

# Optimal magnetization in liquids, generated by triplet–doublet interaction

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This study is an extension of a recent theoretical treatment for calculating the magnetization generated by the encounters of radicals and photoexcited triplets in solution. Whereas the previous study employed a restricted analytical approach to the problem, the present study takes into account a general numerical formulation for the solution of the stochastic Liouville equation to calculate the electron spin polarization generated in the radical, following its encounter with the triplet. This method considers the efficiency of triplet quenching by the radical, which is an important factor in determining the radical polarization and the triplet lifetime in the solution. In addition, numerical calculation of the diffusion process is used to obtain the overall magnetization of the radical and its time dependence. The theory presented here complies with the experimental results and allows for efficient optimization of the magnetization in terms of magnitude and overall lifetime. Such an optimization is accomplished by the proper choice of the chemical system, which is exposed to light excitation, solvent properties and temperature. The ultimate goal of this study is to achieve photo-controlled high magnetization, which can be used in a variety of novel microwave applications.

## 1. Introduction

Many photophysical and photochemical processes can generate transient electron spin polarization (ESP), which is directly related to the phenomenon of chemically induced dynamic electron polarization (CIDEP) [1–4]. Although the basic aspects of CIDEP are well established, the potential use of ESP to various practical applications is much less obvious and rare [5–7]. For example, if spin distribution can be generated with inverted population, it would resemble a situation found in a maser amplifier [8, 9], but with the clear advantage of operating possibly at room temperature, rather than at very low cryogenic temperatures.

The classical CIDEP mechanisms such as the triplet mechanism [10, 11] or the radical pair mechanism (RPM) [3] are not suitable for maser operation at room temperature due to the short lifetime of the polarization, inhomogeneous line broadening and, in many cases, the irreversibility of the processes by photo-degradation. However, a different mechanism, introduced in the last decade, involves the interaction of triplets and stable radicals in liquid solution, and may be more useful for applied purposes. In this case, the generated ESP is based on two fundamental mechanisms, namely

electron spin polarization transfer (ESPT) and the radical–triplet pair mechanism (RTPM) [4, 12–14]. These intermolecular processes can produce high spin polarization, which leads to high and long lived magnetization, even at room temperature [1]. Moreover, by changing the ingredients of the chemical system, one can control the parameters, which determine the temporal behaviour of the magnetization and its magnetic properties, i.e. solvent viscosity, triplet zero field splitting (ZFS) parameter, radical size and EPR linewidth.

To optimize the conditions for generating high and long lived polarized magnetization, due to triplet–radical interaction, one must have a detailed knowledge of the mechanisms involved in this process. Several studies have considered the parameters affecting the ESP magnitude [1, 15–18] and the temporal behaviour of the magnetization [1, 18–20]. For example, a recent and advanced theoretical study has considered the radical polarization as a function of solvent viscosity, where non-efficient triplet quenching during the encounter may occur [17]. Whereas this treatment was confined to non-polarized triplets, a different approach considered the case where a polarized triplet interacts with a stable radical, but only in low viscosity solvents [1]. It is clear that, although significant progress has been accomplished, a complete analysis of this intermolecular photoprocess is still warranted.

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In this study we discuss some open questions regarding the theoretical aspects of the radical polarization and its magnetization. More specifically, we shall discuss the following points (cf. figure 1). First is the effect of solvent viscosity, in which the radical polarization is generated by the encounters of polarized (or non-polarized) triplets with polarized (or non-polarized) radicals. The case of having a polarized radical, prior to the encounter, is of importance. In some recent experiments, the radical exhibited a very long spin-lattice relaxation (SLR) time ( $T_1^R \sim 100 \mu\text{s}$ ) (see [1] and the results presented below). In this case, the encounters of triplets and polarized radicals should affect both the ESPT and RTPM processes. For example, a possibility not discussed in the past is the interaction of a polarized radical and a non-polarized triplet, where the polarization transfer is likely to occur preferentially from the radical to the triplet. Moreover, the involvement of polarized radicals may affect the efficiency of RTPM. Another point is the determination of the radical polarization in terms of the encounter time, and its relation to the SLR times of the triplets and radicals. In some cases, when the triplet-radical encounter time is comparable with the triplet SLR time, a decrease in the radical polarization after separation is expected. Third is the case of the complete depletion of the excited doublet levels as treated recently (figure 1, case A) [1]. This case will be extended to study the generation of the RTPM as a function of excited doublet depletion efficiency. We shall correlate quantitatively the radical polarization and its magnetization as a function of the degree of triplet quenching. The efficiency, by which the excited doublet is depleted, reflects the degree of triplet quenching, and evidently will affect the overall radical magnetization and polarization. In other words, efficient triplet quenching may lead to high radical polarization in a single encounter, but at the same time it will reduce very quickly the triplet population, thus decreasing the overall radical magnetization.

These issues will be treated theoretically by numerical and analytical methods, and will be examined by the experimental results presented in this work. This will allow us to change the controllable parameters, namely the magnetic and chemical systems, enabling us to predict the optimal conditions that should lead to the highest, long lived, radical magnetization and polarization. In the present study we consider only the net radical polarization, without discussing the multiplet polarization, which was found to be negligible in our chemical systems.

## 2. Experimental

Free base tetraphenylporphyrin,  $\text{H}_2\text{TPP}$  (Aldrich) was used without further purification. A derivative of

the trityl radical with good solubility in organic solvents was synthesized by using the procedure detailed in appendix A. The starting material for the synthesis was obtained from Nycomed Innovations in Sweden. The radical was chosen due to its sharp line in liquid solution, which is suitable for FT-EPR measurements, and its high solubility in organic solvents. 1,2-Dichlorobenzene and heavy paraffin oil with viscosity of  $\sim 350$  cP (Sigma) were used as solvents. Samples were prepared by dissolving the porphyrin in 1,2-dichlorobenzene and paraffin in 2 mM concentration, and then mixing the two solvents with varying ratios (5, 10, 20 and 30% of 1,2-dichlorobenzene) to obtain different viscosities (250, 200, 100 and 25 cP, respectively). The radical was then added to the solutions with a concentration of 2 mM. The solutions were inserted in a Pyrex EPR tube (4 mm o.d. and 2.8 mm i.d.) and were sealed under vacuum after several freeze-thaw-pump cycles. FT-EPR measurements were performed with a Bruker ESP 380E spectrometer. The porphyrins in the mixture were photoexcited by a Continuum laser model Surlite II ( $\lambda = 532$  nm, pulse duration 8 ns, pulse repetition rate 10 Hz, pulse energy 5 mJ per pulse). The initial triplet concentration was calculated to be  $\sim 0.25$  mM, taking into consideration the porphyrin extinction coefficient and light intensity. All experiments were performed at room temperature. Additional details regarding the pulse sequences used are given in [1].

