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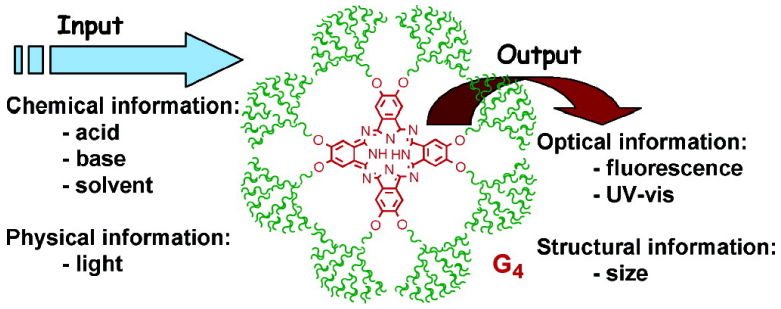
J. Am. Chem. Soc., **2005**, 127 (45), 15762-15770• DOI: 10.1021/ja054797b • Publication Date (Web): 25 October 2005



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Octasubstituted Metal-Free Phthalocyanine as Core of Phosphorus Dendrimers: A Probe for the Properties of the Internal Structure

Julien Leclaire,[†] Rodolphe Dagiral,[†] Suzanne Fery-Forgues,[‡] Yannick Coppel,[†] Bruno Donnadieu,[†] Anne-Marie Caminade,*[,†] and Jean-Pierre Majoral*[,†]

Contribution from the Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 4, France and the Laboratoire IMRCP CNRS UMR 5623, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 4, France

Received July 18, 2005; Revised Manuscript Received September 20, 2005; E-mail: caminade@lcc-toulouse.fr; majoral@lcc-toulouse.fr

Abstract: The synthesis of a new family of phosphorus dendrimers built from an octasubstituted metal-free phthalocyanine core is described up to generation 5. This core is used as a sensor and a probe for analyzing the properties of the internal structure and the influence of each structural part (core, branches, surface) upon the whole structure. UV−visible spectra show both a hyperchromic and bathochromic effect on the Q-bands with increasing generation, indicating that the chromophore is more isolated, and that the dendritic shell mimics a highly polar solvent. There is no evidence for aggregation, except for generation 0, showing again the isolation of the core. However, the dendritic shell is permeable to aqueous acids and bases, as demonstrated by the reversible splitting of the Q-band in an acidic medium (neutral form of the phthalocyanine) and the single Q-band in a basic medium (dianionic form), even for generation 4. The fluorescence quantum yield for the neutral form increases with increasing generation. The dianionic form of generation 0 is poorly fluorescent, whereas generations 3 and 4 (G_3 and G_4) exhibit better fluorescence. The cores of G_3 and G_4 are highly sensitive optical sensors for H_3O^+ and OH^-. These experiments are carried out in THF/water mixtures, and the influence of water on the structure has been checked. The hydrodynamic radius of generation 4 is measured by NMR diffusion (pulse gradient spin−echo) experiments. R_H varies from 35.4 Å at 4 mol % of water to 32.5 Å at 64 mol % of water in THF, indicating the hydrophobic nature of these dendrimers.

Introduction

Dendritic-type architectures are frequently encountered in the biological world, as illustrated by the branches and roots of plants or the neural networks of the higher organisms. The reason for this omnipresence is believed to be a functional optimization in terms of exchange and distribution of energy and of information. Dendrimers[1] constitute a small-scale artificial model of these natural dendritic architectures, and they can be viewed as optimized structures for maximized interactions, both within their network and with the external media, as illustrated for instance by their enhanced solubility when compared to linear polymers.[2] The three structural components of dendrimers, namely an interior core, repeating branching units radially attached to the core, and functional terminal groups attached to the outermost branching units, can be tuned at will. A fine control of the overall size (the generation), shape, and properties of the dendrimer, creating special three-dimensional nanoenvironments, reminiscent of that found in enzymes and proteins, can be achieved. To yield a better understanding of the properties imparted by each component to the whole structure and of the influence of each part on the others, it is highly desirable to introduce environmental probes within the dendritic framework, particularly at the level of the core. Previous works in this field have highlighted the concept of site isolation of the core, leading to enhanced photophysical properties or catalytic effects.[3] The choice of the type of probe located at the core is of crucial importance; ideally, it should be able to afford different types of information, and the variation of its response upon modification of the local environment should be detectable by several techniques. In most cases, the functional probe located at the core is either a photoresponsive system, an electroactive system, or a combination of both, found for instance for porphyrin cores, whose utility has been recognized very early,[4] and which are still widely used as cores of dendrimers.[5] In contrast, relatively few dendrimers incorporating a phthalocyanine core have been synthesized so far, and most physicochemical studies were carried out with either their metallic complexes[6] or with a silicon derivative[7] located within the central macrocycle, even for those that were initially

[†] Coordination du CNRS.
[‡] Université Paul Sabatier.

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10.1021/ja054797b CCC: $30.25

synthesized free.[6b,7b−f,8] However, metal-free phthalocyanines should afford information not only about their degree of steric isolation but also about the modification of basicity or acidity and local polarity, induced by the influence of the dendritic branches.

In this paper we report the synthesis and characterization of a series of phosphorus dendrimers[9] soluble in organic solvents and built from a metal-free phthalocyanine core as well as the information deduced from the modification of their photochemical and diffusional properties. This work is a complement and a very large extension of the work we have previously reported concerning a micellelike water-soluble phosphorus dendrimer possessing hydrophilic end groups and a pthlalocyanine core,[10] whose photo- and physicochemical properties were not studied.

Results and Discussion

Syntheses. Most of the dendrimers possessing a phthalocyanine core are synthesized by the cyclotetramerization of dinitriles bearing a dendritic substituent; only a few of them are synthesized by growing branches from a preexisting functionalized phthalocyanine.[6a,b] Furthermore, in all cases except one,[8b] the phthalocyanine cores are tetrasubstituted. However, this tetrasubstitution induces complications due to regioisomers;[7c] thus, we chose to use an octasubstituted phthalocyanine to avoid these problems. The dendrimer core is an octaformyl phthalocyanine, whose synthesis is inspired by the work done by Wöhrle et al.[11] Dichlorophthalonitrile **1** is reacted with 2 equiv of hydroxybenzaldehyde sodium salt **2** in the first step. The temperature (70, 110, or 150 °C) and the duration of heating (120 or 48 h) were optimized to determine the best conditions to isolate the bisformylphthalonitrile **3** (Scheme 1). Heating at 110 °C for 48 h leads to a 97% disubstitution (^{1}H NMR control), and compound **3** is isolated in 65% yield after washings with water. Single crystals of **3** suitable for X-ray diffraction were

