ENDOR Evidence of Electron-H_2 Interaction in a Fulleride Embedding H_2. Supporting Information

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EXPERIMENTAL

CW-EPR spectra of NMP and H_2@NMP monoanions in 2-MeTHF have been acquired on a Bruker ER200D-SR spectrometer equipped with a TE_{102} cavity and a nitrogen flow cryogenic system (Bruker BVT-1000 temperature control unit). The spectra were recorded in the temperature range 290 – 140 K. In any case, the flow cryogenic system does not allow stabilizing the temperature with a precision better than ± 1 K. The radical concentration in the samples was carefully adjusted to strongly reduce Heisemberg exchange broadening.

Pulsed ENDOR measurements were performed in the range 50 - 100 K using an X-band Elexsys Bruker E580 spectrometer equipped with an ENDOR dielectric Bruker probe head, an Oxford CF 935 cryostat and an Oxford ITC503S variable temperature unit. Each ENDOR spectrum was acquired after the temperature was stabilized for at least one hour. In these conditions, we can estimate a temperature setting precision of about ± 0.1 K. Acquisition parameters: RF pulse length 14 us, MW inversion pulse 400 ns, MW $\pi/2$ pulse 200 ns. Spectra have been recorded in stochastic modality.

CW-EPR SPECTRA

Experimental and simulated CW-EPR spectra of NMP and H_2@NMP monoanions are shown in Figure S1. The spectra of the two anions were recorded under the same nominal experimental conditions. The spectra were simulated using *Win-EPR Simfonia.*[S1] The g-factor (g = 1.9998 ± 0.0005) and ^{14}N and ^{13}C hyperfine coupling constants reported previously (Reference 14b of the main text) were employed, and the same linewidth parameter was used for all of the hyperfine lines in each spectrum, but optimized for each of the spectra. As shown in Figure S1, the resulting fits to the observed spectra are better for H_2@NMP$^-$ than for NMP$^-$. Most notably, the outer lines ($m_I = \pm 1$ components) of the ^{14}N hyperfine triplet of NMP$^-$ are broader and less symmetrical than the central line ($m_I = 0$). The origin of the different linewidth effects for the two anions is unclear, but may be associated with different anisotropic contributions to the linewidths arising from subtle variations in the sample environments.[S2] Nevertheless, a best fit of the central line of NMP$^-$, shown in Figure S1, yields a linewidth, ΔB, of 6 μT, compared to ΔB = 11 μT for H_2@NMP$^-$, suggesting the presence of additional unresolved hyperfine structure in the latter.

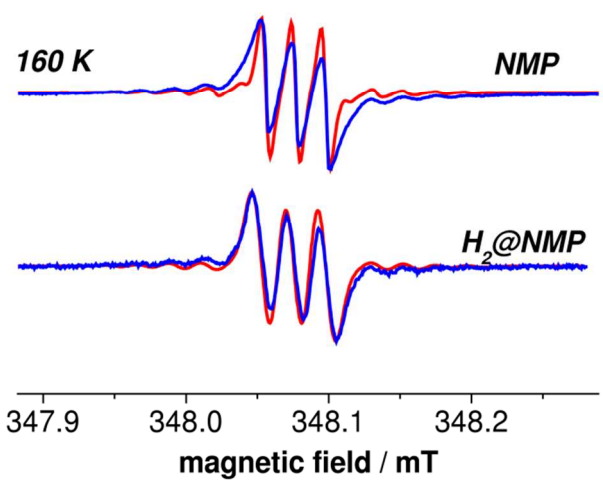

Figure S1. Experimental (blue lines) and simulated (red lines) CW-EPR spectra of NMP and H2@NMP monoanions recorded in solution of 2-MeTHF at T=160 K.

The linewidth difference is of the magnitude expected for the hyperfine coupling to the endo H_2 detected by ENDOR (see Table 1 in the main text). Nevertheless, we do not consider by any means proven that the difference in CW-EPR linewidth for NMP and H_2@NMP monoanions is due to endo H_2 for the following reason. The linewidth in the spectra of fullerene monoanions is strongly temperature-dependent. At temperature larger than about 160 K it has been proposed that the linewidth is mainly determined by a

temperature-dependent Orbach-type process (Reference 14b of the main text) that affects equally the three ^{14}N hyperfine lines, a process that would mimic unresolved hyperfine structure. Small differences in sample temperature might therefore lead to small linewidth differences by this mechanism.

