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Surface, core, and structure modifications of phosphorus-containing dendrimers. Influence on the thermal stability

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Abstract—Three new series of phosphorus-containing dendrimers are described. Their solubility depends on the type of end groups they bear. Perfluoroalkyl chains give dendrimers soluble in chlorofluorocarbons, whereas guanidinium and pyridinium derivatives give water-soluble compounds. The thermal stability of these compounds, as well as of 19 other dendrimers of various generations, having various cores, or various end groups, or branching points is studied. The main feature of this study is that the internal structure of these dendrimers is thermally stable at least up to 376°C. The number of the generation has practically no influence, whereas the principal criterion influencing the thermal stability is the type of end groups. The water-soluble cationic dendrimers are the least stable, but even those are stable up to 225°C. For most of these dendrimers, an important percentage of mass (around 50%) is retained even at a temperature as high as 1000°C. In the best case, up to 70% of the initial mass is retained at 1000°C.

1. Introduction

Dendrimers[1] have attracted a tremendous interest for more than 15 years. The initial studies concerned the synthetic aspects, but efforts are now mainly directed toward applications.[2] In this perspective, the thermal stability appears as a crucial point for most applications of dendrimers, and particularly in the field of materials science. Even though a few papers previously described the thermal behaviour of PAMAM dendrimers,[3] carbosilane dendrimers,[4] or polyphenylene dendrimers,[5] no study has been dedicated to the influence of the number of generations, the nature of the end groups, the core, and the branching points on the thermal stability of dendrimers. Thus, we decided to carry out this study using one of the most easily tunable family of dendrimers, that is the phosphorus-containing dendrimers that we have developed since 1994.[6] Indeed, besides surface modifications,[7] which are commonly used for almost all types of dendrimers, we have also demonstrated the possibility of modifying the type of core,[8] the type of branching points,[9] and the type of skeleton,[10] even after the synthesis of the dendrimer[11] (Fig. 1). This unique behavior is due to the presence of phosphorus as a component of the backbone of these dendrimers.[12] This element brings ease of synthesis, helps with characterization,[6] and gives properties seldom or never found for other dendrimers, such as high dipole moment values,[13] or formation of hydrogels[14] and vesicles[15] in water. Since it is well-known that phosphorus–nitrogen linkages impart an interesting thermal stability to polymers such as polyphosphazenes,[16] an increased stability of our dendrimers (which possess P–N–N linkages), compared to

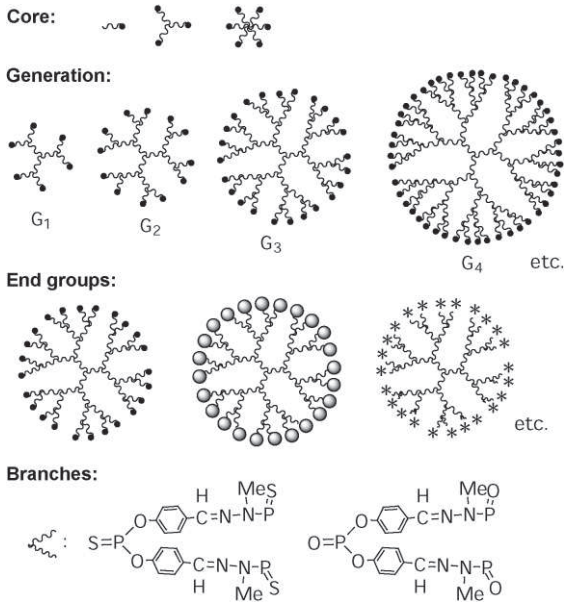
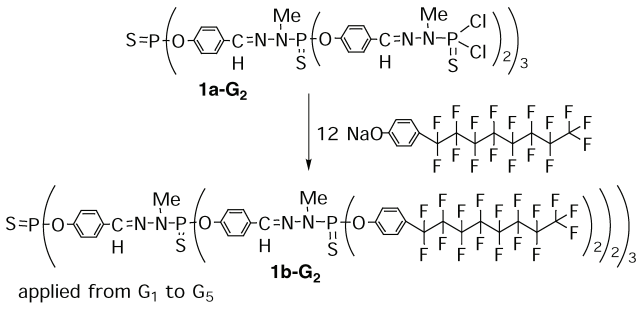


Figure 1. Schematized types of cores, generations, end groups and chemical structure of branches of dendrimers used in this study. For some examples concerning the type of end groups, see Figure 2.

