Supplementary Figure S1 | Multi-stage HPLC chromatograms for the separation of C$_{68}$Cl$_6$. The regions highlighted by the red shadow correspond to the components collected.
Supplementary Figure S2 | HPLC chromatogram for the purified C_{68}Cl_{6}. The chromatogram was monitored at 330 nm and acquired on an analytical buckyprep column (I.D. 4.6 × 250 mm) eluted by toluene at a flow rate of 1 ml·min^{-1}. 
Supplementary Figure S3 | **Mass spectrum of C\textsubscript{68}Cl\textsubscript{6}**. The spectrum was acquired on a Bruker Esquire HCT mass spectrometer interfaced by an atmospheric pressure chemical ionization (APCI) source at evaporation temperature of 300 °C and dry gas temperature of 250 °C in negative ion mode.
Supplementary Figure S4 | Selected diffraction patterns of the single crystal of C_{60}Cl_{6}. The patterns were acquired on an Oxford CCD diffractometer. The insert at right corner is a photo of the single crystal for the present X-ray diffraction analysis.
Supplementary Figure S5 | Packing (a) and intermolecular short contacts (b) in crystal of $C_{68}\text{Cl}_6$. The Cl–C, π–π and Cl–Cl short contacts are represented as red, gray and green dashed lines, respectively.
Supplementary Figure S6 | The experimental mass spectra of bare fullerenes for Exp. B (plotted in blue) and the simulation (in red and black).
Supplementary Figure S7 | The experimental mass spectra of chlorofullerenes for Exp. B (plotted in blue) and the simulation (in red and black).
Supplementary Figure S8  |  The experimental mass spectra of chloro-PAHs for Exp. B (plotted in blue) and the simulation (in red and black).
Supplementary Figure S9 | The experimental and simulated mass spectra of bare fullerenes in Exp. C. The experimental spectra are plotted in blue, and the simulation in red and black.
Supplementary Figure S10 | The experimental and simulated mass spectra of chlorofullerenes in Exp. C. The experimental spectra are plotted in blue, and the simulation in red and black.
Supplementary Figure S11 | The experimental and simulated mass spectra of chloro-PAHs in Exp. C. The experimental spectra are plotted in blue, and the simulation in red and black.
Supplementary Figure S12 | Transition states for a helium atom to penetrate into the cages. (a), $I_6$-$C_{60}$; (b), hepta-$C_{68}$; (c), hepta-$C_{68}\text{Cl}_6$. The helium, carbon and chlorine are colored in cyan, grey and green, respectively. The heptagon is highlighted in red.
**Supplementary Figure S13** | Mass spectra of $C_{68}Cl_6$ species with natural isotopes.

The black, the hepta-$C_{68}Cl_6$ reactant; The blue, the hepta-$C_{68}Cl_6$ treated in the helium encapsulation experiment; The red, the simulated isotopic pattern of $C_{68}Cl_6$; The green, the simulated isotopic pattern of He@$C_{68}Cl_6$. The horizontal and perpendicular dash lines are plotted for clarifying the comparison of mass-to-charge intensities and values.
Supplementary Figure S14  |  Isodensify surfaces (isovalue $\sim 0.03$) of frontier molecular orbitals. (a), HOMO of hepta-C$_{68}$; (b), LUMO of hepta-C$_{68}$; (c), HOMO of hepta-C$_{68}$Cl$_6$; (d), LUMO of hepta-C$_{68}$Cl$_6$. 
Supplementary Figure S15 | Numeration of the C-C and C-Cl bonds in the hepta-C₆₈Cl₆.
Supplementary Figure S16 | Schematic diagram of equipment for the graphite arc-discharge. $R = 9.7$, $r_a = 3.4$, $r_b = 4.3$, and $r_c = 5.2$ cm.
Supplementary Figure S17  |  The relationship of radial temperatures vs. time in the chamber. Points, experimental data at \( r_c = 5.2 \) cm; purple line, correlated at \( r_c = 5.2 \) cm; blue and green lines, calculated at \( r_a = 3.4 \) cm and \( r_b = 4.3 \) cm.
Supplementary Figure S18  | The relationship of radial temperature against radius in the chamber. Points refer to the experimental data at 300 s: 758 K at \( r_a = 3.4 \) cm, 617 K at \( r_b = 4.3 \) cm, 564 K at \( r_c = 5.2 \) cm. Lines, calculated.
Supplementary Figure S19  |  Effect of the convective stream on the $^{13}$C concentration distribution. Line, $u=0$ m·s$^{-1}$; squares, $u=0.0005$ m·s$^{-1}$; triangles, $u=0.01$ m·s$^{-1}$.
Supplementary Figure S20  |  Effect of the thermal diffusion on the $^{13}$C concentration distribution. Line, $\alpha=0$; squares, $\alpha=0.1$. 
Supplementary Figure S21 | Schematic diagram of the graphite anode rods. The area of 2mm-from-arc in hollow rod (left) can be increased ~45% as compared with solid rod (right).
**Supplementary Table S1.** Summary of crystal data and structure refinement for C_{68}Cl_{6}.

| Property                      | Value                          |
|-------------------------------|--------------------------------|
| Compound                      | C_{68}Cl_{6}                   |
| Radiation                     | Cu Kα, 1.54178Å                |
| Experimental formula          | C_{68}Cl_{6}·C_{0.5}Cl_{1.5}   |
| Formula weight                | 1088.56                        |
| Crystal system                | Monoclinic                     |
| Space group                   | C2/c                           |
| Parameters                    | 687                            |
| a (Å)                         | 16.8460(7)                     |
| b (Å)                         | 12.7586(4)                     |
| c (Å)                         | 35.3151(11)                    |
| β (°)                         | 93.615(3)                      |
| V(Å³)                         | 7575.2(5)                      |
| T(K)                          | 173(2)                         |
| Z, D_{calc} (mg·m⁻³)          | 8, 1.909                       |
| F(000)                        | 4308                           |
| μ(mm⁻¹)                       | 5.953                          |
| Ref. collected/unique/[I > 2σ(I)] | 15082/5431/3370           |
| R_{int}                       | 0.0411                         |
| R₁ = 0.0908                   |                                |
| wR₂ = 0.2209                  |                                |
| R₁ = 0.1279                   |                                |
| wR₂ = 0.2419                  |                                |
| Max./min., Δρ (e·Å⁻³)         | 1.667/-0.504                   |

\[ R₁ = \frac{\sum |F_o| - |F_c| \sqrt{\sum |F_o|}}{\sum |F_o|}, \quad wR₂ = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}^{1/2} \]
**Supplementary Table S2.** Atomic coordinates and equivalent isotropic displacement parameters (Å\(^2\)) for C\(_{68}\)Cl\(_6\).

