

Triplet radical pairs from 3-carboxy-proxyl encapsulated in a dendritic box

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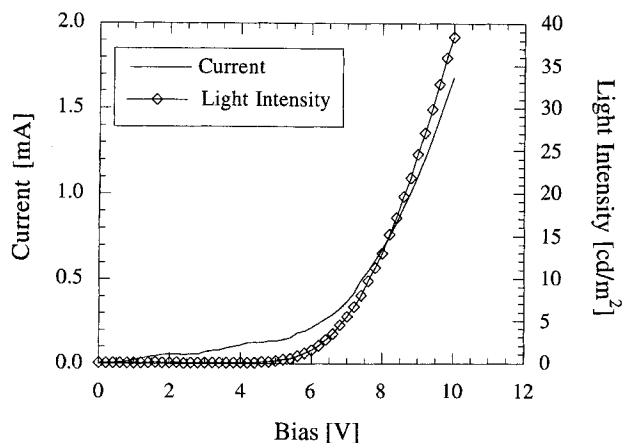


Fig. 4. Current vs. bias voltage and light intensity vs. bias voltage characteristics of an ITO/PANI-DBSA/II/I/Ca device.

40 cd/m^2 at a drive voltage of 10 V. The enhanced performance is considered to be result of better contact between PANi and II, than between ITO and II.

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Triplet Radical Pairs of 3-Carboxyproxyl Encapsulated in a Dendritic Box**

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Dendrimers or cascade molecules are highly branched three-dimensional macromolecules, synthesized stepwise from a central core leading to a well-defined number of generations and end groups.^[1] Recently, it was demonstrated that end-group modification of poly(propylene imine) dendrimers using a bulky substituent produces a rigid outer shell on the dendrimer surface resulting in a "dendritic box".^[2] The possibility to encapsulate small molecules effectively within this box during its construction, opens a plethora of interesting chemical and biochemical applications. Here, we report on the mobility of 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyl-oxyl (3-carboxy-proxyl) radicals in the dendritic box of a fifth generation poly(propylene imine) dendrimer (DAB-dendr-(NH₂)₆₄) with 64 *N*-(*tert*-butoxycarbonyl)-L-phenylalanine (*N*-*t*-BOC-L-Phe) end groups (Fig. 1). In dendritic boxes containing two or more 3-carboxy-proxyl radicals, we observe the intermolecular ferromagnetic alignment of encapsulated radicals into triplet state radical pairs.

The dendritic box used in the present study is based on a flexible poly(propylene imine) dendrimer core synthesized by a divergent route starting from diaminobutane via a repetition of addition-reduction reactions.^[3] The final (fifth generation) dendrimer used for encapsulation contained 64 primary amine end groups. The rigid shell is produced through end-group modification with a bulky group, in this case *N*-*t*-BOC-L-Phe, by reaction of DAB-dendr-(NH₂)₆₄ with the corresponding *N*-hydroxy-succinimide ester in a dichloromethane-triethylamine mixture.^[2] By carrying out the encapsulation reaction in the presence of a varying concentration of 3-carboxy-proxyl, the number of entrapped radicals could be varied from 0.3 to 6.0 molecules per dendritic box as determined by ESR spectroscopy (Fig. 2).^[4]

The number of 3-carboxy-proxyl radicals in the dendritic box does not increase above 6 (Fig. 2), demonstrating that the maximum attainable number of 3-carboxy-proxyl radicals in the dendritic box is restricted by the cavities of the box. The maximum number of 6 is similar to values determined for various encapsulated dyes for which the concentration has been determined accurately using UV/vis spectroscopy.^[2] Excess and/or adhered radicals are removed by extensive washing and dialysis procedures. Various experiments have demonstrated that trapped guest molecules are