## 3. Triplet quenching and the RTPM

Let us consider the encounters between thermal triplets and radicals to generate the RTPM, allowing for some triplet quenching to occur (figure 1, case C). This type of encounter does not consider ESPT, which is relevant only for polarized species. In general, for efficient diffusion-controlled triplet quenching by the radical, one expects the quenching rate of the triplet to be 1/3 of the diffusion-controlled encounter rate [1]. This is due to selection rules, allowing only the two excited doublet levels, out of the six levels (figure 1, cases A and B), to be depleted efficiently to the ground state [21]. In our experiments, however, we have observed quenching rates, that are about 1/40 of the diffusion-controlled values [1]. These low rates were interpreted within the framework of well established theories [22, 23] considering the quenching process due to triplet-radical interaction. Nevertheless, despite the low efficiency of the triplet quenching process, it was found that during the same triplet-radical encounters the RTPM polarization is generated with a relatively high efficiency of about 1/4 of the diffusion-controlled rate. Evidently, the different mechanisms involved in the triplet quenching and the generation of radical polarization, lead to the substantial difference in the rates of these processes [1]. Thus, we

shall discuss the theoretical aspects of how the efficiency of the quenching process (excited doublet depletion) affects quantitatively the RTPM polarization of the radical.

During a radical–triplet encounter, both quartet and excited doublet levels are formed, and the RTPM polarization is generated by the levels mixing (figure 1). In the analytical treatment [1] we assumed complete depletion of the excited doublet levels, while the present study takes into account any degree of excited doublet depletion. To treat the problem properly, we shall use numerical methods, which can model the non-negligible back transition from the excited doublet to the quartet levels in the crossing regions. This back transition is possible provided that the excited doublet depletion to the ground state is inefficient. The present treatment will be based on the ‘two levels’ model [18, 24] modified to incorporate the initial conditions to any degree of triplet quenching. The freedom of choice of the initial conditions will also enable us to consider cases where the radical and/or triplet are polarized prior to the encounter.

The spin Hamiltonian of the triplet–radical pair is

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_{zfs} + \mathcal{H}_{ex}, \quad (1)$$

where  $\mathcal{H}_z$  is the Zeeman part with the energy given in units of  $\text{rad s}^{-1}$ , e.g.  $\omega_0 = g\beta B_0$ , and we assume that the  $g$  factors of the radical and triplet are the same:

$$\mathcal{H}_z = \omega_0(S_R^z + S_T^z). \quad (2)$$

$\mathcal{H}_{zfs}$  is the ZFS part (assuming  $E \ll D$ ), which is given by

$$\mathcal{H}_{zfs} = D \left( S_T^2 - \frac{1}{3} S_T^2 \right), \quad (3)$$

where  $z$  is the principal axis of the ZFS interaction, with the notation that  $X, Y, Z$  and  $x, y, z$  are the frames of reference of the laboratory and molecule, respectively. This axis rotates isotropically in the laboratory frame (triplet tumbling in solution), resulting in a time dependent ZFS interaction. The exchange interaction is expressed by  $J(r) = J_0 e^{-\alpha(r-d)}$ , where  $d$  is the distance of closest approach and  $\alpha$  is a free parameter, and the Hamiltonian is given by

$$\mathcal{H}_{ex} = -J(r)(1 + 2S_R \cdot S_T). \quad (4)$$

Upon approach, the spin angular momentum is added to produce the following states [1].

For  $S = 3/2$ , four quartet states are created:

$$|Q \pm 1/2\rangle = \sqrt{2/3}|0\rangle|\pm 1/2\rangle + \sqrt{1/3}|\pm 1\rangle|\mp 1/2\rangle \quad (5a)$$

$$|Q \pm 3/2\rangle = |\pm 1\rangle|\pm 1/2\rangle. \quad (5b)$$

For  $S = 1/2$ , two excited doublet states are created:

$$|D \pm 1/2\rangle = -\sqrt{1/3}|0\rangle|\pm 1/2\rangle + \sqrt{2/3}|\pm 1\rangle|\mp 1/2\rangle. \quad (6)$$

We focus on the three crossing points marked in figure 1, which contribute most significantly to the RTPM polarization. Second-order contributions due to  $Q \leftrightarrow D$  transitions in the approaching regions are not considered, since they do not affect the general behaviour of the solution [17]. The crossing points of the  $Q$ – $D$  levels exist only for  $J \geq \omega_0$ , a condition that is satisfied in our case at X band frequencies. In high field experiments (e.g. W band), the  $Q$ – $D$  levels do not cross each other, and thus the resulting polarization is much smaller [1]. Such an effect can also be found in the X band if we consider species that cannot approach each other at distances shorter than  $\sim 10$ – $12$  Å, where the exchange interaction is strong enough.

We consider now the matrix elements of the Hamiltonian, for the three interacting pairs in the vicinity of the crossing regions. The root-mean-square of these non-zero matrix elements is averaged over all triplet orientations to obtain the  $Q \leftrightarrow D$  transition rate (figure 1) [15].

For the mixed pair of levels  $|Q - 3/2\rangle$  and  $|D - 1/2\rangle$  we determine the matrix elements, using the wavefunctions in equations (5) and (6) and the full Hamiltonian:

$$\begin{bmatrix} -(3/2)\omega_0 - J(r) & D/\sqrt{45} \\ D/\sqrt{45} & -(1/2)\omega_0 + 2J(r) \end{bmatrix}. \quad (7)$$

For the pairs  $|Q - 3/2\rangle$  and  $|D + 1/2\rangle$  we have

$$\begin{bmatrix} -(3/2)\omega_0 - J(r) & 2D/\sqrt{45} \\ 2D/\sqrt{45} & (1/2)\omega_0 + 2J(r) \end{bmatrix}. \quad (8)$$

Finally, for the pairs  $|Q - 1/2\rangle$  and  $|D + 1/2\rangle$  we have

$$\begin{bmatrix} -(1/2)\omega_0 - J(r) & D\sqrt{15} \\ D/\sqrt{15} & (1/2)\omega_0 + 2J(r) \end{bmatrix}. \quad (9)$$

Here we have neglected the ZFS in the diagonal terms. Recalling that the experiments are carried out in solution, and for  $D\tau_c \ll 1$  ( $\tau_c$  is the triplet rotational correlation time), one should consider only the average value of the ZFS Hamiltonian [15]. This assumption is valid for triplet porphyrins satisfying  $D \sim 1$  GHz and for solvents, in which  $\tau_c < 1$  ns. The opposite case is of relatively slow rotational correlation time, where  $D\tau_c \gg 1$  and  $\tau_c$  is much larger than the encounter time ( $\tau_c \gg (R_R + R_T)^2/D_r$  where  $R_R$  and  $R_T$  are the radical and triplet radii respectively). Due to the ergodic nature of the problem, even for this case, the calculation using the matrix elements (equations (7)–(9)) represents faithfully the average polarization the radical acquires in a large number of such encounters. Using the generalized