|   | x       | y       | z       | U(eq)   | Occupancy |
|---|---------|---------|---------|---------|-----------|
| C1 | 0.1758(9) | 0.7739(6) | 0.3744(4) | 0.088(4) | 1         |
| C2 | 0.1046(7) | 0.6821(9) | 0.4574(3) | 0.079(3) | 1         |
| C3 | 0.3085(4) | 0.2658(5) | 0.39049(18) | 0.039(15) | 1         |
| C4 | 0.3548(4) | 0.4216(6) | 0.35683(19) | 0.0399(17) | 1         |
| C5 | 0.2115(5) | 0.2550(6) | 0.45159(19) | 0.0443(18) | 1         |
| C6 | 0.0116(5) | 0.2952(5) | 0.4208(2) | 0.0472(19) | 1         |
| C7 | 0.2399(4) | 0.1940(5) | 0.3890(2) | 0.0408(17) | 1         |
| C8 | 0.2036(4) | 0.1462(5) | 0.3534(2) | 0.0376(16) | 1         |
| C9 | 0.2678(4) | 0.3029(6) | 0.32399(18) | 0.0384(16) | 1         |
| C10 | 0.3311(4) | 0.3152(6) | 0.4248(2) | 0.0417(17) | 1         |
| C11 | 0.3750(6) | 0.5764(8) | 0.3923(2) | 0.063(3) | 1         |
| C12 | 0.0544(7) | 0.6052(7) | 0.3100(3) | 0.071(3) | 1         |
| C13 | 0.0949(4) | 0.4278(6) | 0.28851(18) | 0.0417(17) | 1         |
| C14 | 0.3439(6) | 0.4740(8) | 0.4582(2) | 0.061(2) | 1         |
| C15 | 0.3209(4) | 0.3236(6) | 0.35588(19) | 0.0412(17) | 1         |
| C16 | 0.0742(4) | 0.1693(5) | 0.3813(2) | 0.0382(16) | 1         |
| C17 | -0.0175(5) | 0.2932(7) | 0.3494(2) | 0.053(2) | 1         |
| C18 | 0.0919(5) | 0.2229(6) | 0.31788(19) | 0.0414(17) | 1         |
| C19 | -0.0524(4) | 0.3940(7) | 0.3527(2) | 0.050(2) | 1         |
| C20 | 0.0083(4) | 0.2414(7) | 0.3829(2) | 0.051(2) | 1         |
| C21 | 0.2356(4) | 0.3876(7) | 0.30174(19) | 0.0464(19) | 1         |
| C22 | 0.1649(5) | 0.3575(6) | 0.27972(18) | 0.0421(17) | 1         |
| C23 | 0.2128(7) | 0.6718(8) | 0.3240(3) | 0.071(3) | 1         |
| C24 | 0.2580(5) | 0.4925(7) | 0.3090(2) | 0.054(2) | 1         |
| C25 | 0.1524(5) | 0.2358(6) | 0.2905(2) | 0.0445(17) | 1         |
| C26 | 0.2166(5) | 0.4520(8) | 0.4863(2) | 0.057(2) | 1         |
| C27 | 0.3247(5) | 0.5062(7) | 0.3342(2) | 0.050(2) | 1         |
| C28 | 0.1390(6) | 0.4020(6) | 0.47808(19) | 0.057(2) | 1         |
| C29 | -0.0264(4) | 0.4573(9) | 0.3214(2) | 0.058(2) | 1         |
| C30 | 0.0703(4) | 0.2337(7) | 0.44754(19) | 0.0453(18) | 1         |
| C31 | 0.1172(5) | 0.1655(5) | 0.3505(2) | 0.0419(17) | 1         |
| C32 | 0.1978(6) | 0.5740(7) | 0.3037(2) | 0.057(2) | 1         |
| C33 | 0.1206(7) | 0.5866(8) | 0.4775(2) | 0.069(3) | 1         |
| C34 | 0.2451(8) | 0.7125(8) | 0.4485(3) | 0.075(3) | 1         |
| C35 | 0.1083(5) | 0.1524(6) | 0.4197(2) | 0.0439(18) | 1         |
| C36 | 0.1974(4) | 0.1909(6) | 0.4217(2) | 0.0428(18) | 1         |
| C37 | 0.3371(6) | 0.6008(8) | 0.3536(3) | 0.068(3) | 1         |
| C38 | 0.2641(7) | 0.6283(7) | 0.4720(2) | 0.070(3) | 1         |
| C39 | 0.0239(4) | 0.2866(6) | 0.3185(2) | 0.0443(18) | 1         |
| C40 | 0.0261(5) | 0.3904(7) | 0.2998(2) | 0.0477(19) | 1         |
| C41 | 0.3842(5) | 0.4673(8) | 0.3942(3) | 0.060(2) | 1  |
|-----|-----------|------------|-----------|---------|---|
| C42 | 0.3719(4) | 0.4173(7)  | 0.4261(2) | 0.0478(19) | 1 |
| C43 | -0.0344(6) | 0.6111(10) | 0.3585(3) | 0.080(3) | 1  |
| C44 | 0.2821(4) | 0.3145(6)  | 0.45597(19) | 0.0443(18) | 1 |
| C45 | 0.2803(6) | 0.6842(6)  | 0.3494(2) | 0.057(2) | 1  |
| C46 | 0.2045(7) | 0.5662(7)  | 0.4859(2) | 0.065(3) | 1  |
| C47 | -0.0498(6) | 0.5590(8)  | 0.3893(3) | 0.072(3) | 1  |
| C48 | -0.0565(5) | 0.6345(8)  | 0.4211(3) | 0.067(3) | 1  |
| C49 | -0.0115(6) | 0.5826(8)  | 0.4285(3) | 0.068(3) | 1  |
| C50 | 0.3337(6) | 0.5788(9)  | 0.4571(2) | 0.069(3) | 1  |
| C51 | 0.2294(4) | 0.2025(6)  | 0.31455(19) | 0.0414(17) | 1 |
| C52 | 0.2844(5) | 0.4053(6)  | 0.47518(19) | 0.0480(19) | 1 |
| C53 | 0.1133(5) | 0.5423(7)  | 0.2951(2) | 0.050(2) | 1  |
| C54 | 0.2916(9) | 0.7209(9)  | 0.4172(3) | 0.096(4) | 1  |
| C55 | 0.2649(9) | 0.7419(8)  | 0.3807(3) | 0.088(4) | 1  |
| C56 | 0.1387(4) | 0.2996(5)  | 0.46332(19) | 0.0469(19) | 1 |
| C57 | -0.0160(5) | 0.5604(8)  | 0.3247(2) | 0.059(2) | 1  |
| C58 | -0.0152(5) | 0.3977(6)  | 0.4228(3) | 0.064(2) | 1  |
| C59 | 0.0474(8) | 0.7360(7)  | 0.3983(3) | 0.076(3) | 1  |
| C60 | 0.0799(5) | 0.4853(10) | 0.4716(2) | 0.071(3) | 1  |
| C61 | 0.0733(9) | 0.6959(8)  | 0.3326(3) | 0.086(4) | 1  |
| C62 | 0.1531(8) | 0.7311(7)  | 0.3387(3) | 0.076(3) | 1  |
| C63 | 0.0227(9) | 0.7042(9)  | 0.3622(3) | 0.096(4) | 1  |
| C64 | 0.1335(10) | 0.7748(7) | 0.4043(3) | 0.093(4) | 1  |
| C65 | 0.0103(5) | 0.4832(8)  | 0.4471(2) | 0.070(3) | 1  |
| C66 | 0.0093(9) | 0.6728(10) | 0.4318(3) | 0.100(5) | 1  |
| C67 | 0.1578(10) | 0.7401(8) | 0.4412(3) | 0.096(4) | 1  |
| C68 | 0.18364(12) | 0.37066(16) | 0.22936(4) | 0.0506(5) | 1  |
| C69 | 0.22823(16) | 0.00920(14) | 0.35199(6) | 0.0627(6) | 1  |
| C70 | 0.12653(13) | 0.15246(16) | 0.25081(5) | 0.0570(6) | 1  |
| C71 | 0.29857(14) | 0.12911(18) | 0.28910(5) | 0.0623(6) | 1  |
| C72 | 0.10312(16) | 0.01964(17) | 0.43552(6) | 0.0650(7) | 1  |
| C73 | 0.01864(12) | 0.1745(2) | 0.48511(5) | 0.0643(7) | 1  |
Supplementary Table S3. Anisotropic displacement parameters (Å^2) for C₆₈Cl₆.

|   | U₁₁  | U₁₂  | U₁₃  | U₂₂  | U₂₃  | U₃₃  |
|---|------|------|------|------|------|------|
| C1| 0.155(12) | 0.013(4) | 0.097(9) | 0.006(5) | 0.030(8) | 0.005(5) |
| C2| 0.115(9) | 0.073(7) | 0.049(5) | 0.046(7) | 0.006(6) | -0.035(6) |
| C3| 0.029(3) | 0.035(4) | 0.039(4) | 0.009(3) | 0.006(3) | 0.002(3) |
| C4| 0.032(4) | 0.052(5) | 0.038(4) | -0.011(3) | 0.011(3) | 0.002(3) |
| C5| 0.053(5) | 0.045(4) | 0.035(4) | -0.014(4) | -0.002(3) | 0.016(3) |
| C6| 0.050(4) | 0.044(4) | 0.051(4) | -0.003(4) | 0.026(3) | 0.111(4) |
| C7| 0.053(4) | 0.025(3) | 0.044(4) | 0.010(3) | 0.008(3) | 0.005(3) |
| C8| 0.043(4) | 0.019(3) | 0.050(4) | 0.008(3) | 0.002(3) | -0.008(3) |
| C9| 0.040(4) | 0.051(4) | 0.025(3) | 0.006(3) | 0.010(3) | -0.007(3) |
| C10| 0.039(4) | 0.043(4) | 0.042(4) | -0.004(3) | -0.008(3) | 0.007(3) |
| C11| 0.071(6) | 0.066(6) | 0.051(5) | -0.050(5) | 0.002(4) | 0.002(5) |
| C12| 0.101(8) | 0.049(5) | 0.062(5) | 0.018(5) | -0.007(5) | 0.023(5) |
| C13| 0.040(4) | 0.057(5) | 0.028(3) | 0.001(4) | -0.003(3) | -0.001(3) |
| C14| 0.068(6) | 0.068(6) | 0.044(4) | -0.043(5) | -0.016(4) | 0.004(4) |
| C15| 0.030(4) | 0.058(5) | 0.036(4) | 0.004(3) | 0.012(3) | -0.002(3) |
| C16| 0.031(4) | 0.029(4) | 0.054(4) | -0.010(3) | 0.003(3) | 0.010(3) |
| C17| 0.040(4) | 0.059(5) | 0.059(5) | -0.016(4) | -0.007(4) | 0.002(4) |
| C18| 0.060(5) | 0.032(4) | 0.032(3) | -0.012(3) | -0.004(3) | -0.007(3) |
| C19| 0.023(4) | 0.062(5) | 0.065(5) | 0.010(3) | -0.007(3) | 0.005(4) |
| C20| 0.042(4) | 0.053(5) | 0.058(5) | -0.016(4) | 0.003(3) | 0.015(4) |
| C21| 0.049(4) | 0.062(5) | 0.029(3) | 0.002(4) | 0.011(3) | 0.004(4) |
| C22| 0.056(5) | 0.042(4) | 0.028(3) | 0.008(3) | 0.001(3) | 0.001(3) |
| C23| 0.099(8) | 0.053(6) | 0.062(6) | -0.010(6) | 0.011(5) | 0.036(5) |
| C24| 0.053(5) | 0.076(6) | 0.035(4) | -0.015(4) | 0.011(3) | 0.020(4) |
| C25| 0.054(5) | 0.039(4) | 0.040(4) | 0.007(4) | 0.001(3) | -0.004(3) |
| C26| 0.074(6) | 0.070(6) | 0.028(4) | -0.011(5) | 0.006(4) | 0.003(4) |
| C27| 0.057(5) | 0.061(5) | 0.033(4) | -0.018(4) | 0.009(3) | 0.013(4) |
| C28| 0.084(6) | 0.066(6) | 0.024(4) | -0.021(5) | 0.013(4) | 0.006(4) |
| C29| 0.034(4) | 0.100(8) | 0.040(4) | 0.019(4) | -0.009(3) | 0.014(5) |
| C30| 0.042(4) | 0.060(5) | 0.035(4) | -0.005(4) | 0.009(3) | 0.014(4) |
| C31| 0.062(5) | 0.024(3) | 0.039(4) | -0.001(3) | -0.004(3) | -0.007(3) |
| C32| 0.087(6) | 0.044(5) | 0.042(4) | -0.026(5) | 0.011(4) | 0.012(4) |
| C33| 0.115(9) | 0.056(6) | 0.037(4) | 0.013(6) | 0.021(5) | -0.019(4) |
| C34| 0.120(9) | 0.051(6) | 0.054(6) | -0.013(6) | -0.005(6) | -0.028(5) |
| C35| 0.058(5) | 0.032(4) | 0.043(4) | -0.006(3) | 0.009(3) | 0.016(3) |
| C36| 0.046(4) | 0.040(4) | 0.044(4) | 0.008(3) | 0.015(3) | 0.022(4) |
| C37| 0.072(6) | 0.072(7) | 0.061(5) | -0.042(5) | 0.018(4) | 0.014(5) |
| C38| 0.124(9) | 0.050(5) | 0.036(4) | -0.030(6) | -0.004(5) | -0.018(4) |
| C39| 0.037(4) | 0.043(4) | 0.051(4) | -0.004(3) | -0.018(3) | 0.002(4) |
| C40| 0.048(5) | 0.054(5) | 0.040(4) | 0.014(4) | -0.007(3) | 0.001(4) |
| C41| 0.046(5) | 0.076(6) | 0.058(5) | -0.029(4) | -0.004(4) | 0.000(5) |
|     |       |       |       |       |       |       |
|-----|-------|-------|-------|-------|-------|-------|
| C42 | 0.025(4) | 0.075(6) | 0.043(4) | -0.011(4) | -0.008(3) | 0.000(4) |
| C43 | 0.068(6) | 0.084(8) | 0.089(7) | 0.058(6) | 0.008(5) | 0.021(6) |
| C44 | 0.043(4) | 0.055(5) | 0.033(4) | 0.003(4) | -0.007(3) | 0.014(4) |
| C45 | 0.086(6) | 0.035(4) | 0.054(5) | -0.034(4) | -0.006(4) | 0.021(4) |
| C46 | 0.117(9) | 0.052(5) | 0.028(4) | -0.023(5) | 0.007(4) | -0.011(4) |
| C47 | 0.064(6) | 0.071(7) | 0.083(7) | 0.037(5) | 0.022(5) | -0.002(6) |
| C48 | 0.029(4) | 0.129(10) | 0.054(5) | 0.010(5) | 0.007(3) | 0.026(6) |
| C49 | 0.084(7) | 0.053(6) | 0.061(6) | -0.035(5) | -0.008(5) | -0.004(5) |
| C50 | 0.073(6) | 0.056(6) | 0.079(6) | 0.042(5) | 0.027(5) | 0.004(5) |
| C51 | 0.083(7) | 0.077(7) | 0.046(5) | -0.030(6) | -0.013(4) | -0.019(5) |
| C52 | 0.052(4) | 0.037(4) | 0.035(4) | 0.005(3) | 0.001(3) | -0.009(3) |
| C53 | 0.067(5) | 0.046(5) | 0.030(4) | -0.006(4) | -0.007(3) | 0.008(3) |
| C54 | 0.059(5) | 0.050(5) | 0.042(4) | 0.016(4) | 0.004(4) | -0.015(4) |
| C55 | 0.161(12) | 0.065(7) | 0.059(6) | -0.063(3) | -0.006(7) | 0.000(5) |
| C56 | 0.154(12) | 0.043(5) | 0.069(7) | -0.058(7) | 0.018(7) | -0.002(5) |
| C57 | 0.041(4) | 0.066(5) | 0.034(4) | -0.007(4) | 0.003(3) | 0.020(4) |
| C58 | 0.061(5) | 0.060(6) | 0.057(5) | 0.033(5) | 0.000(4) | 0.012(4) |
| C59 | 0.046(5) | 0.088(7) | 0.060(5) | 0.008(5) | 0.025(4) | 0.012(5) |
| C60 | 0.113(9) | 0.037(5) | 0.081(7) | 0.044(6) | 0.017(6) | 0.002(5) |
| C61 | 0.064(6) | 0.123(10) | 0.029(4) | 0.011(6) | 0.022(4) | -0.006(5) |
| C62 | 0.141(11) | 0.050(6) | 0.066(6) | 0.047(7) | 0.004(7) | 0.017(5) |
| C63 | 0.120(9) | 0.034(5) | 0.072(6) | -0.015(6) | -0.006(6) | 0.018(5) |
| C64 | 0.158(12) | 0.050(6) | 0.080(8) | 0.071(8) | 0.000(7) | 0.003(5) |
| C65 | 0.177(14) | 0.026(5) | 0.073(7) | 0.025(6) | -0.011(8) | -0.016(5) |
| C66 | 0.081(7) | 0.082(7) | 0.053(5) | 0.003(5) | 0.046(5) | -0.014(5) |
| C67 | 0.157(12) | 0.076(8) | 0.071(7) | 0.083(9) | 0.034(7) | -0.006(6) |
| C68 | 0.198(15) | 0.037(5) | 0.054(6) | -0.014(8) | 0.022(8) | -0.016(5) |
| Cl1 | 0.0669(12) | 0.0590(12) | 0.0264(8) | 0.0026(9) | 0.0059(7) | 0.0073(8) |
| Cl2 | 0.1128(18) | 0.0262(9) | 0.0485(11) | 0.0213(10) | -0.0010(11) | -0.0050(8) |
| Cl3 | 0.0775(14) | 0.0529(12) | 0.0399(10) | -0.0012(10) | -0.0022(9) | -0.0140(9) |
| Cl4 | 0.0775(14) | 0.0664(14) | 0.0436(10) | 0.0260(11) | 0.0092(9) | -0.0124(10) |
| Cl5 | 0.0986(17) | 0.0433(11) | 0.0524(12) | -0.0207(11) | 0.0002(11) | 0.0116(9) |
| Cl6 | 0.0596(12) | 0.0912(17) | 0.0431(10) | -0.0248(11) | 0.0127(9) | 0.0192(11) |
Supplementary Table S4. List of bond lengths (Å) for $C_{68}Cl_6$.