Keywords: dendrimers; perfluoroalkyl chains; chlorofluorocarbons.
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Scheme 1.

other types of dendrimers could be expected. On the other hand, we have shown that the N–N=C linkages also included in the branches of our dendrimers have a somewhat destabilizing effect, since they are sensitive to UV laser irradiation.[17] To know which influence is the most important for the thermal stability, we decided to carry out a large study. First, we have synthesized dendrimers bearing new types of end groups, then we have studied their thermal behavior, together with that of a variety of previously reported dendrimers.

2. Results and discussion

Most of the dendrimers we have described previously are soluble in organic solvents such as THF, dioxane, dichloromethane, or chloroform. However, we have already demonstrated that the grafting of long alkyl chains induces solubility in alkanes,[7i] whereas the grafting of diethylammonium,[18] trimethylammonium[14] or carboxylic acid[10d,15,19] end groups induces solubility in water. In order to vary the type of solvents usable for our dendrimers, we tried to obtain compounds soluble in chlorofluorocarbons (CFC). On the other hand, in view of the increasing importance of water-soluble dendrimers for biological uses, particularly those having positively charged end groups, there is a need for new compounds of this type. The following paragraph will show the synthesis of three new families of dendrimers related to these topics. Then, they are included in the general study concerning the thermal stability.

2.1. Syntheses and solubility

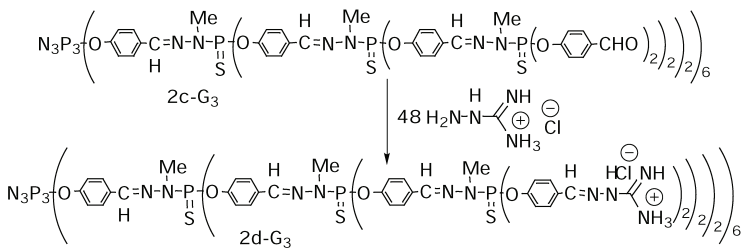
The way that appeared the easiest to obtain dendrimers soluble in CFC consists in the grafting of phenols bearing a long perfluoroalkyl chain. The phenol we chose was 4-perfluorooctane phenol, obtained by the coupling reaction of iodoperfluorooctane and 4-iodophenol with copper.[20] Its sodium salt easily reacts overnight at room temperature with the $P(S)Cl_2$ end groups of dendrimers **1b-G$_x$** in THF for small generation (**x**=1–2) or in THF/CFC113 (ClF_2-$CCFCl_2$) for larger generations (**x**=3–5). The reaction is shown on Scheme 1 for the second generation of the dendrimer, but it was also carried out with all generations from **x**=1 to **x**=5 (6–96 perfluorooctane end groups). Beside singlets corresponding to the internal layers, ^{31}P NMR spectra of **1b-G$_x$** indicate in all cases the presence of one singlet for the phosphorus atoms of the external layer, slightly shielded compared to **1b-G$_x$**. The solubility of these compounds depends on the generation: the first generation is soluble in $CHCl_3$, but generations 2–5 are not. However, they are soluble in CFC as expected, and also in mixtures CFC/$CHCl_3$ (1/1).

We chose another way of grafting functional groups on the surface of dendrimers to obtain water-soluble compounds. In this case, the starting material was the dendrimer **2c-G$_3$** having 48 aldehyde end groups and a cyclotriphosphazene core. A condensation reaction was carried out with aminoguanidine hydrochloride at 60°C in THF/MeOH, leading to the grafting of the guanidinium end groups (Scheme 2). The completion of the reaction was shown both by ^1H NMR and IR, with the total disappearance of signals corresponding to the aldehyde end groups. Dendrimer **2d-G$_3$** is soluble in water as expected, but a few drops of an organic solvent were needed to obtain clear NMR spectra. In the absence of organic solvent, the signals corresponding to the internal hydrophobic layers are not detected.

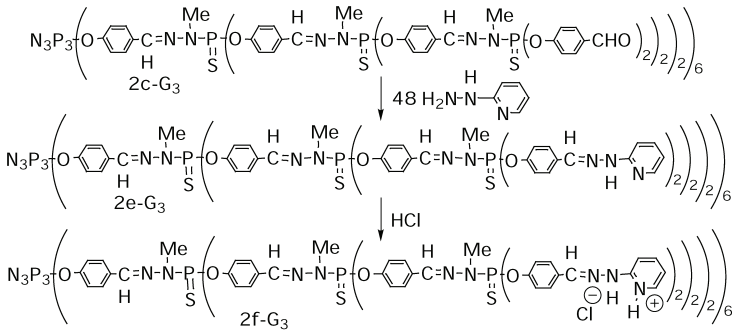
The same type of condensation reaction was carried out in THF at 40°C between 2-hydrazinopyridine and the second or third generation of dendrimers **2c-G$_x$** (**x**=2, 3) (Scheme 3). The reaction occurred easily and was monitored as previously by ^1H NMR and IR, with the total disappearance of the signals corresponding to the aldehydes. The neutral dendrimers **2e-G$_x$** are soluble in organic solvents, but not in water. However, a dramatic change in the solubility is observed when HCl (in water) is added. The protonation of the pyridine easily affords the dendrimer **2f-G$_3$**, which is soluble in water and also in DMSO. Beside modifications of the solubility, the protonation also induces a deshielding of most of the signals corresponding to the pyridine part in the ^1H and ^{13}C NMR spectra.

