Electronic Supplementary Information

Synthesis and Characterization of Bispyrrolidine Derivatives of $H_2@C_{60}$: Differentiation of Isomers Using ^1H 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. $^{*}H_2@C_{60}$ (a mixture of $H_2@C_{60}$ and $HD@C_{60}$) was synthesized according to literature methods.[1] ^{1}H 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.[2] 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 $^{*}H_2@C_{60}$ (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 (SiO_2, eluent: toluene) first gave unreacted $^{*}H_2@C_{60}$ 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 $C_{80}H_{40}N_4O_2$ (M^+) 1088.34, found 719.90 (C_{60}, 77); 1089.04 (M^+).

2.[3] $^{*}H_2@C_{60}$ (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 ^{o}C, the solvent was removed. Column chromagtography (SiO_2, toluene) first gave the unreacted $^{*}H_2@C_{60}$ 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 $C_{72}H_{28}N_2$ (M^+) 920.24, found 719.90 (C_{60}, 75); 919.35 (M^+).

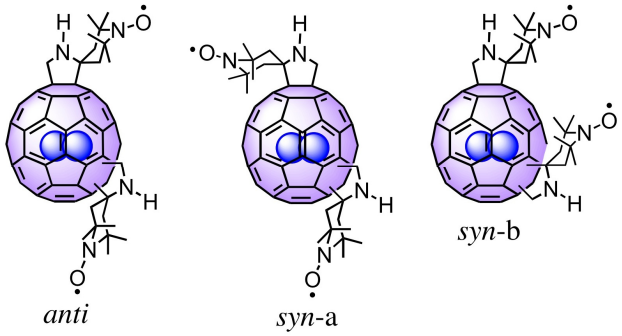

Fig. S1 Possible geometrical isomers of *trans*-2, *trans*-3 and *trans*-4 (for *trans*-1 and *equatorial*-5, *syn*-a and *syn*-b are identical).

Comparison of UV-Vis spectra

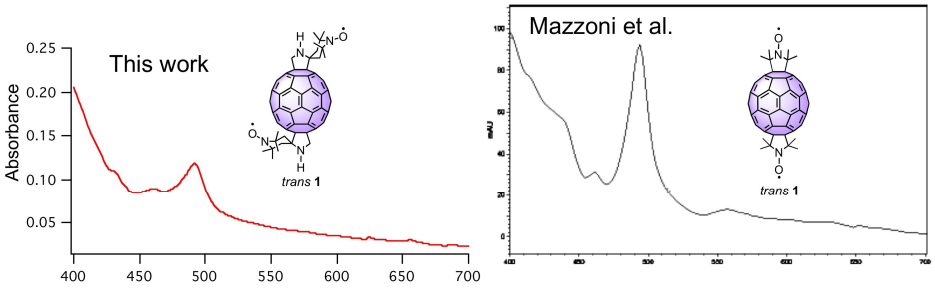

Fig. S2 Comparison of UV-Vis spectra of *trans*-1 in toluene.

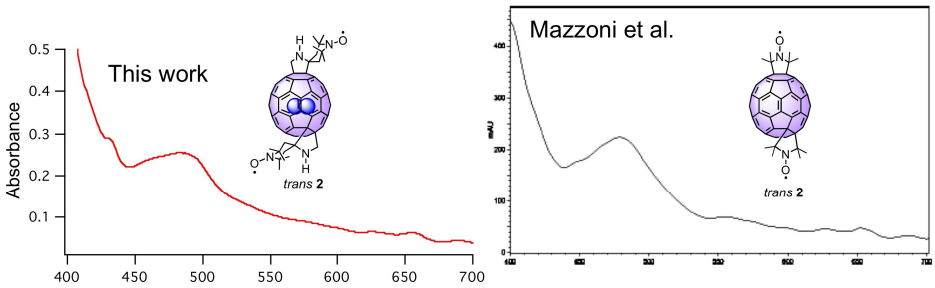

Fig. S3 Comparison of UV-Vis spectra of *trans*-2 in toluene.