SUPPLEMENTARY DIFFERENCE ENDOR SPECTRA

The difference spectra Z calculated using the formula $Z = Y - kX$ (see the main text), for the spectra Y (H_2@NMP$^-$ ENDOR spectrum) and X (NMP$^-$ ENDOR spectrum) recorded in the temperature range 50 –100 K are shown in the Figure S2.

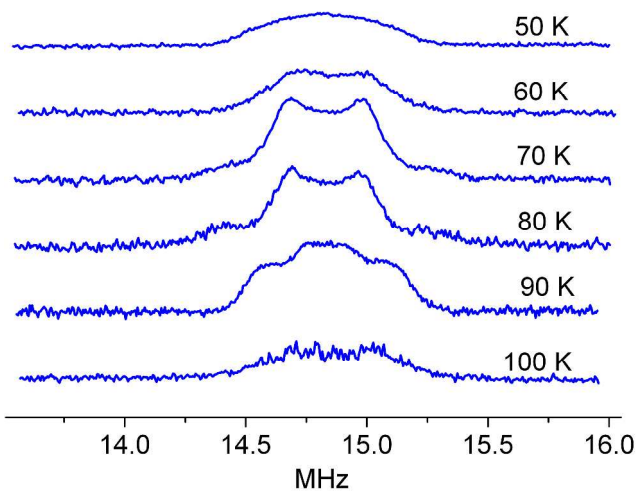

Figure S2. Difference ENDOR spectra between H2@NMP and NMP monoanions in the temperature range 50 - 100 K.

CONTROL EXPERIMENTS

The excitation pulse width and the instrumental set up can be a relevant problem in ENDOR experiments, because artifacts could appear in the ENDOR profile when weak couplings are measured. In order to verify the experiment reproducibility, each ENDOR spectrum was acquired twice, on two different days, and was perfectly well reproduced. In order to check for pulse width effects, we carried out the same ENDOR experiments using a shorter RF pulse length (12 μs instead of 14 μs) at T=80 K, for both NMP and H_2@NMP anions.[S3] The ENDOR spectra acquired for both samples with RF pulse lengths of 12 μs (blue line) and 14 μs (red line) are shown in Figure S3: no evident differences between the spectra recorded with different RF pulse lengths are observable. The length of microwave (MW) pulses could be a relevant problem too, when weak couplings are measured with ENDOR. The effect of the different length of MW pulses on the ENDOR profile has been investigated by recording ENDOR spectra of H_2@NMP monoanion at T=80 K and using different MW pulse lengths. In Figure S4 the ENDOR spectra of H_2@NMP monoanion acquired at 80 K with MW inversion pulse of 320 ns (red line), 400 ns (black line) and 800 ns (blue line) are shown. In every experiment the RF pulse length was set to 14 μs and the MW π/2 pulse length was set to coincide with half the MW inversion pulse length. It is apparent that the ENDOR spectra acquired with 400 ns and 800 ns MW inversion pulses are quite similar (blue and black lines), while the ENDOR spectrum with 320 ns MW inversion pulse is characterized by a dip in the center of the line. The dip could be due to selectivity effects. Selectivity effects occur when the MW inversion pulse width is larger than the hyperfine couplings to be measured. In that case the intensity of the corresponding ENDOR lines is reduced. With a MW inversion pulse of 320 ns, the pulse width is larger than the smallest hyperfine couplings of our spectrum, and the corresponding ENDOR lines (close to the center of the spectrum) become weaker, causing the appearance of the dip. However, with a MW inversion pulse of 400 ns the ENDOR lines corresponding to the smallest hyperfine couplings are not significantly suppressed, since a longer inversion pulse (800 ns) does not change the ENDOR profile. Therefore a MW inversion pulse of 400 ns is suitable to get an undistorted ENDOR spectrum of our samples.

