Supplementary Material (ESI) for Chemical Communications

First observation of the hyperfine structure of an excited quintet state in liquid solution.

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Supplementary Information.

The simulation of the steady state EPR spectrum of **1** has been carried out by finding the eigenvalues and eigenvectors of the Hamiltonian:

$$H = g\beta B\, S_z(1) + g\beta B\, S_z(2) + a_N\, S_z(1)I_z(a) + a_N\, S_z(2)I_z(b) - 2J\, \mathbf{S}(1)\mathbf{S}(2)$$

The calculated spectrum takes into account the linewidth variations due to molecular rotational diffusion and due to J modulation induced by conformational changes. The linewidths depend on the particular transition considered i.e. they depend on the total nuclear spin quantum number M_I and on the single nuclear spins m_{I1} and m_{I2}. The linewidth is described by the following formulas [ref. 9]:

$$\frac{1}{T_2} = \frac{1}{T_2}(M_I) + \frac{1}{T_2}(m_{I1}, m_{I2})$$

$$\frac{1}{T_2}(M_I) = A + BM_I + CM_I^2$$

$$\frac{1}{T_2}(m_{I1}, m_{I2}) = \frac{a^2(m_{I1} - m_{I2})^2}{4J^2} j(J)$$

where $j(J)$ is the spectral density at the J frequency. The best-fit EPR spectrum together with the experimental spectrum are shown in Figure 1 and best-fit parameters a ,J, g, A, B, C are reported in Table 1

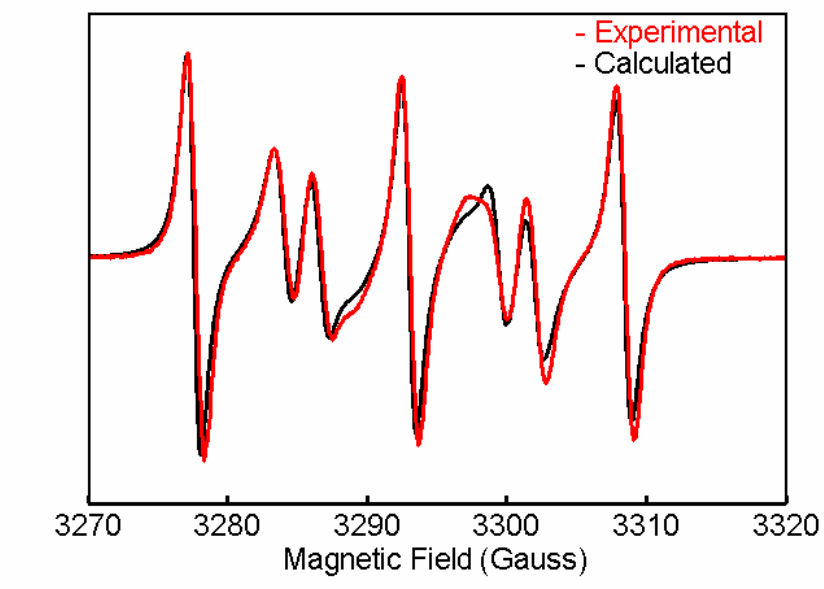

Figure 1. Experimental steady-state EPR Spectrum (red) and computer simulation (black) for the nitroxide biradical ***1.***

Parameter	***Value***
g-factor	2.0062 ± 0.0005
Hyperfine Coupling Constant a_N	15.4 Gauss
Exchange Interaction Constant J	45 Gauss.
A	0.9 Gauss
B	-0.025 Gauss
C	0.001 Gauss
j(J)	12.31 Gauss

*Table 1. Simulation parameters for nitroxide biradical **1** in the ground state*

The Time Resolved EPR spectrum recorded after pulsed photoexcitation, at a delay of 0.5 microseconds after the laser pulse, is simulated by the superposition of the EPR lines of the biradical **1** in its ground state and of additional five lines, with intensity ratios 1:2:3:2:1, as shown in figure 2. The ground state lines are polarized and are either in enhanced absorption or in emission due to a selective population of the spin sublevels from the excited states [ref. 10].

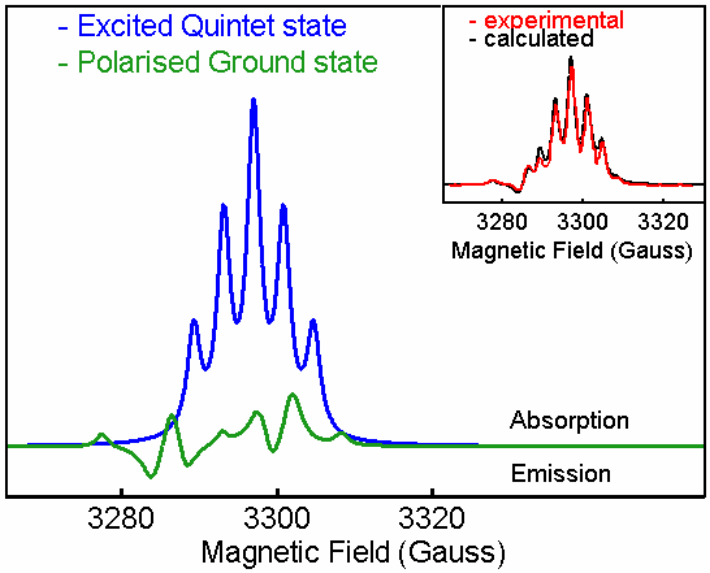

*Figure 2. Calculated Time Resolved EPR Spectrum for the ground state (green) and excited quintet state (blue) of nitroxide biradical **1**. The superposition of the two spectra give the experimental TR-EPR spectra reported in the insert.*

Parameter	***Value***
g-factor	2.0039 ± 0.0005
Hyperfine Coupling Constant	3.85 Gauss
Linewidth	1.02 Gauss

*Table 2. Simulation parameters for nitroxide biradical **1** in the excited quintet state*