Supplementary Information

Isolation and analysis of C_{100} containing fractions

The fullerene soot was synthesized by a Krätschmer-Huffman DC-arc discharging method with undoped graphite rods. About 100 g soot was Soxhlet extracted by toluene for *ca*. two weeks. The solution contained mainly C_{60}, C_{70} and small amounts of higher fullerene up to C_{96} according to MALDI-TOF mass spectrometry. This toluene extract was not used. The remaining soot was Soxhlet extracted by *o*-dichlorobenzene for further two weeks. The MALDI MS analyses showed the presence of C_{60}, C_{70} and larger amounts of higher fullerenes up to C_{130}. The *o*-dichlorobenzene solution was dried in vaccum at heating at 150°C. The solid was partially dissolved in toluene and subjected to HPLC separation using a preparative Buckyprep column (20 × 250 mm, Nacalai Tesque, Japan; flow rate 25.0 mL min^{-1}; injection volume 10 mL) and toluene as the eluent (Fig. S1). The several fractions have been collected with elution time up to 120 min. The fraction collected between 84 and 92 min contained C_{100} and C_{106}-C_{112} fullerenes (Fig. S2). It was further separated by recycling HPLC with a semi-preparative Buckyprep column (10 × 250 mm, Nacalai Tesque, Japan) in toluene at flow rate at 6.9 mL min^{-1} (injection volume 5 mL) affording several subfractions (Fig. S3) as mixtures of C_{100} and C_{106}-C_{112} fullerenes in different proportions according to MALDI-TOF MS data. The central subfraction **B** contained mainly C_{100} and smaller amounts of C_{108} and C_{110} fullerenes (Fig. S4). Concentration of subfraction B resulted in precipitation of black solid which was shown to be pure C_{100} fullerene (Fig. S5).

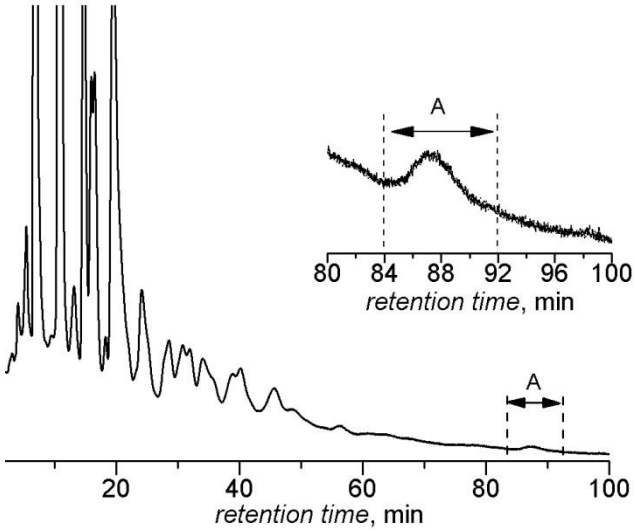

Fig. S1 HPLC trace of the *o*-dichlorobenzene extract recorded in toluene. Fraction **A** has been collected between 84 and 92 min.

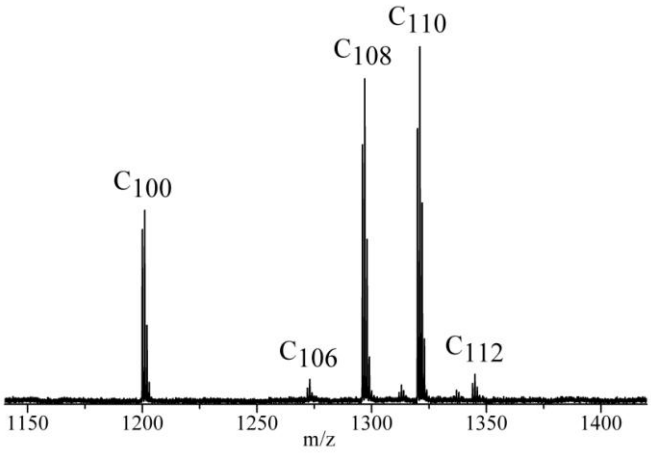

Fig. S2 Negative MALDI-TOF mass spectra of fraction **A** showing the presence of C_{100} and C_{106}-C_{112} fullerenes.