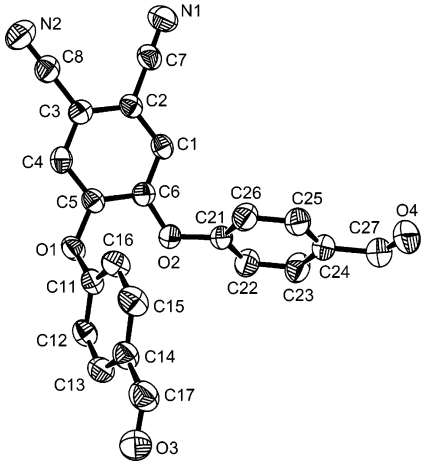
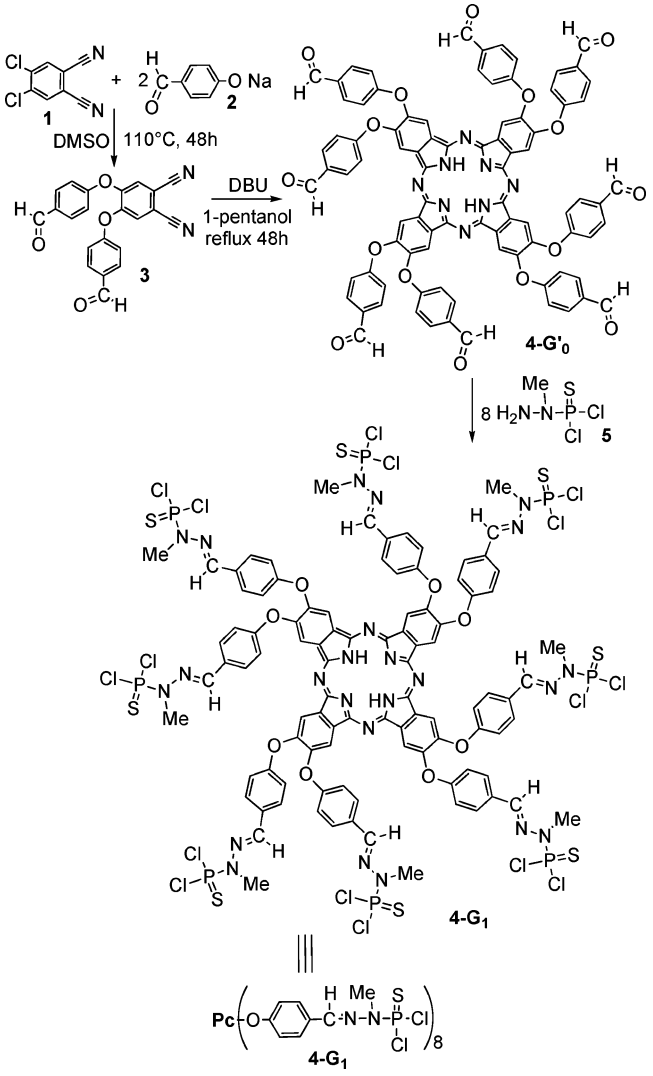


Figure 1. ORTEP view of compound **3**.

Scheme 1



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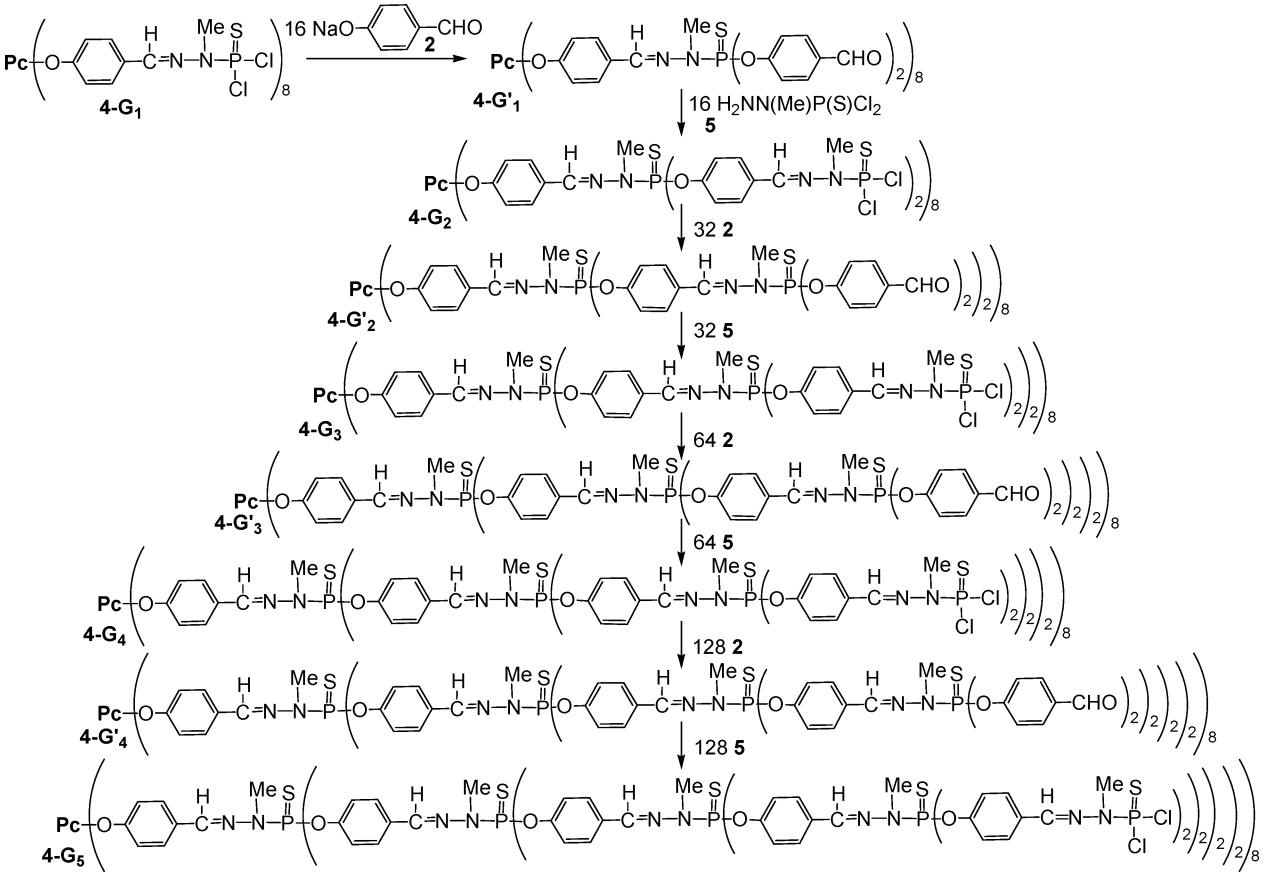
Scheme 2



obtained by slow evaporation in THF/pentane at room temperature. The ORTEP drawing of the X-ray structure is shown in Figure 1. The benzaldehyde groups are not coplanar with the phthalonitrile moieties; thus, there is no stacking phenomenon at this step in the solid state and, therefore, neither in solution.

The next step consists of the cyclization reaction of 4 equiv of compound **3** in refluxing 1-pentanol in the presence of DBU. This procedure affords metal-free phthalocyanines (Pc) in relatively good yields. Here, the phthalocyanine **4-G$_0'$** is isolated in 56% yield, as a poorly soluble dark-green powder. Due to this poor solubility, only low-quality NMR spectra could be obtained in solution, but compound **4-G$_0'$** is unambiguously characterized by mass spectrometry (FAB, $m/z = 1474$). Starting from the aldehydes, the dendrimer is grown by our classical two-step method,[12] whose first step is a condensation reaction with the phosphorhydrazide **5**. Generally, these reactions afford the condensation products in nearly quantitative yields. However, the first-generation **4-G$_1$** is isolated in only 37% yield after work up, due to the poor solubility of **4-G$_0'$**. Dendrimer **4-G$_1$** is much more soluble than **4-G$_0'$**; it is characterized by ^{31}P, ^{1}H, and ^{13}C NMR and IR spectroscopies; no trace of aldehyde is detected, showing the completion of the condensation reactions.

The next steps, i.e., the nucleophilic substitution of Cl by hydroxybenzaldehyde sodium salt **2**, the condensation reaction of the aldehyde with the phosphorhydrazide **5**, and then the repetition of both steps, occur without any problem (Scheme 2). This means that the known tendency of phthalocyanines to stack, which causes their insolubility, is largely diminished, even for the first generation. All compounds up to the fifth generation **4-G$_5$** are isolated in nearly quantitative yields. The completion of the reaction in each case is monitored by NMR. ^{31}P NMR is useful for the nucleophilic substitution (**4-G$_n$** → **4-G$_n'$**), which induces a slight but clearly detectable shielding ($\Delta\delta = -0.3$ ppm) of the signal corresponding to the phosphorus that undergoes the reaction. A deshielded signal ($\Delta\delta = 6$ ppm), corresponding to the monosubstitution reaction, is detected during the course of the reaction; it totally disappears when the reaction has gone to completion. ^{1}H NMR is useful for the condensation reaction (**4-G$_n'$** → **4-G$_{n+1}$**), which induces the total disappearance of the signal corresponding to the aldehydes, also detected by ^{13}C NMR and IR spectroscopies.

Having this series of phosphorus dendrimers soluble in organic solvent (**4-G$_n'$**), we studied their UV−visible and fluorescence properties, using the phthalocyanine core as a sensor and a probe.

UV−Visible Absorption Spectroscopy. UV−visible absorption spectroscopy is an easy and informative way to study phthalocyanines and to detect changes in their environment. The $\pi-\pi^*$ transitions of the 14-electron aromatic phthalocyanine ring are characterized by two types of absorption bands, named B- and Q-bands, centered at ∼300 and ∼670 nm, and corresponding to $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ transitions, respectively. For the dendritic phthalocyanines described here, the near-UV band should correspond to the superposition of the B-band of the core and of the absorption band characteristic of the arylhydrazones constituting the skeleton of the dendrimer. We have

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Table 1. Spectral Characteristics of Dendrimers **4-G′$_n$** in $CHCl_3$ ([C] = 1.00×10^{-5} mol L^{-1}); Wavelength, Molar Absorption Coefficient (log ϵ), Q-Band Energy, and Energy Difference between the Splitted Bands

	B-band λ (nm) (log ϵ (M^{-1} cm^{-1}))		Q-band λ (nm) [Q, cm^{-1}] (log ϵ (M^{-1} cm^{-1}))				splitting ($Q_y - Q_x$)
dendrimer			$Q_y(0,1)$	$Q_x(0,1)$	$Q_y(0,0)$	$Q_x(0,0)$	(cm^{-1})
4-G′$_0$[a]	275	(4.25)	608	637	663 [15080]	699 [14300]	777
	348	(3.99)	(4.20)	(4.37)	(4.65)	(4.67)	
4-G′$_1$	259		607	643	667 [14990]	701 [14270]	727
	(5.71)		(4.07)	(4.27)	(4.66)	(4.71)	
4-G′$_3$	264	274	611	643	672 [14880]	704 [14200]	676
	(6.16)	(6.16)	(4.36)	(4.52)	(4.97)	(5.02)	
4-G′$_4$	263	277	611	643	672 [14880]	704 [14200]	676
	(6.48)	(6.48)	(4.46)	(4.62)	(5.07)	(5.11)	

[a] The ϵ values given for **4-G′$_0$** are the apparent values, not corrected for the effects of aggregation

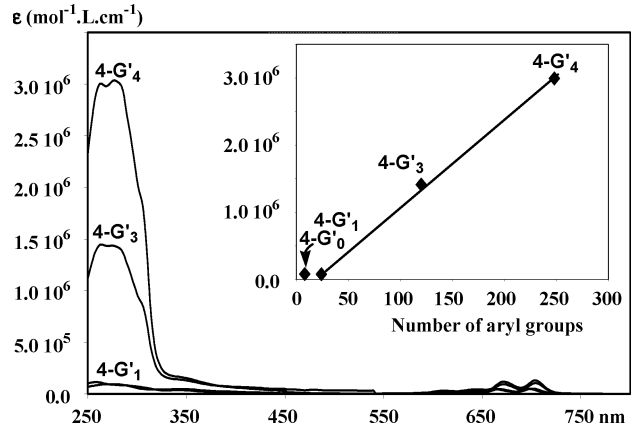

Figure 2. UV−visible absorption spectra of dendrimers **4-G′$_n$** in $CHCl_3$. (Insert) Variation of the value of ϵ (mol^{-1} L cm^{-1}) at 264 nm with the number of aryl groups.

