**Supporting Information**

# Indirect $^1$H NMR characterization of $H_2@C_{60}$ nitroxide derivatives and their nuclear spin relaxation

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## 1. Analysis of reduction of $C_{60}$ nitroxide for NMR characterization

Three requirements have to be fulfilled in order to realize the in situ NMR characterization: 1) the reducing process should be conveniently monitored; 2) a suitable reducing reagent has to be chosen in which the NMR signals from both the reducing reagent and its oxidative product would not interfere with the NMR signals of the reduced $C_{60}$ nitroxide product–hydroxylamine; 3) the reduction must occur on a convenient time scale for the EPR and NMR analysis. The first requirement is fulfilled by quantitatively monitoring the EPR signals of $C_{60}$ nitroxides during the reducing process. The reduction reaction takes less than an hour at room temperature. Hydrazobenzene is a mild reducing reagent and has been demonstrated to reduce nitroxide radicals to hydroxylamines effectively (Eq. 1).[1] The $^1$H NMR of hydrazobenzene is very simple: two multiplets in the aromatic region (~7 ppm) and one narrow peak of the -NH-NH- moiety (~5 ppm). The oxidized product azobenzene has only two aromatic peaks shifted to further low field (>7 ppm). By observing the structural features of $C_{60}$ nitroxide derivatives, both fulleropyrrolidines and methanofullerenes, we expected that NMR signals of the corresponding functional groups should appear in 1−5 ppm region, in which the NMR signals from hydrazobenzene and azobenzene would not interfere with that of the hydroxylamine products.
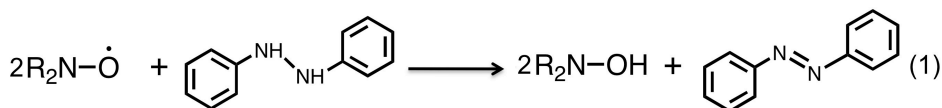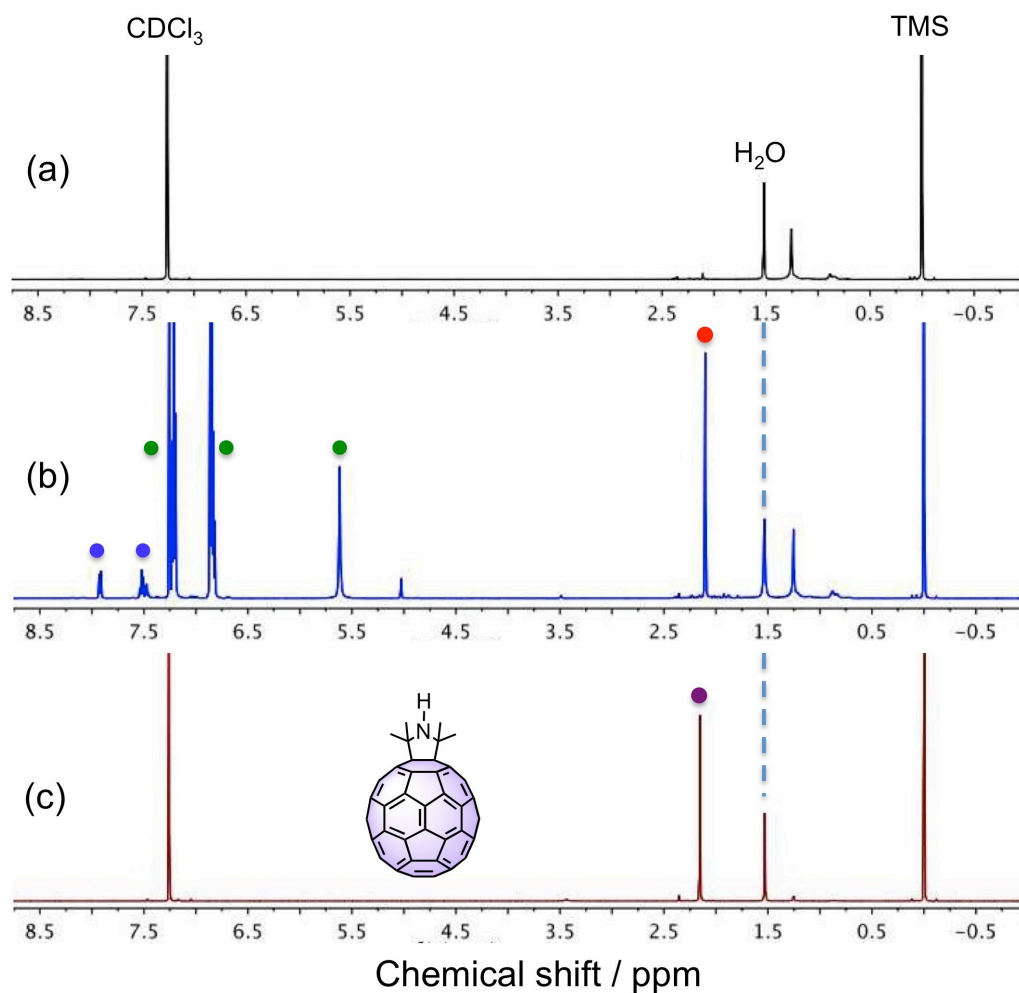
**Fig. S1** $^1$H NMR in CDCl$_3$ solutions. (a) **1**; (b) **1** after reduction by hydrazobenzene; new peaks labeled with red dots; peaks from azobenzene labeled with blue dots; hydrazobenzene peaks labeled with green dots; (c) **3** (synthetic precursor of **1**); methyl groups labeled with purple dot.