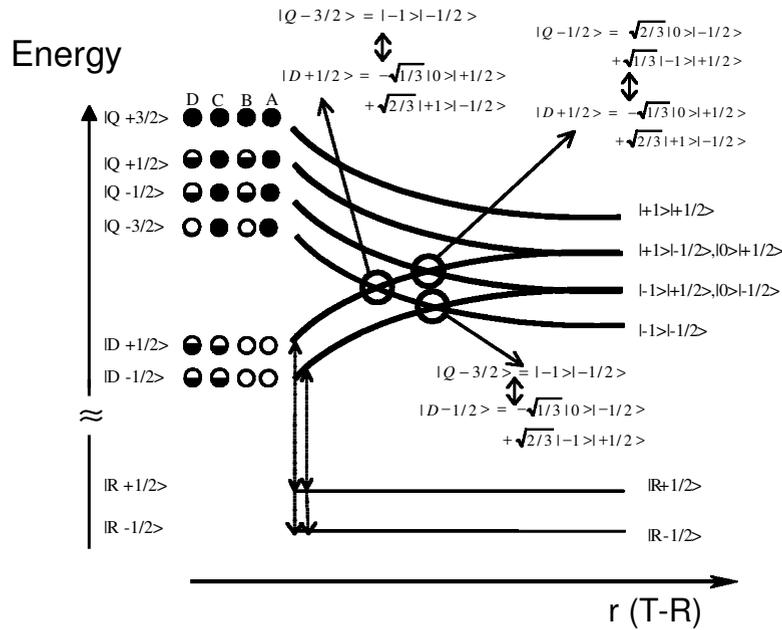


Figure 1. Energy levels (schematics) in a triplet–doublet encounter, emphasizing the crossing points (marked by circles), between the excited doublet and quartet levels, where the main contribution to the RTPM occurs. According to equations (5) and (6), each crossing point characterizes a specific  $Q \leftrightarrow D$  transition, which corresponds to transitions between the radical and triplet levels. Various cases, describing the initial conditions at the distance of closest approach, are discussed. A, Triplet encounters a radical, both in Boltzmann population. The excited doublet levels are completely depleted since the transitions  $|R \pm 1/2\rangle \rightarrow |D \pm 1/2\rangle$  (dotted arrows) are allowed (see text), while the quartet levels have equal population and do not deplete to ground state. Note that a complete depletion of the excited doublet levels leads to  $1/3$  triplet population quenching. B, A non-polarized radical encounters a triplet (in emission) with a complete depletion of the doublet levels. Similar initial conditions will result from a spin-polarized radical (in emission) encountering thermal triplets. C, Same as case A, except that the depletion of the doublet levels is inefficient. D, Same as case B, but with inefficient doublet levels depletion.

Bloch equations in the vector presentation [25] we can write the differential equations, based on the stochastic Liouville equation (SLE), for each of the three pairs described by matrices (7)–(9) [18, 24, 26, 27].

$$\begin{aligned} \frac{\partial(r\rho_0)}{\partial t} &= D_r \frac{\partial^2(r\rho_0)}{\partial r^2} \\ \frac{\partial(r\rho_q)}{\partial t} &= D_r \frac{\partial^2(r\rho_q)}{\partial r^2} + \mathbf{\Omega}(r) \times (r\rho_q). \end{aligned} \quad (10)$$

These equations describe the mixing of the two  $Q \leftrightarrow D$  levels during the diffusion process, associated with the wavefunction  $\Psi = C_Q(t)|Q\rangle + C_D(t)|D\rangle$ , where  $\rho_q(r, t)$  and  $\rho_0(r, t)$  are a vector and a scalar, respectively, containing the density matrix elements for each of the three Q–D pairs:

$$r^2 \rho_0(r, t) \equiv C_D C_D^* + C_Q C_Q^*, \quad (11)$$

$$r^2 \rho_q(r, t) = r^2 \begin{pmatrix} \rho_x \\ \rho_y \\ \rho_z \end{pmatrix} \equiv \begin{pmatrix} C_Q C_D^* + C_D C_Q^* \\ -i C_Q C_D^* + i C_D C_Q^* \\ C_D C_D^* - C_Q C_Q^* \end{pmatrix},$$

and  $\mathbf{\Omega}(r)$  is the analogous Bloch ‘magnetic field’, that operates on the analogous ‘magnetization vector  $\rho_q(r, t)$  and is defined as

$$\mathbf{\Omega}(r) \equiv \begin{pmatrix} \mathcal{H}_{12} + \mathcal{H}_{12}^* \\ i(\mathcal{H}_{12} - \mathcal{H}_{12}^*) \\ \mathcal{H}_{22} - \mathcal{H}_{11} \end{pmatrix}. \quad (12)$$

$\mathcal{H}_{ij}$  are the matrix elements of the  $2 \times 2$  matrices appearing in equations (7)–(9). By solving equation (10) one obtains the evolution of the spin population for each pair of levels. Equations (7)–(9) and (12) can be used to express in detail the three pairs of  $\mathbf{\Omega}_i(r)$  ( $i = 1-3$ , corresponding to the matrices in equations (7)–(9), respectively):

$$\mathbf{\Omega}_1(r) \equiv \begin{pmatrix} \frac{2}{\sqrt{45}} \\ 0 \\ \omega_0 + 3J(r) \end{pmatrix}, \quad \mathbf{\Omega}_2(r) \equiv \begin{pmatrix} \frac{4}{\sqrt{45}}D \\ 0 \\ 2\omega_0 + 3J(r) \end{pmatrix},$$

$$\mathbf{\Omega}_3(r) \equiv \begin{pmatrix} \frac{2}{\sqrt{15}}D \\ 0 \\ \omega_0 + 3J(r) \end{pmatrix}. \quad (13)$$

The time evolution of the vector  $\rho_q(r, t)$  (without considering the diffusion) in the analogous Bloch presentation is described by the precession of the magnetization vector  $\rho_q(r, t)$  about the 'magnetic field'  $\mathbf{\Omega}(r)$ . Thus, for example, if we start the mixing process with complete excited doublet levels depletion, leaving only quartet levels populated, the components of  $\rho_q(r, t)$  will be  $(0, 0, -1)$ . In this case,  $\rho_q(r, t)$  will be tipped from the  $Z$  axis, only if at a certain time during the mixing process the analogous field  $\mathbf{\Omega}$  has a substantial component in the  $XY$  plane. Such a case corresponds to quartet population loss to the excited doublet levels. In a situation where non-efficient excited doublet depletion occurs, the initial condition for  $\rho_q(r, t)$  is different, as will be considered below.

We solve equation (10) by employing the finite difference approach of Freed and Pedersen [28]. In the present numerical scheme, the time dependence of equation (10) is treated by the Laplace transform to obtain simpler expressions for the scalar  $\hat{\rho}_0(r, s)$ ,

$$s\hat{\rho}_0(r, s) - \hat{\rho}_0^0(r) = D_r \frac{\partial^2 \hat{\rho}_0(r, s)}{\partial r^2}, \quad (14a)$$

and for the vector  $\hat{\rho}_q^0(r)$ ,

$$s\hat{\rho}_q(r, s) - \hat{\rho}_q^0(r) = D_r \frac{\partial^2 \hat{\rho}_q(r, s)}{\partial r^2} + \mathbf{\Omega}(r) \times \hat{\rho}_q(r, s), \quad (14b)$$

where we define

$$\hat{\rho}_p(r, s) = \int_d^\infty e^{-st} r \rho_p(r, t) dt \quad (15)$$

and the subscript  $p$  of  $\hat{\rho}$  can be either  $p = 0$ , for the scalar part of  $\hat{\rho}$  or  $p = q$ , for the vector part of  $\hat{\rho}$  (equation (10)). The Laplace variable is  $s$  and  $\hat{\rho}_p^0(r)$  is the initial condition in the Laplace domain, which is related to the initial conditions in the time domain at the distance of closest approach, i.e. at  $r = d$ :

$$\hat{\rho}_p^0(r) = r \rho_p(r, 0). \quad (16)$$

The interval between  $d$  and the fully separated distance, taken as  $\sim 15\text{--}20 \text{ \AA}$  in our case, is divided into  $N$  finite small distances  $\Delta r$ . The fully separated distance is chosen such that further increase in separation will not change the polarization value in the radical after a single encounter. Unlike in the RPM, re-encounter of the original species is not required to generate radical polarization. The derivatives in equation (14) are replaced by

finite differences, which may be expressed in a matrix form. The matrix parameters describe the diffusion  $D_r$  and the interaction  $\mathbf{\Omega}$  between the two levels. Thus, this interaction matrix consists of the following  $4N \otimes 4N$  matrices, which combine the spatial domain ( $N$ -dimensional) and the spin domain (4-dimensional, i.e. 0,  $x$ ,  $y$ ,  $z$ ) [28]:

$$\mathbf{A} = (s\mathbf{1} - \mathbf{W} - \mathbf{\Theta}). \quad (17)$$

Where  $\mathbf{1}$  is a unit matrix,  $s$  is the Laplace variable and  $\mathbf{W}$  is the matrix describing the diffusion operator:

$$\mathbf{W} = \frac{D_r}{\Delta r} \begin{pmatrix} -2 \left[ 1 + \frac{\Delta r}{d} \right] & 2 & 0 & \dots & \dots & \dots & \dots & \dots \\ 1 & -2 & 1 & 0 & \dots & \dots & \dots & \dots \\ 0 & 1 & -2 & 1 & 0 & \dots & \dots & \dots \\ \dots & \dots \\ \dots & \dots \\ \dots & \dots & \dots & \dots & 1 & -2 & 1 & \dots \\ \dots & \dots & \dots & \dots & \dots & 1 & -2 & 0 \\ \dots & \dots & \dots & \dots & \dots & 0 & 2 & 0 \end{pmatrix}. \quad (18)$$

In this description of  $\mathbf{W}$ , each term represents a diagonal  $4 \otimes 4$  submatrix, which is not shown explicitly since the diffusion operator is the same (equation (14)) for all the components of  $\rho$ . The expression for  $\mathbf{\Theta}$  is a  $4N \otimes 4N$  matrix with the components  $\Omega_x, \Omega_y, \Omega_z$ , of the vector  $\mathbf{\Omega}$  (equation (13)), which in this case is different for the various pairs considered and is given by

$$\mathbf{\Theta} = \begin{pmatrix} 0 & 0 & 0 & 0 & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & -\Omega_z & \Omega_y & \dots & \dots & \dots & \dots & \dots \\ 0 & \Omega_z & 0 & -\Omega_x & \dots & \dots & \dots & \dots & \dots \\ 0 & -\Omega_y & \Omega_x & 0 & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & 0 & 0 & 0 & 0 & \dots \\ \dots & \dots & \dots & \dots & 0 & 0 & -\Omega_z & \Omega_y & \dots \\ \dots & \dots & \dots & \dots & 0 & -\Omega_y & \Omega_x & 0 & \dots \end{pmatrix}. \quad (19)$$

Thus, the total  $4N \otimes 4N$  matrix corresponds to the linear equations

$$\mathbf{A}\hat{\rho}(s) = \hat{\rho}^0. \quad (20)$$

The solution is  $\hat{\rho}(s) = \mathbf{A}^{-1}\hat{\rho}^0$ , which is a  $4N$ -component vector that represents both the 4-dimensional spin domain of the density matrix ( $\rho_0, \rho_x, \rho_y, \rho_z$ ) and the small intervals  $N$  in the spatial domain. Two cases will be considered for solving equation (20).

### 3.1. Complete depletion of the excited doublet levels

In this case, at the distance of closest approach, only the quartet level is populated (figure 1, cases A and B). Thus, in terms of equation (11), we can write  $C_D = 0$ ,  $C_Q = 1$ , which corresponds to  $\rho_0(d, 0) = 1/d^2$  and  $\rho_q(d, 0) = (0, 0, -1/d^2)$ . Using equation (16), which provides the relation between the initial conditions in the time and the Laplace domains, one obtains

$$\hat{\rho}^0 = [(1/d), 0, 0, (-1/d); 0, 0, 0, 0, \dots], \quad (21)$$

where, in this presentation,  $1/d$  and  $(0, 0, -1/d^2)$  correspond to  $\hat{\rho}_0^0(d)$  and  $\hat{\rho}_q^0(d)$ , respectively. Note that all other components are equal to zero. Solving the set of linear equations (equation (20)) with  $s$  as a parameter, provides us with  $\hat{\rho}(s)$ . The results for the radical polarization at full separation are obtained for  $t \rightleftharpoons \infty$  in the time domain, which corresponds to  $s \rightleftharpoons 0$  in the Laplace domain. Thus, the radical polarization due to each  $Q \leftrightarrow D$  mixing process can be calculated using  $\hat{\rho}(s)$  by the expression [28]:

$$R_p^q = \lim_{s \rightarrow 0} s \cdot \eta_q \sum_{i=1}^N (\hat{\rho}_{4(i-1)+1} + \hat{\rho}_{4i}). \quad (22)$$

The index  $q$  runs over each pair of the three mixed levels, contributing to the overall radical polarization in terms of

$$R_p = \sum_{q=1}^3 R_p^q. \quad (23)$$

The indices of  $\hat{\rho}$  (equation (22)) are chosen such that the expression in parentheses is  $\hat{\rho}_0 + \hat{\rho}_z$ , which corresponds to the population of the excited doublet levels after the encounter. In the present case, i.e. complete depletion of the excited doublet level at the distance of closest approach, the population of the excited doublet after the encounter can result only from population transfer due to the  $Q \leftrightarrow D$  mixing process. In other words, if only doublet quenching occurs, without any  $Q \leftrightarrow D$  mixing, all the four quartet levels remain equally populated and no radical polarization will be generated after the encounter. The term  $\eta_q$ , presented here is a numerical factor determining the degree of polarization, and can be generated in the radical for each of the three pairs. One can calculate  $\eta_q$  with the assumption that the excited doublet level depletion occurs at the distance of closest approach or very close to it. This assumption is reasonable because at such a short distance  $J$  is maxi-

mum and decreases exponentially with distance. Since the depletion rate is proportional to  $J^2$  [21–23], it implies that any further depletion occurring at larger distances is negligible. This additional population of the excited doublet levels is assumed not to deplete to the ground state. With this assumption, we can calculate  $\eta_q$  by using equations (5) and (6) (see appendix B).