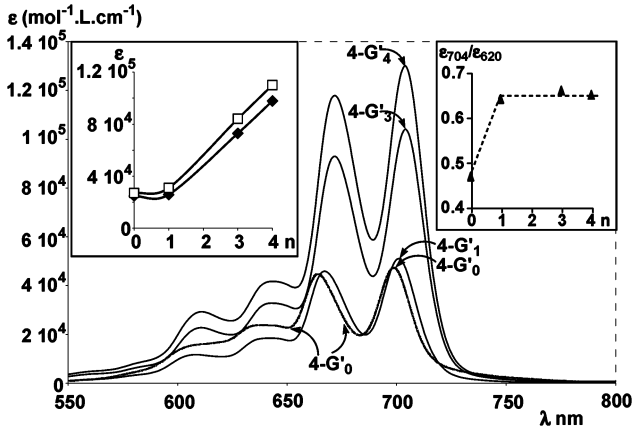

Figure 3. Q-band of dendrimers **4-G′$_n$**. (Left insert) Value of ϵ at 670 nm (◆) and 700 nm (□) versus the generation (*n*). (Right insert) Ratio of the value of ϵ at 704 and 620 nm versus generation (*n*).

already shown that the molar absorption coefficient ϵ depends on the number of chromophoric units, in an essentially additive way, for dendrimers having azobenzene units in the branches;[13] the same behavior is observed for the series **4-G′$_1$**, **4-G′$_3$**, **4-G′$_4$** in chloroform, and thus each branch and each segment of the branch is electronically independent (Table 1). The strong band in the UV area is mainly due to the aryl groups constituting the skeleton of the dendrimer (Figure 2), and the increase of ϵ is directly linked to the multiplication of their number with growing generations, except for **4-G′$_0$** which does not possess any arylhydrazone groups (Figure 2, insert). Thus, the B-band of the phthalocyanine is hidden and cannot offer any interesting information. On the other hand and very interestingly, the dendritic skeleton is totally transparent in the area of the Q-band.

The spectra of dendrimers **4-G′$_0$**, **4-G′$_1$**, **4-G′$_3$**, and **4-G′$_4$** in chloroform in the visible area are gathered in Figure 3. In all cases, the Q-band is splitted into two components $Q_y(0,0)$ and $Q_x(0,0)$, giving two main absorptions at ∼670 and ∼700 nm, as expected for the D_{2h} symmetry of neutral phthalocyanines; two vibrational bands $Q_y(0,1)$ and $Q_x(0,1)$ are also observed at ∼610 and ∼640 nm, respectively. The energy difference between the $Q_x(0,0)$ and $Q_y(0,0)$ bands decreases with the energy of the Q-band (see splitting in Table 1), as previously reported for "classical" phthalocyanines.[14] At first glance, the most salient feature of Figure 3 is the hyperchromic effect observed when the number of generation increases from 1 to 4 (Table 1). This increase is linear for the maxima of the absorption of both bands centered at ∼670 and ∼700 nm, except for **4-G′$_0$**, presumably because of a different electronic effect of the substituents of the chromophoric units (aldehydes for **4-G′$_0$** versus hydrazones for all the others) (Figure 3, left insert). The very high value measured for the molar absorption coefficient of the Q-band of **4-G′$_4$** shows that the chromophore is highly isolated; similar values were already reported for chromophores encapsulated in liposomes,[15] or in a liposome/dendrimer system.[6d]

The isolation of the chromophoric unit is also confirmed by Figure 3; except for **4-G′$_0$**, there is no evidence for any aggregation phenomenon, which should give a very broad band at ∼620 nm. The ratio of the intensity of the absorption at 704 and 620 nm, depending on the generation *n*, is practically constant for $n = 1$, 3, and 4 but is different for $n = 0$ (Figure 3, right insert), indicating that the aggregation band is superposed to the vibrational band in the latter case. These data can be correlated to the observation made previously concerning the poor solubility of **4-G′$_0$** compared to those of **4-G′$_1$**−**4-G′$_4$**.

The last point to be emphasized concerning Figure 3 is the slight bathochromic effect observed for the maxima of absorption of the Q-band when generation *n* increases. Reichardt[16] proposed a relation between a solvatochromic effect and changes in a polarity parameter ($E_T(30)$), which increases with the polarity of the solvent. With all spectra of **4-G′$_n$** being recorded in the same solvent ($CHCl_3$), the observed bathochromic effect

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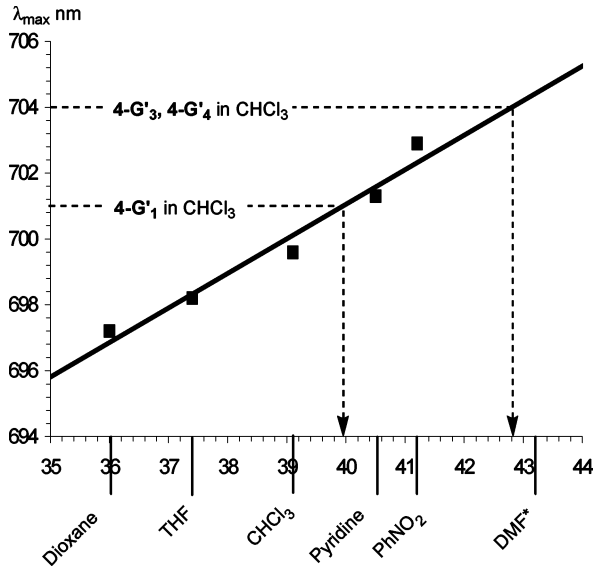

Figure 4. Bold straight line: variation of the λ_{max} value of the Q-band of **4-G′$_0$** in various solvents versus their $E_T(30)$ Reichardt's parameter.[16] DMF*: **4-G′$_0$** has a single Q-band; the corresponding data are not plotted. Dotted horizontal lines: λ_{max} of the Q-band of **4-G′$_1$**, **4-G′$_3$**, and **4-G′$_4$** in $CHCl_3$; dotted vertical lines: estimation of the polarity induced by the branches, deduced from the intercept with the bold line.

might be related to changes in polarity induced by the dendritic layers upon the core. To estimate the modification of the local polarity induced by the branches, we plotted first the variation of the λ_{max} value of the Q-band of **4-G′$_0$**, recorded at ~700 nm in solvents of different polarities, versus their $E_T(30)$ parameters (Figure 4) as a calibration curve; a linear correlation (as expected from Dimroth and Reichard's model) is observed. No value could be obtained in DMF, which affords a single-band spectrum different from all the other (splitted) spectra and which should correspond to a deprotonated species; this phenomenon will be emphasized in the next paragraph. Dendrimers **4-G′$_n$** ($n \geq 1$) can be considered to be made of **4-G′$_0$** encapsulated within a dendritic solvation sphere; this approximation is often used for dendritic systems.[17] Thus, plotting the λ_{max} values measured for **4-G′$_n$** ($n \geq 1$) in $CHCl_3$ on the straight line of Figure 4 (dotted lines) gives information about the influence of the dendritic shell upon the chromophoric core. This shell mimics a highly polar solvent, the branches of both **4-G′$_3$** and **4-G′$_4$** in $CHCl_3$ seem to have an influence close to that of DMF upon the phthalocyanine core, but no deprotonation is observed in $CHCl_3$.