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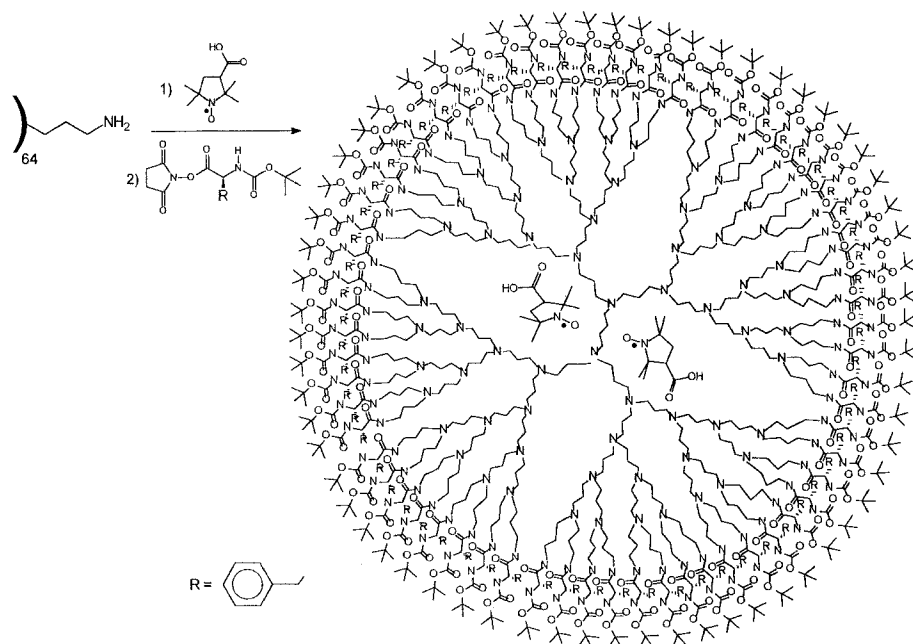


Fig. 1. Two-dimensional representation of a DAB-dendr-(NH-*t*-BOC-L-Phe)₆₄ box containing two 3-carboxy-proxyl radicals.

physically encapsulated and not chemically bound to the dendrimer.^[2]

The ESR spectra of 3-carboxy-proxyl@DAB-dendr-(NH-*t*-BOC-L-Phe)₆₄^[5] dissolved in 2-methyltetrahydrofuran (2MeTHF) (5 mg mL⁻¹; 6 guests per box) are strongly temperature dependent (Fig. 3). At 305 K an essentially isotropic ¹⁴N-coupled ESR spectrum is observed, characteristic for

motion (anisotropic) spectrum is observed. The isotropic hyperfine coupling is fairly constant over the temperature range from 150–305 K and amounts to $A_{iso}(N) = 1.40\text{--}1.42$ mT. The parallel ¹⁴N-hyperfine coupling is temperature dependent and reaches a constant value of $A_{zz}(N) = 3.38$ mT below 120 K. This temperature-dependent behavior is observed irrespective of the concentration of the dendritic box (0.1–10.0 mg mL⁻¹) and the number of guests per box (0.3–6.0).

The superposition of motionally-narrowed and slow-motion spectra indicates that the micro-environment of encapsulated 3-carboxy-proxyls is not uniform over the

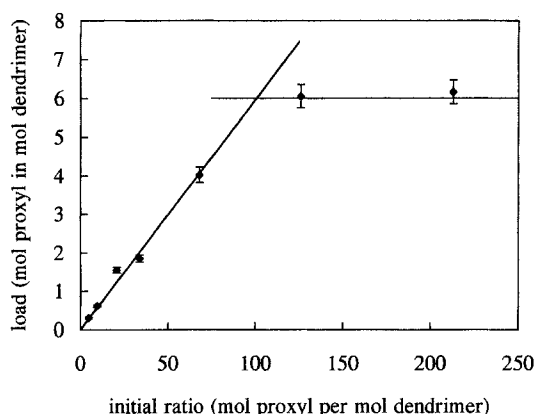


Fig. 2. Number of 3-carboxy-proxyl radicals trapped in the dendritic box as determined by ESR spectroscopy versus the molar ratio of 3-carboxy-proxyl and dendrimer in the initial solution prior to the encapsulation reaction.

rapid rotational diffusion of the 3-carboxy-proxyl spin probe.^[6] Lowering the temperature results in a decreasing intensity of the isotropic spectrum (Figs. 3 and 4) and the appearance of an anisotropic ESR spectrum, consistent with a more restricted motion of the spin probe.

In the temperature range from 150 to 250 K a superposition of the motionally narrowed (isotropic) spectrum and the slow-

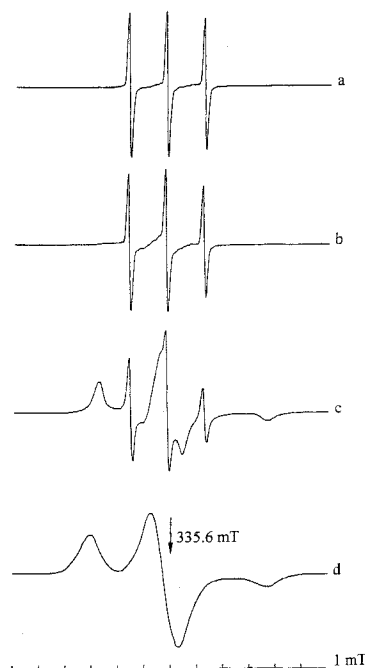


Fig. 3. ESR spectra of 3-carboxy-proxyl@DAB-dendr-(NH-*t*-BOC-L-Phe)₆₄ in 2MeTHF (5 mg mL⁻¹; 6 guests per box) at: a) 305 K; b) 235 K (rel. gain: × 1.3); c) 175 K (rel. gain: × 8.5); d) 105 K (rel. gain × 5.7).

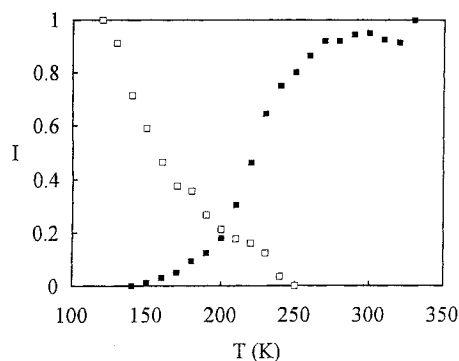


Fig. 4. Normalized intensity ($\Delta m_l = +1$ transition) of isotropic (■) and anisotropic (□) ESR spectra of 3-carboxy-proxyl@DAB-dendr-(NH-*t*-BOC-L-Phe)₆₄ in 2MeTHF (1 mg mL⁻¹; 6 guests per box) versus temperature.

interior of the dendritic box. The spectra shown in Figure 3 suggest that at least two different trapping sites exist for 3-carboxy-proxyl radicals, one allowing relative free motion and another where the spin-probe is almost immobilized, while the exchange rate between the different sites is slow on the ESR time scale. It is tempting to speculate that these sites correspond to cavities with different size that result from the architecture of the dendrimer. A distribution of sites is in accordance with a recent observation by Ottaviani *et al.* that three different complexes of Cu^{II} exist with each of the groups composed of a carboxylate-terminated poly(amidoamine) dendrimer.^[7] On the other hand, a distribution of correlation times for rotational diffusion of spin probes is not unique to the present dendritic box and is frequently observed in various systems.^[8, 9]

The ESR spectrum of a solid sample of 3-carboxy-proxyl @DAB-dendr-(NH-*t*-BOC-L-Phe)₆₄ exhibits the characteristic anisotropic ¹⁴N pattern of a nitroxide radical. In contrast to a solid sample of pure 3-carboxy-proxyl, no discernible exchange narrowing is observed with ESR spectroscopy, even with 6 guests per box. However, a (partial) ferromagnetic alignment of 3-carboxy-proxyl radicals encapsulated in the dendritic box occurs for high concentrations. The observation of a $\Delta m_s = 2$ ESR transition exhibiting a partially resolved 1:2:3:2:1 hyperfine coupling pattern due to two ¹⁴N nuclei with $A(\text{pair}) = 1/2 A(3\text{-carboxy-proxyl})$ gives unambiguous spectral evidence of the presence of a triplet-state radical pair (Fig. 5). The intensity of the $\Delta m_s = 2$ signal follows Curie law ($I = C/T$) between 4.2 and 100 K, consistent with a triplet ground state. Unfortunately, the $\Delta m_s = 1$ region of the ESR spectrum does not show any

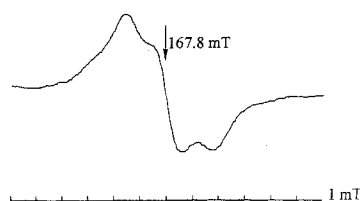


Fig. 5. $\Delta m_s = 2$ ESR spectrum of a solid sample of 3-carboxy-proxyl@DAB-dendr-(NH-*t*-BOC-L-Phe)₆₄ at 4.2 K.

evidence of the presence of a triplet state radical pair, preventing the evaluation of the zero-field splittings (D and E) that would have given an estimate to the distance between the two radicals in the pair via the dipole-dipole approximation. The absence of triplet signals in the $\Delta m_s = 1$ region indicates that the concentration of pairs is low as compared to free radicals or that a distribution of geometries for triplet radical pairs exists. The $\Delta m_s = 2$ signal is only observed for samples with an average load of more than 1.6 guests per box. In addition, the $\Delta m_s = 2$ transition is also observed for frozen 2MeTHF solutions of 3-carboxy-proxyl@DAB-dendr-(NH-*t*-BOC-L-Phe)₆₄ (1 mg mL⁻¹; 6 guests per box), excluding the possibility of box-box interactions as being responsible for the observed triplet state.

