Supporting Information for "*A bimetallic endohedral fullerene: PrSc@C$_{80}$*"

Simon R. Plant,[a] Tsz Cheong Ng,[a] Jamie H. Warner,[a] Géraldine Dantelle,[a,b] Arzhang Ardavan,[c] G. Andrew D. Briggs[a] and Kyriakos Porfyrakis*[a]

[a] *QIPIRC, Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, United Kingdom; E-mail:* kyriakos.porfyrakis@materials.ox.ac.uk
[b] *Laboratoire de Photonique Quantique et Moléculaire, ENS Cachan, 61 Avenue Président Wilson, 94235 Cachan Cedex, France*
[c] *Clarendon Laboratory, Department of Physics, University of Oxford, Parks Road, Oxford OX1 3PU, United Kingdom*

1. Experimental methods

Energy dispersive X-ray (EDX) analysis was performed using a JEOL JEM-2010 transmission electron microscope fitted with an Oxford Instruments LZ5 energy dispersive X-ray spectrometer. For this purpose, samples were dissolved in CS_2 and then deposited onto copper grids covered with carbon. Samples were allowed to dry in air before being inserted into the microscope. The beam, at an acceleration voltage of 200 kV, was focused down onto crystalline areas of the sample. The acquisition time was 1000 s.

^{13}C NMR spectroscopy was conducted using a Bruker AV (III) 500 Cryoprobe. For this purpose, 0.153 mg of PrSc@C$_{80}$ was dissolved in CS_2 with the addition of Cr(acac)$_3$ (2 mg) as the relaxant and $CDCl_3$ as the reference. The data were accumulated over 65,536 scans at room temperature for a spectrometer frequency of 126 MHz.

EPR spectroscopy was conducted using an X-band Bruker EMX Micro EPR spectrometer at (frequency, 9.40 GHz) starting at liquid helium temperature and rising to room temperature. For this study, the sample was dissolved in toluene, degassed and sealed in a quartz tube under vacuum. The modulation frequency and the amplitude modulation were set at 100 kHz and 10 G respectively. The microwave power was varied between at 0.2 and 20 mW.

2. Comments on the environmental stability of PrSc@C$_{80}$

PrSc@C$_{80}$ was isolated and remained in solution (toluene) for approximately one month prior to mass spectrometry analysis. During this time, the sample was held in a transparent vessel, exposed to air at ambient temperature, and yet there was no evidence of oxidation, decomposition or precipitation. As required for each method of characterization, PrSc@C$_{80}$ was dried and transferred into a new solvent under ambient conditions, readily dissolving in both CS_2 and toluene. None of the solvents used were de-gassed.

3. NMR spectroscopy

The NMR spectrum of PrSc@C_{80}, obtained by the methods outlined in the manuscript, is shown below in Figure S1. The NMR spectrum of a control sample containing CS_2, Cr(acac)$_3$ and $CDCl_3$ was used for comparison with the NMR spectrum of the sample containing PrSc@C_{80}. This enabled identification of lines in the NMR spectrum that only arose from the fullerene. We were also able to determine, therefore, those peaks arising from impurities in the solvent. Lines 18 and 19 in Figure S1 are approximately half intensity as compared to lines 1-17.

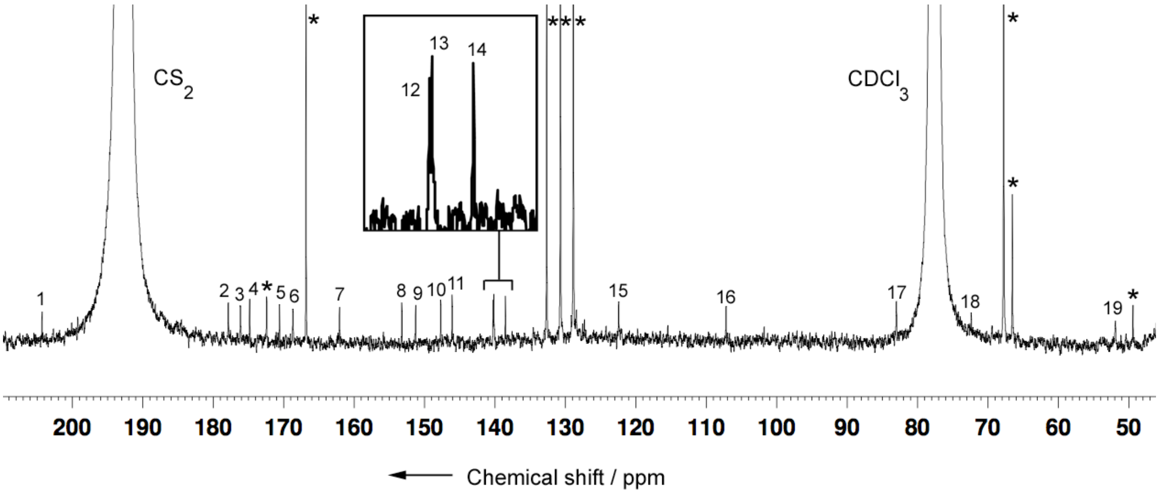

Figure S1: ^{13}C NMR spectrum of PrSc@C_{80} in CS_2 with $CDCl_3$ as the reference and Cr(acac)$_3$ as the relaxant. The lines arising from the fullerene are labelled 1-19, with lines arising from impurities indicated using (*). The assigned peaks correspond to the following chemical shifts, δ: 1 (δ = 204.24), 2 (177.85), 3 (176.13), 4 (174.81), 5 (170.58), 6 (168.67), 7 (162.05), 8 (153.21), 9 (151.24), 10 (147.69), 11 (146.07), 12 (140.24), 13 (140.15), 14 (138.50), 15 (122.41), 16 (107.16), 17 (82.99), 18 (72.35), 19 (51.87). Lines 18 and 19 are approximately half intensity compared with lines 1-17.