However, the particular behavior of **4-G′$_0$** in DMF incited us to have a deeper insight on the acido/basicity properties of the phthalocyanine ring. Contrarily to porphyrins, this type of property is much less studied for phthalocyanines, especially in an organic environment.[18] The four pyrrole nitrogen atoms can theoretically undergo protonation/deprotonation reactions, which modify the symmetry of the phthalocyanine ring and affect particularly the Q-band's shape and location. Although metalated phthalocyanines exhibit a sole Q-band, the corresponding free-base band is classically splitted. This fact is characteristic of the free-base symmetry, which is D_{2h}, whereas metalation induces a D_{4h} symmetry of the aromatic ring.[19] Complete protonation or deprotonation of the pyrrole nitrogens has been reported to induce a unique Q-band absorption, restoring D_{4h} symmetry,[20] whereas the monoanionic and monocationic derivatives also exhibit a splitted Q-band, but these species are generally considered as energetically less favored[18] (Figure 5).

The experiments were first conducted with **4-G′$_0$** in THF, which is both a good solvent for dendrimers **4-G′$_n$** and miscible with water. The initial spectrum of **4-G′$_0$** in THF closely resembles that in $CHCl_3$ (Figure 6a), and no change is observed when bases such as NEt_3 or DBU are added in stoichiometric amounts (2 equiv per **4-G′$_0$**). Thus, the thermodynamic stable form of **4-G′$_0$** in THF is the neutral form (2 NH and 2 N**:** for the four central pyrrole rings). On the other hand, the addition of 2 equiv of strong bases, such as sodium or potassium hydroxide, in water to generation 0 in THF induces dramatic changes of the Q-band, which merges in a single band, as expected for a totally deprotonated dianionic phthalocyanine (Figure 6b). An increased amount of aggregated phthalocyanines is observed, characterized by a band at ~630 nm. The addition of HCl allows for the recovering of a splitted Q-band, characteristic of the neutral phthalocyanine (Figure 6c). The protonation of the four pyrrole nitrogens, which would give a single Q-band, is never observed, even when an excess of acid is used, whatever the acid (HCl, trifluoroacetic acid, or H_2SO_4). Another deprotonation/protonation cycle has been done, adding successively KOH and HCl (Figure 6d,e); the phenomena observed are the same as for the first cycle but with an increased amount of aggregated species, which is presumably a hydrophobic effect due to the increased polarity of the solvent[6d] induced by an increased amount of water in THF added together with KOH and HCl.

Surprisingly, dendrimers **4-G′$_3$** and **4-G′$_4$** in THF gave a unique Q-band (see Figure 7a, for **4-G′$_3$**), whereas they gave a splitted Q-band in $CHCl_3$. Thus, it seems that the stable form of the cores of **4-G′$_3$** and **4-G′$_4$** in THF is the deprotonated, doubly negatively charged form. This finding has to be related to a strong increase of the local polarity induced by the branches toward the core, as deduced previously from Figure 4. The addition of 1 equiv of water induces a partial protonation; Figure 7b displays a spectrum corresponding to the superposition of a unique Q-band and a splitted Q-band, indicating that at least two species exist in the THF−water solution. The addition of HCl totally affords the neutral species, characterized by the splitted Q-band (Figure 7c). As already observed for **4-G′$_0$**, no protonation of the four-pyrole nitrogen could be detected here, even with an excess of acid. Deprotonation and protonation cycles can be carried out for **4-G′$_3$** with KOH and HCl (Figure 7d−f). The phenomena observed are the same as for **4-G′$_0$** but with one noticeable difference: no aggregation problem is observed for **4-G′$_3$**, confirming the protecting effect induced by the dendritic shell toward the core.

Thus, it can be concluded from these data that the dendritic shell influences the pK_a of the core.

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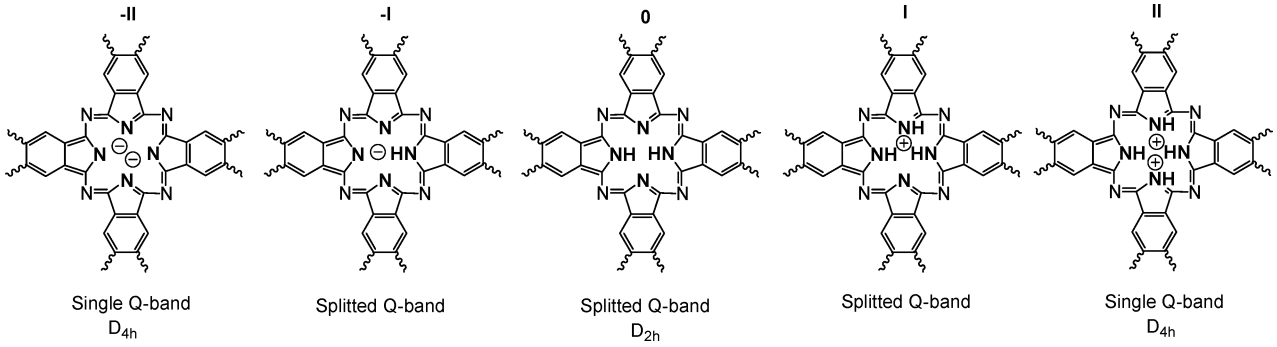

Figure 5. Protonation and deprotonation of phthalocyanines, influence on the symmetry and on the appearance of the Q-band.

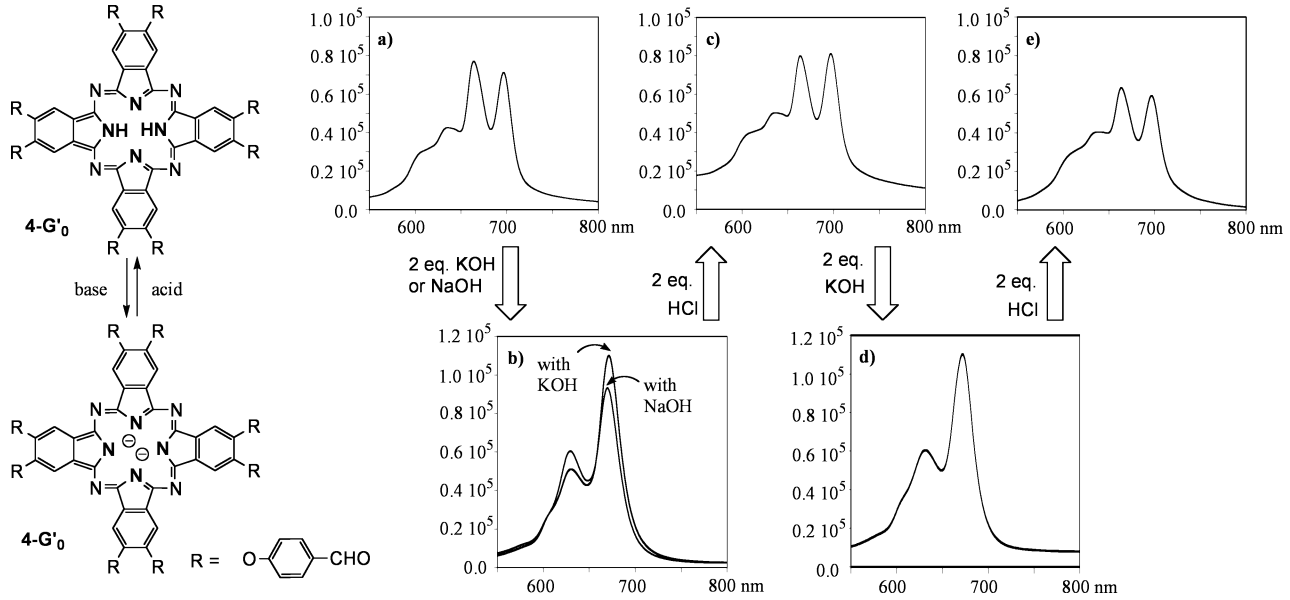

Figure 6. Variation of the Q-band of **4-G′$_0$** in THF, depending on the acido/basicity, with successive additions of base and acid. ϵ (M^{-1} cm^{-1}) versus λ (nm).