### 3.2. Incomplete depletion of the excited doublet levels

As mentioned above, one of the reasons for carrying out the numerical treatment of solving the SLE is the ability to take into consideration a situation where the excited doublet levels are not completely depleted (i.e. inefficient triplet quenching). Different initial conditions will result in different values for  $\hat{\rho}$  at full separation. Thus, for the case where the excited doublet levels are partially depleted, we define  $X$  as the fraction of the depleted population. With this definition, the normalized difference between the doublet and quartet population will be

$$\Delta = \frac{-X}{2-X}. \quad (24)$$

In this case, the initial condition for  $\hat{\rho}$  will be (it should be noted that due to the uncorrelated nature of the spin wavefunctions, in a single encounter (Adrian in [3]),  $\hat{\rho}_x = \hat{\rho}_y = 0$ ).

$$\hat{\rho}(0) = (1/d, 0, 0, \Delta/d, 0, 0, 0, 0, \dots). \quad (25)$$

Thus, the two limiting cases,  $X = 0$  and  $X = 1$ , correspond to no depletion and full depletion of the excited doublet, respectively. The value of  $X$  can be calculated via the expressions given in previous publications [1, 22, 23]:

$$X = \frac{(k_{\text{ISC}}\tau_{\text{ex}})^2}{(k_{\text{ISC}}\tau_{\text{ex}})^2 + 1}, \quad (26)$$

where  $\tau_{\text{ex}}$  is a characteristic time during which the species are in the vicinity of closest approach distance, and the rate of triplet depletion to ground state is given by

$$k_{\text{ISC}} = \frac{2\pi|H_{\text{ex}}|^2 F}{\hbar H_{\text{v}}}, \quad (27)$$

where  $H_{\text{ex}}$  is the matrix element of the exchange interaction during the encounter,  $F$  is the Frank–Condon factor and  $H_{\text{v}}^{-1}$  is the density of the final vibrational energy states (after the quenching) [1].

We recall that in the complete depletion case the excited doublet population after the encounter is due only to the level mixing process. In the incomplete depletion case,  $\hat{\rho}_0 + \hat{\rho}_z$  (equation (22)) consists of the initial excited doublet population and the population that was added during the mixing process. Thus, to obtain the net population transfer from the quartet to the excited

doublet, the initial population should be subtracted from the final excited doublet population as calculated by equation (22). Therefore, the modified equation for the radical polarization in the case of inefficient excited doublet levels depletion is

$$R_p^q = -(1 + \Delta) + \lim_{s \rightarrow 0} s \cdot \eta_q \sum_{i=1}^n r_i (\hat{\rho}_{4(i-1)+1} + \hat{\rho}_{4i}). \quad (28)$$

In this case we also assume that quenching of the excited doublet levels occurs mainly at the distance of closest approach.

An additional factor, affecting the radical polarization in the RTPM, is related to the thermal relaxation of the combined radical–triplet pair, during the encounter. Our treatment of this factor is rather simplified, but still accurate. We can follow the level population at separation via the SLR of the triplet,  $T_1^T$ , and the diffusion-controlled encounter time,  $\tau_e$ . It is evident that for  $\tau_e \gg T_1^T$ , the radical polarization will be small. Therefore, the final expression for the radical polarization can be written as

$$R_p = e^{-\tau_e/T_1^T} \sum_{q=1}^3 A_q R_p^q, \quad (29)$$

where  $A_q$  is a numerical factor,  $0 < A_q < 1$ , related to the initial polarization of the triplet and radical before

the encounter. This factor will be discussed in detail in the next section.

Figure 2 presents typical results for the radical polarization in the RTPM during an encounter with a thermal triplet for various values of  $X$ , as a function of viscosity. It can be seen that the analytical calculation, which neglects back transition from the excited doublet to the quartet levels, results in high polarization values at high viscosities. Obviously this approach is inadequate at high viscosity values [17, 18]. In contrast to the analytical approach, the numerical calculation gives much smaller polarization values at high viscosities. The numerical solution fits the analytical solution only at low viscosities. In the case of non-efficient excited doublet depletion, one obtains even lower results for the RTPM polarization. This is conceivable because the smaller the depletion rate of the excited doublet levels, the larger their population will be during the encounter. This will result in inefficient population transfer  $Q \leftrightarrow D$ , giving rise to smaller RTPM polarization. In the following section we shall discuss the case where both encountering species are spin polarized prior to the encounter (figure 1, cases B and D).

#### 4. Encounters between polarized triplets and radicals

To provide a complete description of the radical's magnetization as a function of time, one should consider