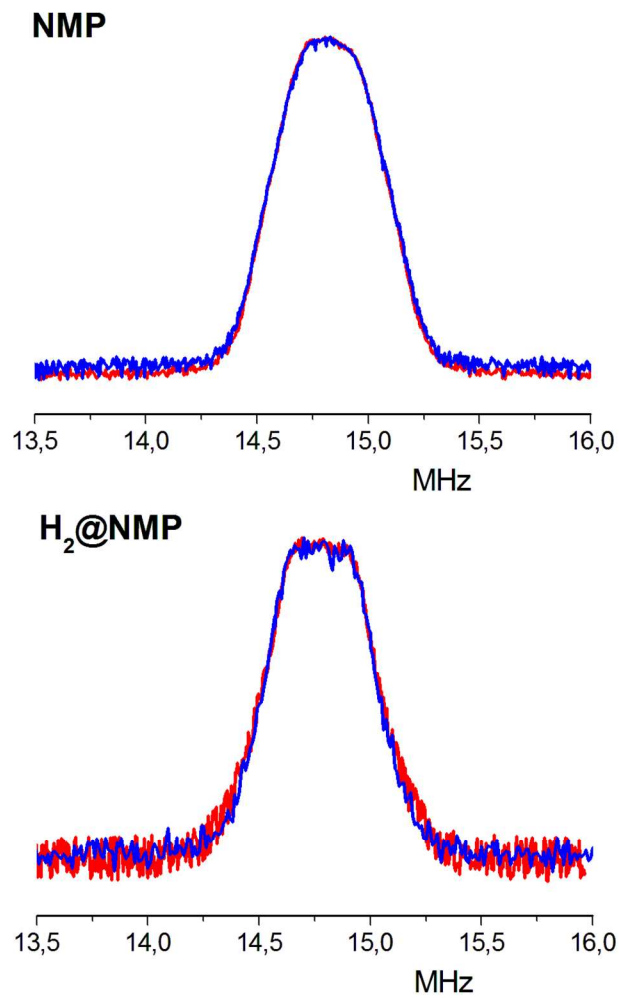

Figure S3. ENDOR spectra acquired at T = 80 K for NMP and H_2@NMP monoanions (in 2-MeTHF solution) with a RF pulse length of 12 μs (blue lines) and 14 μs (red lines).

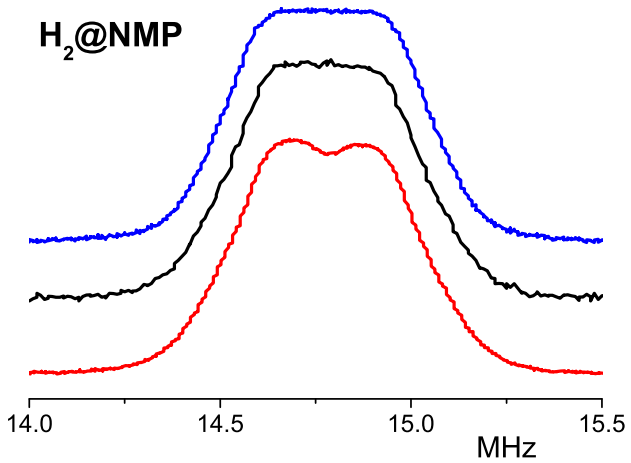

Figure S4. ENDOR spectra acquired at T=80 K for H_2@NMP monoanions (in 2-MeTHF solution) with a MW inversion pulse length of 320 ns (red line), 400 ns (black line) and 800 ns (blue line). In all cases: RF pulse length = 14 μs; MW π/2 pulse length = ½ MW inversion pulse.

REFERENCES

(S1) *Win-EPR SimFonia* is a user-friendly commercial computational package for spectral EPR simulations running on the Windows platform. For more details, please visit the Bruker-Biospin website: *http://www.bruker-biospin.com/simfonia.html* .

(S2) A simulation of the monoanion EPR spectra taking into account anisotropic linewidth contributions is beyond the scope of this work.

(S3) A π RF pulse of shorter length cannot be obtained with the available RF amplifier.