{12}$C in the $^{13}$C-enriched (99%) amorphous carbon target. $^{12}$C_{2} may be produced by fragmentation of the parent C_{60}, which can also incorporate into $^{12}$C_{60} to form $^{12}$C_{62}. There is also $^{12}$C_{1}$^{13}$C_{1} addition that corresponds to ~3% of the isotopic distribution for C_{62}. The $^{12}$C incorporation likely results from atom exchange events, because our DFT calculations show that ingestion of atomic $^{13}$C results in ejection of $^{12}$C, which can subsequently act as a catalyst or insert as a dimer into the fullerenes during growth. The monoisotopic peak corresponding to $^{12}$C_{64} is extremely weak for the C_{64} isotopic profile, and no monoisotopic peaks are detected in larger fullerenes. The formation of $^{12}$C_{60}$^{13}$C_{4} (and all larger fullerenes formed) is achieved by $^{13}$C or $^{13}$C_{2} ingestion (or combinations thereof) into C_{60}. Atom exchange processes occur for all larger fullerenes. All growth is consistent with $^{13}$C ingestion into the desorbed C_{60} fullerene.
Supplementary Figure S5 | Formation route for ground state C_{62} by direct carbon atom ingestion and C transfer between two C_{61} fullerenes followed by internal rearrangement of C_{62}. (a)→(b), C_{60} ingests atomic carbon, forming C_{60}C. (b)→(c), A second C_{60} ingests carbon to form another C_{60}C. (c)→(d), A carbon adatom is transferred between the C_{60}C fullerenes upon collision, generating C_{60}CC and C_{60}. The C_{60}CC species possesses two carbon adatoms which can then propagate through the structure via intrafullerene exchange (Figure 4a, process 2). (d)→(e), The carbon adatoms meet within the structure to form the ground state C_{62} fullerene, the same structure formed by direct C_{2} incorporation. (b)→(d), C_{60}C can directly ingest a carbon atom to produce C_{60}CC that will subsequently form C_{62} via (d)→(e).
Supplementary Figure S6 | Formation route for ground state C_{62} by direct C_{2} ingestion. A portion of the fullerene is shown for clarity. (a)→(b), Isolated C_{2}, found to be most stable in the triplet state, initially forms a “stick” structure with C_{60}. (b)→(c) or (d), the structure rearranges into (c) or (d) after C_{2} associates with a hexagon-hexagon or hexagon-pentagon bond upon spin relaxation. (c) or (d)→(e), C_{2} incorporates into the structure forming a stable C_{62} fullerene possessing fused pentagons surrounded by a heptagon.
Supplementary Figure S7  |  Diffusion barrier for bond rotation from (left) $I_h$-$C_{60}$ to (right) $C_{2v}$-$C_{60}$ catalysed by CH. The barrier occurs in two steps, first a barrier of 80.4kcal/mol needs to be overcome to switch the binding site of the hydrogen atom, followed by a barrier of 35.6kcal/mol to perform the C-C bond rotation. The barrier for the total process is thus 80.4kcal/mol (52.4kcal/mol for the reverse reaction).
Supplementary Figure S8  |  Isolation and fragmentation of La$_2$@C$_{88}$ grown from La$_2$@C$_{80}$.

a, SWIFT-isolated La$_2$@C$_{88}$. b, Fragmentation of La$_2$@C$_{88}$ grown from La$_2$@C$_{80}$ showing C$_2$ loss with retention of both La atoms. All larger endohedral fullerenes grown from La$_2$@C$_{80}$ exhibit this fragmentation pattern, confirming that the larger species are endohedral metallofullerenes.
Supplementary Figure S9 | Growth of La$_2$@C$_{80}$ in carbon vapor. Results of the vaporization of a La$_2$@C$_{80}$ coated graphite target with mass scale expansions, unequivocally demonstrating that growth of La$_2$@C$_{80}$ occurs with retention of both La atoms by the CNG mechanism. The low abundance La@C$_{2n}$ and C$_n$ fullerenes form by growth of La@C$_{80}$ and C$_{80}$ produced from La$_2$@C$_{80}$ parent by La atom loss produced by fragmentation of La$_2$@C$_{80}$ from laser ablation (see Supplementary Figure S10).
Supplementary Figure S10 | Laser irradiation of La$_2$@C$_{80}$ film without exposure to carbon vapor at low and high laser intensities. 

**a.** Simple desorption spectrum of the La$_2$@C$_{80}$ starting material. The mass spectrum shows the very high purity of the La$_2$@C$_{80}$ sample used in the growth experiments. The film was irradiated at a fluence of 3 mJ/cm$^2$. 

**b.** Irradiation of a La$_2$@C$_{80}$ film on a quartz rod at the higher laser fluence (50 mJ/cm$^2$) used for the growth experiment. A small amount of La$_2$@C$_{80}$-2n results from C$_2$ loss of the parent La$_2$@C$_{80}$. The ejection of La atoms results in formation of La@C$_{80}$ and C$_2$ loss fragment ions. Very weak signals for C$_{80}$, and C$_2$ loss product ions, are formed by loss of both La atoms from the La$_2$@C$_{80}$. 
Supplementary Figure S11  | Laser irradiation of Gd@C₈₂ film without exposure to carbon vapor at low and high laser fluence. a, Desorption mass spectrum produced by laser irradiation of a Gd@C₈₂ sample film at low laser fluence (3 mJ/cm²). Although Gd@C₈₂ is the only endohedral fullerene in the sample (the weak Gd@C₈₀ signal is due to fragmentation of Gd@C₈₂), empty cage nanostructure impurities are evident from the weaker signals at C₁₀₂-C₁₁₀. b, The encapsulated Gd atom is ejected under the higher laser power (50 mJ/cm²) used during the growth experiments due to fragmentation of the Gd@C₈₂ parent ion. Ejection forms empty cage C₈₂ and C₂ loss fragment ions, however, Gd@C₈₂ is primarily desorbed intact.
Supplementary Figure S12 | Exposure of Gd@C_{82} to carbon vapor. Vaporization of a Gd@C_{82} coated graphite target demonstrating growth to larger metallofullerenes by the CNG mechanism. The empty cage impurities (see Supplementary Figure S11a) of C_{102}-C_{110} grow to larger carbon nanostructures as well. Empty cage peaks at low relative abundance also result from the growth of C_{82}, formed by ejection of a Gd atom during laser irradiation at higher fluence (50 mJ/cm^2).

Supplementary Figure S13 | Isolation and fragmentation of Gd@C_{92} grown from Gd@C_{82}. a, SWIFT-isolated Gd@C_{92}. b, Fragmentation pattern. Gd@C_{92} fragments by C_2 loss with retention of the encapsulated Gd atom. All Gd@C_{2n} ions probed by CID grown from Gd@C_{82} after exposure to carbon vapor reveal this fragmentation pattern, confirming that all larger growth clusters are endohedral metallofullerenes.
Supplementary Figure S14 | Purity of C_{60}, C_{70}, C_{76}, C_{78}, and C_{84} starting material samples. a-e, Laser irradiation of fullerene films (made from the fullerene samples used in the growth experiments) deposited on a 6.35 mm diameter quartz target rod in the source at 3 mJ/cm². The purity of the samples is clearly evident, and further shows that the larger clusters are not present until after gas-phase reactions of the fullerene with carbon vapor. Weak signals corresponding to fragmentation of the desorbed fullerene are observed.