2.2. Thermal stability

In order to determine all the criteria influencing the thermal stability of phosphorus-containing dendrimers, we studied the behaviour of 24 dendrimers, including representative examples of the three families described above (Table 1).



Scheme 2.



Scheme 3.

This exhaustive study was carried out with the aim of determining the importance of the generation (comparison from **1c-G$_0$** to **1c-G$_5$**), of the internal structure (comparison **1c-G$_3$/3c-G$_3$**), of the core (comparison between **1c-G$_x$**, **2c-G$_x$**, and **4c-G$_x$**), and of the end groups (from **a** to **n**) (Fig. 2). Compounds possessing aldehyde end groups (series **c**) serve as a reference in all cases. Indeed, these end groups are the most easily available, since they are obtained at each generation during the synthesis of all our phosphorus-containing dendrimers. Furthermore, we have already used these aldehyde-dendrimers for studying some physical properties using thermostimulated currents and broadband dielectric spectroscopy,[21a,b] and enthalpy relaxation.[21c]

Since some samples may contain 1–2% of solvent (detected by ^{1}H NMR), we considered the temperature to which a loss of 5% in weight is observed as an indication of the beginning of the degradation (noted $T_{95\%}$ in Table 1). Figure 3 displays the influence of the generation on the thermal stability from **1c-G$_0$** to **1c-G$_5$** under an inert gas. It appears from these graphs that the least stable compound is **1c-G$_0$**, but all dendrimers from **1c-G$_1$** to **1c-G$_5$** have roughly the same thermal behaviour. They are stable (less than 5% loss) up to 300–330°C. These phosphorus-containing dendrimers having aldehyde end groups are much more stable than PAMAM dendrimers (5% loss around 110°C)[3] and carbosilane dendrimers (5% loss between 100 and 200°C, depending on the structure),[4] but less stable than polyphenylene dendrimers (5% loss around 500°C).[5] The shape of the decomposition curve indicates a first loss (of approximately 15%) around 350°C, followed by a plateau up to ~450°C. Then a second loss of 15–20% was observed, followed by a plateau up to 850–900°C, irrespective of the generation. The percentage of mass retained at 1000°C is close to 50%, which is a very high value.

This fact incited us to check the thermal behaviour of these

Table 1. Thermal behaviour of dendrimers **1c-G$_{0\text{-}5}$**, **1b-G$_3$**, **1a-b-G$_5$**, **1g-k-G$_5$**, **1n-G$_5$**, **2c-f-G$_3$**, **3c-G$_3$**, **4c-G$_{2,3}$**, **4l,m-G$_3$**

Compound	Number of R	MW	–Ar[a]% [a]	C% [b]	$T_{95\%}$ [c]	$M_{500°C}$% [d]	$M_{700°C}$% [c]	$M_{900°C}$% [d]	$M_{1000°C}$% [d]
1c-G$_0$	3	426	50.7[e]	59.2	305	70.9	62.7	56.5	49.8
1c-G$_1$	6	1423	55.6	55.7	329	80.8	66.7	57.0	43.0
1c-G$_2$	12	3417	63.1	54.8	315	78.8	65.2	56.9	47.5
1c-G$_3$	24	7405	65.9	54.5	319	79.8	69.1	60.0	47.0
1c-G$_4$	48	15381	67.2	54.4	326	79.6	68.8	60.7	48.0
1c-G$_5$	96	31331	67.7	54.3	329	78.5	68.7	56.0	51.9
1c-G$_5$ under O_2	96	31331	67.7	54.3	272	73.8	20.0	16.2	16.2
1a-G$_5$	96	23108	85.3[f]	38.7	234	71.1	67.0	54.1	47.6
1b-G$_3$	24	16766	29.1	36.1	228	17.8	9.7	7.0	7.0
1b-G$_5$	96	68776	30.8	36.5	327	18.7	16.4	13.6	11.4
1g-G$_5$	96	28643	74.2	55.4	350	52.2	45.3	34.4	20.7
1h-G$_5$	96	47655	44.5	59.9	376	73.8	69.2	64.8	54.7
1i-G$_5$	96	43832	48.5	52.0	228	52.8	45.8	38.9	35.1
1j-G$_5$	96	47657	44.6	52.6	225	51.2	44.7	35.6	32.8
1k-G$_5$	96	35368	60.0	54.6	270	67.4	60.2	50.2	48.7
1n-G$_5$	96	39415	53.9	63.6	343	45.7	34.1	22.1	20.0
2c-G$_3$	48	14819	66.0	54.5	349	80.7	69.9	63.5	52.0
2d-G$_3$	48	19260	50.8	44.9	275	62.1	28.8	6.6	2.3
2e-G$_3$	48	19192	50.9	57.1	294	64.2	58.4	52.3	33.5
2f-G$_3$	48	20943	46.7	52.3	211	63.0	50.0	32.7	23.5
3c-G$_3$	24	7052	64.2	57.2	384	81.7	67.2	56.3	44.7
4c-G$_2$	8	2525	66.7	56.1	348	86.8	80.6	76.5	70.0
4c-G$_3$	16	5184	67.5	55.1	323	76.6	64.0	48.0	29.6
4l-G$_3$	16	5425	64.6	56.2	268	63.7	59.8	50.4	42.4
4m-G$_3$	16	5136	68.2	55.7	274	56.7	52.0	39.8	33.9

