Supporting Information

$C_{72}Cl_4$: A Pristine Fullerene with Favorable Pentagon-Adjacent Structure

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1. Multi-stage separation of $C_{72}Cl_4$ through HPLC.

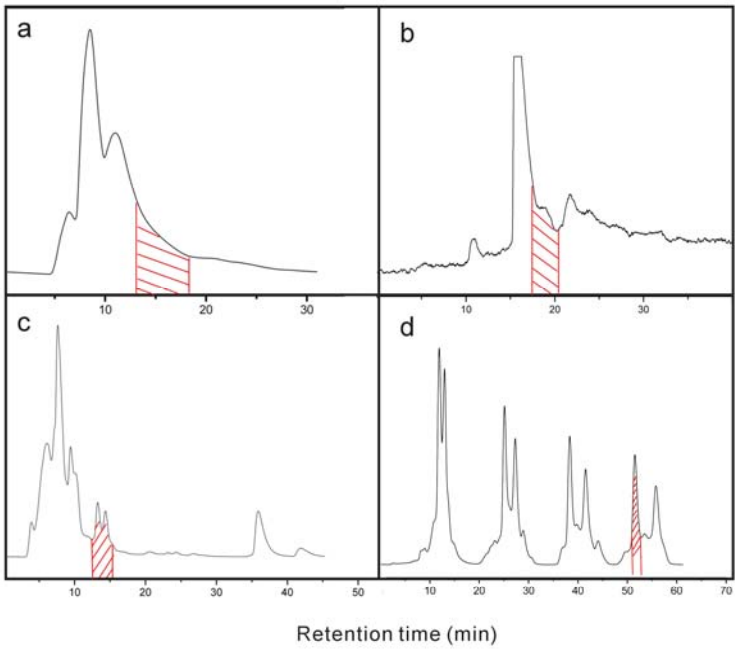

Figure S1. Multi-stage HPLC chromatograms for the separation of $C_{72}Cl_4$. The regions of collected components are highlighted as red shadow.

The procedure for the separation and purification of $C_{72}Cl_4$ requires four stages of HPLC runs, of which the last isolation was carried out in a recyclic mode. All the separations were performed at the room temperature using toluene as the eluent. The crude toluene extraction of carbon soot was separated into several components using a pyrenebutyric acid bonded silica column (I.D. 20 × 250 mm) at a flow rate of 10 ml/min, and the components with the retention time ranging from 13.4 to 18.5 min were collected for the secondary HPLC stage (Fig. S1a). The primarily separated sample was separated using a buckyprep column (I.D. 10 × 250 mm) at a flow rate of 4 ml/min, and then the components with the retention time ranging from 17.5 to 20.5 min were collected (Fig. S1b). These two separation stages are similar to the first two isolation procedures for $C_{78}Cl_8$ recently reported by our group.[S1] The subsequent isolation was carried out on a 5PBB column (I.D. 10 × 250 mm) at a flow rate of 4 ml/min, and the components ranging from 12.6 to 16.0 min was collected (Fig. S1c). Then the recyclic isolation under the same HPLC conditions (5PBB column and flow rate of 4 ml/min) was utilized. After four cycles of HPLC runs, the purified $C_{72}Cl_4$ was collected at the corresponding retention time (Fig. S1d). The purity of the collected $C_{72}Cl_4$ was analyzed by analytical HPLC on a buckyprep column (I.D. 4.6 ×

250 mm) at a flow rate of 1 ml/min. As shown in Fig. S2, only a dominant peak with the retention time of 16.6 min was shown in the chromatogram of $C_{72}Cl_4$, confirming the high purity of the purified $C_{72}Cl_4$.

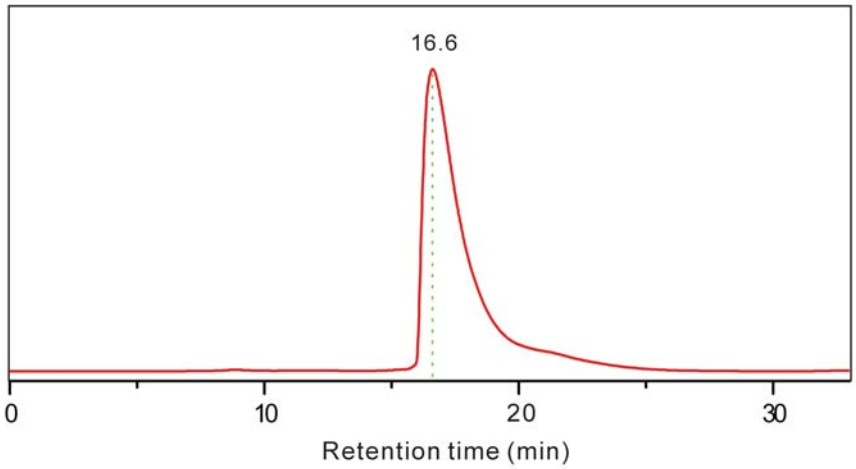

Figure S2. Analytical HPLC of the purified $C_{72}Cl_4$.