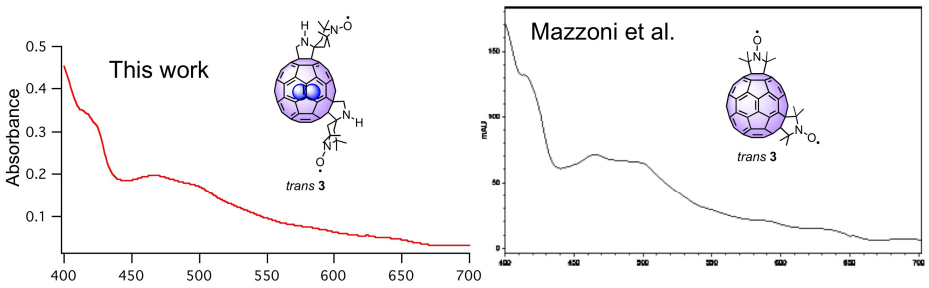

Fig. S4 Comparison of UV-Vis spectra of *trans*-3 in toluene.

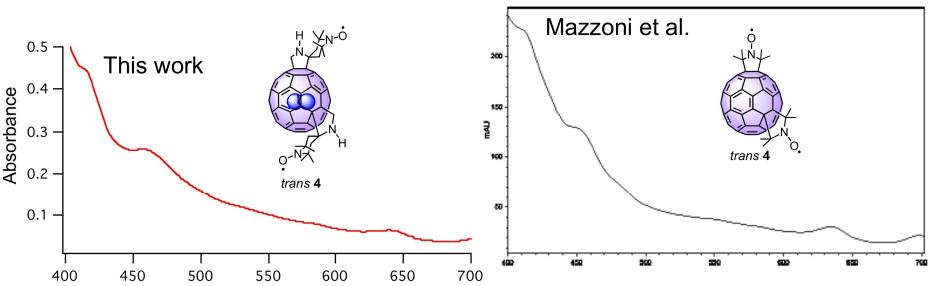

Fig. S5 Comparison of UV-Vis spectra of *trans*-4 in toluene.

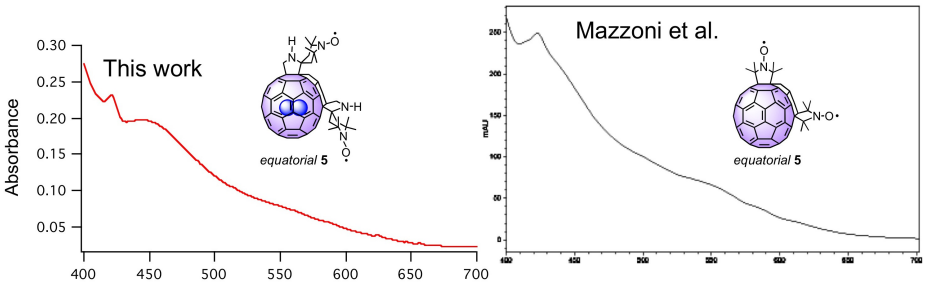

Fig. S6 Comparison of UV-Vis spectra of *equatorial*-5 in toluene.

Reference: Mazzoni, M.; Franco, L.; Corvaja, C. Zordan, G.; Menna, E.; Scorrano, G.; Maggini, M. *ChemPhysChem.* **2002**, 527-531.

^{1}H NMR spectra of endohedral H_2 and HD of bisadduct isomers of 1

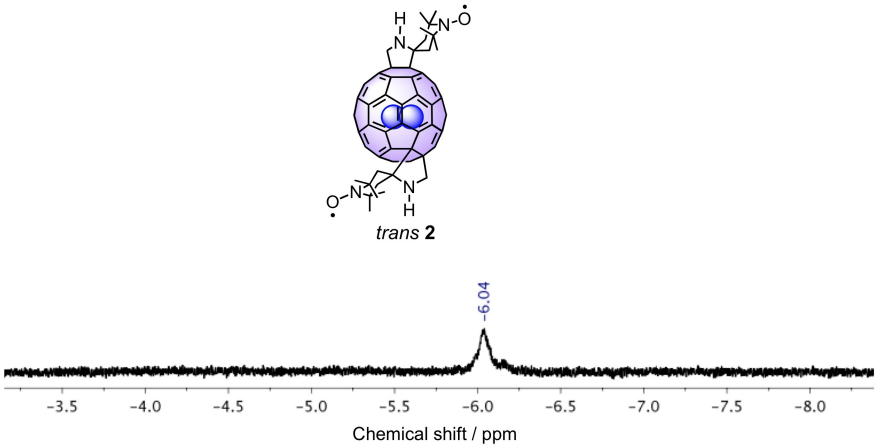

Fig. S7 ^{1}H NMR spectrum of endohedral H_2 and HD of *trans*-2 in $CDCl_3/CS_2$.