[a] Theoretical percentage of mass remaining after loss of all end groups by cleavage of the O–Aryl bonds.
[b] Percentage of carbon in the starting compound.
[c] Temperature to which the material retains 95% of its mass.
[d] % of mass retained at 500°C, 700°C, 900°C, or 1000°C.
[e] Loss of two aryl groups.
[f] Loss of Cl.

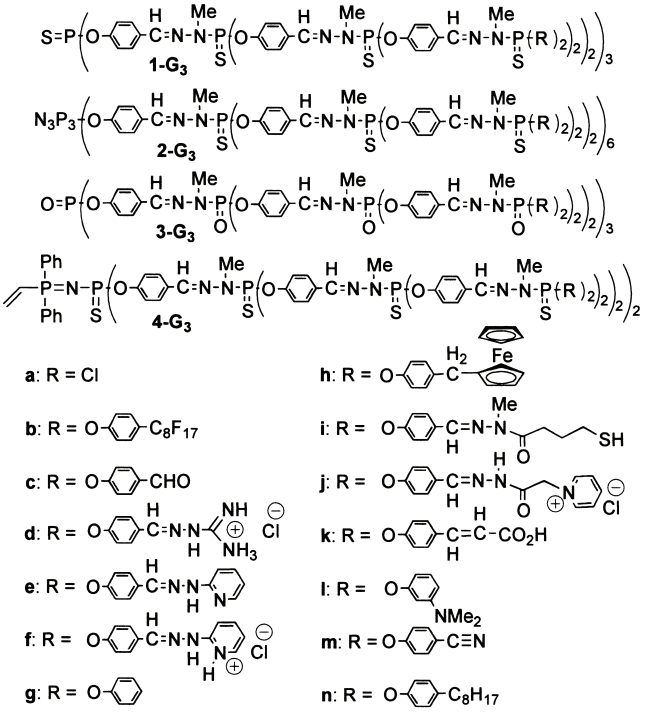


Figure 2. Types of core, structure, and end groups.

dendrimers under oxygen. Figure 4 displays the comparison between **1c-G$_5$** under N_2 and under O_2. Obviously, **1c-G$_5$** is less stable under O_2: the degradation begins 60°C earlier, and the percentage of mass retained at 1000°C is only 16.2%, compared with 51.9 under N_2. However, the percentage of mass retained at 500°C is close in both cases: 78.5% under N_2, and 73.8% under O_2.

In order to know if the first degradation observed at 300–330°C under N_2 was due to the structure of the dendrimer or the nature of the end groups, we decided to study the thermal behavior of dendrimers having various types of functionalized end groups. These experiments were all performed with the fifth generation dendrimer under an inert gas, in order to change only one parameter at a time. Nine compounds were used, i.e. **1a-c-G$_5$**, **1g-k-G$_5$** and **1n-G$_5$** (Fig. 5). Compound **1g-G$_5$**, which differs only from **1c-G$_5$** by the absence of aldehyde end groups, was synthesized especially to check their influence on stability. It appears from the TGA curves that compound **1g-G$_5$** is more stable ($T_{95\%}$=350°C) than **1c-G$_5$** ($T_{95\%}$=329°C), and presents a

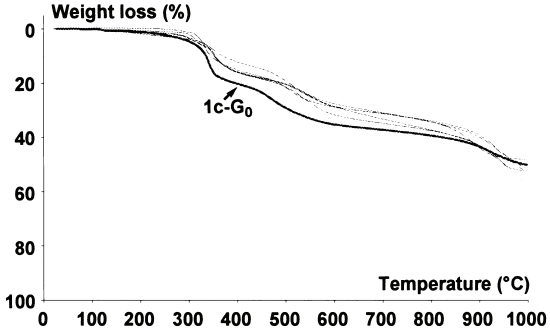


Figure 3. TGA curves for dendrimers **1c-G$_0$** and **1c-G$_{1\text{-}5}$** (thin lines).