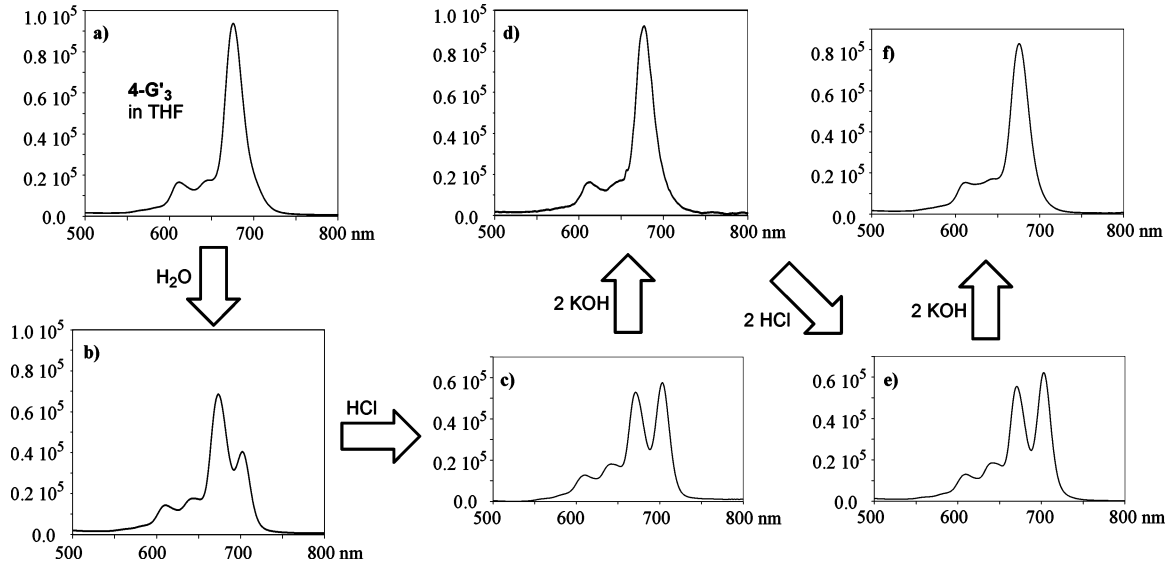

Figure 7. Variation of the Q-band of **4-G′$_3$** in THF, depending on the acido/basicity, with successive addition of acid and base. ϵ (M^{-1} cm^{-1}) versus λ (nm).

Fluorescence. Due to the particular behavior of the phthalocyanine core in THF, the steady-state fluorescence properties of the series **4-G′$_n$** (n = 0, 3, 4) were investigated in this solvent. Taking into account the high-sensitivity of the central chromophore to pH (see above), the fluorescence experiments of the neutral species were carried out by adding first aqueous HCl 10^{-4} M (1/1000 v/v H_2O/THF) to the solution of dendrimer. First, it was checked that the excitation spectra did not vary with the emission wavelength, confirming that there was a single emitting species. Second, it was checked that the position of the emission spectrum did not depend on the excitation wavelength. Having verified both points, the fluorescence

Table 2. Fluorescence Characteristics of Dendrimers 4-G′$_n$

dendrimer	λ_{em} (nm)	$\Phi_{4-G'n}$	τ (ns)	k_r (10^8 s^{-1})	k_{nr} (10^8 s^{-1})
			4-G′$_0$		
neutral	700	0.33 ± 0.02	4.5 ± 0.5	0.73 ± 0.11	1.49 ± 0.23
dianionic	682	0.03 ± 0.01	<0.3		
			4-G′$_3$		
neutral	704	0.43 ± 0.02	5.0 ± 0.3	0.86 ± 0.09	1.14 ± 0.11
dianionic	684	0.07±0.01	<0.3		
			4-G′$_4$		
neutral	708	0.42 ± 0.02	4.6 ± 0.3	0.92 ± 0.10	1.26 ± 0.13
dianionic	686	0.11 ± 0.01	<0.3		

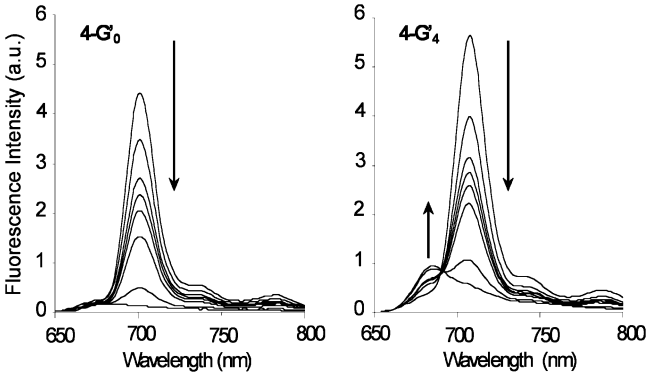

Figure 8. Variation of the fluorescence spectrum of **4-G′$_0$** (2.0×10^{-6} M, left) and **4-G′$_4$** (1.2×10^{-6} M, right) induced by the addition of aqueous NaOH to a solution of THF containing HCl 10^{-4} M (after correction of the dilution). From top to bottom, [NaOH] = 0; 9.95×10^{-5}; 1.98×10^{-4}; 2.96×10^{-4}; 3.92×10^{-4}; 4.88×10^{-4}; 5.85×10^{-4}; and 6.76×10^{-4} M.

properties were investigated by exciting in the Q-band of the central chromophore at 646 nm. An intense unresolved emission band accompanied by a weak vibrational component was observed for the three compounds studied. A slight bathochromic effect was observed for the emission from 700 to 708 nm when the generation (the size) of the dendrimer increased from **4-G′$_0$** to **4-G′$_4$** (Table 2). This slight increase has to be related to an increased local polarity, as already demonstrated from the absorption spectra.