## 2. Monitor the reduction process by EPR

The reduction process of C$_{60}$ nitroxides **1** and **2** was monitored by EPR spectroscopy in toluene solutions at the radical concentration of 0.25 mM. For comparison, reduction of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) by hydrazobenzene was also performed. The resulting reduction profiles are shown in Fig.

S2. Both $C_{60}$ nitroxides are clearly reduced faster than that of the small molecule TEMPO. It has been reported[2] that electron-accepting groups attached to a nitroxide moiety accelerate the reduction reaction. As $C_{60}$ is a good electron acceptor, it might help the electron transfer process via stabilization of the reaction intermediates.
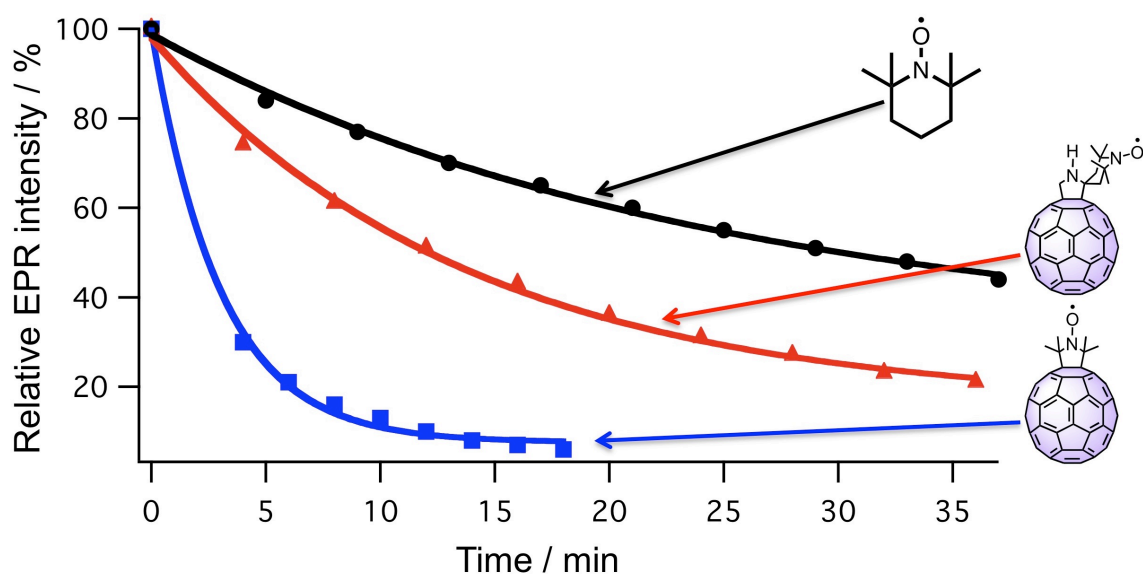