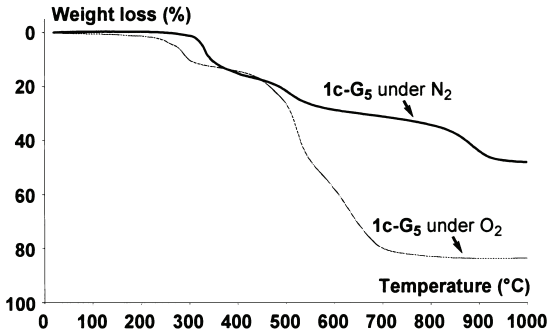


Figure 4. TGA curves of **1c-G$_5$** under N_2 and under O_2.

single loss instead of two (compare Figs. 4 and 5). Thus, the first loss observed for **1c-G$_5$** may be ascribed to the aldehyde groups, which might generate carbon monoxide. We have also tested six other compounds, all of generation five, with very different end group. Figure 5 shows that the thermal stability is highly dependent on the type of end groups. Indeed, the least stable compound (**1j-G$_5$**) decomposes at 225°C, whereas the most stable compound (**1h-G$_5$**) decomposes at 376°C. This last result indicates that it is not the internal structure of the dendrimers that is involved in the degradation observed at lower temperature, but the end groups.

In most cases, there is a rather good correlation between the percentage of mass retained at the level of the plateau observed between ca. 500 and 900°C and the theoretical value that should remain after the loss of all the Aryl end group, by cleavage of the O–Aryl bonds (compare values from the columns '–Ar%' and $M_{700°C}$% in Table 1). However, there are a few noticeable exceptions. Dendrimer **1a-G$_5$** differs from all the other **1-G$_5$**, since it possesses chlorine atoms as end groups instead of O–Ar end groups. If the value of the plateau corresponded to the cleavage of the P–Cl bonds, it should be 85.3%; if it corresponded to the cleavage of the internal O–Ar (O–C_6H_4CHNNMeP(S)Cl_2), it should be 44.7%. Both values are far from the value measured in the middle of the plateau at 700°C ($M_{700°C}$%=67%); however, the cleavage of the N–NMeP(S)Cl_2 bonds or of the CH=NNMeP(S)Cl_2 bonds gives values (66.1 and 63.2%, respectively) close to the value measured. Analogous remarks can be made for the behavior of **1g-G$_5$** (at 500°C). Thus, besides the external O–Ar bonds, the hydrazone linkage appears as a second fragile point in these dendrimers, as already shown by mass

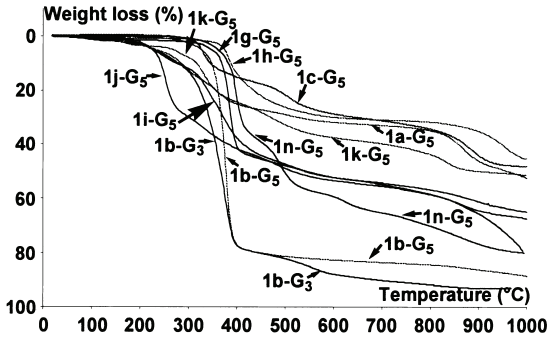


Figure 5. TGA curves of dendrimers **1a-c-G$_5$**, **1g-k-G$_5$**, and **1b-G$_3$**.

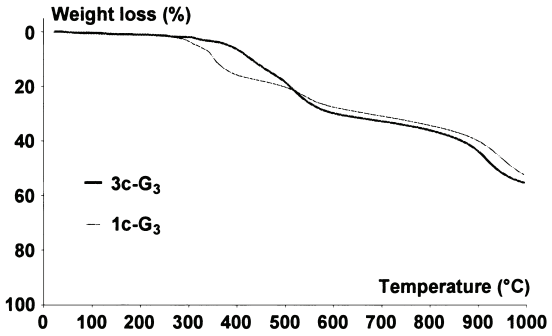


Figure 6. TGA curves for dendrimers **1c-G$_3$** and **3c-G$_3$**.