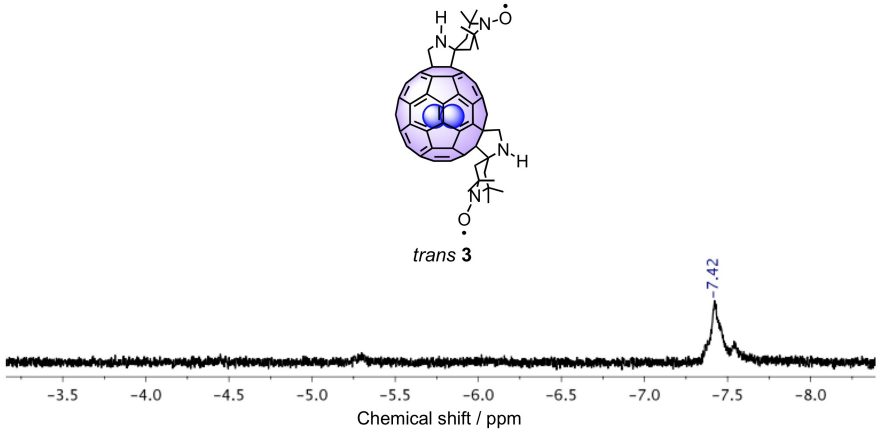

Fig. S8 ^{1}H NMR spectrum of endohedral H_2 and HD of *trans*-3 in $CDCl_3/CS_2$.

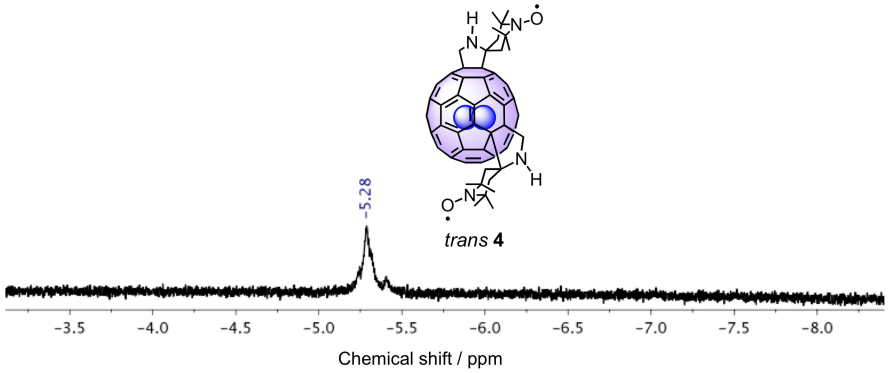

Fig. S9 ^{1}H NMR spectrum of endohedral H_2 and HD of *trans*-4 in $CDCl_3/CS_2$

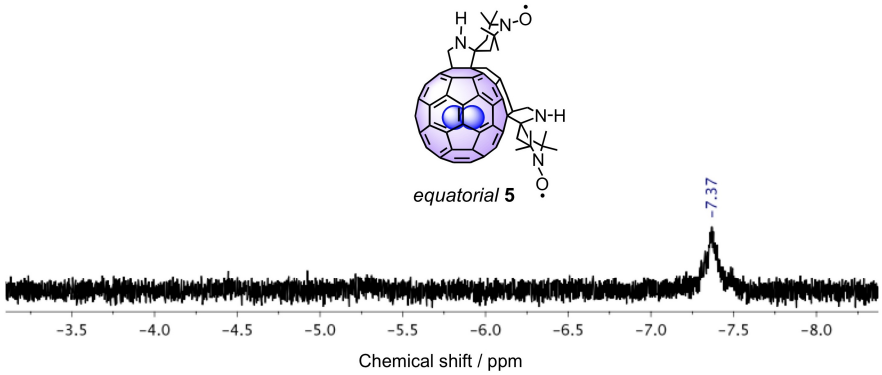

Fig. S10 ^{1}H NMR spectrum of endohedral H_2 and HD of *equatorial*-5 in $CDCl_3/CS_2$.

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.

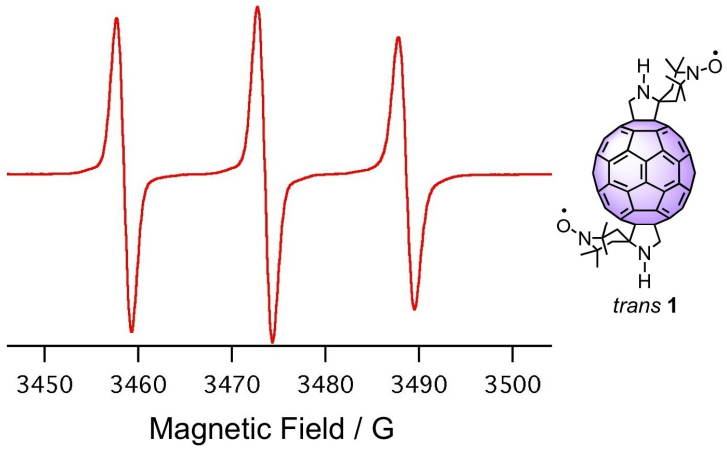

Fig. S11 EPR spectrum of *trans*-1 at room temperature.

