Highly regioselective cycloaddition of diphenylnitrilimine to $Sc_3N@I_h$-C_{80} affording a very stable, unprecedented pyrazole-ring fused derivative of endohedral metallofullerenes

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Experimental details

General considerations.

All the commercial reagents were used without further purification except o-dichlorobenzene for the reaction which was freshly distilled before use. $Sc_3N@I_h$-C_{80} were produced with acr-discharge method and isolated with HPLC. Analytical and preparative HPLC were performed on different Buckyprep columns (ø10×250 mm or ø20×250 mm, Cosmosil), respectively. Toluene was used as eluent. NMR spectra were recorded on a Bruker AV-II 500 MHz NMR spectrometer, locked on deuterated solvents and referenced to the solvent peak. Matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectra were recorded with a Biflex III (Bruker Daltonics Inc., Germany) mass spectrometer using 1,1,4,4-tetraphenyl-1,3-butadiene as matrix in a positive ion linear mode. The UV-vis experiments were carried out on a PE Lambda 750S UV-vis-NIR spectrophotometer.

Synthesis of the pyrazole-ring fused derivative 2.

To a 40 ml o-dichlorobenzene solution containing 5.0 mg $Sc_3N@I_h$-C_{80} (4.6 μmol, 1 eq) and 5.3 mg N'-phenylbenzohydrazonoyl chloride (23 μmol，5 eq) was added triethylamine (50 μl), and the reaction mixture were stirred at 120°C under argon for 5h. The reaction progress was followed with HPLC on a semi-preparative Buckyprep column (ø10×250 mm, Cosmosil). Then, the solvent was evaporated and the solid residue was dissolved in CS_2 and subjected to silica gel column chromatography. The polarity of the eluant was increased from CS_2 to toluene, which allows separation of the unreacted $Sc_3N@I_h$-C_{80}. The eluant of 1:1 CS_2/toluene gave the desired product **2** which was

further purified by HPLC using a Buckyprep column (ø20×250 mm, Cosmosil) with 8.0 mL/min toluene flow rate. After evaporation, 2.5 mg of the product **2** was obtained (38% isolated yield).

^{1}H NMR (500 MHz, CS_2/C_3D_6O=4:1, 298K) δ_H = 6.36 (d, *J*=7.5 Hz, 1H), 6.44 (t, *J*= 7.5 Hz, 1H), 6.50 (t, *J*= 7.5 Hz, 1H), 6.54 (t, *J*= 7.5 Hz, 1H), 6.67 (t, *J*= 8.0 Hz, 2H), 6.73-6.75 (m, 1H), 6.67 (t, *J*= 8.0 Hz, 2H), 6.78 (t, *J*= 8.5 Hz, 2H), 7.39 (d, *J*= 6.5 Hz, 2H).

MS (MALDI-TOF): *m/z* =1303 $[M+H]^+$; Calcd for $Sc_3C_{120}H_{21}F_{10}N_6$: *m/z* = 1303.

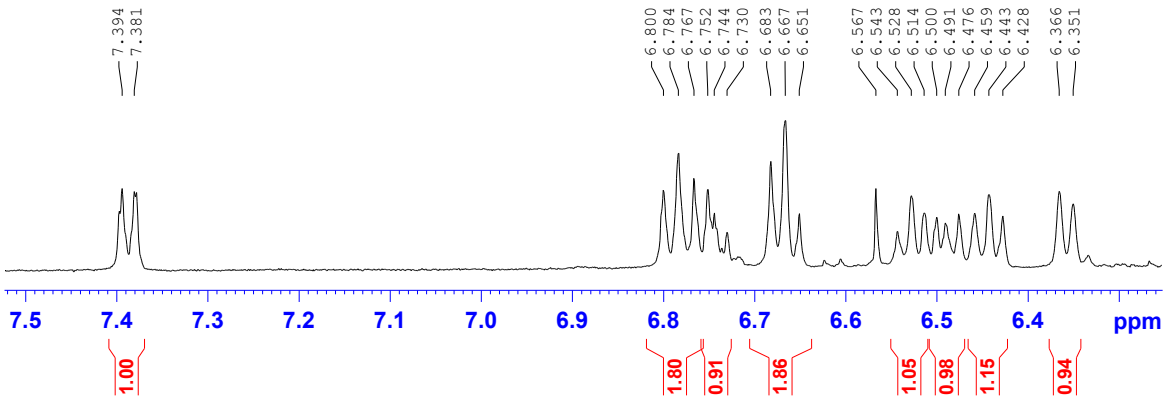

Figure S1. ^{1}H NMR spectrum of **2**, 298 K, C_3D_6O/CS_2.

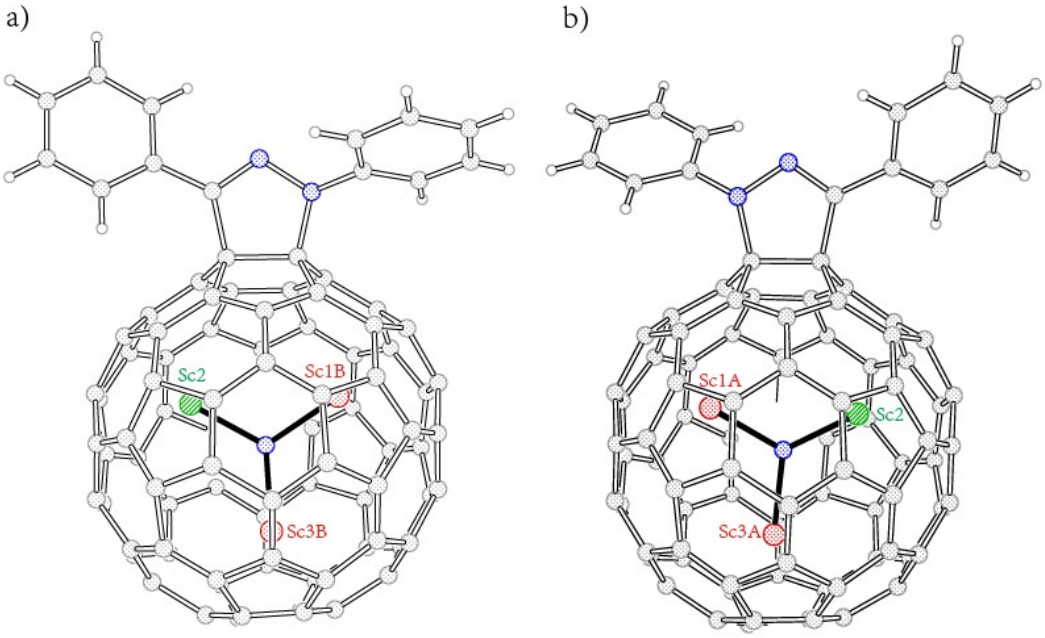

Figure S2. Geometric features of **2**. a) minor cage with minor Sc_3N cluster, occupation: 0.33 for the cage and 0.40 for Sc1B & Sc3B, b) major cage with major Sc_3N unit, occupation: 0.67 for the cage and 0.60 for Sc1A & Sc3A.