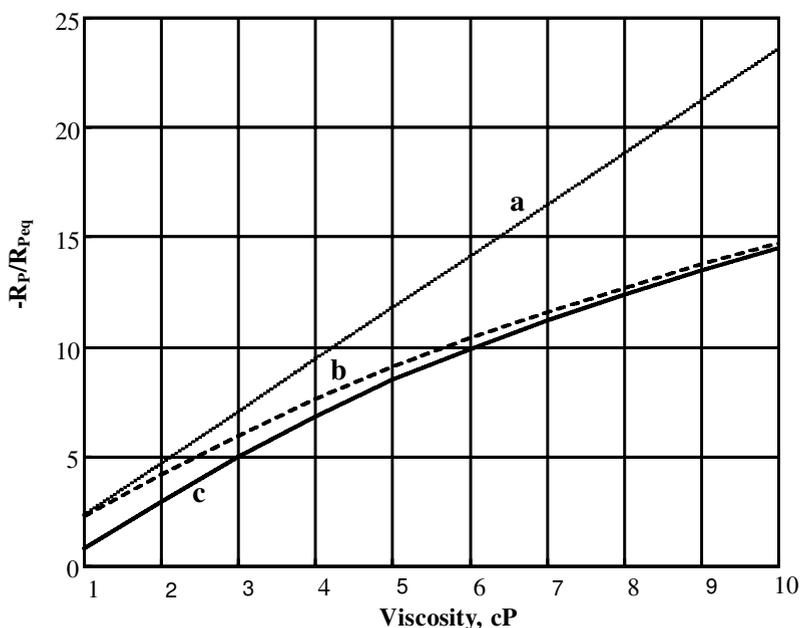


Figure 2. RTPM polarization calculated for the following cases: dotted line (a), analytical calculation; dashed line (b), numerical calculation assuming complete doublet quenching; and solid line (c), numerical calculation assuming non-efficient doublet quenching. The following parameters were used for the calculations:  $D = 6 \times 10^9$  rad s<sup>-1</sup>, magnetic field  $B_0 = 0.34$  T,  $J_0 = -9.4 \times 10^{10}$  rad s<sup>-1</sup>,  $\alpha = 2.5 \text{ \AA}^{-1}$ , triplet and radical radii are 5 Å. The quenching efficiency for case *c* was calculated using equations (26) and (27) and the expressions are presented elsewhere [1]. The triplet SLR time (equation (29)) in various viscosities was calculated by the expressions in [1, 30].

cases where the SLR time of the radical is longer than the mean time between the encounters. In such a case, the polarized radical can re-encounter the triplet (polarized or thermal). The SLR time, which satisfies this requirement, should be larger than  $10\ \mu\text{s}$  (determined in this work). Such cases will be discussed below for both ESPT and the RTPM. The ESPT phenomenon will be treated by modifying the expressions developed earlier [1], while the effect of a long  $T_1$  on the RTPM will be analysed by taking into account the initial triplet and radical polarizations.

#### 4.1. Electron spin polarization transfer (ESPT)

We consider the relative population rates,  $A_x$ ,  $A_y$ ,  $A_z$  to the  $x$ ,  $y$ ,  $z$  levels in the triplet molecular frame, which enables us to estimate the relative populations ( $P_{T_i}$ ) of the triplet levels ( $T_0$  and  $T_{\pm 1}$ ) [11]:

$$P_{T_0} = (1/3)(A_x + A_y + A_z), \quad (30a)$$

$$P_{T_{\pm 1}} = P_{T_0} \pm (2/15)(D/B_0)(A_x + A_y - 2A_z). \quad (30b)$$

For an arbitrary relative population of the radical (doublet),  $P_{R_{+1/2}}^0$  and  $P_{R_{-1/2}}^0$ , prior to the encounter (initial conditions), we can calculate the relative population of the quartet ( $P_Q$ ) and excited doublet ( $P_D$ ) levels using equations (5) and (6):

$$P_{Q_{\pm 3/2}} = P_{T_{\pm 1}} P_{R_{\pm 1/2}}^0 \quad (31a)$$

$$P_{Q_{\pm 1/2}} = \frac{1}{3} P_{T_{\pm 1}} P_{R_{\mp 1/2}}^0 + \frac{2}{3} P_{T_0} P_{R_{\pm 1/2}}^0 \quad (31b)$$

$$P_{D_{+1/2}} = \frac{1}{3} P_{T_0} P_{R_{+1/2}}^0 + \frac{2}{3} P_{T_{+1}} P_{R_{-1/2}}^0 \quad (31c)$$

$$P_{D_{-1/2}} = \frac{1}{3} P_{T_0} P_{R_{-1/2}}^0 + \frac{2}{3} P_{T_{-1}} P_{R_{+1/2}}^0. \quad (31d)$$

The populations in equation (31) are determined by multiplying the components of each level (the triplet and radical), to obtain the relative contribution to the quartet and excited doublet level populations. Thus, when the triplet and/or the radical are polarized, the quartet and excited doublet levels are also polarized and, consequently, radical polarization will be generated after separation. The relative population of the radical after the encounter (figure 1, cases B and D) can be calculated in terms of the radical and triplet wavefunctions, mixed into the quartet and excited doublet levels (equations (5) and (6)), with the triplet quenching efficiency  $X$  (equation (26)):

$$P_{R_{+1/2}} = P_{Q_{+3/2}} + \frac{2}{3} P_{Q_{+1/2}} + \frac{1}{3} P_{Q_{-1/2}} + (1 - X) \left( \frac{1}{3} P_{D_{+1/2}} + \frac{2}{3} P_{D_{-1/2}} \right), \quad (32a)$$

$$P_{R_{-1/2}} = P_{Q_{-3/2}} + \frac{2}{3} P_{Q_{-1/2}} + \frac{1}{3} P_{Q_{+1/2}} + (1 - X) \left( \frac{1}{3} P_{D_{-1/2}} + \frac{2}{3} P_{D_{+1/2}} \right). \quad (32b)$$

For example, case B in figure 1 corresponds to  $X = 1$ , while case D corresponds to  $X \neq 1$ . Therefore, the radical polarization ( $R_{P, \text{ESPT}}$ ), as a result of its encounter with the polarized triplet via the ESPT mechanism, is

$$R_{P, \text{ESPT}} = (P_{R_{+1/2}} - P_{R_{-1/2}}) / (P_{R_{+1/2}} + P_{R_{-1/2}}) \quad (33)$$

which can be calculated using equations (30)–(32).

An interesting feature concerning ESPT with polarized radicals is that the radical can lose some of its polarization (equations (31) and (32)). This situation is exemplified in figure 3, which demonstrates the fact that for a particular chemical system, even after many encounters with the triplet, the radical polarization cannot exceed a certain value. Such behaviour is due to the opposite contribution of ESPT and the RTPM to the overall radical polarization.

#### 4.2. Radical triplet pair mechanism (RTPM)

The numerical treatment presented in §3 dealt with the induced transitions at the crossing levels, considering the case of thermal triplets interacting with thermal radicals (figure 1, cases A and C). Hence, the overall radical polarization was calculated by summing the contributions at the three crossing regions (equation (29)). For triplets and radicals that are not polarized, all the transitions at the crossing points have the same relative contribution (i.e.  $A_q = 1$  in equation (29)). However, if we consider the case of a polarized triplet and/or a polarized radical, prior to the encounter, first we must calculate the initial quartet and excited doublet level populations by equation (31), and with this information to determine  $A_q$ . For example, if both the radical and triplet species are highly polarized, e.g. in emission as depicted by cases B and D in figure 1, then the  $|Q - 3/2\rangle$  level will be almost empty during the encounter, and therefore  $A_q$ , which is related to the particular crossing regions of this level, is small. In the present notation, the relative  $A_q$  are calculated using equations (30) and (31):

$$A_1 : A_2 : A_3 = P_{Q_{-3/2}} + P_{D_{-1/2}} : P_{Q_{-3/2}} + P_{D_{+1/2}} : P_{Q_{-1/2}} + P_{D_{+1/2}}. \quad (34)$$

Therefore, we conclude that equation (29) provides us with the solution of the problem when considering the general case of polarized or non-polarized triplets and radicals. Moreover, the effect of non-efficient doublet level depletion during the encounter, as well as the effect of SLR during the encounter, are also taken into account. Figure 4 provides an example of such a calculation that describes the effect of the radical polarization on the RTPM for three different cases.