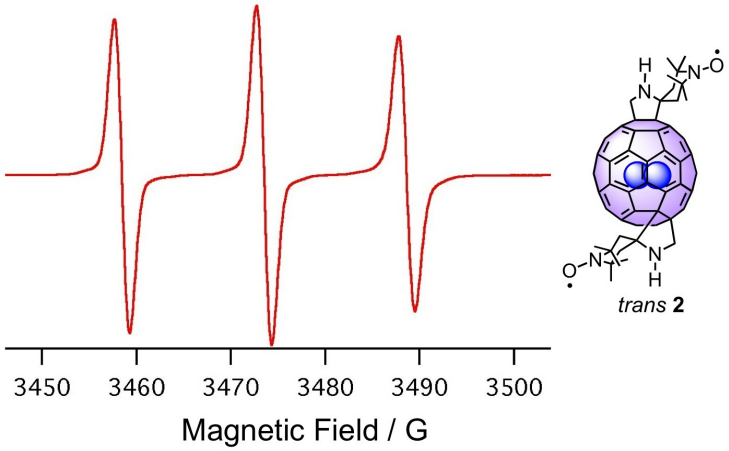

Fig. S12 EPR spectrum of *trans*-2 at room temperature.

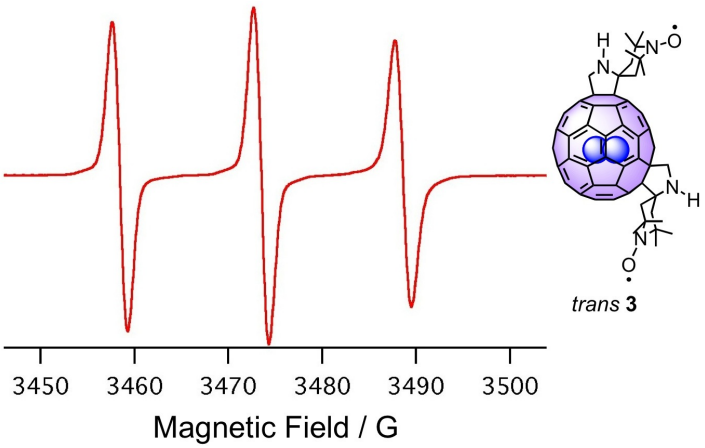

Fig. S13 EPR spectrum of *trans*-3 at room temperature.

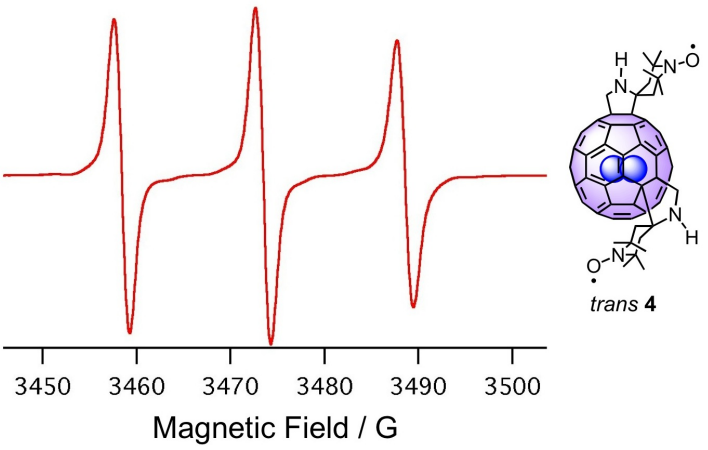

Fig. S14 EPR spectrum of *trans*-4 at room temperature.

