

Supporting Information

Functionalised Endohedral Fullerenes in Single-Walled Carbon Nanotubes

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S1. Synthesis and characterisation of *N*-methyl-2-(4-(liponyloxy)benzyl)-[5,6]-Sc₃N@C₈₀ fulleropyrrolidine (1):

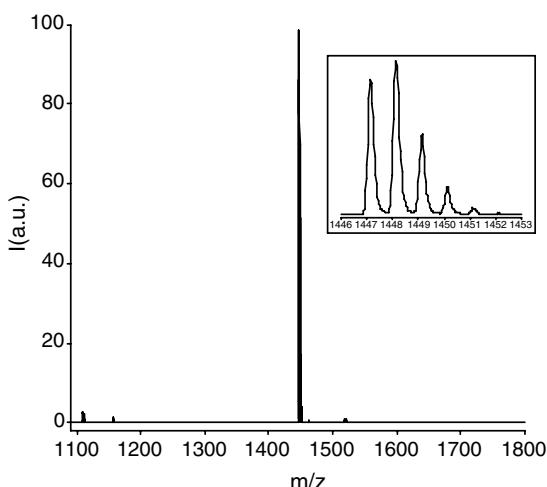
All other reagents and solvents were purchased from Aldrich and were used without further purification. ¹H and ¹³C NMR spectra were obtained on a Bruker AV(III)500 spectrometers. Coupling constants (*J*) are denoted in Hz, and chemical shifts (δ), in ppm. Mass spectrometry was carried out on a Bruker Ultraflex III MALDI-TOF spectrometer using DCTB as matrix (355 nm).

A mixture of 0.8 mg of Sc₃N@C₈₀ (Luna Innovations; 7.6 10⁻⁴ mmol), 1.1 mg of sarcosine (0.013 mmol) and 13.0 mg of 4-(liponyloxy)benzaldehyde (0.04 mmol) was heated and stirred at 110 °C in 15 mL of dry toluene for 270 min. The crude product was purified by column chromatography (silica gel/toluene; R_f = 0.13) affording compound **1** in 34 % yield. MALDI-MS 1447.14 *m/z* [M]⁺. ¹H NMR {500 MHz, CDCl₃:CS₂ (1:6), 300 K} δ _H 4.38 (d, *J* = 9.7 Hz, 1H, -CH₂ pyrrolidine), 3.76 (s, 1H, -CH pyrrolidine), 3.15 (s, 3H, -NCH₃), 3.08 (d, *J* = 9.7 Hz, 1H, -CH₂ pyrrolidine) ppm. Heteronuclear Multiple Quantum Correlation (HMQC) {500 MHz, CDCl₃:CS₂ (1:6), 300 K} δ _C 85.0 (-CH₂ pyrrolidine), 72.5 (-CH pyrrolidine), 41.4 (-NCH₃) ppm.

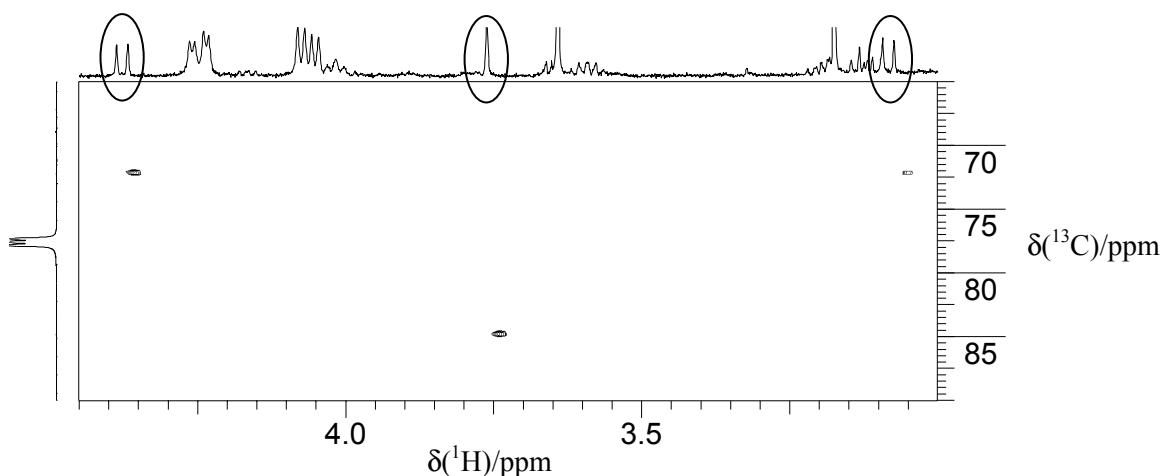
S2. Insertion of molecules into carbon nanotubes:

5 mg of SWNT (*NanoCarbLab*, arc discharge, 80% purity) heated in air at 520 °C for 38 min were added immediately after the heating to a solution of compound **1** (50 µg) in 0.05 ml of chloroform at room temperature. The solvent was evaporated, additional amount of chloroform was added (0.05 ml) and the resultant mixture was stirred vigorously until the solvent evaporated again. This procedure was repeated three times. The resultant black powder was dispersed in 20 ml of chloroform under ultrasonic agitation; the suspension was filtered onto a PTFE filtration membrane (pore size 0.5 µm), washed with an additional 10 ml portion of chloroform and dried in air.

MALDI-TOF mass spectrum of **1** (inset: isotopic distribution pattern confirming the composition of monoadduct **1**).



Heteronuclear Multiple Quantum Correlation (HMQC) of **1** {500 MHz, CDCl₃:CS₂ (1:6), 300 K} δ_C 85.0 (–CH₂ pyrrolidine), 72.5 (–CH pyrrolidine), 41.4 (–NCH₃) ppm.



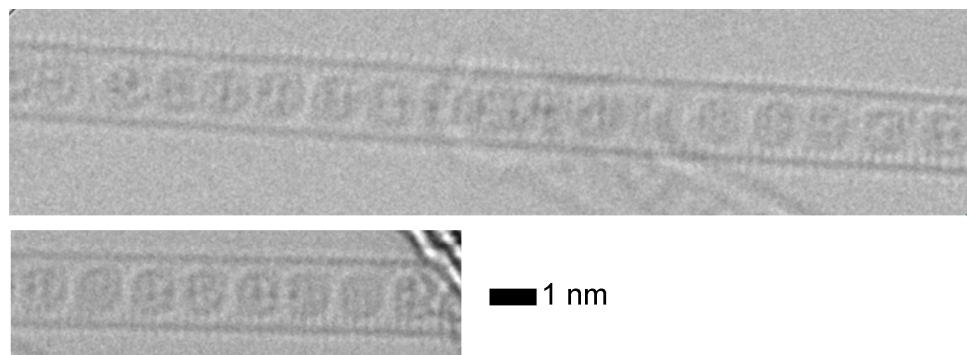
S3. TEM image simulation.

TEM image simulations were performed using a custom-made programme (MUSLI code [1]). Coherent aberrations corresponding to those in the experimental images were used. Parameters for dumping envelope were as follows: focal distance 1.5 mm (tabulated value for Titan 80-300), coefficient of chromatic aberration 1.4 mm (measured experimentally), energy spread of electron source 0.2 eV (measured experimentally), stability of high tension 10⁻⁶ (tabulated value for Titan 80-300), stability of objective lens current 3·10⁻⁷ (fitted by simulations), convergence semi-angle 0.5 mrad (this parameter does not measurably influence aberration corrected imaging). Thermal vibrations were treated using frozen phonons approach with 100 phonon configurations averaged for every image at corresponding Debye–Waller factor of 0.005 nm². The sampling rate was 0.017 nm/pixel. Images were calculated at the electron dose of 10⁶ e⁻/nm² and further processed using the same routine as for experimental images.

Figure 1d was processed by Fourier filtering of back and front walls of the nanotube and by applying an Gaussian blur filter. The latter did not sacrifice the resolution, due to image oversampling.

S4. Spacing between unfunctionalised M₃N@C₈₀ in nanotube.

Spacing between M₃N@C₈₀ is independent of the nature of endohedral metal atoms and is fully determined by the diameter of the icosahedral C₈₀ cage, identical for all molecules of this type. Our measurements confirm that this distance is the same for Sc₃N@C₈₀ and Ho₃N@C₈₀ molecules. While the endohedral Ho atoms can be easily visualised, Sc atoms are more difficult to observe in unfunctionalised M₃N@C₈₀. Sc₃N cluster, however, becomes clearly visible when the functional group is fragmented by the e-beam.



[1] A. Chuvalin and U.Kaiser *Ultramicroscopy* **104** (2005) 73-82