**Fig. S2** The profiles of reduction of **1** (blue curve, 1 eq of hydrazobenzene), **2** (red curve, 2 eq of hydrazobenzene) and TEMPO (black curve, 2 eq of hydrazobenzene) in 0.25 mM toluene solutions.
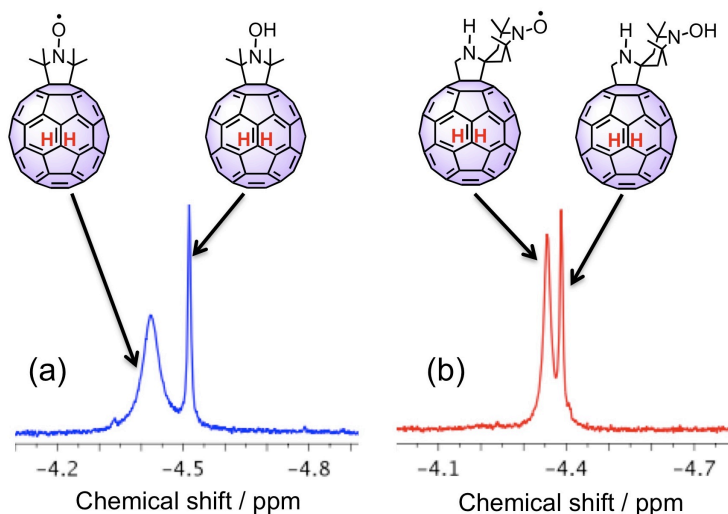


**Fig. S3** $^1$H NMR of endohedral $H_2$ in $CDCl_3$ solutions (a) $H_2@1$ and the corresponding hydroxylamine; (b) $H_2@2$ and the corresponding hydroxylamine at [c] = 3.34 mM.

## 3. Analysis of possible contact shift and hyperfine coupling

Previously, we have reported distance-dependent relaxivity of endohedral $H_2$ in a series of $H_2@C_{60}$ nitroxide derivatives.[3] It was found that the measured value of the spin-lattice relaxation rate of $H_2@1$ in 1,2-dichlorobenzene-$d_4$ (ODCB-$d_4$) at room temperature is slightly faster than can be accounted for by the dipolar interaction with the unpaired electron of the nitroxide using an estimate of the distance between the spins based on molecular modeling. It was suggested that this discrepancy could be accounted for by invoking a small contribution to $T_1$ from a hyperfine interaction modulated by relaxation of the electron spin. If present, however, this interaction would also be expected to (1) produce a contact shift, $\Delta_c$, of the resonance of the endohedral $H_2$ in the radical relative to the diamagnetic hydroxylamine and (2) make an even larger contribution to $1/T_2$, i.e. the linewidth, than to the spin-lattice relaxation rate, $1/T_1$.

The spectra in Fig. S3 do indeed exhibit downfield shifts of 45±1 Hz (-0.09 ppm) and 20±1 Hz (-0.04 ppm) for $H_2@1$ and $H_2@2$, respectively, and, as noted above, significant line broadening of the nitroxide. Shifts of this magnitude would require a proton hyperfine splitting (hfs), $a_H$, on the order of 1 milligauss.[4] A hyperfine interaction of this magnitude would also be expected to produce an additional contribution of *ca*. 8 s$^{-1}$ to the value of $1/T_2$, but have a negligible effect on $1/T_1$, for a reasonable value,[5,6] $10^{-7}$ s, for the electron relaxation time[7] since the rate of modulation of the hfs by electron relaxation is much slower than the electron larmor frequency, $2 \times 10^{12}$ rad s$^{-1}$. The observed paramagnetic contribution to the linewidth of $H_2@1$, obtained by subtracting the linewidths of the hydroxylamine from that of the nitroxide, is, however, only *ca*. 20 percent larger than expected from spin-lattice relaxation ($1/T_1 \approx 50$ s$^{-1}$, $1/T_2 \approx 60$ s$^{-1}$). This increase is consistent with the $T_1/T_2$ ratio of 7/6 expected for dipolar relaxation when the rotational rate is slower than the electron larmor frequency, but no slower than the nuclear larmor frequency.[8]

*We therefore conclude: (1) within the accuracy of the current measurements there is no detectable contribution of scalar coupling to $T_2$ in $H_2@1$, and that any hyperfine coupling between the nitroxide electron and the endo-$H_2$ nuclei must therefore be substantially smaller than 1 milligauss; (2) it therefore seems likely that the unexpectedly short $T_1$ of $H_2@1$ reported previously[3] is explainable by a somewhat shorter than*

*expected effective distance between the unpaired electron and the endo-$H_2$ nuclei (This would not affect the $T_1/T_2$ ratio expected from dipolar relaxation); and (3) the observed chemical shift difference between the endo-$H_2$ in the nitroxide and hydroxylamine arises primarily from differences in shielding of the nuclei in the slightly different electronic environments.[9]*

**References:**

(1) A. D. Malievskii and A. B. Shapiro, *Kinet. Catal.* 2005, **46**, 472.