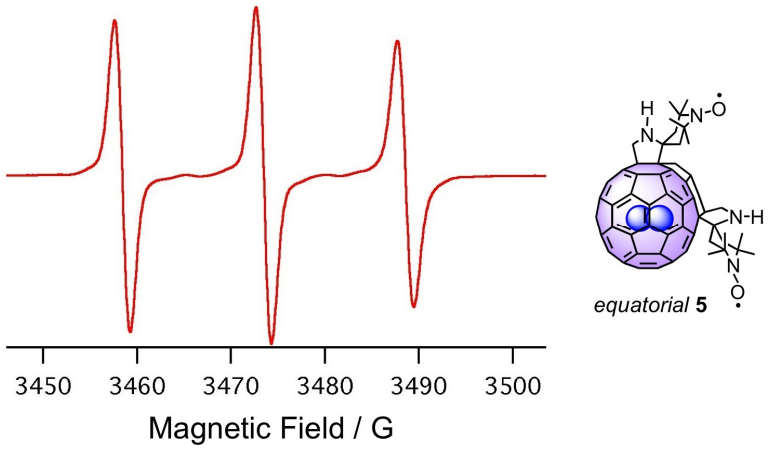

Fig. S15 EPR spectrum of *equatorial*-5 at room temperature.

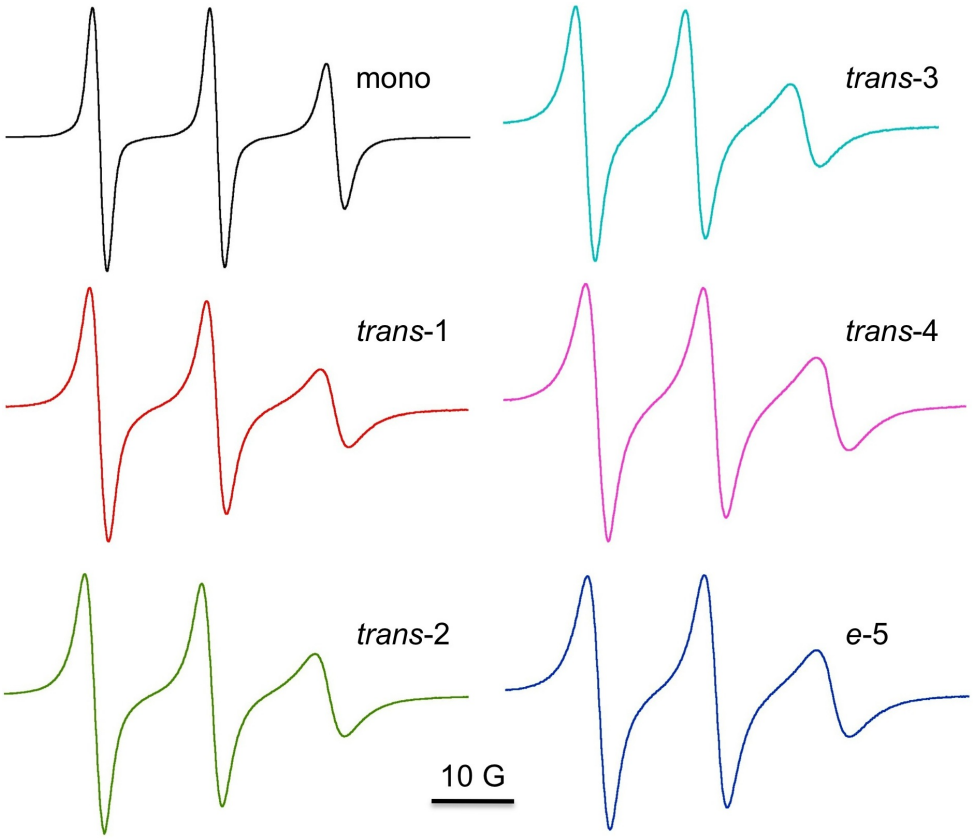

Fig. S16 EPR spectra of monoadduct and bisadduct isomers of **1** in deoxygenated toluene solutions at 213 K (EPR parameters: Modulation amplitude: 1 G; Resolution: 1024 points; Sweep width: 70 G).

References:

1. (a) Murata, M.; Murata, Y.; Komatsu, K. *J. Am. Chem. Soc.* **2008**, *128*, 8024-8033.

(b) Murata, Y.; Murata, M.; Komatsu, *Chem. Eur. J.* **2003**, *9*, 1600-1609.

2. Arena, F.; Bullo, F.; Conti, F. Corvaja, C.; Maggini, M.; Prato, M.; Scorrano, G. *J. Am. Chem. Soc.* **1997**, *119*, 789-795.

3. Schick, G.; Levitus, M.; Kvetko, L.; Johnson, B. A.; Lamparth, I.; Lunkwitz, R.; Ma, B.; Khan, S. I.; Garcia-Garibay, M. A.; Rubin, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3246-3247.