| Atoms   | Distance  | Atoms   | Distance  | Atoms   | Distance  |
|---------|-----------|---------|-----------|---------|-----------|
| C1—C65 | 1.309(18) | C13—C22 | 1.529(10) | C30—Cl6 | 1.798(7)  |
| C1—C63 | 1.406(16) | C14—C51 | 1.347(14) | C32—C54 | 1.492(12) |
| C1—C56 | 1.557(18) | C14—C42 | 1.452(13) | C33—C46 | 1.449(14) |
| C2—C68 | 1.322(17) | C14—C53 | 1.485(11) | C33—C61 | 1.471(15) |
| C2—C33 | 1.427(15) | C16—C31 | 1.344(11) | C34—C38 | 1.384(14) |
| C2—C67 | 1.515(18) | C16—C20 | 1.446(11) | C34—C55 | 1.397(17) |
| C3—C10 | 1.396(10) | C16—C35 | 1.456(10) | C34—C68 | 1.518(19) |
| C3—C15 | 1.454(10) | C17—C39 | 1.336(12) | C35—C36 | 1.576(11) |
| C3—C7  | 1.471(10) | C17—C20 | 1.400(12) | C35—C51 | 1.787(7)  |
| C4—C15 | 1.375(11) | C17—C19 | 1.421(12) | C37—C45 | 1.433(14) |
| C4—C27 | 1.417(11) | C18—C39 | 1.406(11) | C38—C46 | 1.391(14) |
| C4—C41 | 1.498(11) | C18—C31 | 1.408(10) | C38—C51 | 1.460(16) |
| C5—C36 | 1.345(11) | C18—C25 | 1.456(11) | C39—C40 | 1.482(11) |
| C5—C44 | 1.412(11) | C19—C48 | 1.364(13) | C41—C42 | 1.321(12) |
| C5—C57 | 1.436(11) | C19—C29 | 1.458(12) | C43—C47 | 1.316(15) |
| C6—C59 | 1.388(5)  | C21—C24 | 1.411(12) | C43—C58 | 1.411(14) |
| C6—C20 | 1.500(12) | C21—C22 | 1.433(11) | C43—C64 | 1.529(19) |
| C6—C30 | 1.540(11) | C22—C25 | 1.615(10) | C44—C53 | 1.343(11) |
| C7—C36 | 1.397(10) | C22—Cl1 | 1.834(7)  | C45—C56 | 1.365(14) |
| C7—C8  | 1.495(10) | C23—C63 | 1.384(16) | C47—C48 | 1.517(16) |
| C8—C31 | 1.473(11) | C23—C45 | 1.412(13) | C47—C50 | 1.518(15) |
| C8—C52 | 1.631(10) | C23—C32 | 1.454(14) | C48—C59 | 1.501(12) |
| C8—Cl2 | 1.798(6)  | C24—C27 | 1.398(12) | C49—C55 | 1.484(18) |
| C9—C15 | 1.418(10) | C24—C32 | 1.457(13) | C49—C51 | 1.497(14) |
| C9—C21 | 1.423(11) | C25—C52 | 1.564(10) | C50—C67 | 1.341(18) |
| C9—C52 | 1.464(11) | C25—Cl3 | 1.792(7)  | C50—C66 | 1.465(14) |
| C10—C44 | 1.418(11) | C26—C53 | 1.369(12) | C52—Cl4 | 1.781(7)  |
| C10—C42 | 1.472(11) | C26—C28 | 1.466(12) | C55—C56 | 1.365(15) |
| C11—C49 | 1.345(14) | C26—C46 | 1.471(14) | C59—C66 | 1.436(12) |
| C11—C41 | 1.402(14) | C27—C37 | 1.397(13) | C60—C64 | 1.379(16) |
| C11—C37 | 1.505(13) | C28—C57 | 1.407(5)  | C60—C67 | 1.479(16) |
| C12—C54 | 1.405(13) | C28—C61 | 1.464(13) | C60—C65 | 1.535(18) |
| C12—C62 | 1.431(16) | C29—C58 | 1.331(14) | C61—C66 | 1.413(5)  |
| C12—C58 | 1.442(14) | C29—C40 | 1.476(12) | C62—C64 | 1.392(17) |
| C13—C40 | 1.338(11) | C30—C57 | 1.506(11) | C62—C63 | 1.420(17) |
| C13—C54 | 1.507(12) | C30—C35 | 1.591(11) | C65—C68 | 1.413(16) |
**Supplementary Table S5.** List of bond angles in C<sub>68</sub>Cl<sub>6</sub>