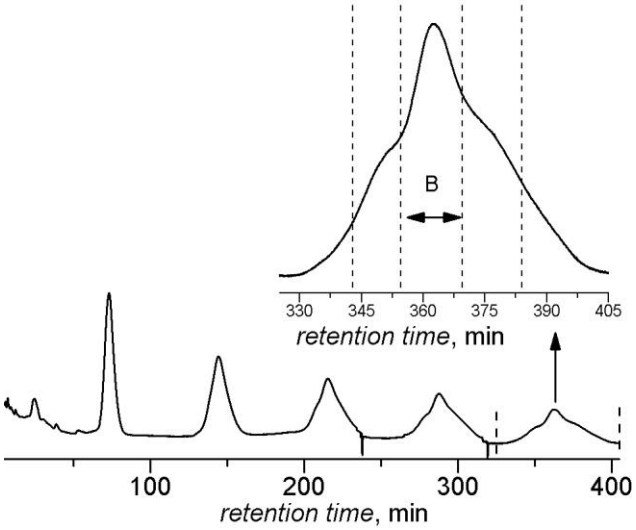

Fig. S3 Recycling HPLC of the fraction A in toluene. Fraction B has been collected

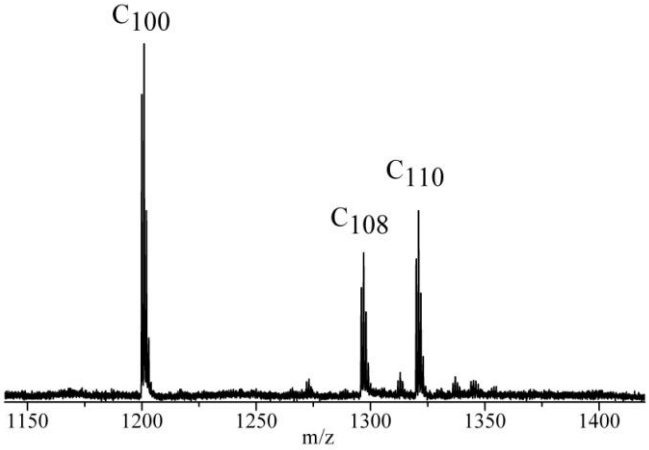

Fig. S4 Negative MALDI-TOF mass spectra of subfraction **B** showing the presence of mainly C_{100} still admixed with other higher fullerenes.

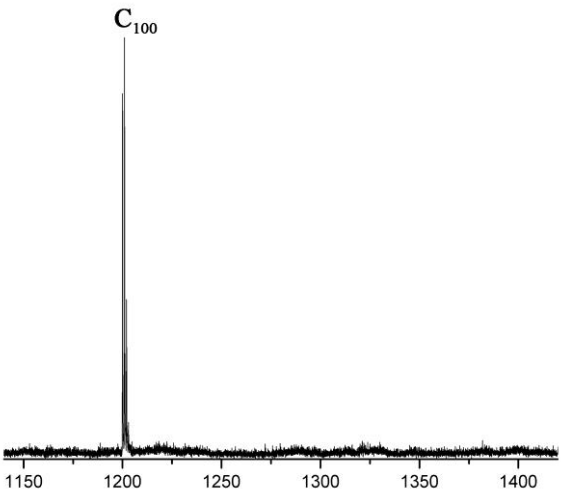

Fig. S5 Negative MALDI-TOF mass spectra of the solid precipitated from subfraction **B** evidencing the presence of pure C_{100}.

Subfraction **B** and the solid precipitated from it were used for chlorination in ampoules with excess VCl_4 plus a drop of $SbCl_5$ as chlorinating agent affording red-coloured, plate-like crystals of $C_{100}Cl_{12}{\cdot}2SbCl_5$. The presence of vanadium chloride as solvated molecule was excluded based of the EDX analysis with a JEOL JSM-6060 instrument (Fig. S6).

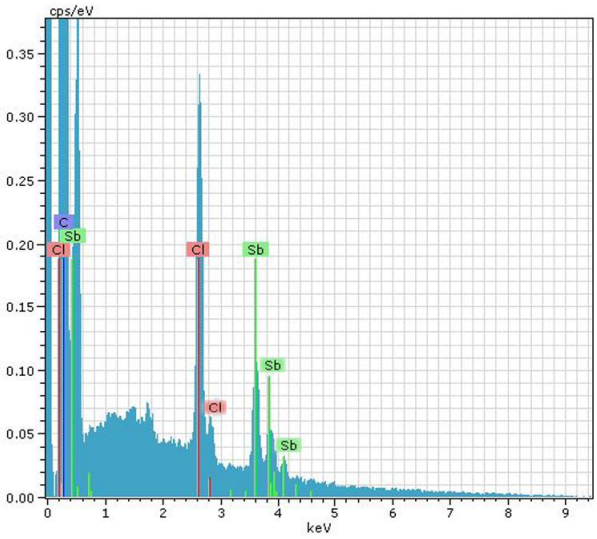

Fig. S6. EDX analysis of the crystal used for X-ray diffraction study demonstrating the presence of only C, Cl, and Sb elements.