Sc₃CH@C₈₀: selective ¹³C enrichment of the central carbon atom

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Supporting Information

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Experimental Details

The arc-discharge synthesis was performed in a static 250 mbar He atmosphere in the presence of a several mbar of CH₄. Graphite rods were drill-holed and packed with a mixture of Sc/graphite or Sc/Ti/graphite powder. Reducing the amount of residual nitrogen in the generator is crucial for the successful synthesis since nitride clusterfullerenes are readily formed in the presence of nitrogen

MALDI mass-spectra were measured with Bruker autoflex mass-spectrometer using sulfur as a matrix.

NMR measurements were performed on a Bruker Avance 500 spectrometer equipped with a multiprobe head 1152Z. The measurements were performed for compounds dissolved in CS_2 with d⁶-acetone placed in a coaxial tube as a lock.

FT-IR spectra were measured using Bruker Vertex 80v spectrometer, the samples were drop-casted from CS_2 solution on KRS-5 substrates and then dried in vacuum. The spectra were measured in attenuated total reflectance (ATR) mode.

UV-Vis-NIR spectra were measured in toluene solution using Shimadzu 3100 spectrophotometer.

Luminescence spectra were measured in toluene solution using Omicron PhoxX+ diode laser with 405 nm wavelength for excitation and Avantes HS1024x122TEC spectrometer with back-thinned TE-cooled CCD image sensor for detection. The spectra were corrected for a drop of sensitivity in the NIR range using certified halogen lamp AvaLight-DH-CAL (Avantes).

Electrochemical measurements were performed in a glovebox with 3-electrode cell (Pt wire are a working and counter electrodes, Ag wire as a pseudoreference electrode; potentials were calibrated versus $Fe(Cp)_2$ and $Fe(Cp^*)_2$ as internal standards).

Separation of Sc₃CH@C₈₀-I



Figure S1a. HPLC curves of the raw fullerene extracts (2 analytical BP columns, 1.6 ml/min, 40°C) obtained in Sc/CH₄ and Sc/Ti/CH₄ systems. The fractions containing Sc₃CH@C₈₀-I elute at 30-33 min. Other components in the fractions are Sc₄C₂@C₈₀ (main), Sc₃N@C₇₈, and small amounts of Sc₃N@C₈₀-I and Sc₂C₇₆. Sc₃CH@C₈₀-II elutes at a later time (34-35 min) together with Sc₃N@C₈₀-II.



Figure S1b. Mass-spectrum of the fraction containing Sc₃CH@C₈₀.



Figure S2. Second step of the Sc₃CH@C₈₀-I separation: 1 semi-prep BC column, 1.0 ml/min, 40°C. At this step, Sc₄C₂@C₈₀, Sc₂C₇₆ and large part of Sc₃N@C₇₈ are removed, leaving only residual Sc₃N@C₇₈ and Sc₃N@C₈₀-I as impurities to the target compound. These impurities are then removed at the 3rd step (see Fig. S3).



Figure S3. Third step of the $Sc_3CH@C_{80}$ -I separation: 4 analytical BP columns, 0.8ml/min, 40°C. At this step, residual $Sc_3N@C_{78}$ and $Sc_3N@C_{80}$ -I are removed leaving pure $Sc_3CH@C_{80}$ -I.

NMR Measurements

Discussion:

The two-line ¹³C NMR pattern of $Sc_3CH@C_{80}$ proves that the hydrogen atom is not attached to the carbon cage but is a part of the Sc_3CH cluster and that the cluster is rotating freely inside the fullerene.

The possibility to distinguish $Sc_3CH@C_{80}$ from $Sc_3N@C_{80}$ by ⁴⁵Sc NMR is crucial taking into account their close mass-numbers. The presence of the $Sc_3N@C_{80}$ admixture in the $Sc_3CH@C_{80}$ may result in erroneous analysis of the isotopic distribution by mass-spectrometry, which is important for the mechanistic studies discussed below. Figure 1b in the manuscript proves that the possible content of the $Sc_3N@C_{80}$ in the purified samples of $Sc_3CH@C_{80}$ is below the sensitivity limit of the ⁴⁵Sc NMR (ca 5%) and hence its influence of the isotopic distribution analysis can be safely excluded

Very negative ¹H chemical shift in Sc₃CH@C₈₀ facilitates its assignment (i.e., it cannot be confused for solvent or impurity signals since organic compounds have their ¹H resonances at much lower field). The high-field chemical shifts of carbon-bonded protons are usually associated with electron-donating substituents at the carbon atom. E.g., δ (¹H) chemical shifts in CH₃Li and (CH₃)₂Mg are –2.1 and –1.4 ppm, respectively.¹ Since each Sc atom in the Sc₃CH cluster formally donates one electron to the central carbon atom, the large negative chemical shift of the proton in Sc₃CH@C₈₀ is not unexpected. Furthermore, large negative chemical shift in the center of the C₈₀⁶⁻ hexaanion was calculated to be –24 ppm.² The ¹J_{C-H} coupling constant in Sc₃CH@C₈₀ is quite small, 78.5 Hz, which is also typical for protons bonded to carbon atoms with highly electropositive substituents: the ¹J_{C-H} values in CHCl₃, CH₄, CH(SiMe₃)₃, and CH₃Li are 209.0, 125.0, 100.0, and 97.0 Hz, respectively.^{1,3} Thus, the measured ¹J_{C-H} constant is in line with the large negative charge on the central carbon atom predicted for Sc₃CH@C₈₀.⁴the ¹J_{C-H} values in CHCl₃, CH₄, CH(SiMe₃)₃, and CH₃Li are 209.0, 125.0, 100.0, 125.0, 100.0, and 97.0 Hz, respectively.^{1,3}