(2) A. D. Malievskii, S. V. Koroteev and V. V. Kasparov, *Russ. Chem. Bull.* 1993, **42**,1027.

(3) Y. Li, X. Lei, R. G. Lawler, Y. Murata, K. Komatsu and N. J. Turro, *J. Phys. Chem. Lett.*, 2010, **1**, 2135.

(4) The chemical shift, $\Delta_c$, induced by scalar coupling at temperature T is given by:[10]

$$\Delta_c \text{ (ppm)} = -(\mu_0/4\pi)(u_B/\gamma_I)Ag(g-1)S(S+1)(3k_BT)^{-1}$$

where A is the hyperfine coupling in rad s$^{-1}$ [A = $17.6 \times 10^6$ $a_H$ (gauss)], g is the isotropic g-factor, and the other symbols have the usual meaning.

(5) The contribution of the scalar coupling to the relaxation rates is given by:[11,12]

$$1/T_{1p,c} = (2/3)A^2S(S+1)\tau_e(1+\omega_S^2\tau_e^2)^{-1}$$

$$1/T_{2p,c} = (1/3)A^2S(S+1)\tau_e[1 + (1 + \omega_S^2\tau_e^2)^{-1}]$$

where A is the hyperfine coupling in rad s$^{-1}$ and $\tau_e$ is the electron relaxation time.

(6) This somewhat non-intuitive conclusion is a consequence of nuclear spin-lattice relaxation occurring in this case via simultaneous flips of the electron and nuclear spins in a transition whose frequency is dominated by the electron larmor frequency; the linewidth, however, also has a contribution that does not involve spin flips and is therefore frequency independent.[13]

(7) Christina Schubert, personal communication.

(8) The Solomon-Bloembergen equations[11,12] for dipolar relaxation of a nuclear spin by an unpaired electron are:

$$1/T_{1p,dd} = \Omega_{dd}^2\tau_c[6/(1+\omega_I^2\tau_c^2) + 14/(1+\omega_S^2\tau_c^2)]$$

$$1/T_{2p,dd} = \Omega_{dd}^2\tau_c[4 + 3/(1+\omega_I^2\tau_c^2) +13/(1+\omega_S^2\tau_c^2)]$$

where $\Omega_{dd}{}^2 = (1/15)(\mu_0/4\pi)^2\gamma_I^2 g^2 \mu_B{}^2 S(S+1)r^{-6}$, $\tau_c$ is the rotational correlation time of the radical and the other parameters have their usual meaning. The ratio $(1/T_{2p,dd}/1/T_{1p,dd})$ should therefore be independent of r but increase as $\omega_I^2\tau_c^2$ becomes larger (assuming that $\tau_c > 0.5$ ps so that $\omega_S^2\tau_c^2 > 1$ ).

(9) A small contribution to the chemical shift, $\Delta_p$, in the nitroxide could arise from the pseudo-contact interaction which arises from cross-correlation of the electron-nuclear dipolar interaction and g-factor anisotropy.[14] This is usually negligible for radicals such as the nitroxides with small g-factor anisotropies. Such shifts could be detectable at high fields, however, in cases such as ours where the shifted lines are narrow. An accurate estimate of this effect requires detailed knowledge of the geometry of the nitroxide and the g-factor anisotropy which is not presently available for $H_2@\mathbf{1}$ or $H_2@\mathbf{2}$.

(10) J. Reuben, *Prog. NMR Spectros.* 1975, **9**, 1.

(11) I. Solomon, *Phys. Rev.* 1955, **99**, 559.

(12) N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, 1961, **34**, 842.

(13) A. Abragam, *The Principles of Nuclear Magnetism,* 1961, Oxford at the Clarendon Press; pp 308-312.

(14) G. N. La Mar, W. DeW. Horrocks, Jr. and L. C. Allen, *J. Chem. Phys.,* 1964, **41**, 2126.