| Atoms (i, j, k) | Angle (i, j, k) | Atoms (i, j, k) | Angle (i, j, k) | Atoms (i, j, k) | Angle (i, j, k) |
|----------------|----------------|----------------|----------------|----------------|----------------|
| C65—C1—C63    | 126.5(14)      | C45—C23—C32   | 121.1(9)       | C56—C45—C37   | 118.5(9)       |
| C65—C1—C56    | 117.2(12)      | C27—C24—C21   | 115.4(8)       | C23—C45—C37   | 119.3(8)       |
| C63—C1—C56    | 103.4(10)      | C27—C24—C32   | 121.3(8)       | C38—C46—C33   | 122.8(9)       |
| C68—C2—C33    | 125.5(11)      | C21—C24—C32   | 118.5(7)       | C38—C46—C26   | 117.7(10)      |
| C68—C2—C67    | 110.5(11)      | C18—C25—C52   | 101.6(6)       | C33—C46—C26   | 108.2(8)       |
| C33—C2—C67    | 110.8(11)      | C18—C25—C22   | 111.9(6)       | C43—C47—C48   | 118.8(9)       |
| C10—C3—C15    | 117.0(6)       | C52—C25—C22   | 105.9(6)       | C43—C47—C50   | 123.9(11)      |
| C10—C3—C7     | 118.9(6)       | C18—C25—C13   | 107.8(5)       | C48—C47—C50   | 105.6(8)       |
| C15—C3—C7     | 116.1(6)       | C52—C25—C13   | 114.5(5)       | C19—C48—C59   | 123.0(9)       |
| C15—C4—C27    | 123.1(7)       | C22—C25—C13   | 114.5(5)       | C19—C48—C47   | 118.0(8)       |
| C15—C4—C41    | 119.3(7)       | C53—C26—C28   | 120.3(8)       | C59—C48—C47   | 107.0(9)       |
| C27—C4—C41    | 106.7(7)       | C53—C26—C46   | 123.0(8)       | C11—C49—C55   | 124.9(9)       |
| C36—C5—C44    | 121.2(7)       | C28—C26—C46   | 108.0(8)       | C11—C49—C51   | 117.7(9)       |
| C36—C5—C57    | 110.9(6)       | C37—C27—C24   | 120.5(9)       | C55—C49—C51   | 105.7(9)       |
| C44—C5—C57    | 118.9(7)       | C37—C27—C4    | 110.1(7)       | C67—C50—C66   | 126.2(10)      |
| C59—C6—C20    | 119.0(7)       | C24—C27—C4    | 120.5(7)       | C67—C50—C47   | 115.9(10)      |
| C59—C6—C30    | 130.3(8)       | C57—C28—C61   | 129.0(8)       | C66—C50—C47   | 108.5(9)       |
| C20—C6—C30    | 107.5(6)       | C57—C28—C26   | 117.4(8)       | C14—C51—C38   | 121.5(9)       |
| C36—C7—C3     | 115.5(6)       | C61—C28—C26   | 107.7(7)       | C14—C51—C49   | 117.8(9)       |
| C36—C7—C8     | 118.7(7)       | C58—C29—C19   | 121.7(8)       | C38—C51—C49   | 107.5(9)       |
| C3—C7—C8      | 124.3(6)       | C58—C29—C40   | 122.5(8)       | C9—C52—C25    | 103.0(6)       |
| C31—C8—C7     | 109.9(6)       | C19—C29—C40   | 106.8(8)       | C9—C52—C8     | 109.4(5)       |
| C31—C8—C52    | 100.6(6)       | C57—C30—C6    | 112.9(6)       | C25—C52—C8    | 108.6(6)       |
| C7—C8—C52     | 114.3(6)       | C57—C30—C35   | 105.3(6)       | C9—C52—C14    | 106.4(5)       |
| C31—C8—Cl2    | 112.9(5)       | C6—C30—C35    | 102.8(5)       | C25—C52—Cl4   | 114.6(5)       |
| C7—C8—Cl2     | 109.6(5)       | C57—C30—C16   | 110.9(5)       | C8—C52—Cl4    | 114.2(5)       |
| C52—C8—Cl2    | 109.3(5)       | C6—C30—C16    | 110.2(5)       | C44—C53—C26   | 121.5(8)       |
| C15—C9—C21    | 119.8(7)       | C35—C30—C16   | 114.5(5)       | C44—C53—C14   | 107.8(7)       |
| C15—C9—C52    | 126.2(7)       | C16—C31—C18   | 119.5(7)       | C26—C53—C14   | 117.1(8)       |
| C21—C9—C52    | 113.0(6)       | C16—C31—C8    | 122.1(7)       | C12—C54—C32   | 117.1(8)       |
| Bond          | Angle (°) | Bond          | Angle (°) |
|---------------|-----------|---------------|-----------|
| C3—C10—C44   | 122.0(7)  | C18—C31—C8   | 112.9(7)  |
| C3—C10—C42   | 121.9(6)  | C23—C32—C24  | 116.8(8)  |
| C44—C10—C42  | 106.0(7)  | C23—C32—C54  | 117.9(9)  |
| C49—C11—C41  | 123.2(8)  | C24—C32—C54  | 118.7(7)  |
| C3—C10—C42   | 106.0(7)  | C23—C32—C54  | 118.7(7)  |
| C54—C12—C62  | 122.3(10) | C46—C33—C61  | 108.2(8)  |
| C4—C15—C9    | 115.4(7)  | C30—C35—Cl5  | 113.3(5)  |
| C39—C17—C19  | 111.3(8)  | C34—C38—C46  | 120.6(11) |
| C31—C16—C20  | 120.6(7)  | C7—C36—C35   | 120.6(7)  |
| C31—C16—C35  | 123.2(7)  | C27—C37—C45  | 120.9(8)  |
| C20—C16—C35  | 108.4(7)  | C27—C37—C11  | 108.0(8)  |
| C39—C17—C20  | 120.7(8)  | C45—C37—C11  | 119.2(9)  |
| C39—C17—C19  | 111.3(8)  | C34—C38—C46  | 120.6(11) |
| C20—C17—C19  | 117.9(8)  | C34—C38—C51  | 106.2(9)  |
| C39—C18—C31  | 119.5(7)  | C46—C38—C51  | 119.6(9)  |
| C39—C18—C25  | 123.3(7)  | C17—C39—C18  | 121.2(7)  |
| C31—C18—C25  | 114.5(7)  | C17—C39—C40  | 109.7(7)  |
| C48—C19—C17  | 120.7(8)  | C18—C39—C40  | 117.8(7)  |
| C48—C19—C29  | 118.2(9)  | C13—C40—C29  | 120.4(8)  |
| C17—C19—C29  | 107.1(7)  | C13—C40—C39  | 119.9(7)  |
| C17—C20—C16  | 117.7(8)  | C29—C40—C39  | 104.7(7)  |
| C17—C20—C6   | 121.9(8)  | C42—C41—C11  | 119.9(9)  |
| C16—C20—C6   | 109.9(6)  | C42—C41—C4   | 120.1(7)  |
| Bond        | Angle (°)  | Bond        | Angle (°)  | Bond        | Angle (°)  |
|-------------|------------|-------------|------------|-------------|------------|
| C24—C21—C9 | 122.1(7)   | C11—C41—C4 | 108.3(8)   | C1—C65—C60 | 116.4(11)  |
| C24—C21—C22| 123.9(7)   | C41—C42—C14| 120.1(9)   | C68—C65—C60| 104.0(13)  |
| C9—C21—C22 | 111.8(7)   | C41—C42—C10| 119.9(7)   | C61—C66—C59| 125.8(9)   |
| C21—C22—C13| 110.9(6)   | C14—C42—C10| 107.0(6)   | C61—C66—C50| 115.7(9)   |
| C21—C22—C25| 104.2(6)   | C47—C43—C58| 122.3(11)  | C59—C66—C50| 109.4(8)   |
| C13—C22—C25| 113.8(6)   | C47—C43—C64| 118.6(11)  | C50—C67—C60| 121.8(11)  |
| C21—C22—Cl1| 108.3(5)   | C58—C43—C64| 104.9(10)  | C50—C67—C2 | 121.6(10)  |
| C13—C22—Cl1| 109.0(5)   | C53—C44—C5 | 121.2(7)   | C60—C67—C2 | 103.2(13)  |
| C25—C22—Cl1| 110.5(5)   | C53—C44—C10| 112.8(7)   | C2—C68—C65 | 114.3(14)  |
| C63—C23—C45| 106.1(10)  | C5—C44—C10 | 116.5(7)   | C2—C68—C34 | 118.3(10)  |
| C63—C23—C32| 123.1(10)  | C56—C45—C23| 112.8(11)  | C65—C68—C34| 116.8(13)  |
**Supplementary Table S6. Response to the questions raised in the Check CIF Reports**

| Alert level | Question Description | Response |
|-------------|----------------------|----------|
| B           | (1) Ratio of reflections to parameters is < 8 for acentrosymmetric structure | **Response:** The small size of measured crystal and weak diffraction power of light elements (carbon, chlorine, Z<20) lead to the weak diffraction intensity, especially for the peaks at the high diffraction angle, which lower the ratio of sine(theta_max)/wavelength, the ratio of data/parameter and measured diffraction fraction. Although great efforts have been made, we failed to obtain bigger size of the single crystal. The recorded ratios, however, are just a little bit lesser than the required values, for example, by only 0.008 for the ratio of sine(theta_max)/wavelength, 0.09 for the ratio of data/parameter and 0.02 for the measured diffraction fraction. Such a difference is tolerant for the structural identification of C_{68}Cl_{6}.

Proportion of unique data used 1.0000  
Ratio reflections to parameters 7.9054  
Poor Data / Parameter Ratio 7.91  

(2) The value of sine(theta_max)/wavelength is less than 0.575  
Calculated sin(theta_max)/wavelength = 0.5672  

(3) diffrn_measured_fraction_theta_full  
Low 0.94  

| Alert level | Question Description | Response |
|-------------|----------------------|----------|
| B           | (4) Low Bond Precision on C-C Bonds (x 1000) Å 13 | **Response:** The lower precision on C-C bond lengths can be attributed to the small size of measured crystal and disorder phenomena of the C_{68}Cl_{6} crystal. The precision with C-C bond lengths in 0.013 Å (the required precision on C-C bond lengths is less than 0.010 Å), however, does not influence the structural discussion regarding C_{68}Cl_{6} in the manuscript.

Proportion of unique data used 1.0000  
Ratio reflections to parameters 7.9054  
Poor Data / Parameter Ratio 7.91  

(2) The value of sine(theta_max)/wavelength is less than 0.575  
Calculated sin(theta_max)/wavelength = 0.5672  

(3) diffrn_measured_fraction_theta_full  
Low 0.94  

(4) Low Bond Precision on C-C Bonds (x 1000) Å 13
**Supplementary Table S7.** List of the species detected in the toluene extraction of the crude products.

| Chlorofullerene | Retention time (min) | Bare fullerene | Retention time (min) | Chloro-PAH | Retention time (min) |
|-----------------|----------------------|----------------|----------------------|------------|----------------------|
| Formula         |                      | Formula        |                      | Formula    |                      |
| #271 C₅₀Cl₁₀    | 60.6                 | #1812 C₆₀      | 74.4                 | C₆Cl₆      | 8.7                  |
| #1889 C₆₀Cl₈    | 61.2                 | #8149 C₇₀      | 91.4                 | C₇₀Cl₈     | 16.1                 |
| #1913 C₆₈Cl₄    | 73.9                 | #1915 C₇₆      | 108.8                | C₇₆Cl₈     | 24.1                 |
| Hepta-C₆₆Cl₆    | 77.1                 | C₇₈             | 112.6                | C₇₈Cl₆     | 18.6 [1], 29.4 [2]   |
| #9913 C₅₆Cl₁₀   | 60.4                 | C₈₂             | 125.7                | C₈₂Cl₁₀    | 21.7 [1], 30.9 [2], 43.5 [3] |
| #4169 C₆₆Cl₆    | 66.5                 | C₈₄             | 130.5                | C₈₄Cl₁₀    | 41.0 [1], 57.2 [2]   |
| C₆₆Cl₄          | 72.8                 |                |                      |            |                      |

* The number in the brackets represents different isomers for a given formula.

**Supplementary Table S8.** Symmetries, PBE/DNP-predicted relative energies (ΔE, in kcal·mol⁻¹) and HOMO-LUMO gap (E_g, eV) of low-energy C₆₈ isomers.

| Spiral code | Symmetry | N_{pp}^a | ΔE^b | E_g |
|-------------|----------|----------|------|-----|
| 6290        | C₂       | 4        | 0.0  [0.0] | 1.38 |
| 6328        | C₂       | 4        | 2.0  [1.7] | 0.94 |
| hepta-C₆₈   | C₁       | 4        | 2.7  [7.1] | 0.95 |
| 6094        | C₃       | 4        | 8.1  [15.7] | -    |
| 6146        | C₃       | 4        | 9.7  [15.5] | -    |
| 6148        | C₁       | 4        | 10.4 [20.0] | 0.38 |
| 6270        | C₁       | 4        | 11.7 [8.7]  | 1.07 |
| 6198        | C₁       | 4        | 12.4 [9.5]  | 0.41 |
| 6309        | C₁       | 6        | 15.2 [18.4] | 0.85 |
| 6269        | D₂       | 4        | 25.1 [19.5] | 0.68 |

^a N_{pp} (Number of pentagon-pentagon fusions).

^b The PM3-predicted relative energies are given in brackets.

^c The isomer has a triplet ground state.
Supplementary Table S9. PBE/DNP-predicted relative Gibbs free energies (kcal·mol$^{-1}$) and abundances (%) of the three lowest-energy C$_{68}$ isomers at different temperatures.

| Temperature (K) | $^{90}C_{68}$ | $^{92}C_{68}$ | Hepta-C$_{68}$ |
|----------------|----------------|----------------|----------------|
| 0              | 0.0(83.1)      | 2.1(10.0)      | 2.5(6.9)       |
| 500            | 0.0(79.9)      | 2.1(9.4)       | 2.0(10.6)      |
| 1000           | 0.0(73.7)      | 2.2(8.3)       | 1.4(18.0)      |
| 1500           | 0.0(64.2)      | 2.3(6.7)       | 0.8(29.1)      |
| 1900           | 0.0(54.1)      | 2.3(5.3)       | 0.3(40.5)      |
| 2000           | 0.0(51.4)      | 2.3(5.0)       | 0.2(43.6)      |
| 2100           | 0.0(48.6)      | 2.3(4.7)       | 0.0(46.7)      |
| 2200           | 0.0(45.8)      | 2.4(4.3)       | -0.1(49.9)     |
| 2300           | 0.0(42.9)      | 2.4(4.0)       | -0.2(53.1)     |
| 2400           | 0.0(40.1)      | 2.4(3.7)       | -0.3(56.2)     |
| 2500           | 0.0(37.3)      | 2.4(3.4)       | -0.5(59.6)     |
| 3000           | 0.0(24.6)      | 2.5(2.1)       | -1.1(73.3)     |

* Relative abundances of the three C$_{68}$ isomers are given in parentheses.

Supplementary Table S10. The PBE/DNP-computed activation energies (in kcal·mol$^{-1}$), imaginary frequency (in cm$^{-1}$) and the shortest He-C distance ($R_{\text{He-C}}$, in Å) for the transition states of a helium atom to penetrate into the hepta-C$_{68}$, hepta-C$_{68}$Cl$_6$ and $I_h$-C$_{60}$ cages.

|                  | Activation energy | Imaginary | $R_{\text{He-C}}$ |
|------------------|-------------------|-----------|-------------------|
| Hepta-C$_{68}$   | 123.0             | -854      | 1.73              |
| Hepta-C$_{68}$Cl$_6$ | 128.4             | -786      | 1.73              |
| $I_h$-C$_{60}$   | 225.1             | -1112     | 1.58              |

Supplementary Table S11. Bond length (Å) and Wiberg bond order of C-C bonds in the heptagon region of hepta-C$_{68}$Cl$_6$.

| C-C bond | bond length | Expt. | PBE/DNP | B3LYP/6-31G* | Wiberg bond order |
|----------|-------------|-------|---------|--------------|-------------------|
| a        | 1.54        | 1.51  | 1.52    |              | 0.9989            |
| b        | 1.39        | 1.39  | 1.39    |              | 1.4664            |
| c        | 1.44        | 1.48  | 1.49    |              | 1.0990            |
| d        | 1.41        | 1.40  | 1.40    |              | 1.4303            |
| e        | 1.46        | 1.48  | 1.48    |              | 1.1067            |
| f        | 1.41        | 1.39  | 1.39    |              | 1.4755            |
| g        | 1.51        | 1.52  | 1.52    |              | 0.9962            |

* see Supplementary Figure S15 for the labeling of C-C bonds.
**Supplementary Table S12.** PBE/DNP-predicted C-Cl bond lengths (Å) in hepta-C₆₈Cl₆ and the relative energies (in kcal·mol⁻¹) of hepta-C₆₈Cl₅*⁺ isomers derived from hepta-C₆₈Cl₆.

| C-Cl bond | C-Cl bond length | Relative energy of hepta-C₆₈Cl₅⁺ | Relative energy of hepta-C₆₈Cl₅⁻ |
|-----------|------------------|----------------------------------|---------------------------------|
| Expt.     | PBE/DNP          |                                  |                                 |
| I         | 1.80             | 1.81                             | 4.9                             | 8.8                             |
| II        | 1.79             | 1.80                             | 10.8                            | 9.7                             |
| III       | 1.80             | 1.82                             | 5.1                             | 3.6                             |
| IV        | 1.78             | 1.80                             | 12.6                            | 10.8                            |
| V         | 1.79             | 1.79                             | 16.2                            | 12.4                            |
| VI        | 1.83             | 1.83                             | 0.0                             | 0.0                             |

* see Supplementary Figure S15 for the labeling of C-Cl bonds.

**Supplementary Table S13.** Gas pressure and ¹³C percentage in the graphite rod and CCl₄

| Experimental series | CCl₄ pressure (atm) | Helium pressure (atm) | ¹³C content in graphite rod (%) | ¹³C content in CCl₄ (%) |
|---------------------|---------------------|-----------------------|--------------------------------|------------------------|
| Exp. A              | 0.0132              | 0.3816                | 1.1                            | 1.1                    |
| Exp. B              | 0.0211              | 0.3737                | 1.1                            | 99.0                   |
| Exp. C              | 0.0132              | 0.3816                | 21.8                           | 1.1                    |

**Supplementary Table S14.** The measured temperature at rₖ = 5.2 cm during the experimental period of 300 seconds.

| Time (s) | Temperature (K) | Time (s) | Temperature (K) | Time (s) | Temperature (K) |
|----------|-----------------|----------|-----------------|----------|-----------------|
| 0        | 290             | 50       | 429             | 140      | 523             |
| 5        | 319             | 60       | 439             | 150      | 533             |
| 10       | 331             | 70       | 453             | 160      | 540             |
| 15       | 343             | 75       | 473             | 170      | 547             |
| 20       | 356             | 80       | 482             | 180      | 552             |
| 25       | 369             | 85       | 488             | 200      | 557             |
| 30       | 383             | 90       | 499             | 220      | 560             |
| 35       | 393             | 105      | 509             | 240      | 563             |
| 40       | 404             | 120      | 513             | 300      | 564             |
| 45       | 416             | 130      | 517             |          |                 |
Supplementary Methods

Multi-stage separation of C_{68}Cl_6 through HPLC.

The procedure for the purification of C_{68}Cl_6 included three stages of regular HPLC runs and one stage of recyclic separation. All the separations were performed at room temperature using toluene as the eluent. At the first stage, the crude toluene extraction was separated into several components by a pyrenebutyric acid bonded silica column (I.D. 20 × 250 mm) at a flow rate of 10 ml·min⁻¹, and then the component with retention time ranging from 9 to 13 min was collected (Supplementary Figure S1a). Then the collected sample was further isolated using a Buckyprep column (I.D. 10 × 250 mm) at a flow rate of 6 ml·min⁻¹, collecting the component with retention time ranging from 13 to 17 min (Supplementary Figure S1b). The following separation was carried out using a 5PBB column (I.D. 10 × 250 mm) at a flow rate of 4 ml·min⁻¹. The second peak of the chromatography, as shown in Supplementary Figure S1c, containing C_{68}Cl_6 was collected for further purification. The final procedure was also performed on a 5PBB column (I.D. 10 × 250 mm) at a flow rate of 4 ml·min⁻¹ in a recyclic mode. After nine times of recyclic isolation, the purified C_{68}Cl_6 was obtained (Supplementary Figure S1d). To further validate the purity of separated C_{68}Cl_6, it was analyzed by analytic HPLC and mass spectrometry (Supplementary Figures S2 and S3).

Crystallographic information.

The sample of C_{68}Cl_6 is soluble in organic solvents commonly used for fullerene research, such as toluene, carbon disulfide and chloroform. To obtain a single crystal suitable for X-ray diffraction analysis, slow evaporation of solvent from a C_{68}Cl_6 solution was attempted. Amorphous solid of C_{68}Cl_6 was obtained from either carbon disulfide or chloroform solution, but the mixed solvent of carbon disulfide and chloroform (2:1 in volume) is a right solution for the growth of single crystals of C_{68}Cl_6. The crystals of C_{68}Cl_6 we obtained were black with characteristic luster but quite small in size (see the inset in Supplementary Figure S4). A single crystal with three dimensions of 0.20 × 0.12 × 0.10 mm³ was selected for X-ray diffraction analysis.
The diffraction data were collected on an Oxford CCD diffractometer using a graphite-monochromated Cu Kα radiation source \((\lambda = 1.54178 \text{ Å}, V = 40 \text{ KV}, I = 40 \text{ mA})\) with the ω scan mode. The crystal was measured at 173 K controlled by an Oxford Cryosystems nitrogen gas-flow apparatus. A total of 964 diffraction pattern frames were acquired with the exposure time of 30 s per frame and a resolution of 1024×1024 pixels (Supplementary Figure S4). The X-ray diffraction data were calculated and reduced using Oxford CrysAlisPro Gemini Ultra System program. Absorption correction was carried out in multi-scan mode. The reduced X-ray diffraction data including HKL index, intensities and unit cell parameters were analyzed with XPREP program in SHELX-97 package\(^4\). Then the initial structure was obtained by direct methods with SHELXS-97 program\(^4\) and refined by full-matrix least-squares calculations with SHELXL-97 program\(^4\) based on \(F^2\).

