Electronic Supplementary Information

Synthesis and Characterization of Bispyrrolidine Derivatives of H$_2$@C$_{60}$ : Differentiation of Isomers Using $^1$H NMR Spectroscopy of Endohedral H$_2$

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General Experimental Details:

All chemicals were available from commercial sources and used as received without further purification. All solvents were reagent grade and used as received. *H2@C60 (a mixture of H2@C60 and HD@C60) was synthesized according to literature methods.1 1H NMR was recorded on a Bruker (500 MHz) spectrometer. EPR spectra were measured with a Bruker EMX X-band spectrometer. UV-Vis spectra were measured with an Agilent UV8453 spectrometer. Mass spectra were obtained by FAB+ method.

Synthesis:

1. 4-Amino-4-carboxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TOAC) (12.0 mg, 0.056 mmol) and paraformaldehyde (8.4 mg, 0.28 mmol) was added to a solution of *H2@C60 (20 mg, 0.028 mmol) in toluene (20 mL). The mixture was refluxed for 1.5 h. The solvent was removed under vacuum. Column chromatography (SiO2, eluent: toluene) first gave unreacted *H2@C60 followed by the monoadduct. Then mixing solvents (toluene:ethanol / 95:5) were used as the eluent. The mixture of bisadduct isomers was collected. After removing solvents, the brown solid was subjected to preparative TLC with toluene/ethanol (95:5) as the eluent. Four separated bands were clearly shown on the TLC plate and each band was carefully collected. MS (FAB+, m/z, %) (a mixture of the isomers) calculated for C80H40N4O2 (M+) 1088.34, found 719.90 (C60, 77); 1089.04 (M+).

2. *H2@C60 (20 mg, 0.028 mmol) was dissolved in chlorobenzene (50 mL). Then 2-aminoisobutyric acid (5.8 mg, 0.056 mmol) and acetone (1 mL) was added to the solution. The mixture was placed in a pressure glass tube and sealed. After heated for 24 h at 120 °C, the solvent was removed. Column chromatography (SiO2, toluene) first gave the unreacted *H2@C60 followed by the monoadduct. Then the mixing solvents
(toluene/ethyl acetate 7:3) were used as eluent. The fraction was collected as a mixture of five bisadduct isomers. MS (FAB\(^+\), m/z, %) (a mixture of the isomers) calculated for C\(_{72}\)H\(_{38}\)N\(_2\) (M\(^+\)) 920.24, found 719.90 (C\(_{60}\), 75); 919.35 (M\(^+\)).

Fig. S1 Possible geometrical isomers of trans-2, trans-3 and trans-4 (for trans-1 and equatorial-5, syn-a and syn-b are identical).

Comparison of UV-Vis spectra

Fig. S2 Comparison of UV-Vis spectra of trans-1 in toluene.
Fig. S3 Comparison of UV-Vis spectra of trans-2 in toluene.

Fig. S4 Comparison of UV-Vis spectra of trans-3 in toluene.

Fig. S5 Comparison of UV-Vis spectra of trans-4 in toluene.

Fig. S6 Comparison of UV-Vis spectra of equatorial-5 in toluene.

1H NMR spectra of endohedral H₂ and HD of bisadduct isomers of 1

Fig. S7 1H NMR spectrum of endohedral H₂ and HD of trans-2 in CDCl₃/CS₂.

Fig. S8 1H NMR spectrum of endohedral H₂ and HD of trans-3 in CDCl₃/CS₂.
Fig. S9 $^1$H NMR spectrum of endohedral H$_2$ and HD of *trans*-4 in CDCl$_3$/CS$_2$.

Fig. S10 $^1$H NMR spectrum of endohedral H$_2$ and HD of *equatorial*-5 in CDCl$_3$/CS$_2$.

EPR spectra of bisadduct isomers of 1 in deoxygenated toluene solutions at room temperature.

EPR parameters for all of spectra: Modulation amplitude: 1 G; Resolution: 1024 points; Sweep width: 70 G.
Fig. S11 EPR spectrum of trans-1 at room temperature.

Fig. S12 EPR spectrum of trans-2 at room temperature.

Fig. S13 EPR spectrum of trans-3 at room temperature.
**Fig. S14** EPR spectrum of *trans*-4 at room temperature.

**Fig. S15** EPR spectrum of *equatorial*-5 at room temperature.
Fig. S16 EPR spectra of monoadduct and bisadduct isomers of 1 in deoxygenated toluene solutions at 213 K (EPR parameters: Modulation amplitude: 1 G; Resolution: 1024 points; Sweep width: 70 G).

References: