Radical Dendrimers: A Family of Five Generations of Phosphorus Dendrimers Functionalized with TEMPO Radicals

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ABSTRACT

Five novel generations of phosphorous dendrimers based on a cyclotriphosphazene core with stable TEMPO radicals end groups have been synthesized and studied by EPR, SQUID, ¹H NMR, ³¹P NMR, FT-IR and UV-Vis spectroscopy. The nitroxyl radicals exhibit a strong exchange interaction, which depends on the dendrimer generation and the temperature. An $|\Delta m_s|$

= 2 transition has been observed in each generation in dilution conditions demonstrating the intra-molecular origin of the radicals interaction. There exists a direct proportionality between the EPR $|\Delta m_s| = 2$ transition intensity and the number of radicals by generation, consequently, the utility of EPR for the determination of the substitution efficiency on dendrimers by paramagnetic species is quite good. From the UV-Vis characterization we have observed that the molar extinction coefficient value is also proportional to the number of TEMPO groups. The magnetic properties of the zero, first and fourth generation dendrimers studied by SQUID magnetometry show antiferromagnetic interaction between radicals.

Introduction

To study the magnetic behavior of paramagnetic species, different materials can be used as scaffolds, like polymers,¹ metallic nanoparticles,² SAMs³ or dendrimers. Dendrimers are a very special class of hyperbranched macromolecules, which are synthesized step-by-step in order to ensure a good monodispersity. The three-dimensional structure of these molecules proceed from the central core with exponentially increasing number of repeated units and terminal groups.⁴ Caminade *et al.* have described several series of dendrimers built with phosphorus as branching points and with end groups that can be functionalized.⁵ The reactivity of these end groups has already led to various applications of these phosphorus-containing dendrimers in Nanomedicine and Materials Science.⁶ Combination of the globular structure of dendrimers with functional properties is one of the focal points of current research in dendritic molecules. Molecules with many unpaired electrons, which possess high-spin ground states and are stable at room temperature, are particularly challenging and promising targets. Only a few dendrimers have been functionalized with stable organic radicals and studied by EPR to date.^{7,8} However, a complete and deep study of these systems by EPR has never been done, in the best of our

knowledge. Magnetic interactions between radicals, not only in radical dendrimers but also in radical polymers, gold nanoparticles or other supramolecular species, determine the most important properties of these kinds of compounds in different applications.⁹

Here we describe the first example of five generations of phosphorus-containing dendrimers with stable radical end groups. Their synthesis and study by EPR, SQUID, ¹H NMR, ³¹P NMR, FT-IR and UV-Vis spectroscopy. The magnetic interactions between pendant stable radicals of the dendritic surface and their dynamic behavior are reported.

Results and Discussion

We have synthesised a family of phosphorus dendrimers based on a cyclotriphosphazene core, and containing 6, 12, 24, 48 and 96 aldehyde groups on their surface (Gc₀', Gc₁', Gc₂', Gc₃' and Gc₄' respectively) in the same way than previously reported.¹⁰ These dendrimers have been condensed with 4-amino-TEMPO (**2**) to obtain the corresponding imine TEMPO derivatives **3-Gc₀T**, **3-Gc₁T**, **3-Gc₂T**, **3-Gc₃T** and **3-Gc₄T** in 73-97 % yields (Scheme 1). We followed the conditions already reported for compound **3-Gc₀T**.⁷ An extended structure of dendrimer **3-Gc₃T** is depicted in Scheme 2.

Scheme 1. Synthesis of **3-Gc₀T**, **3-Gc₁T**, **3-Gc₂T**, **3-Gc₃T** and **3-Gc₄T** dendrimers, with 6, 12, 24, 48 and 96 TEMPO radicals, respectively, at the periphery.

Scheme 2. Extended structure of dendrimer **3-Gc₃T**.

^1H NMR and FT-IR allowed us to determine if reactions had gone to completion (by disappearance of the aldehyde signal at $\delta = 10$ ppm and 1760 cm^{-1} , respectively). Even though the signals of the ^1H NMR spectra were broad, due to the presence of the paramagnetic radical units, it was possible to establish the position of each group of protons of the molecule enabling also to follow the course of their preparation with this technique. Moreover, the shift of ^{31}P NMR signals (which were not too much affected by the presence of the radicals) permitted also the monitoring of the reaction and determination of the purity of the new dendrimers. The ^{31}P NMR chemical shifts of the starting materials (dendrimers with aldehyde termination) and the final dendrimers functionalized with TEMPO radical are reported in Table 1. In all cases a shift up to lowest field is observed, in agreement with similar modifications described in the literature.^{5f}

Table 1. ^{31}P NMR chemical shifts of dendrimers Gc_0' , Gc_1' , Gc_2' , Gc_3' and Gc_4' with aldehyde termination compared to those of dendrimers **3-Gc₀T**, **3-Gc₁T**, **3-Gc₂T**, **3-Gc₃T** and **3-Gc₄T** functionalized with TEMPO radical.

Compound	$^{31}\text{P}\{^1\text{H}\}$ NMR (101.3 MHz, CDCl_3) δ (ppm)
Gc_0'	5.0
3-Gc₀T	5.6
Gc_1'	5.8, 58.5
3-Gc₁T	6.4, 60.1
Gc_2'	6.2, 58.3, 60.3
3-Gc₂T	6.7, 60.8, 61.4
Gc_3'	6.2, 58.0, 59.9, 60.1
3-Gc₃T	6.4, 60.2, 61.1
Gc_4'	5.8, 58.0, 59.9, 60.3 (br)
3-Gc₄T	5.8, 60.6, 61.7, 62.6

By MALDI–TOF mass spectrometry it was possible to analyze compound **3-Gc₀T**, of zero generation, containing 6 radicals on its surface.⁷ However, it was not possible to analyze by this technique dendrimers from the 1st to the 4th generations, as it is usual for these kinds of compounds.^{5^f,11} In addition to this, in the dendrimer of zero generation **3-Gc₀T**, it was also possible to confirm its structure by X-ray diffraction showing the same orientation of the dendrimer branches in solution as in the solid state.⁷

We performed the EPR temperature study of all the generations synthesised **3-Gc₀T**, **3-Gc₁T**, **3-Gc₂T**, **3-Gc₃T** and **3-Gc₄T**. The EPR spectrum of the 4-amino-TEMPO free radical **2** shows

three lines with relative intensities 1:1:1 (Figure 1) from the coupling with the ^{14}N atom ($a_{\text{N}} = 15.5 \text{ G}$) and this pattern is independent on the temperature.

Figure 1. EPR spectra of a $5 \times 10^{-4} \text{ M}$ solution of 4-amino-TEMPO **2** in dichloromethane:toluene (1:1) at 300 K and 120 K (frozen solution).

In contrast, the EPR spectrum of **3-Gc₀T** shows seven lines centred at $g = 2.0066$ and separated by 5.0 G (Figure 2), indicating that there is a strong spin exchange interaction $|J| \gg |a_{\text{N}}|$ between three nitroxides ($1/3 a_{\text{N}}$).⁷ In addition, the relative intensity lines and linewidths change upon cooling from 350 to 220 K showing an alternating linewidth effect. This clearly indicates that the intramolecular exchange interaction is modulated by the temperature because $|J|$ critically depends on the frequency of collisions of the spin-bearing functional groups.¹² As the temperature is gradually lowered, the alternate lines 2nd, 3rd and 5th, 6th broaden and disappear because the frequency of collisions decreases and the spectra are less affected by spin exchange interaction.

Figure 2. EPR spectra of 10^{-4} M solution of dendrimer **3-Gc₀T** in dichloromethane:toluene (1:1) from 300 K to 120 K. Inset: spectrum at 350 K.

In frozen solutions (120 K) the spectrum is sensitive to the dipole-dipole interaction between neighboring nitroxides which substantially alters the shape of the spectrum. We can observe in Figure 2 that the spectrum of **3-Gc₀T** at 120 K is somewhat different than the corresponding to the 4-amino-TEMPO free radical, **2**, showing significant contribution of dipole-dipole interactions among adjacent spin labels. This effect could be estimated by the empirical ratio of peak heights d_1/d of a frozen EPR spectrum (Figure 1). This parameter was shown to be sensitive to the distance between adjacent nitroxides (e. g., the higher the ratio, the shorter the distance between the radical centres) and hence a convenient measure of the strength of the dipole-dipole interactions.^{13,14} The d_1/d parameter for **3-Gc₀T** is 0.77, whereas for 4-amino-TEMPO (**2**) is only 0.53.

The evolution of the shape of the spectra with temperature for the other dendrimer generations is similar among them, from the 1st to the 4th ones. As an example, we show in Figure 3 the evolution of the EPR spectra with temperature of dendrimer **3-Gc₃T** and in Figure S1, S2 and S3 the ones corresponding to a **3-Gc₁T**, **3-Gc₂T** and **3-Gc₄T**, respectively.

Figure 3. Evolution of the EPR spectra with temperature of a 3×10^{-4} M solution of dendrimer **3-Gc₃T** in dichloromethane:toluene (1:1).

As we can see in **Figure 3** the spectrum at high temperature shows a polyradical spectral pattern, which is dominated by a single, intense broad line. This line results from spin exchange and dipole-dipole interactions between several nitroxide radicals anchored close together on the dendrimer surface, averaged over different interaction distances.² As the temperature goes down the single broad line starts to decrease meanwhile three lines are maintained, as in the zero generation case. Thus, this three-line pattern is not attributed to a residual amount of free radical

impurity as we can find in the literature but to the non-interacting radicals contribution (see the Supporting Information, Figure S4). In this case, the d_1/d value extracted from the frozen spectrum at 120 K is 0.87.

In Figure 4 we show both the EPR spectra at 300 K and 120 K of generations **3-Gc₁T**, **3-Gc₂T**, **3-Gc₃T** and **3-Gc₄T** coming from solutions of the same molarity (5×10^{-4} M). The spectra are made in dilution conditions to be sure that we study the intra-molecular interactions present in each dendrimer. At 300 K (Figure 4a), all the EPR spectra show a similar polyradical spectral pattern, as explained above, dominated by a single, intense broad line. In fact, only for compound **3-Gc₀T** of zero generation (Figure 2) the spectral resolution allow us to determine the number of TEMPO interacting radicals, but from the 1st ($n = 12$) to the 4th ($n = 96$) generations the spectral resolution does not allow the observation of the everdecreasing spacing between the various hyperfine transitions (decrease of the splitting value a_N/n and increase of the number of lines $2n + 1$). It is worth mentioning that the linewidth of the broad line decreases from the 1st to the 4th generations (Figure 4a). This is consistent with the fact that at higher generations the radical ensembles will become larger, more compact and therefore more uniform. The tighter packing is expected to produce stronger spin exchange effects, leading to a narrower, Lorentzian line.¹⁵

Figure 4. a) EPR spectra, at 300K and b) at 120 K (frozen solution), of 5×10^{-4} M solutions of dendrimers **3-Gc₁T**, **3-Gc₂T**, **3-Gc₃T** and **3-Gc₄T** in dichloromethane:toluene (1:1).

At 120 K (Figure 4b) the dipole-dipole interactions are reflected in the d_1/d parameter calculated which is 0.83, 0.85, 0.87 and 0.94 for dendrimer **3-Gc₁T**, **3-Gc₂T**, **3-Gc₃T** and **3-Gc₄T**, respectively, much higher than for monoradical 4-amino-TEMPO (0.53). It is clearly seen the progressive increase of the d_1/d value which means that the intra-molecular dipolar interaction is higher from generation to generation. Moreover, we also observed at 120 K an $|\Delta m_s| = 2$ transition at half-field in each generation (see Figure 5a) which gives direct evidence of the presence of a high-spin state. No $|\Delta m_s| = 3$ or other lower-field transitions could be observed. We determined the EPR relative signal intensities of the $|\Delta m_s| = 2$ transition at half-field for every generation and we observed that there exists a direct proportionality between the EPR

signal intensity and the number of radicals of each generation (Figure 5b). Thus, the utility of EPR for the determination of the substitution efficiency on dendrimers by paramagnetic species is quite good.

Figure 5. a) EPR spectra of $|\Delta m_s| = 2$ transitions at half-field for dendrimers **3-Gc₀T**, **3-Gc₁T**, **3-Gc₂T**, **3-Gc₃T** and **3-Gc₄T** at 120 K in dichloromethane:toluene (1:1) with the same concentration: 5×10^{-4} M. b) EPR relative signal intensities (double integrals) of each spectrum of Figure 5a vs the number of attached radicals of each generation.

Further, we made an EPR concentration study for all the dendrimer generations (**3-Gc₀T** to **3-Gc₄T**). As an example, we show in Figure 6 the EPR spectra of the first generation dendrimer, **3-Gc₁T**, from 10^{-2} M to 10^{-4} M in dichloromethane:toluene 1:1, at 120 K. An $|\Delta m_s| = 2$ transition at half-field was observed in all the concentrations studied even in very diluted solutions (5×10^{-5} M). This phenomenon was the same in all the generations of dendrimers and gives direct evidence of the intra-molecular origin of the dipolar interactions.

Figure 6. EPR study of different concentrations of dendrimer **3-Gc₁T** in dichloromethane:toluene 1:1, from 10^{-2} M to 10^{-4} M, at 120 K (spectra of $|\Delta m_s| = 2$ transition at half-field). Spectra of 10^{-2} M and 5×10^{-3} M solutions are depicted in the inset and in a different scale.

The magnetic properties of dendrimers **3-Gc₀T**, **3-Gc₁T** and **3-Gc₄T** were also investigated on a polycrystalline sample by SQUID magnetometry in the temperature range of 2 to 300 K. The temperature dependence of the molar magnetic susceptibility χ_M , is given in Figure 7 as a plot of $\chi_M T$ versus T. The $\chi_M T$ value of these compounds remains constant from 300 K to *ca.* 30 K and then decreases at lower temperature. Such behaviour is indicative of antiferromagnetic interaction between the radicals. The $\chi_M T$ values given at 300 K are of 2.23, 4.46 and 30.56 $\text{cm}^3\text{Kmol}^{-1}$ for dendrimers **3-Gc₀T**, **3-Gc₁T** and **3-Gc₄T**, respectively. Such values are close to the expected contribution of the number of radicals by each dendrimer generation.¹⁶

Figure 7. Temperature dependence of the experimental $\chi_M T$ for dendrimers **3-Gc₀T**, **3-Gc₁T** and **3-Gc₄T**.

Dendrimers **3-Gc₀T**, **3-Gc₁T**, **3-Gc₂T**, **3-Gc₃T** and **3-Gc₄T** were also characterized by UV-Vis spectroscopy (Figure 8).

Figure 8. UV-Vis spectra of dendrimers **3-Gc₀T**, **3-Gc₁T**, **3-Gc₂T**, **3-Gc₃T** and **3-Gc₄T** in dichloromethane at room temperature.

We can observe that the UV-Vis spectra show the typical TEMPO n- π^* absorption band at *ca.* 450 nm (Table 2).¹⁷ Interestingly, the value of the molar extinction coefficient (ϵ) increases by a factor of two generation by generation, thus, ϵ increases with the number of TEMPO groups in a simple additive way. Indeed, each TEMPO group contributes *ca.* 10 M⁻¹cm⁻¹ to the value (Table 2), which is the molar extinction coefficient of the free TEMPO radical.^{17,18}

Con formato: Inglés (Reino Unido), Superíndice

Table 2. UV-Vis spectroscopy data for dendrimers **3-Gc₀T**, **3-Gc₁T**, **3-Gc₂T**, **3-Gc₃T** and **3-Gc₄T** in dichloromethane at room temperature.

Dendrimer	λ_{max} (nm)	ϵ (M ⁻¹ cm ⁻¹) [a]	ϵ per TEMPO (M ⁻¹ cm ⁻¹) [a]
3-Gc ₀ T	456	61.8	10.3
3-Gc ₁ T	455	117.6	9.8
3-Gc ₂ T	452	240.9	10.0
3-Gc ₃ T	450	484.8	10.1
3-Gc ₄ T	443	1065.6	11.1

[a] Estimated error on the molar absorption coefficient ϵ is ± 10 %.

Conclusions

A family of five generations phosphorus containing dendrimers has been functionalized with pendant nitroxyl radicals (**3-Gc₀T**, **3-Gc₁T**, **3-Gc₂T**, **3-Gc₃T** and **3-Gc₄T**). The nitroxyl radicals show a strong magnetic exchange interaction. We have made an exhaustive study by EPR of these interactions, examining carefully their dynamic behaviour with temperature as well as the

effect of the concentration on them. We have explained the presence of the three-line signal overlapping the broad line at high temperature that becomes the main contribution at low temperature. The direct evidence of the high-spin states has been given by the observation of $|\Delta m_s| = 2$ transitions in each generation. This forbidden transition is observed at diluted concentrations giving direct evidence of the intra-molecular origin of such interactions. We have observed that there exists a direct proportionality between the intensity of the half-field transition and the number of radicals of each generation. From the UV-Vis characterization we have observed that the value of the molar extinction coefficient it is also proportional to the number of TEMPO groups. The magnetic properties studied by SQUID magnetometry showed antiferromagnetic interaction between the spin carriers.

Experimental Section

Materials and Methods. IR spectra were recorded in the attenuated total reflectance mode (ATR) in a Perkin Elmer Spectrum One Fourier transform spectrometer. NMR spectra were recorded with a Bruker AC250 instrument. ^1H NMR (250 MHz) chemical shifts are reported relative to tetramethylsilane; coupling constants are reported in Hz. $^{31}\text{P}\{^1\text{H}\}$ NMR (101.3 MHz) spectra are reported relative to H_3PO_4 85% in water. EPR spectra were obtained with an X-Band Bruker ELEXYS 500 spectrometer equipped with a TE102 microwave cavity, a Bruker variable temperature unit, a field frequency lock system Bruker ER 033 M and equipped with a NMR Gaussmeter Bruker ER 035 M. The modulation amplitude was kept well below the line width, and the microwave power was well below saturation. Magnetic measurements down to 2 K were carried out in a Quantum Design MPMS-5S SQUID magnetometer. The molar susceptibility was

corrected for the sample holder and for the diamagnetic contribution of all atoms by means of Pascal's tables.^{18,19}

All preparations of dendrimers were performed under inert atmosphere with Schlenk type glassware. Anhydrous solvents were used thoroughly.

Synthesis.

Synthesis of 3-Gc₁T. Dendrimer Gc₁' (0.10 g, 0.04 mmol) and free radical 4-amino-TEMPO **2** (0.08 g, 0.49 mmol) were dissolved in THF (1 mL). The mixture was stirred overnight. Pentane was added to the solution until the formation of an orange precipitate. The mixture was stirred for 10 min and filtered via cannula. The solid was washed with THF-pentane (1:10) several times and dried to afford 0.12 g of the imine (73 %) as an orange solid. IR (ATR) 2976, 2932, 2861, 1644, 1602, 1503, 1465, 1361, 1184, 1157, 913 cm⁻¹. ³¹P{¹H} NMR (101.3 MHz, CDCl₃) δ 6.4, 60.1.

Synthesis of 3-Gc₂T. The same procedure for 3-Gc₁T was followed, using 0.10 g (0.01 mmol) of dendrimer Gc₂' and 0.07 g (0.41 mmol) of radical 4-amino-TEMPO **2**. We obtained 0.13 g of the imine (86 %) as an orange solid. IR (ATR) 2973, 2934, 2869, 1644, 1602, 1503, 1467, 1361, 1187, 1157, 913 cm⁻¹. ³¹P{¹H} NMR (101.3 MHz, CDCl₃) δ 6.7, 60.8, 61.4.

Synthesis of 3-Gc₃T. The same procedure for 3-Gc₁T was followed, using 0.10 g (6.75·10⁻³ mmol) of dendrimer Gc₃' and 0.06 g (0.35 mmol) of radical 4-amino-TEMPO **2**. We obtained 0.14 g of the imine (97 %) as an orange solid. IR (ATR) 2973, 2932, 2862, 1644, 1601, 1502, 1466, 1361, 1187, 1157, 909 cm⁻¹. ³¹P{¹H} NMR (101.3 MHz, CDCl₃) δ 6.4, 60.2, 61.1.

Synthesis of 3-Gc₄T. The same procedure for 3-Gc₁T was followed, using 0.10 g (3.36·10⁻³ mmol) of dendrimer Gc₄' and 0.06 g (0.35 mmol) of radical 4-amino-TEMPO **2**. We obtained

0.13 g of the imine (89 %) as an orange solid. IR (ATR) 2973, 2934, 2857, 1645, 1601, 1502, 1466, 1361, 1187, 1157, 909 cm⁻¹. ³¹P{¹H} NMR (101.3 MHz, CDCl₃) δ 5.8, 60.6, 61.7, 62.6.

ASSOCIATED CONTENT

Supporting Information Available: Experimental spectra of **3-Gc1T** to **3-Gc4T**, EPR temperature study of **3-Gc1T**, **3-Gc2T** and **3-Gc4T** and additional EPR data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

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ABBREVIATIONS

TEMPO: (2,2,6,6-Tetramethylpiperidin-1-yl)oxy.

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Radical Dendrimers: A Family of Five Generations of Phosphorus Dendrimers Functionalized with TEMPO Radicals

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