

Time-resolved EPR characterisation of radical–triplet pairs formed by host–guest interaction of a photoexcited C₆₀–crown ether with an ammonium aminoxyl in liquid solution

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A time resolved EPR (TR-EPR) spectrum of a radical–triplet pair (RTP) in the quartet excited state has been recorded by irradiating with visible laser light a solution of a [60]fullerene–crown ether conjugate and an ammonium aminoxyl radical; this is the first direct observation of a RTP in liquid solution for a stable host–guest complex between a macrocyclic ligand bearing a triplet precursor and an aminoxyl ammonium cation.

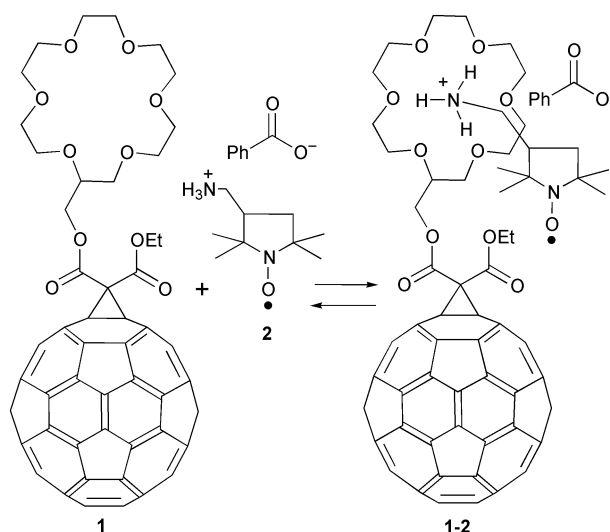
Several investigations have shown that triplet excitations are quenched in the presence of free radicals, with a mechanism involving the formation of radical–triplet pairs (RTP).¹ The radical–triplet encounter can form a pair either in a quartet (⁴[RTP]) or in a doublet state, whose energies are separated by the exchange interaction *J*. These two states are mixed by the electron–electron dipolar interaction.

In a magnetic field, the doublet character of the four quartet components is not the same and they decay with different rates to the ground state, causing a transient deviation of the radical sublevel populations from the thermal equilibrium values. This spin polarisation is revealed as an anomalous EPR line intensity.^{2,3} The TR-EPR spectrum of a radical recorded in the presence of a triplet precursor after a laser pulse presents lines in enhanced absorption (A) or in emission (E). Spin polarisation derives also by the radical quenching of the excited singlet state, *i.e.* by enhanced ISC. In this case the polarisation is opposite to that caused by triplet quenching.⁴

The observation of spin polarised EPR spectra of a stable radical, such as aminoxyl radicals, in the presence of a triplet precursor is an indication of the formation of RTPs. However, the direct observation of a RTP in its excited quartet state by EPR spectroscopy is not feasible since collision pairs, in solutions of moderately viscous liquids, have lifetimes too short⁵ to be detected *via* their ⁴[RTP] EPR spectrum. On the other hand, ⁴[RTP] spectra could be recorded for molecular systems where the radical and triplet precursor were (i) covalently linked,⁶ (ii) coordinated⁷ or (iii) linked to a molecular template.⁸

In this paper we report the first observation of a RTP that forms upon photoexcitation of a host–guest complex between [60]fullerene–crown ether conjugate **1** and the benzoate ammonium salt of 3-aminomethyl-[2,2,5,5-tetramethylpyrrolidin-1-oxyl] **2**.

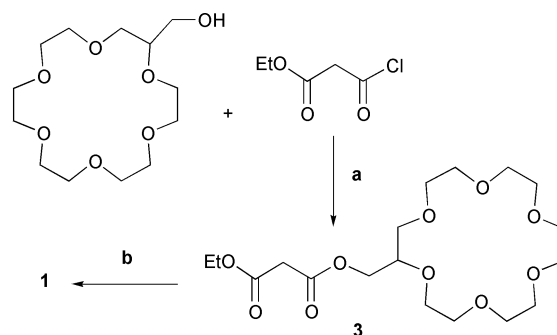
Derivative **1** combines in one molecule both the 18-crown-6 ionophore and the [60]fullerene triplet precursor, that has been selected for the long lifetime and high quantum yield of its triplet excited state.¹⁰ The synthetic strategy toward derivative **1** is outlined in Scheme 1 and requires two steps. Esterification between commercially available hydroxymethyl-18-crown-6 and ethylmalonyl chloride in the presence of solid NaHCO₃ afforded ester **3** in 33% isolated yield. Cyclopropanation of C₆₀¹¹ with **3** in the presence of I₂ and 1,8-diazab-



cyclo[5.4.0]undec-7-ene (DBU) in toluene at rt gave **1** in 42% isolated yield.

All spectroscopic and analytical data were consistent with the proposed molecular structure.[†] Ammonium aminoxyl **2** was obtained by mixing equimolar amounts of the corresponding aminomethyl aminoxyl and benzoic acid in diethyl ether. Pink crystals were isolated after crystallization from isopropyl ether.

The TR-EPR spectrum recorded by laser excitation of **1** in CHCl₃ solution at 235 K consists of a single broad line ($\Delta B = 1.66 \pm 0.02$ mT) centred at $g = 2.0016 \pm 0.0002$ which is attributed to the excited triplet state. The line is broadened because of the incomplete averaging of the electron dipolar interaction. The signal decay is accounted for by two exponential functions with time constants $\tau_1 = 0.9$ μ s and $\tau_2 =$



Scheme 1 Reagents and conditions: a, solid NaHCO₃, toluene, reflux, 8 h, 33%; b, C₆₀, I₂, DBU, toluene, rt, 2 h, 42%.

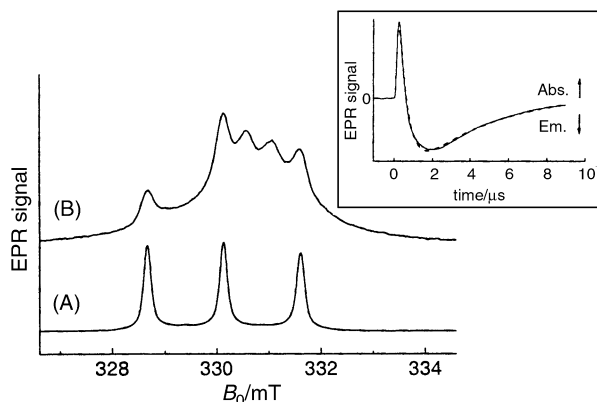


Fig. 1 EPR spectra of a 2 mM CHCl_3 solution of **1** and **2** at 235 K. (A) Integrated EPR spectrum. Microwave attenuation 20 dB. (B) TR-EPR spectrum recorded by laser excitation. Time delay from the laser pulse 250 ns. Microwave attenuation 5 dB. In the insert the signal decay of the central quartet line (solid line) and the fitting to a tri-exponential function (dotted line) are shown.

9.2 μs . The first decay time is to be assigned to the spin relaxation process which brings the initially spin polarised sublevel populations to thermal equilibrium values. The larger constant τ_2 is the triplet lifetime.

The EPR spectrum of a 2 mM CHCl_3 solution of both **1** and **2** consists of three lines with $g_{\text{NO}} = 2.0057 \pm 0.0002$ and hyperfine separation $a_{\text{N}} = 1.47 \pm 0.02$ mT, which are the typical values for an aminoxyl free radical, such as TEMPO, in that solvent (Fig. 1A).

When the solution was illuminated by a laser pulse, a strong spin polarised spectrum was recorded, as shown in Fig. 1B. It consists of three lines at the field positions corresponding to the aminoxyl lines and of three additional lines centred at a lower g value ($g = 2.0031 \pm 0.0002$), with a separation of 0.46 ± 0.02 mT. The central line of the aminoxyl spectrum and the low field line of this second multiplet coincide. A broad signal is superimposed to these narrow features.

The three lines with 0.46 mT splitting are assigned to the host-guest complex **1-2**.¹² They are typical of the aminoxyl-fullerene triplet pair in the quartet excited state where the three unpaired electron spins interact with a single ^{14}N nuclear spin.⁶ Since the electron spins are distributed 2/3 on fullerene and 1/3 on the aminoxyl group, the coupling constant is reduced to 1/3 the typical value for an aminoxyl radical. Also the g factor agrees with the value expected for a quartet, obtained from the g factor of the triplet state of **1** ($g_{\text{T}} = 2.0016$) and of the aminoxyl ($g_{\text{NO}} = 2.0057$) according to the formula $g_{\text{Q}} = 2/3g_{\text{T}} + 1/3g_{\text{NO}}$.¹³ The TR-EPR spectrum of an equimolar amount of **1** and toluene-*p*-sulfonic ester of 3-hydroxymethyl-[2,2,5,5-tetramethylpyrrolidin-1-oxyl]¹⁴ in CHCl_3 does not show the quartet special features observed for **1-2**.

The lifetime of the quartet signal, recorded at 235 K, is about 4 μs (see insert of Fig. 1). This value is much larger than the lifetime of a collisional pair made by the encounter of **1** and **2** in the same solvent at the same temperature, which can be calculated by using⁵ the following Einstein-Smoluchowski equation that gives the escape rate of a RTP partner:

$$k_{\text{E}} = 2(D_{\text{R}} + D_{\text{T}})/(\rho_{\text{R}} + \rho_{\text{T}})^2$$

where D_{R} and D_{T} are the diffusion coefficients of the two partners and ρ_{R} and ρ_{T} their van der Waals radii. D_{R} and D_{T} are obtained from the Stokes-Einstein relation:

$$D = kT/6\pi\eta\rho.$$

Using $\eta = 1.2 \text{ cP}^{15}$ and for ρ_{R} and ρ_{T} the estimated values 0.35 and 0.70 nm, the RTP lifetime $1/k_{\text{E}} = 1.1 \text{ ns}$ is obtained.

In the TR-EPR spectra there are signals of three species: excited triplet **1**, **2** and the associated form **1-2** in the quartet state. The EPR spectrum of the **1-2** host-guest complex in the ground state is not expected to differ significantly from that of free **2**. Unfortunately, the relative concentrations of **2** and **1-2** could not be measured directly from the TR-EPR spectra because the signal intensity depends not only on their concentration, but also on the amount of spin polarisation, which is not known. This method for observing host-guest interaction can be extended to other systems, where a partner contains a triplet precursor and the other a free radical.

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Notes and references

† Selected data for **1**: ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.49 (t, 3H, $\text{COOCH}_2\text{CH}_3$), 4.07–3.60 (m, 2H, OCH_2CH_2), 4.57 (q, 2H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.67 (d, 2H, $\text{CO}_2\text{CH}_2\text{CH}$); λ_{max} (CH_2Cl_2)/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 324 (2700), 257 (8570), 226 (71400); m/z (ESI-MS): 1149 ($\text{M} + \text{Na}^+$), 1165 ($\text{M} + \text{K}^+$).

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