The quantum yield (Φ) of the fluorescence of **4-G′$_0$**, **4-G′$_3$**, and **4-G′$_4$** was measured using 3,3′-diethyloxatricarbocyanine iodide (DOTCI) in absolute ethanol as a reference.[21] $\Phi_{4-G'n}$ was found to be higher for the dendrimers **4-G′$_3$**, and **4-G′$_4$** than for the parent species **4-G′$_0$** despite a longer emission wavelength (Table 2). This result seems to contradict a correlation previously reported between short wavelengths and high quantum yields for a series of nondendritic phthalocyanines[22] and illustrates the specificity of dendrimers. The relatively high values obtained show that each phthalocyanine is isolated from the others by the dendritic shell, which inhibits the quenching due to self-assembly. However, despite its physical isolation, the phthalocyanine core remains very sensitive to its environment. Indeed, the modifications that occur in basic conditions and which are evidenced by the UV−visible spectra also have a tremendous influence on fluorescence emission. The addition of aqueous NaOH induced in all cases a dramatic decrease of the fluorescence intensity (Figure 8). The fluorescence of **4-G′$_0$** practically disappeared, whereas a new fluorescence band of low intensity appeared for **4-G′$_3$** and **4-G′$_4$** at 684 and 686 nm, respectively. The quantum yield of this new band increased for the highest generations of the dianionic species because it passed from 0.03 for **4-G′$_0$** to 0.11 for **4-G′$_4$**, illustrating here also an increased isolation. To the best of our knowledge, no fluorescence data of dianionic metal-free phthalocyanines has been reported so far. The observation of this new band, practically undetectable for the small compound **4-G′$_0$** but relatively intense for **4-G′$_4$**, illustrates again the protective influence of the dendritic shell.

On the other hand, it has been often reported previously that the luminescence of phthalocyanines is totally quenched in water, due to aggregation in polar solvents.[23] However, this aggregation is always accompanied by a broadening and a large blue-shift of the absorption Q-band, which is not observed here for **4-G′$_n$** dendrimers of high generations; thus, aggregation of the phthalocyanine rings due to the presence of water is unlikely to explain the phenomenon observed. This phenomenon is also not related to the interaction of the phthalocyanine core with water. Indeed, the "tiny" amount of water added at the beginning to ensure the neutrality of the phthalocyanine ring is, in fact, very large compared to the amount of dendrimer (from 21 000 to 41 000 molecules of water for one molecule of **4-G′$_0$** to **4-G′$_4$**), and it does not quench fluorescence. Furthermore, no decrease of fluorescence is observed when slightly acidic water is added, even in larger amounts than for the experiments done with basic water. It can be also noted that when neutral water is added to the THF solution, the decrease of fluorescence intensity observed is closely related to the formation of the deprotonated species. Thus, the dramatic modification of the fluorescence is most likely due to the chemical modification of the phthalocyanine induced by deprotonation. In fact, the core of these dendrimers is a highly sensitive sensor to detect optically H_3O^+ and OH^- without any interference of quenching phenomena due to aggregation, contrary to classical phthalocyanines.

The high fluorescence efficiency of the neutral species in THF allowed an easy determination of the fluorescence lifetimes τ, measured by a stroboscopic technique (Table 2). In each case, the decay was found to be monoexponential, with a χ^2 value lower than 1.25 that indicates the quality of the fit. Lifetime values of a few nanoseconds were measured in relatively good accordance with the values already reported for nondendritic phthalocyanines.[22] This corroborates the quasi-absence of influence of the phosphorus dendrimer skeleton on τ, previously shown for pyrene derivatives grafted to the internal layers.[24] On the other hand, the fluorescence lifetime of the dianionic species is too short to be measured by this technique. For the neutral form, kinetic data concerning the chromophoric core were obtained from Φ/τ for the radiative deexcitation constant k_r (Table 2). An increase of k_r with the generation number was observed. One possibility is that this effect corresponds to an improvement of the emissive properties of the phthalocyanine, resulting from increasing isolation. However, the difference in k_r values is mainly due to the low quantum yield obtained for **4-G′$_0$** with respect to that of the other analogues, and the lifetimes are close for the three dendrimers considered, if taking

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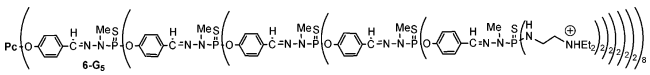
into account the experimental error. This situation is totally in line with the fact that the solution of the **4-G′$_0$** dendrimer contains some aggregates that contribute to absorption but not to emission, thus decreasing the fluorescence quantum yield without affecting the fluorescence lifetime. In this case, the difference found in the k_r values would indirectly reflect the prevention of aggregation due to the dendritic shell in the highest generations. As for the nonradiative deexcitation constant k_{nr} obtained for the neutral species from $(1 - \Phi)/\tau$, it is found to be poorly sensitive to the generation number.

It results from these fluorescence studies that water does not seem to play a central role in the phenomenon observed. This finding could appear to contradict the results we reported previously from the diffusion NMR experiments for a "micelle-like" water-soluble ammonium-terminated dendrimer whose branches were dramatically folded up upon the influence of water.[10] The occurrence of a shrinkage here should modify the fluorescence properties by an increased interaction of the branches with the core, which is not observed. Thus, diffusion NMR measurements are carried out with **4-G′$_4$** to check if a contraction of the size upon the influence of water is observed for these aldehyde-terminated dendrimers.

NMR Diffusion. High-field NMR experiments using pulse-field gradient spin−echo sequences have already been used to probe size and geometrical parameters of various dendrimers upon the influence of pH,[25] temperature,[26] concentration,[27] or type of branching.[28] As indicated above, we have already shown the usefulness of this technique to detect the dramatic increase of the size of the water-soluble phosphorus dendrimers **6-G$_5$**, upon the addition of THF to water.[10] Dendrimer **4-G′$_4$**, which is soluble in THF, affords the opportunity to carry out the "reverse" experiment, that is studying the eventual variation of the hydrodynamic radius upon addition of water to THF.



Self-diffusion NMR experiments (DOSY-type) give access to diffusion coefficients D, which are related to the hydrodynamic radius R_H (for spherical particles) by the Stokes−Einstein equation $R_H = k_BT/6\pi\eta_0D$, where k_B is the Boltzmann constant, T the temperature in Kelvin, and η_0 the dynamic viscosity of the solvent. Because we have shown that the presence of the dendrimer may modify the viscosity of the solution,[10] the value of η_0 is unknown. To circumvent this problem, a reference whose hydrodynamic radius is invariant must be added to the solution. In previous experiments, we used NMe_4Cl as an internal diffusion reference in water, but this compound is not soluble in pure THF. On the other hand, $SiMe_4$ (TMS) is soluble in organic solvents and has already been used as a reference compound in DOSY studies to determine relative variations of hydrodynamic radius, using the equation $R_H/R_{H(TMS)} = D_{(TMS)}/D$.[29] Being interested in the absolute value of hydrodynamic radius, it was necessary to have access to the value of $R_{H(TMS)}$.