The triplet pair of 3-carboxy-proxyl in a dendritic box is an example of ferromagnetic ordering in a non-crystalline guest-host assembly. The triplet pairs are likely to be associated with specific and rigid intermolecular orientations. In order to obtain a positive value of the exchange integral, J , the direct overlap of the singly occupied molecular orbitals must be negligible or zero. This can occur when the face-to-face orbital overlap is small, e.g. by a twist of the radicals in the pair into a (pseudo) D_{2d} geometry.^[10] Recent interest in intermolecular ferromagnetic interactions of nitroxide radicals in the solid state has resulted in a number of organic nitroxide crystals that show a transition to a truly three-dimensional ferromagnetic phase at low temperatures.^[10-12] X-ray crystallographic studies on these materials show that fairly long distances between radical centers can be involved and it has been suggested that superexchange interaction through intervening bonds may be operative.^[10, 12] Detailed geometrical requirements necessary for ferromagnetic interactions between nitroxide radicals, however, are still unknown. Since there is little information on the shape or size of the cavities in the dendritic box, we propose that triplet radical pairs occur in a statistical fashion.

As a first step towards the organic synthesis of nanometer-size magnetic particles Rajca *et al.* have shown that intramolecular ferromagnetic interactions can occur in π -conjugated dendritic polyradicals, resulting in an average spin of about 5/2 for a dendrimer with 31 radical centers.^[13] The present study on 3-carboxy-proxyl@DAB-dendr-(NH-*t*-BOC-L-Phe)₆₄ demonstrates that intermolecular ferromagnetic exchange interactions can occur when free radicals are incorporated as guests in a supramolecular assembly. Further research will be focused towards exploring this phenomenon in more detail employing other stable radicals.

Experimental

The preparation of poly(propylene imine) dendrimers and the procedure for encapsulation with *N*-*t*-BOC-L-Phe have been described elsewhere.^[2, 3] ESR spectra were recorded on a Bruker ER200D SRC X-band spectrometer. Temperature was controlled by Bruker ER4111 variable temperature unit between 100 K and 350 K, or by an Oxford 3129 temperature controller combined with an ESR900 continuous flow cryostat in the range from 3.8–100 K.

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- [5] The notation 3-carboxy-proxyl@DAB-dendr-(NH-t-BOC-L-Phe)₆₄ means 3-carboxy-proxyl encapsulated in a DAB-dendr-(NH-t-BOC-L-Phe)₆₄ dendrimer (see [2,3]). The @ sign is taken from the notation for endohedral metallofullerene complexes.
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Dielectric Relaxation Processes in an Antiferroelectric Liquid Crystal**

By M. Rosario de la Fuente,* Santos Merino, Yolanda González, Miguel A. Pérez Jubindo, Blanca Ros, José A. Puértolas, and Miguel Castro

Since the first antiferroelectric liquid-crystalline phase was discovered by Chandani et al. in 1989,^[1,2] a number of series of materials showing ferroelectric, ferrielectric and antiferroelectric mesophases have been found. In spite of the large amount of experimental and theoretical work devoted to this subject, a clear explanation of the structure of these new phases has not yet been achieved. The phenomenology they exhibit is complex: many transitions that cannot be detected by means of the usual characterization techniques such as X-ray or DSC,^[3,4] transition temperature changes with the cell thickness, anomalous behavior of the helical pitch,^[5] phases that disappear changing the optical purity,^[6] different (qualitative and quantitative) results in the same phase of different compounds,^[7,8] etc.

Dielectric and electrooptic experiments have become very important in this field because of their capability of providing information about the collective modes involved in these polar phases: soft mode, ferroelectric Goldstone mode, helix related ferrielectric and antiferroelectric modes, etc.^[4,9-13] In this paper we present dielectric and polarization studies of (R)-1-methylheptyl-4'-(4'-n-decyloxybenzoyloxy)-biphenyl-4-carboxylate (hereafter called MHD0BBC).

This compound was first synthesized by the group of Goodby and the reported phase sequence, on cooling, was:^[3] I-124.5 °C-SmA-104.9 °C-SmC_β*-77.6 °C-SmC_γ*-72.1 °C-SmC_α*-47.5 °C-SmJ*. As we shall see later, our study allows us to include two new phases. One between the SmA and the SmC_β*, the so called SmC_z* and another between the SmC_α* and the SmJ*, that could be a SmI_z* phase. If we interpret our dielectric results in the light of a recent phenomenological theory,^[4,9] some of the reported transition temperatures should be modified.

The structure of the SmC_z* phase was found to be antiferroelectrically ordered with molecules in adjacent layers tilted in opposite directions.^[1,2] The SmC_γ* is ferrielectric and

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