2. Crystallographic Information

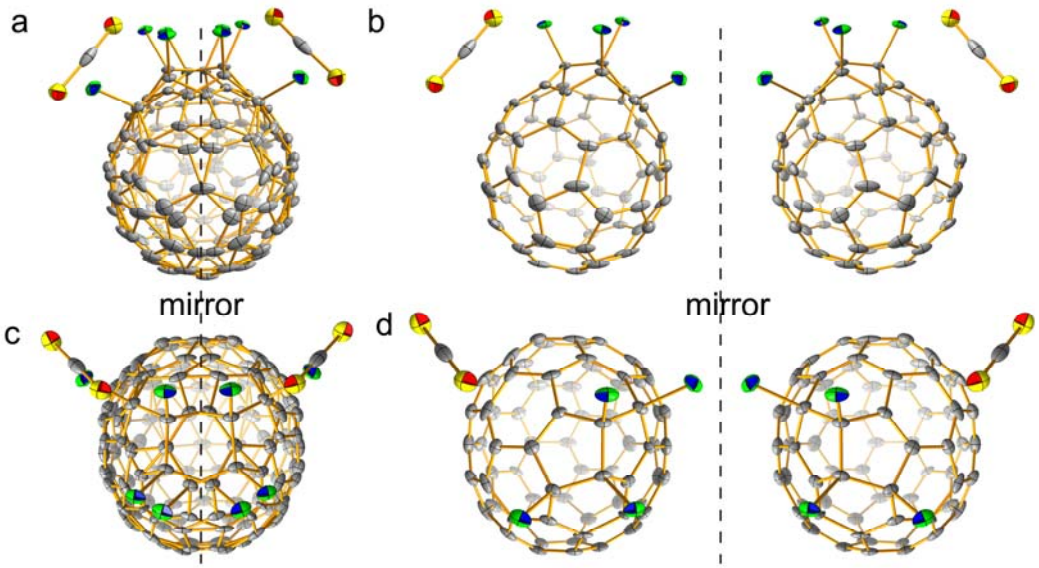

Figure S3. The disordered $C_{72}Cl_4$ in the crystal. (a, b,) the side view. (c, d,) the top view. Containing two enantiomers, the $C_{72}Cl_4$ is disordered on a mirror plane.

The Crystals of **1**: 0.30 × 0.20 × 0.10 mm^3; orthorhombic; space group *Pnma*; a = 20.377(4), b = 16.863(3), c = 10.972(2); V = 3770.4(13); Z = 4; T = 173(2) K; no. reflections = 28208; no. independent reflections = 4442; full-matrix least-squares refinement on F^2; final R indices ($F_o > 4\sigma(F_o)$) are R_1 = 0.0783 and wR_2 = 0.2211 (R_1(all data) = 0.0842 and wR_2(all data) = 0.2277). In the crystal, $C_{72}Cl_4$ is disordered with its own mirror image. Each of the atoms has 0.5 occupancy (Fig. S3). We also used other non-centrosymmetric space groups such as $P_{2(1)2(1)2(1)}$ to resolve the crystal structure. Even though the structure can be obtained, the resolved $C_{72}Cl_4$ is still disordered. We suppose that the disorder of $C_{72}Cl_4$ is not derived from the symmetry of space group, but likely from crystal twinning. 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. Only one 'level B' error about the 'Parameter Ratio of 6.35' is shown. This is due to the disorder making the double number of atom coordinates in an asymmetrical unit and leading to the doubled parameters of refinement. As a result, the ratio of the diffraction number *vs.* parameters is lower than 10 (~6.35), even though the measured diffraction angle θ is quite high (27.6°).

3. Multi-stage mass spectra of $C_{72}Cl_4$.

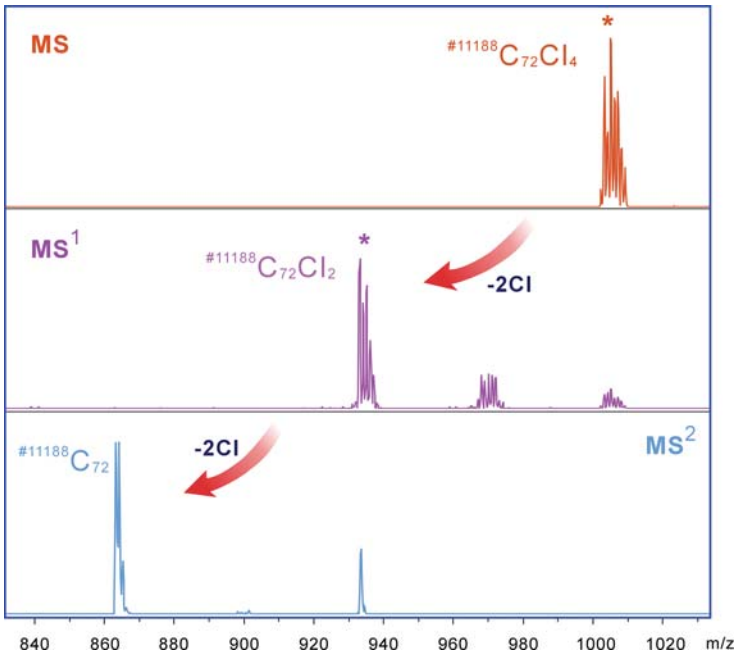

Figure S4. Multi-stage mass spectra of $C_{72}Cl_4$.

The multi-stage spectra of $C_{72}Cl_4$ (Fig. S4) was obtained using a Bruker Esquire HCT mass spectrometer with an atmospheric pressure chemical ionization (APCI) source, in which a furnace vaporizer equipped with a spray needle (nebulizer) and a corona needle. The APCI allows the sample solution nebulized in a setting temperature (ranging from 100 to 500 °C) supplied by a tubular furnace, where the sample droplets can be vaporized, desolvented, heated, and partially decomposed in turn. The stepwise dissociation of chlorine was achieved by collision of $C_{72}Cl_4$ molecules with helium buffer gas in ion trap.

Supplementary reference

S1. Tan, Y. Z.; Li, J.; Zhou, T.; Feng, Y. Q.; Lin, S. C.; Lu, X.; Zhan, Z. P.; Xie, S. Y.; Huang, R. B.; Zheng, L. S. *J. Am. Chem. Soc.* 2010, *132*, 12648.