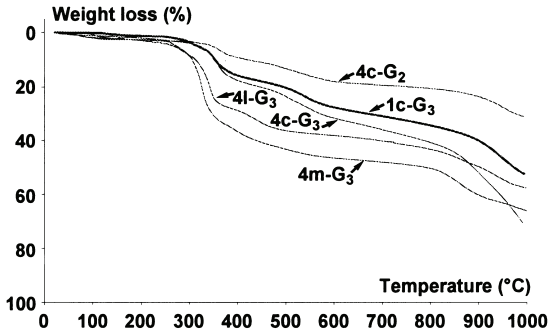


Figure 8. TGA curves for dendrons **4c-G$_{2,3}$** and **4l,m-G$_3$** compared to **1c-G$_3$**.

spectrometry.[17] On the other hand, it must be emphasized that the percentage of mass retained at 1000°C (47.6%) is much higher than the total percentage of carbon in **1a-G$_5$** (38.7%). Thus, an important part of the heteroelements remains at 1000°C.

Another 'abnormal' result concerns dendrimer **1b-G$_5$**, which decomposes abruptly and nearly totally. The percentage of mass remaining at the level of the plateau ($M_{700°C}$%=16.4) is much lower than the value expected for the cleavage of the O–$C_6H_4C_8F_{17}$ end groups (30.8%). To be sure that this behavior was due to the structure of the compound and not to a technical incident, we also performed the experiment with the third generation **1b-G$_3$**. This compound was even less stable than **1b-G$_5$**. However, both generations present an analogous behavior, which is totally unexpected in view of the chemical structure, except if one remembers that perfluorinated compounds have the ability to trap and carry oxygen. We postulate that the long perfluoroalkyl chains linked to the surface of **1b-G$_x$** may trap oxygen, which induces the 'burning' of the dendrimer during the TGA experiments. In order to consolidate this assumption, an analogue of **1b-G$_5$** in which all the fluorine atoms are replaced by hydrogen atoms was synthesized (compound **1n-G$_5$**). Both compounds have a different thermal behavior since **1n-G$_5$** has a much higher percentage of mass remaining at 700°C, as expected ($M_{700°C}$%=34.1). This assumption is also supported by the relatively close value obtained at 700°C for the TGA analysis of **1c-G$_5$** under O_2 (20% for **1c-G$_5$** under O_2; 9.7% for **1b-G$_3$**; 16.4% for **1b-G$_5$**). The difference in stability observed between both generations tested could be due to a longer exposure to air of **1b-G$_3$** compared to **1b-G$_5$**. The last data worthy of mention concern dendrimer **1h-G$_5$**, which is the most stable ($T_{95\%}$=376°C). It has also the highest percentage of mass retained at 700°C (69.2%) as well as at 1000°C (54.7%). These values are much higher than the theoretical values corresponding to the cleavage of the O–Ar surface bonds (44.5%).

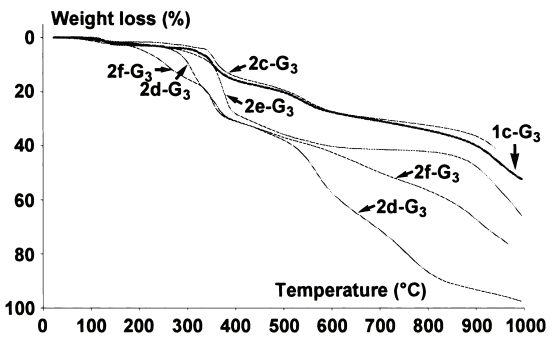


Figure 7. TGA curves for dendrimers **2c,e-g-G$_3$** compared to **1c-G$_3$**.

After studying the influence of the surface groups on stability, we wanted to check the influence of structural modifications, first by modifying the nature of the branching points. Indeed, our dendrimers have generally thiophosphoryl groups (P=S) as branching units, but they can also have phosphoryl groups (P=O). However, the latter generally induce a lower stability of the dendrimers upon long storage (several months), thus we generally use thiophosphoryl groups. Surprisingly, the comparison between the TGA analysis of **3c-G$_3$** (P=O groups) and **1c-G$_3$** (P=S groups) shows that **3c-G$_3$** is thermally more stable (Fig. 6). Indeed, the thermal degradation of **3c-G$_3$** begins at 384°C instead of 319°C for **1c-G$_3$** (Table 1).