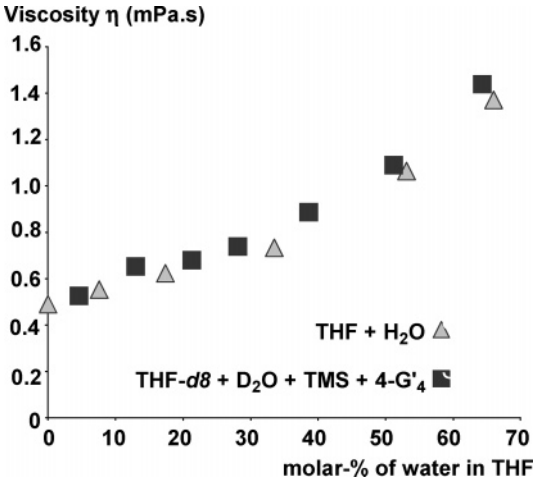


Figure 9. Viscosity of THF/water mixtures. Data deduced from NMR diffusion experiments on the TMS signal in the presence of **4-G′$_4$** (■). Data from the literature[31] (▲).

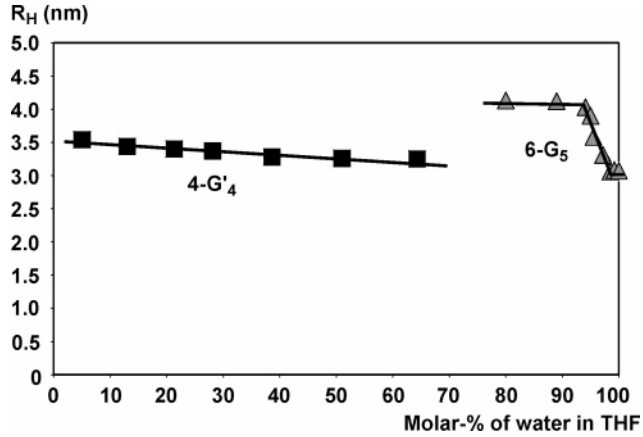


Figure 10. Variation of the hydrodynamic radius of dendrimers **4-G′$_4$** (■) and **6-G$_5$** (▲),[10] depending on the molar percentage of water in THF.

For this purpose, we have carried out a preliminary experiment with TMS and NMe_4Cl, both dissolved in a mixture of THF-d_8 and D_2O (v/v). Applying the value of 2.9 Å for $R_{H(NMe4)}$[30] afforded a value of 1.9 Å for $R_{H(TMS)}$.

Self-diffusion NMR experiments are carried out with micromolar amounts of **4-G′$_4$** ($[C] = 9.2 \times 10^{-5}$ M) dissolved first in THF-d_8 in the presence of TMS. Small quantities of D_2O are progressively added, and the diffusion data are recovered in each case. Hydrodynamic radii are deduced by applying the equation shown above; the viscosity is also deduced by applying the Stokes−Einstein equation and using the data measured on TMS. We have previously shown that the unimolecular micelle-type/amphiphilic dendrimer **6-G$_5$** induces dramatic changes in the viscosity of water/THF mixtures due to the presence of positive charges on the end groups.[10] This phenomenon is not expected to occur with the neutral dendrimer **4-G′$_4$** and is not observed. Indeed, Figure 9 shows that there is a good correlation between the values of viscosity obtained from the NMR data and the values from the literature.[31]

The variation of the hydrodynamic radius of **4-G′$_4$** versus the molar percentage of D_2O in THF-d_8 is shown in Figure 10. The first experiment is done after the addition of a small quantity

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of water in the NMR tube to have the same initial water/dendrimer ratio as that in the fluorescence experiments; the ratio here is 44 000 D_2O/1 **4-G$_4'$** versus 41 000 H_2O/1 **4-G$_4'$** for the fluorescence experiments. The measured hydrodynamic radius is 35.4 Å at this step. Repetitive additions of water (D_2O) slightly modify the value of R_H, which is 32.5 Å at 64 mol % of D_2O in THF (Figure 10). This is the last point obtainable due to the precipitation of **4-G$_4'$** when a higher percentage of water is used. This slight shrinkage confirms the relatively hydrophobic character of these phosphorus dendrimers and the quasi-absence of influence of water on the structure and topology of these aldehyde-terminated dendrimers deduced from fluorescence experiments. Indeed, the largest amount of water used in the latter case was 16 mol % of water in THF, corresponding to a zone in which R_H is quasi-constant.

These data show that a small and even relatively large amount of water in THF has only a slight influence on the hydrodynamic radius of lipophilic **4-G$_4'$**, whereas a small amount of THF in water had a tremendous influence on amphiphilic **6-G$_5$**. Indeed, a simple chemical modification of the surface groups induces totally different physicochemical behavior.

Conclusion

We have elaborated a series of phosphorus dendrimers especially designed to get a better understanding of the influence of the diverse components (core, branches, surface) on the whole structure of dendrimers. The phthalocyanine used as the core allowed for the exploration of the internal structure by optical methods, which provided a lot of information. The UV−visible spectra show the physical isolation of the core preventing aggregation, even for the first generation. A hyperchromic effect with increasing generations indicates that the core is more isolated for higher generations, whereas a bathochromic effect indicates the high polarity of the skeleton. Furthermore, the basicity of this skeleton is shown by the absence of the splitting of the Q-band in THF for the high generations, and NMR diffusion experiments have shown the rather lipophilic character of the branches.

It results from these data that the branches of these phosphorus dendrimers exert their influence upon the core in terms of polarity, basicity, and lipophilicity in addition to a physical isolation. However, this does not mean a chemical isolation of the core; indeed, the dendritic shell is permeable enough to allow acids and bases to attain the core, reversibly, even for the fourth generation, as shown in particular by the dramatic changes in the fluorescence properties. Thus, the phthalocyanine core of G_3 and G_4 can be considered as a sensitive optical sensor for H_3O^+ and OH^-, without any interference or quenching.

In fact, these complex macromolecules can be viewed as an outline of intelligent systems, in interaction with their external environment and able to translate reversibly chemical or physical information into optical or structural information.

Acknowledgment. Thanks are due to the Centre National de la Recherche Scientifique (CNRS) for financial support.

Supporting Information Available: Experimental section, methods of synthesis, analytical and spectroscopic characterization data, experimental procedures for fluorescence, NMR diffusion, X-ray diffraction, crystallographic information tables, and NMR spectra (^{31}P for all compounds, selected ^{1}H and ^{13}C). This material is available free of charge via the Internet at http://pubs.acs.org.

JA054797B