With this numerical approach, we can model accurately the time dependence of the radical magnetization following photoexcitation by employing the same

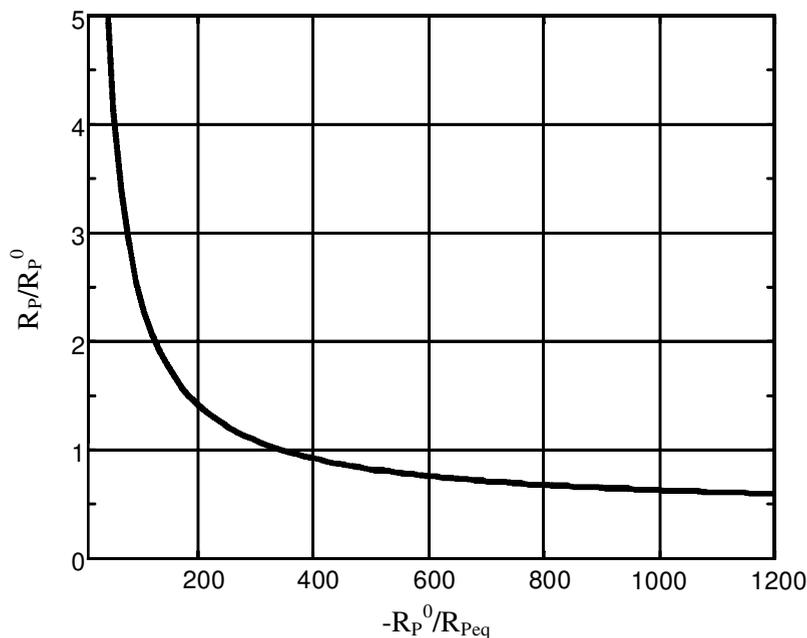


Figure 3. Ratio between the final and initial radical polarizations,  $R_p/R_p^0$ , as a function of  $R_p^0$  under the conditions:  $T = 300$  K;  $B_0 = 0.34$  T, distance of closest approach  $d = 10$  Å; triplet radius = 5 Å;  $J_0 = -2 \times 10^{11}$  rad s $^{-1}$ ,  $\alpha = 2$  Å $^{-1}$ ; triplet ZFS,  $D = 6.8 \times 10^9$  rad s $^{-1}$ ; viscosity, 25 cP. For example, for initial radical polarization  $R_p^0 = 200 \times R_{P_{eq}}$ , after the encounter the polarization will be  $\sim 1.4 \times 200 = 280 R_{P_{eq}}$ . The figure shows that for these conditions, radical polarization cannot exceed  $\sim 350 R_{P_{eq}}$ .

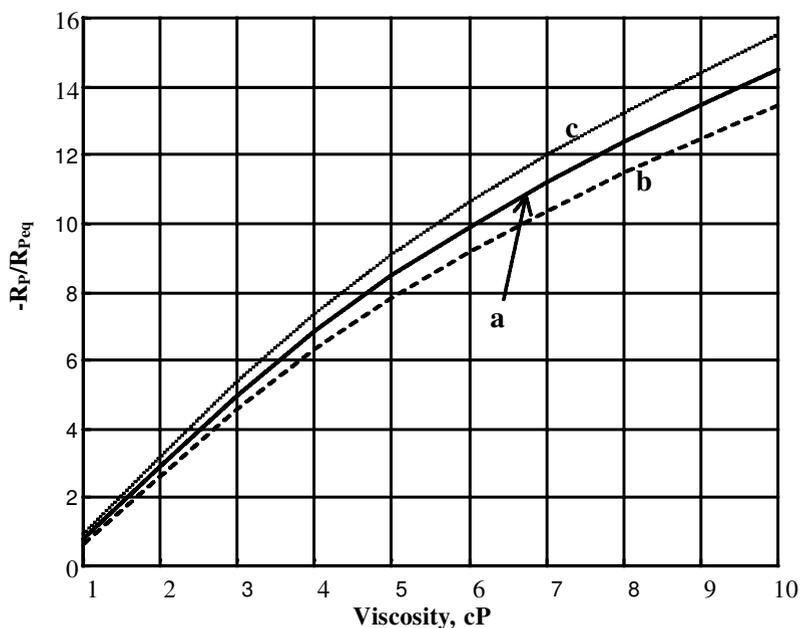


Figure 4. Solid line (a) is the numerical calculation of the radical polarization due to the RTPM under the same conditions as in figure 2, curve (c); Dashed line (b) is related to the same conditions but with a polarized radical having  $100P_{eq}$  in emission prior to the encounter. Dotted line (c) corresponds to the same conditions as for curve (b) but  $100P_{eq}$  in absorption. In all cases, the triplet is in Boltzmann equilibrium. For a highly polarized radical in emission, prior to the encounter (see figure 1, case B), the contribution of the RTPM will be smaller due to the lower population in the lower quartet levels. This results in less effective  $Q \leftrightarrow D$  transitions.