Another way to induce structural modifications consists in using other types of cores. First, we chose to use the cyclotriphosphazene core (N_3P_3) instead of the P=S core, because it is well known that the thermal ring opening of cyclotriphosphazenes is one of the best methods to synthesise polyphosphazenes.[16] This expected behaviour could induce a higher percentage of mass to be retained at high temperatures. However, comparison between **2c-G$_3$** and **1c-G$_3$**, which differ only by the core and thus by the number of end groups, showed very similar behaviors (Fig. 7). We have also studied, for dendrimers built from the cyclotriphosphazene core, a few examples to check the influence of the end groups on stability. The pyridinium derivative **2f-G$_3$** was the least stable compound in this series ($T_{95\%}$=211°C). This fact can be correlated with the low stability of the other pyridinium derivative **1j-G$_5$** series. It is interesting to note that dendrimer **2e-G$_3$**, which differs only from **2f-G$_3$** by the absence of proton on pyridine, is much more stable ($T_{95\%}$=294°C). Thus, it seems that the water-soluble cationic dendrimers are thermally less stable than the dendrimers soluble in organic solvents, presumably because of the ionization state of the end groups.

The absence of influence of the cyclotriphosphazene core on the thermal stability incited us to use another core, which could polymerize more easily. The CH_2=CH–PPh_2=N–P=S group located at the core of dendrons **4-G$_x$** appeared suitable for this purpose. The thermal behavior of **4c-G$_3$** is almost identical to that of **1c-G$_3$** (at least up to 500°C) (Fig.

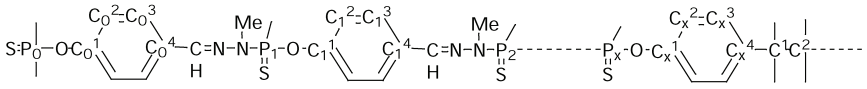


Figure 9. Numbering used for NMR.

8). On the other hand, a dramatic difference is observed for **4c-G$_2$**. This second generation has an increased $T_{95\%}$ value (323°C for **4c-G$_3$**, 348°C for **4c-G$_2$**), but the most spectacular difference concerns the percentage of mass retained at high temperature (76.5% at 900°C and 70.0% at 1000°C). These are the highest values observed for all the compounds we have tested, and also for all dendrimers whose TGA behavior was previously reported. To explain this particular behavior, we think that the polymerization of the vinyl group located at the core occurs as expected for **4c-G$_2$**, but not for **4c-G$_3$**, because of increased steric hindrance. The presence of dimethylamino groups (**4l-G$_3$**) or nitrile groups (**4m-G$_3$**) on the surface of the dendron induces a lower stability compared to the aldehyde groups.

3. Conclusion

The reported TGA analysis of 24 phosphorus-containing dendrimers and dendrons allows conclusions to be drawn about the thermal stability of these compounds. The most important point is that the internal structure of these dendrimers is stable up to at least 376°C for the thiophosphoryl dendrimers (P═S as branching points), and even up to 384°C for the phosphoryl dendrimers (P═O as branching points). These are high values. Furthermore, there is practically no influence of the generation on the thermal stability. In fact, the most important point concerning stability is the nature of the end groups. Indeed, for the thiophosphoryl dendrimers, the thermal stability ranges from 225 to 376°C, depending on the end groups. It appears that the least stable compounds are the cationic dendrimers soluble in water, particularly the pyridinium derivatives. However, the most important use of water-soluble dendrimers concerns biology, and stability under 225°C is sufficient for such purposes. On the other hand, the stability of most phosphorus-containing dendrimers soluble in organic solvents is over 300°C. We have also shown that the nature of the core has practically no influence on the thermal behavior, however, with one noticeable exception. A second generation dendron having a vinyl group at the core, able to polymerize, retains 70% of its mass at 1000°C. This very unusual behavior offers interesting perspectives for novel surface coating materials. Thus, it appears from all these data that phosphorus-containing dendrimers offer an excellent compromise between thermal stability and ease of functionalization.

4. Experimental

4.1. General

All manipulations were carried out with standard high-vacuum and dry-argon techniques. ^{1}H, ^{13}C, ^{31}P NMR and ^{19}F spectra were recorded with Bruker AC 200, AC 250, DPX 300, or AMX 400 spectrometers. References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P NMR, $SiMe_4$ for ^{1}H and ^{13}C NMR and CF_3CO_2H for ^{19}F. The attribution of ^{13}C NMR signals has been done using *J*mod, two-dimensional HBMC and HMQC, broad band, or CW ^{31}P decoupling experiments when necessary. The numbering used for NMR is depicted in Figure 9. TGA measurements were recorded on a TGA7 Perkin–Elmer or Setaram 92.16.18 apparatus operating between 20 and 1500°C. Curves were recorded between 20 and 1000°C (20°C min^{-1}) using an Al_2O_3 sample boat, and helium or nitrogen as a vector (1 l h^{-1}). All dendrimers were synthesized in our laboratory, according to the procedures we previously reported (**1a-G$_x$** and **1c-G$_x$**;[6,7a] **1h-G$_5$**;[10c] **1i-G$_5$**;[7o] **1j-G$_5$**;[14] **1k-G$_5$**;[19] **2c-G$_x$**,[8a] **3c-G$_3$**;[9b] **4c-G$_{2,3}$** and **4l,m-G$_3$**[8c]).