The possibility to detect ¹³C satellites in the proton NMR spectrum enables determination of the ¹³C chemical shift of the central carbon atom. Figure S4a shows ¹H spectra measured with selective ¹³C decoupling at different ¹³C irradiation frequencies. The satellites are well visible at 165 or 180 ppm, but disappear completely at 173–174 ppm. The main ¹H peak at 173 ppm excitation is also noticeably broader. Taking into account the ¹³C irradiation bandwidth of 5 ppm, the ¹³C chemical shift of the central atom in Sc₃CH@C₈₀ can be determined as 173±1 ppm. Interestingly, this value is noticeably more shielded than ¹³C chemical shifts of endohedral carbon atoms in other carbide clusterfullerenes (see Table 1).

We also measured ¹H-¹³C HSQC measurements to determine the chemical shift of the internal carbon (Fig. S4b) and observed a signal corresponding to the 13C chemical shift of ca 165 ppm, which is somewhat different from the value determined by a sequence of selective decoupling measurements. However, the measurement required several days of accumulation, which results in a drift of the field. Hence 173 ppm should be considered as a more reliable value.



Figure S4a. Decoupled ${}^{1}H-{}^{13}C$ NMR spectra of Sc₃CH@C₈₀ measured with continuous wave ${}^{13}C$ decoupling at different irradiation frequencies (the values are given in ppm, the irradiation band width is 5 ppm in all measurements). Left: broad range of irradiation frequencies, lower signal-to-noise ration; right: smaller steps in irradiation frequencies, better signal to noise ratio.



Figure S4b. HSQC measurements of Sc₃CH@C₈₀. The peak corresponding to δ (¹³C) = 165 ppm can be seen. However, the measurement requires several days of integration, which results in an unavoidable drift of the field.

¹H NMR spectra of ¹³C-enriched samples



Figure S5. ¹H NMR spectra in the range of internal proton signal for the sample synthesized with natural abundance CH₄ and graphite powder (left, "CH₄/C"), ¹³CH₄ and natural abundance graphite powder (middle, "¹³CH₄/C"), and natural abundance CH₄ with ¹³C-rich carbon powder (right, "CH₄/¹³C"). Enhancement of the spectra in the range of ¹³C satellites is shown in Figure 4 of the manuscript together with corresponding mass-spectra. Note that the total amount of the "CH₄/C" sample was much higher allowing better signal-to-noise ratio. Measurement of the sample "¹³CH₄/C" required several days, and the small drift of the magnetic field over this period resulted in an apparent "broadening" of the signals. This effect was taken into account in the measurements of the "CH₄/¹³C" sample: the spectrum was measured in several 4-hour periods with recalibration of the chemical shift after each period.

¹H NMR spectra of Sc₃CH@C₈₀-II

The fraction containing $Sc_3CH@C_{80}$ -II was eluted at 34-35 min (see Fig. S1) and, according to the mass-spectrum (Fig. S6a), also contained $Sc_3N@C_{80}$ -II (main component) along with $Sc_2C_2@C_{82}$ and $Sc_4C_2@C_{80}$. $Sc_3CH@C_{80}$ -II is the only Sc_3CH -type clusterfullerene in this fraction, which enables determination of its ¹H chemical shift by ¹H NMR measurement without further separation (Fig. S6b).



Figure S6a. Positive-ion mass spectrum of the fraction containing $Sc_3CH@C_{80}$ -II. $Sc_3CH@C_{80}$ and $Sc_3N@C_{80}$ have overlapping mass-spectra, but $Sc_3CH@C_{80}$ is still recognizable as it appears one a.m.u. below $Sc_3N@C_{80}$ as can be seen in the inset.



Figure S6b. ¹H NMR of the fraction containing Sc₃CH@C₈₀-II.

FTIR spectra of Sc₃CH@C₈₀ versus Sc₃N@C₈₀



Figure S7. FT-IR spectra of $Sc_3CH@C_{80}$ (black) and $Sc_3N@C_{80}$ (cyan). The strong band at 1507 cm⁻¹ is due to CS₂. The inset shows the range of antisymmetric metal/nitrogen(carbon) stretching vibration. In $Sc_3N@C_{80}$ this mode is observed at 599 cm⁻¹, whereas in $Sc_3CH@C_{80}$ the frequency is shifted to 630 cm⁻¹. At the same time, all cage vibrations in both molecules occur at virtually identical frequencies.

References

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