The crystal belongs to monoclinic lattice and \(C2/c\) space group with the cell parameters: \(a = 16.8460(7), b = 12.7586(4), c = 35.3151(11), \beta = 93.615(3), V = 7575.2(5), Z = 4\). A total of 15082 reflections were measured and 5431 were independent. Lorentz-polarization and absorption correction were applied. The final \(R\) indices \((F_o > 4(F_o))\) are \(R_1 = 0.0908\) and \(wR_2 = 0.2209\) \((R_1(\text{all data}) = 0.1279\) and \(wR_2(\text{all data}) = 0.2419\) \) (summarized in Supplementary Table S1). The atomic coordinates, equivalent isotropic displacement parameters, anisotropic displacement parameters, bond lengths and bond angles for \(C_{68}Cl_6\) are list in Supplementary Tables S2-S5. CCDC 817336 contains the supplementary crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) as well.

The refined CIF was checked at the web site ‘http://checkcif.iucr.org/’. All the alert questions in the ‘Check CIF Reports’ have been carefully checked to make sure the validity of the reported crystallographic data (CCDC 817336). An explanation table (see Supplementary Table S6) is provided in response to the questions listed as Alert level A/B in the ‘Check CIF Reports’.

Each unit cell in the crystal of \(C_{68}Cl_6\) contains eight \(C_{68}Cl_6\) molecules and six co-crystallized solvent chloroform. The chloroform is disorder between two
orientations with 0.66(2)/0.34(2) occupancies. There are three kinds of intermolecular short contacts, i.e. the Cl-C, π-π and Cl-Cl short contacts, contributing to the packing in crystalline, as shown in Supplementary Figure S5.

**HPLC-MS analysis of the products from the $^{13}$C-labeled experiments and simulation of the $^{13}$C-riched mass spectra.**

The products of $^{13}$C-labeled experiments were extracted by toluene in ultrasonic bath. Then the extraction was analyzed by HPLC-MS using a Discovery C18 column (4.6 I.D. × 250 mm) of SUPELCO eluted by a gradient methanol-ethanol-cyclohexane. The mass spectra were acquired on a Bruker mass spectrometer interfaced by APCI at evaporation temperature of 300 °C and dry gas temperature of 250 °C in negative ion mode. The species detected in the crude products are listed in Supplementary Table S7. We failed to detect any more species by the HPLC-MS, likely due to their relatively low abundance or poor solubility in toluene solvent.

The mass spectrum of each individual component in the products was recorded during the HPLC-MS analysis. The $^{13}$C content was estimated based on the experimental isotopic distribution pattern in the corresponding mass spectrum of each product by the software Isopro, which was designed for computational simulation of isotopic distribution based on ref 49. The simulated isotopic patterns were generated by the same software. The detailed experimental and simulated mass spectra of the detected species, sorted by bare fullerenes, chlorofullerenes and chloro-PAHs, are shown in Supplementary Figures. S6-S11.
Theoretical computations on stability and temperature-dependent abundance of hepta-C\textsubscript{68} relative to its isomers without heptagon.

To evaluate the stability of pristine hepta-C\textsubscript{68} relative to its classical isomers without heptagon, the time-saving semiempirical PM3 method\textsuperscript{50} implemented in Gaussian09\textsuperscript{51} was used to optimize hepta-C\textsubscript{68} together with all possible 6332 classical isomers of C\textsubscript{68}. Supplementary Table S8 lists the PM3-predicted relative energies of ten lowest-energy isomers of C\textsubscript{68}. Among them, the hepta-C\textsubscript{68} is the third one, being 7.1 kcal\cdot mol\textsuperscript{-1} higher in energy than the most stable \textsuperscript{6290}C\textsubscript{68}. More reliable first-principle density functional theory (DFT) calculations were performed to re-optimize the structures of these ten C\textsubscript{68} isomers by using the Perdew-Burke-Ernzerhof (PBE)\textsuperscript{52} functional with all-electron double numerical plus polarization (DNP) basis set as implemented in Dmol\textsuperscript{3,53,54}. At the PBE/DNP theoretical level, the three lowest-energy isomers, i.e. \textsuperscript{6290}C\textsubscript{68}, \textsuperscript{6328}C\textsubscript{68} and hepta-C\textsubscript{68}, are quite close in energy (i.e., spanning within 2.7 kcal\cdot mol\textsuperscript{-1}), while other isomers are, at least, 5.4 kcal\cdot mol\textsuperscript{-1} higher (Supplementary Table S8). Thus, the DFT calculations suggest that the hepta-C\textsubscript{68} cage might be as attainable as the two non-heptagon fullerene isomers (\textsuperscript{6290}C\textsubscript{68} and \textsuperscript{6328}C\textsubscript{68}) in the carbon arc process.

Fullerenes are formed in the high-temperature area around the arc center as alluded in main text. Note that at the PBE/DNP theoretical level the entropy of hepta-C\textsubscript{68} with a heptagon ring is 1.051 and 1.085 cal\cdot mol\textsuperscript{-1}\cdot K\textsuperscript{-1} higher than that of \textsuperscript{6290}C\textsubscript{68} and \textsuperscript{6328}C\textsubscript{68} at room temperature, respectively. Since these three lowest-energy C\textsubscript{68} isomers (\textsuperscript{6290}C\textsubscript{68}, \textsuperscript{6328}C\textsubscript{68} and hepta-C\textsubscript{68}) have very small energy differences (\(\Delta E < 3\) kcal\cdot mol\textsuperscript{-1}, Supplementary Table S8), it is expected that at high temperatures the entropy factor play a decisive role in their relative free energies\textsuperscript{55} and, consequently, alter their relative concentrations in the carbon arc chamber. Supplementary Table S9 lists the PBE/DNP-computed relative Gibbs free energies of the three C\textsubscript{68} isomers as well as their relative concentrations at different temperatures ranging from 0 to 3000 K. Indeed, upon elevation of temperature, the Gibbs free energy of hepta-C\textsubscript{68} relative to \textsuperscript{6290}C\textsubscript{68} gradually decreases and eventually turns to be negative at temperature higher than 2100 K. Accordingly, the relative concentration/abundance of hepta-C\textsubscript{68} (Supplementary Table S9) increases upon temperature elevation and becomes even
higher than the classical fullerene isomers \( ^{6290}\text{C}_{68} \) and \( ^{6328}\text{C}_{68} \) in the temperature region \( T > 2100 \text{ K} \), likely accounting for the isolatable abundance of hepta-C\(_{68}\), which has been stabilized as hepta-C\(_{68}\)Cl\(_6\), in the chlorine-involving arc-discharge conditions.

**DFT computation of the activation energies for encapsulating a helium atom into hepta-C\(_{68}\), hepta-C\(_{68}\)Cl\(_6\) and \( \text{I}_h\)-C\(_{60}\) cages.**

An obvious advantage of a heptagon-containing fullerene is that the penetration of a small atom such as He or H through its heptagon ring into the fullerene cage is much easier than through a hexagon ring of a classical fullerene without heptagon. The transition states (TS) for helium atom to penetrate through a hexagon of \( \text{I}_h\)-C\(_{60}\) and through the heptagon of hepta-C\(_{68}\)/hepta-C\(_{68}\)Cl\(_6\) (Supplementary Figure S12) were optimized at the PBE/DNP theoretical level. Supplementary Table S10 lists the predicted activation energies. For \( \text{I}_h\)-C\(_{60}\), the PBE/DNP-computed activation barrier is 225.1 kcal\( \cdot \)mol\(^{-1}\), in accordance with the previous predictions.\(^{56,57}\) For hepta-C\(_{68}\) and hepta-C\(_{68}\)Cl\(_6\), the activation energies are respectively reduced to 123.0 kcal\( \cdot \)mol\(^{-1}\) and 128.4 kcal\( \cdot \)mol\(^{-1}\), by 100 kcal\( \cdot \)mol\(^{-1}\) lower than that of \( \text{I}_h\)-C\(_{60}\). The shortest He-C distance in the transition state of penetration is 1.73 \( \text{Å} \) for the cases of hepta-C\(_{68}\) and hepta-C\(_{68}\)Cl\(_6\) and 1.58 \( \text{Å} \) for the case of \( \text{I}_h\)-C\(_{60}\), implying much smaller steric repulsion exerted to helium by the heptagon of hepta-C\(_{68}\) cage than the hexagon of \( \text{I}_h\)-C\(_{60}\).

Suggested by the theoretical calculations, we attempted to encapsulate He atom into C\(_{68}\)Cl\(_6\) cage by high pressure. About 0.3 mg C\(_{68}\)Cl\(_6\) powder with natural isotopes was added into a 2 ml glass bottle. The bottle was put into a high pressure vessel reactor (50 ml) and then the vessel was sealed. Replacing air by He gas, the vessel was pressurized up to 650 atm by a motor driven plunger pump (Superpressure, Newport Scientific, Inc.) with He atmosphere and heated to 70 \( ^\circ\text{C} \). The vessel was maintained at 650 atm and 70 \( ^\circ\text{C} \) for 4 h. The crude products of C\(_{68}\)Cl\(_6\) species were dissolved in toluene and analyzed by a Bruker HCT mass spectrometer interfaced by an APCI source.

Shown in Supplementary Figure S13 are the experimentally recorded and theoretically simulated mass spectra of the reactant/product of C\(_{68}\)Cl\(_6\) species. The MS isotopic distribution pattern of C\(_{68}\)Cl\(_6\) reactant (black) matches well with the simulated
one (red). Deformed pattern (blue) with extra abundances at the mass-to-charge (m/z) peaks larger than 1029.9, however, are shown for the C$_{68}$Cl$_6$ species after treatment with 650 atm helium. The extra intensities of the m/z peak are very likely attributed to the addition of small quantities of He@C$_{68}$Cl$_6$ produced in the high pressure helium encapsulation experiment. As shown in Supplementary Figure S13, the experimentally acquired MS of the crude products (blue) from the helium encapsulation experiment is approximately a combination of the MS of C$_{68}$Cl$_6$ (black) and He@C$_{68}$Cl$_6$ (green), rather than the pure C$_{68}$Cl$_6$. Note that, theoretically, the MS pattern of He@C$_{68}$Cl$_6$ (green) is completely merged into that of C$_{68}$Cl$_6$ with simply 4 m/z units more.

Accordingly, formation of He@C$_{68}$Cl$_6$ in the pressure of 650 atm and the temperature of 70 °C was supported by the mass spectrometric evidence. These reaction conditions are considerably milder than those for He@C$_{60}$ formation. The chief method to encapsulate helium into C$_{60}$ fullerene (with ~1% yield) is to heat fullerene in the presence of the gas at 650 °C and 3000 atm.$^{58}$ Such a difference in reaction conditions is in accordance with the prediction that the activation energy for helium encapsulated into hepta-C$_{68}$Cl$_6$ is lower than into a regular hexagonal/pentagonal fullerene such as C$_{60}$.