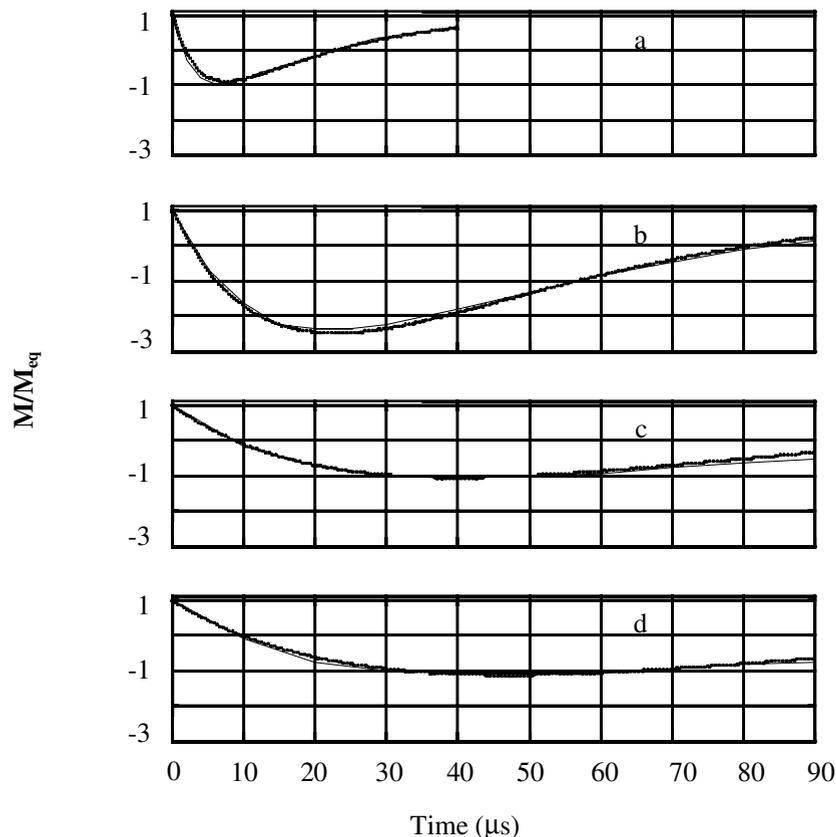


Figure 5. Experimental (dotted) and calculated (solid) magnetization of the radical (trityl) with  $\text{H}_2\text{TPP}$  (see experimental section) as a function of time, as measured by FT-EPR. The viscosity in the experiments was 25, 100, 200, 245 cP for (a)–(d), respectively. The parameters used for calculating the magnetization in all curves are:  $J_0 = 3 \times 10^{11} \text{ rad s}^{-1}$ ,  $\alpha = 2.5 \text{ \AA}^{-1}$  and the independently measured radical SLR times are 17, 24, 36, 40  $\mu\text{s}$  for (a)–(d), respectively. The quenching efficiency was calculated using equations (26) and (27). Triplet initial polarization was taken from [31]. Further details regarding the experimental techniques (FT-EPR pulse sequences) are given in [1, 20].

kinetic equations, which were discussed recently [1]. The difference between the present and the previous approach is the procedure by which we calculate the radical polarization,  $R_p$ . The numerical approach allows us to analyse separately the radical polarization at any time frame after the laser pulse. It enables us to evaluate the different radical polarizations, which are a function of the instantaneous radical and triplet polarizations, generated by triplet-radical encounters at various intervals after the laser pulse. An example to provide a comparison between the calculation using this method and our experimental observations is presented in figure 5.

### 5. Conclusion

High controllable magnetization and polarization by light excitation are necessary requirements in microwave applications [5–7]. A mechanism that fulfils these requirements is based upon the interaction of stable radicals and photoexcited triplets in liquid solution,

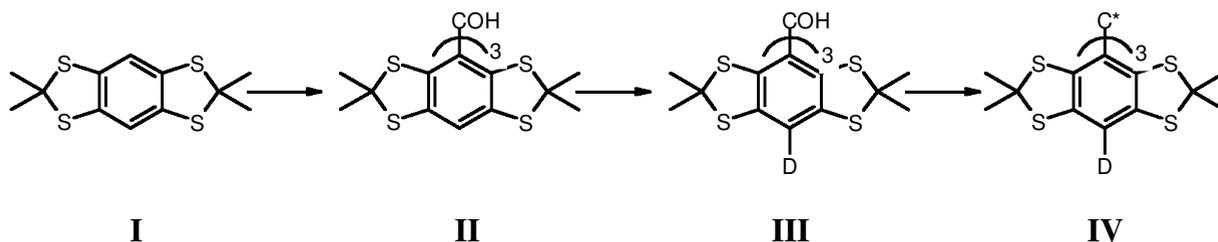
i.e. ESPT and the RTPM. Therefore, to acquire optimal conditions for generating high and long lived magnetization and polarization, an in-depth analysis of ESPT and the RTPM, as functions of molecular and magnetic parameters, has been presented. The analysis enables us to calculate accurately the radical polarization as a function of several parameters, such as solvent viscosity, triplet and radical initial polarization, and triplet quenching rate and its efficiency. With these accomplishments we could take a step further by developing a preliminary prototype of a microwave device [29].

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## Appendix A

## Radical synthesis

The radical synthesis was performed from the starting material using the following three-step procedure:



(1) 17.36 g of the starting material (I), was suspended in 360 ml dry ether and then 26.7 ml of n-BuLi was added to the suspension, under an argon atmosphere. After 80 min stirring at room temperature, trimerization was initiated by adding very slowly 2.21 ml of diethyl carbonate dissolved in 50 ml of cyclohexane. The addition took 60 min. The reaction mixture was then stirred over night. The product of the first stage (II) was filtered off as a lithium salt and dissolved in 350 ml ether + 100 ml  $\text{CH}_2\text{Cl}_2$ , washed with 100 ml of 1 M  $\text{NaH}_2\text{PO}_4$  and with 100 ml water, and after drying was recrystallized from 50 ml THF.

(2) 5.3 g of the trimer (II) were dissolved in 320 ml of dry N,N,N',N'-tetramethylethylenediamine, cooled to  $0^\circ\text{C}$ , under argon, and added to a solution of n-BuLi in hexane (19.2 ml, 48 mM). After 30 min stirring at  $0^\circ\text{C}$ , 3 ml  $\text{D}_2\text{O}$  was added into the reaction flask, while raising the temperature slowly to room temperature. The product (III) was obtained by evaporating the organic solvent in a rotating vacuum drier.

(3) 3 g of material (III) were suspended in 180 ml acetonitrile. 2 ml trifluoromethanesulphonic acid were added and, after stirring for 8 minutes, a fresh solution of 0.7 g tin chloride in 70 ml  $\text{CH}_3\text{CN}$  was added. After stirring for 7 min, 180 ml 1 M  $\text{NaH}_2\text{PO}_4$  was added. The radical product (IV, green) was precipitated. It was filtered and checked by standard analytical methods.

## Appendix B

Calculation of the numerical factor  $\eta_q$ 

The numerical factor  $\eta_q$  in equation (22), for the polarization, relates the change in the quartet and excited doublet populations to the change in the population of the radical  $|R \pm 1/2\rangle$  after separation. For example, a transition  $|Q - 3/2\rangle \leftrightarrow |D + 1/2\rangle$ , in terms of the radical population (figure 1), is a transition  $|R - 1/2\rangle \leftrightarrow |R - 1/2\rangle$  with 2/3 of the population and to  $|R + 1/2\rangle$  with 1/3 of the population (equations (5)

and (6)). It implies that  $\eta_q$  for generating radical polarization, due to the mixing of this  $Q \leftrightarrow D$  pair is 1/3. Similarly, the transition  $|Q - 3/2\rangle \leftrightarrow |D - 1/2\rangle$ , in which the population of  $|R - 1/2\rangle$  is transferred both to  $|R - 1/2\rangle$  with 1/3 of the population and to  $|R + 1/2\rangle$  with 2/3 of the population, results in  $\eta_q = 2/3$ . Finally, for the transition  $|Q - 1/2\rangle \leftrightarrow |D + 1/2\rangle$ ,  $\eta_q = 0$ . From this analysis, it is obvious that the transition  $|Q - 1/2\rangle \leftrightarrow |D + 1/2\rangle$ , under our basic assumptions, does not contribute to the radical polarization.

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