**Theoretical computations on chemical reactivity of hepta-C$_{68}$ and hepta-C$_{68}$Cl$_6$.**

The chemical reactivity of fullerenes is mainly determined by the structure of surface carbon rings.$^{59}$ For example, the fused pentagon unit was considered more active than the hexagon-hexagon-hexagon unit.$^{32,60}$ Furthermore, the chemical reactivity of a molecule is generally related its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Supplementary Figure S14 depicts the HOMOs and LUMOs of pristine hepta-C$_{68}$ and hepta-C$_{68}$Cl$_6$ from PBE/DNP calculations, respectively. The HOMO of hepta-C$_{68}$ is predominantly distributed over the pentagon-pentagon fusions, indicating these sites are active for further addition reactions, e.g., chlorination to form the isolated hepta-C$_{68}$Cl$_6$. For hepta-C$_{68}$Cl$_6$, its HOMO has remarkable contribution from the p$_\pi$-orbitals of the ring atoms of heptagon, while its LUMO is also p$_\pi$-like and distributed widely over the unsaturated C$_{62}$ network.
Accordingly, the heptagon (except the sp³-hybridized C(Cl) atom) in hepta-C₆₈Cl₆ is nucleophilic and likely reactive upon electrophilic attack by electrophiles.

To further understand the reactivity pertaining to the heptagon region of hepta-C₆₈Cl₆ (Supplementary Figure S15), the C-C bond lengths from PBE/DNP and B3LYP/6-31G* calculations are listed in Supplementary Table S11, together with experimental data. In addition, Natural Bond Orbital (NBO 3.1) analysis on the B3LYP/6-31G*-computed Kohn-Sham wavefunctions of hepta-C₆₈Cl₆ was performed to obtain the Wiberg bond orders of these C-C bonds (Supplementary Table S11). The a, c, e, g bonds are obviously C-C single bonds with much longer bond lengths and bond orders around 1.0, the b, d and f bonds with shorter bond lengths and bond orders around 1.46 are approximately C=C double bonds, indicating the heptagonal ring of hepta-C₆₈Cl₆ is cycloheptatriene-like. Conceivably, electrophilic additions or ring-opening reactions should preferentially occur at the b, d and f bonds.

To explore the reactivity of the six C-Cl bonds in hepta-C₆₈Cl₆ to substitution reactions, the relative energies of hepta-C₆₈Cl₅⁺/₀ isomers resulted from heterolytic/homolytic cleavage of a C-Cl bond of hepta-C₆₈Cl₆ were computed at the PBE/DNP level of theory. Supplementary Table S12 lists the predicted relative energies of hepta-C₆₈Cl₅⁺/₀ isomers and the C-Cl bond lengths of hepta-C₆₈Cl₆.

It is expected that the longer is the C-Cl bond, the weaker is the C-Cl bond, and the more stable is the corresponding hepta-C₆₈Cl₅⁺/₀ isomer obtained by heterolytic/homolytic cleavage of the C-Cl bond. As shown in Supplementary Table S12, the C-Cl bond length follows the order: VI > I = III > V > II > IV, the corresponding hepta-C₆₈Cl₅⁺ isomer is in the order of stability: VI > I > III > II > IV > V. Among them, the C-Cl(VI) bond located at a hexagon-hexagon-pentagon vertex is the longest, the corresponding hepta-C₆₈Cl₅⁺/₀ isomer VI is the most stable. Accordingly, the C-Cl(VI) bond is the most reactive towards nucleophilic substitution.

In general, those C-Cl bonds at pentagon-pentagon fusion sites are generally stronger than those at hexagon-hexagon-pentagon vertexes. However, it should be noted that the C-Cl(I) bond at the heptagon-pentagon-pentagon vertex appears to be more reactive than the C-Cl(III) bond in nucleophilic substitution, hepta-C₆₈Cl₅⁺(I) is more...
stable than hepta-C$_{68}$Cl$_5^+$ (III) by taking advantage of the local aromaticity of its 6-electron $\pi$-conjugated C$_7^+$ tropylium-like ring.

**Simulation on $^{13}$C concentration and temperature distributions in the reactor.**

$^{13}$C-Labeled experiments. Supplementary Figure S16 shows the schematic diagram of the experimental equipment for the $^{13}$C-labeled experiments, in which a spherical glass chamber was equipped with two graphite electrodes: a block cathode (130 mm diameter, 15 mm length) and a rod anode (6 mm diameter, 150 mm length). The glass chamber was evacuated to a pressure of $10^{-2}$ torr, and then fed with CCl$_4$ vapor and helium. Listed in Supplementary Table S13 are the composition of the two gases (He and CCl$_4$), and $^{13}$C content in the graphite rod and CCl$_4$ for the $^{13}$C-labeled synthetic experiments (Expts. A, B and C). The arc current was set at 60 A, and the voltage varied from 28 to 38 V. The graphite consumption rate $r_R$ was $1.05 \times 10^{-4}$ mol·s$^{-1}$. The temperatures at the radius of $r_a=3.4$, $r_b=4.3$, and $r_c=5.2$ cm were monitored by thermocouples (Supplementary Figure S16).

**Mass conservation equation.** Fick’s second law of diffusion in a spherical coordinate is conveniently used for the mass conservation in the chamber for arc-discharge.$^{49}$

$$\frac{\partial c}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D \frac{\partial c}{\partial r} \right) \quad (r \neq 0) \tag{S1}$$

with the initial and boundary conditions (I.C. and B.C.)

I.C.: $c = 0, t = 0 \quad (0 < r \leq R)$

B.C.1: $c = r_R/t V_t \quad (r = 0^+)$ \tag{S2}

B.C.2: $c = 0 \quad (r = R)$

where $c$ is the concentration of carbon produced from graphite, $V_t$ is the volume of the spherical chamber, $r$ is the distance from the arc center. The temperature dependent diffusion coefficient $D$ (ref. 67) for carbon in helium is calculated with Eq.(S3), with an additional term exp(ac) accounting for the concentration dependence ($a$ is an undetermined parameter).
\[
D = \frac{0.0002745}{P} \left( \frac{T}{\sqrt{T_c1T_c2}} \right)^{1.823} (P_1/P_2)^{1/3} (T_c1T_c2)^{5/12} (1/M_1 + 1/M_2)^{1/2} \exp(ac) \quad (S3)
\]

where subscriptions 1 and 2 represent carbon and helium respectively, subscription \( c \) denotes critical point, \( P \) is the pressure, \( M \) is the molecular weight (the critical temperature and pressure of carbon are from ref. 68). The percentage content of \( ^{13}\text{C} \) can then be calculated with

\[
^{13}\text{C}\% = \left[ c \times ^{13}\text{C}\% \text{ in graphite rod} + c_{\text{Cl}} \times ^{13}\text{C}\% \text{ in } \text{CCl}_4 \right] / (c + c_{\text{Cl}}) \quad (S4)
\]

or

\[
^{13}\text{C}\% = \left[ c_{13} + c_{\text{Cl}} \times ^{13}\text{C}\% \text{ in } \text{CCl}_4 \right] / (c + c_{\text{Cl}}) \quad (S5)
\]

where \( c_{\text{Cl}} \), the concentration of \( \text{CCl}_4 \), is calculated by the ideal gas equation of state at different temperatures obtained from the energy conservation equation. \( c_{13} \), the concentration of \( ^{13}\text{C} \) in the produced carbon, is calculated from Eqs.\((S1)-(S3)\) with \( c_{13} \) instead of \( c \) and B.C.1: \( c_{13} = r_{Rt}/V_t \times ^{13}\text{C}\% \text{ in graphite rod} \ (r = 0+) \). Eq.\((S4)\) indicates that \( ^{13}\text{C} \) diffuses out of the arc-discharge center following the bulk carbon, while Eq.\((S5)\) represents that \( ^{13}\text{C} \) diffuses out of the center independently. Consequently, the average percentage content of \( ^{13}\text{C} \) is calculated with

\[
^{13}\text{C}\% = 0.9 \times ^{13}\text{C}\% \text{ from Eq.}(S4) + 0.1 \times ^{13}\text{C}\% \text{ from Eq.}(S5) \quad (S6)
\]

**Energy conservation equation.** By considering the heat conduction of helium as the major component of the chamber atmosphere and the heat radiation due to \( \text{CCl}_4 \) in the atmosphere, the energy conservation equation can be expressed as

\[
\rho c_p \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 (k \frac{\partial T}{\partial r}) + \sigma (T_r^4 - T^4) \right] \quad (r \neq 0) \quad (S7)
\]

with the I.C. and B.C.

I.C.: \( T = T_r, \ t = 0 \ (0 < r \leq R) \quad (S8) \)

B.C.1: \( T = T_{\text{max}} - T_{\text{max}} \exp[ -b(t + t_0)] \ (r = 0+) \)

B.C.2: \( T = T_r \ (r = R) \)

where \( T \) is the temperature, \( T_r \) is the room temperature (293 K). The thermal conductivity of helium \( k = (17.201 + 6.704 \times 1.0^{-2}T - 1.25 \times 1.0^{-6} T^2) \times 10^{-5} \) cal·m\(^{-1}\)·K\(^{-1}\)·s\(^{-1}\) (ref. 69). Helium’s density \( \rho = 0.176 \text{ Kg} \cdot \text{m}^{-3} \). Helium’s thermal capacity
\( c_p = 20.79 \text{ J mol}^{-1} \text{ K}^{-1} \) (ref. 70). \( \sigma = 5.669 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \). The B.C.1 of Eq.(S8) is an empirical formula containing parameters \( b \) and \( t_0 \). \( T_{\text{max}} \) is a steady-state temperature at the center of the container determined by the energy balance.

\[
 r_R \ c_{\text{pg}} (T_{\text{max}} - T_i) = VI - r_l h - \sigma (0.003^2 \pi + 0.006 \pi L_c) (T_{\text{max}}^4 - T_i^4)
\]

(S9)

In Eq.(S9), \( V = 33 \text{ V (an average)}, I = 60 \text{ A}, \) the sublimation heat of graphite \( h = 735.8 \times 10^3 \text{ J mol}^{-1} \) (ref. 71). Graphite’s thermal capacity \( c_{\text{pg}} = 6.23 + 0.0161T \text{ J mol}^{-1} \text{ K}^{-1} \) (ref. 71). Eq.(S9) reveals that only part of the rod graphite anode takes part in the arc-discharge with a length of \( L_c \).

**Modeling results and experimental data.** Eqs.(S1) and (S7) are coupled partial differential equations, they can be numerically solved by discretization to algebraic equations with the Crank-Nicholson scheme. The parameters in Eqs.(S8) and (S9), namely, \( b (= 0.02 \text{ s}^{-1}) \), \( t_0 (= 25 \text{ s}) \) and \( L_c = 0.4 \text{ cm} \) were correlated from the experimentally measured temperatures at \( r_c = 5.2 \text{ cm} \). From the correlation, \( b \) and \( t_0 \) behavior sensitive to the temperature profile, while \( L_c \) is decisive to the steady state temperature (564 K) at \( r_c = 5.2 \text{ cm} \). As shown in Supplementary Figure S17, the correlations and the experimental data (Supplementary Table S14) are in good agreement, indicating the rationalization of the model. Supplementary Figure S18 shows the calculated temperature profiles at different times. The calculated data are in good agreement with the three experimental points, further supporting the validation of the model. The measured temperature are: \( T_a = 758 \text{ K at } r_a = 3.4 \text{ cm}, T_b = 617 \text{ K at } r_b = 4.3 \text{ cm}, T_c = 564 \text{ K at } r_c = 5.2 \text{ cm} \).

On the other hand, part of the produced carbon from the arc-discharge will lose its activity by condensation following the decrease of temperature along the radius direction inside the spherical glass container. Then a factor \( \beta \) is empirically introduced which represents the ratio of active carbon concentration to the overall carbon concentration

\[
 \beta = 1 \quad (T \geq T_\beta) ; \quad \beta = P^\ast(T) / P^\ast(T_\beta) \quad (T < T_\beta)
\]

(S10)

where \( P^\ast(T) \) is the carbon vapor pressure at \( T \) (ref. 70), \( T_\beta \) could be adjustable. This \( T_\beta \) value suggests that the carbon at relative low temperature may not totally lose its
activity probably due to the postponed condensation. The calculated $^{13}$C percentages vs. radius in chamber are shown in Fig. 4 of the manuscript. Conformity of the reaction area with the obtained $^{13}$C content of fullerenes and chlorinated PAHs in both Exp. B and Exp. C validates the model of the mass conservation equation.

It is worthy to note that the pressure diffusion, the convective stream and the thermal diffusion (the Soret effect) are negligible in the proposed models, considering the following reasons:

(1) If the pressure diffusion was considered, a term of pressure (i.e. the pressure of the investigated system, see ref. 69) gradient should be added into the mass conservation equation. As shown in Supplementary Table S13, the helium pressure is about 40000 Pa, while the carbon vapor pressure is very low [e.g., about $1.75 \times 10^{-11}$ Pa at 1004 K and $r = 1.46$ cm (ref. 71)]. So it is reasonable to assume the insignificance of bulk flow in the system, indicating the pressure of the system is almost constant. That is, the pressure gradient is approximately zero, and the pressure diffusion can be neglected.

(2) If the convective stream was considered, the mass conservation equation and energy conservation equation, respectively, were changed into:

$$\frac{\partial c}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D \frac{\partial c}{\partial r} \right) - u \frac{\partial c}{\partial r}$$

$$\rho_c c_p \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 (k \frac{\partial T}{\partial r}) + \sigma(T^4 - T^4) \right] - u \rho c_p \frac{\partial T}{\partial r}$$

(S11)

The solution of these new governing equations shows that the concentration profile at $u = 0.0005$ m·s$^{-1}$ is almost overlapped with that at $u = 0$ m·s$^{-1}$ (see Supplementary Figure S19) (the average relative deviation of all the 41 points in Supplementary Figure S19 is 0.0147%, the maximum relative deviation is 0.0671%), and at $u = 0.01$ m·s$^{-1}$ the profile slightly changes (the average relative deviation of all the 41 points in Supplementary Figure S19 is 0.4%, the maximum relative deviation is 2.6%). For the arc-discharge experiment, the time of reaching steady state (constant concentration or constant temperature) is larger than 3 min (Supplementary Figure S17). So, the
estimated velocity $u$ should be slower than 0.0005 m·s$^{-1}$, indicating the convective stream can be neglected (with maximum relative derivation less than 0.0671%).

(3) The flux regarding both ordinary (concentration) diffusion and thermal diffusion can be expressed as (assume the gas phase mainly contains helium since the vapor pressure of carbon is very low):

$$J = -\frac{Ddc}{dr} - (Dc\alpha/T)\frac{dT}{dr} \quad (S12)$$

Where $\alpha$ is the thermal diffusion factor. At low pressure, the experimental $\alpha$ values of binary gas mixtures are in the order of 0.1 or smaller$^{72}$. When $J = -\frac{Ddc}{dr} - (Dc\alpha/T)\frac{dT}{dr}$ is used instead of $J = -\frac{Ddc}{dr}$ in the mass conservation equation, Supplementary Figure S20 shows that the thermal diffusion with $\alpha = 0.1$ does not have obvious effect on the final results (the average relative deviation of the 41 points shown in Supplementary Figure S20 is 0.13 %, and the maximum relative deviation is 0.70%).

**Improvement of fullerenes yields by increasing the area for fullerenes growth.**

As discussed in this contribution, the $^{13}$C-labeled experiments and mass/energy conservation equation simulations suggest that fullerenes grow from carbon atom or small carbon clusters in a bottom-up fashion around the high temperature zone of 2-3 mm from the arc center. According to this suggestion, fullerenes yields could be improved if the area of 2-3 mm from arc was increased under the optimal reaction conditions. Considering the center of the arc-discharge is on the top of anode rod, we designed an arc-discharge experiment in which the anode rod was dug as a hollow rod with an inner diameter of ~4 mm. As shown in Supplementary Figure S21, this hollow rod allows the area of 2mm-from-arc in the arc-discharge reaction increased up to ~45% in relative to the solid rod. Of interest is that yields of fullerenes ($I_{h-C_{60}}$, $D_{sh-C_{70}}$ and $^{8109}_{C_{60}}Cl_8$) were indeed increased up to double of the original yields under otherwise the same reaction conditions (the same with the arc-discharge conditions of $^{13}$C-labeled experiments). This experimental evidence supports the simulation about fullerenes growth in the area close to the arc center.
Supplementary References

48. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **A64**, 112-122 (2008).

49. Yergey, J.A. A general approach to calculating isotopic distributions for mass spectrometry. *Int. J. Mass Spectrom. Ion Phys.* **52**, 337-349 (1983).

50. Stewart, J.J.P. Optimization of parameters for semi-empirical methods I. Method. *J. Comp. Chem.* **10**, 209-220 (1989).

51. Gaussian 09, Revision A.02, Frisch, M.J. *et al.* Gaussian, Inc., Wallingford, CT, 2009.

52. Perdew, J.P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865-3868 (1996).

53. Delley, B. An all-electron numerical method for solving the local density functional for polyatomic molecules. *J. Chem. Phys.* **92**, 508-517 (1990).

54. Delley, B. From molecules to solids with the DMol³ approach. *J. Chem. Phys.* **113**, 7756-7764 (2000).

55. Slanina, Z. Equilibrium isomeric mixtures potential energy hypersurfaces as the origin of the overall thermodynamics and kinetics. *Int. Rev. Phys. Chem.* **6**, 251-267 (1987).

56. Mowrey, R.C., Ross, M.M. & Callahan, J.H. Molecular dynamics simulations and experimental studies of the formation of endohedral complexes of buckminsterfullerene. *J. Phys. Chem.* **96**, 4755-4761 (1992).

57. Patchkovskii, S. & Thiel, W. How does helium get into buckminsterfullerene? *J. Am. Chem. Soc.* **118**, 7164-7172 (1996).

58. Saunders, M., Jiménez-Vázquez, H.A., Cross, R.J., Mroczkowski, S., Gross, M.L., Giblin, D.E., & Poreda, Incorporation of helium, neon, argon, krypton, and xenon into fullerenes using high pressure. *R.J. J. Am. Chem. Soc.* **116**, 2193-2194 (1994).
59. Hirsch, A. & Brettreich, M. Fullerenes: Chemistry and Reactions. (Wiley-VCH Verlag GmbH & Co. KGaA, London 2005).

60. Simeonov, K.S., Amsharov, K.Y. & Jansen, M. C\textsubscript{80}Cl\textsubscript{12}: a chlorine derivative of the chiral \emph{D\textsubscript{2}}-C\textsubscript{80} isomer - empirical rationale of halogen-atom addition pattern. \textit{Chem. Eur. J.} 15, 1812-1815 (2009).

61. Becke, A.D. Density-functional thermochemistry. III. The role of exact exchange. \textit{J. Chem. Phys.} 98, 5648-5652 (1993).

62. Lee, C., Yang, W. & Parr, R.G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. \textit{Phys. Rev. B: Condens. Matter} 37, 785-789 (1988).

63. NBO Version 3.1, Glendening E. D., Reed A. E., Carpenter J. E., Weinhold F.

64. Weinhold, F. & Landis, C.R. Natural bond orbitals and extensions of localized bonding concepts. \textit{Chem. Educ. Res. Prac. Eur.} 2, 91-104 (2001).

65. Weinhold, F. & Landis, C.R. Valency and bonding. A natural bond orbital donor-acceptor perspective. (Cambridge University Press, Cambridge, UK and New York, 2005).

66. Pauling, L., Brockway, L.O. & Beach, J.Y. The dependence of interatomic distance on single bond-double bond resonance. \textit{J. Am. Chem. Soc.} 57, 2705-2709 (1935).

67. Bird, R.B., Stewart, W.E. & Lightfoot, E.N. Transport Phenomena. (John Wiley & Sons, 1960).

68. Bundy, F.P., Basset, W.A., Weathers, M.S., Hemley, R.J., Mao, H.K. & Goncharov, A.F. The pressure-temperature phase and transformation diagram for carbon, updated through 1994 \textit{Carbon} 34, 141-153 (1996).

69. Saxena, V.K. & Saxena, S.C. Measurement of the thermal conductivity of helium using a hot-wire type of thermal diffusion column. \textit{Brit. J. Appl. Phys.} 1, 1341-1351 (1968).

70. Dean, J.A. Lange's Handbook of Chemistry, 15th Ed. (McGraw-Hill New York, 1999).
71. Marshall, A.L. & Norton, F.J. Carbon vapor pressure and heat of vaporization. *J. Am. Chem. Soc.* 72, 2166-2171 (1950).

72. Kempers L.J.T.M. A thermodynamic theory of the Soret effect in a multicomponent liquid. *J. Chem. Phys.* 90, 6541-6548 (1989).