4.2. General procedure for the synthesis of dendrimers 1b-G$_x$ (x=1, 2, 3, 4, 5)

To a solution containing 200 mg of dendrimer **1b-G$_x$** (**x**=1, 0.220 mmol; **x**=2, 0.084 mmol; **x**=3, 0.037 mmol; **x**=4, 0.018 mmol; **x**=5, 0.009 mmol) in a mixture of CFC113 (ClF_2CCFCl_2) (10 mL) and THF (10 mL) was added dropwise a solution of THF (10 mL) containing the sodium salt of 4-perfluorooctylphenol (**x**=1, 775 mg, 1.452 mmol; **x**=2, 593 mg, 1.110 mmol; **x**=3, 522 mg, 0.977 mmol; **x**=4, 508 mg, 0.950 mmol; **x**=5, 508 mg, 0.950 mmol). The reaction mixture was stirred overnight at room temperature and then centrifuged to remove sodium chloride. After solvent removal under reduced pressure the crude material was washed with a mixture of ether and pentane (1/1, 3×10 mL) to afford the expected perfluorinated dendrimers **1b-G$_x$** as white powders.

4.2.1. First generation 1b-G$_1$. 90% Yield; ^{31}P{^{1}H} NMR ($CDCl_3$) δ 52.1 (s, P_0), 60.7 (s, P_1); ^{1}H NMR ($CDCl_3$) δ 3.42 (d, $^3J_{HP}$=10.8 Hz, 9H, N–CH_3), 7.1–7.8 (m, 36H, Ar, CH═N); ^{19}F NMR ($CDCl_3$) δ −50.5 (br s, 12F, C^7F_2), −47.0 (br s, 12F, C^6F_2), −46.1 (br s, 18F, $C^{2,3,4}F_2$), −45.6 (br s, 12F, C^5F_2), −34.6 (t, $^3J_{FF}$=14 Hz, 12F, C^1F_2), −5.2 (t, $^3J_{FF}$=10 Hz, 18F, C^8F_3); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 32.8 (d, $^2J_{CP}$=13.5 Hz, N–CH_3), 103–121 (m, C^i–F), 121.6 (d, $^3J_{CP0,1}$=4.6 Hz, $C^2_{0,1}$), 126.1 (t, $^2J_{CF}$=24.7 Hz, C^4_1), 128.5 (s, C^3_0), 128.6 (t, $^3J_{CF}$=7.7 Hz, C^3_1), 132.4 (s, C^4_0), 139.1 (d, $^3J_{CP1}$=13.8 Hz, CH═N), 151.4 (d, $^2J_{CP0}$=7.8 Hz, C^1_0), 153.3 (d, $^2J_{CP1}$=6.3 Hz, C^1_1). Calcd for $C_{108}H_{48}F_{102}N_6O_9P_4S_4$ (3764): C, 34.47; H, 1.29; N, 2.23. Found: C, 34.51; H, 1.26; N, 2.29.

4.2.2. Second generation 1b-G$_2$. 95% Yield; ^{31}P{^{1}H} NMR ($CDCl_3$/CFC113, 1/1) δ 53.3 (s, P_0), 61.3 (s, P_2), 62.4 (s, P_1); ^{19}F NMR ($CDCl_3$/CFC113, 1/1) δ −50.6 (br s, 24F, C^7F_2), −47.1 (br s, 24F, C^6F_2), −46.2 (br s, 36F, $C^{2,3,4}F_2$), −45.6 (br s, 24F, C^5F_2), −34.8 (br s, 24F, C^1F_2), −5.4 (br s, 36F, C^8F_3); ^{1}H NMR ($CDCl_3$/CFC113, 1/1) δ 3.42 (bd, $^3J_{HP}$=10.0 Hz, 27H, N–CH_3), 7.1–7.8 (m, 93H, Ar, CH═N). Calcd for $C_{240}H_{120}F_{204}N_{18}O_{21}P_{10}S_{10}$ (8098): C, 35.60; H, 1.49; N, 3.11. Found: C, 35.78; H, 1.56; N, 3.22.

4.2.3. Third generation 1b-G_3. 93% Yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$/CFC113, 1/1) δ 53.3 (s, P_0), 61.4 (s, P_3), 62.2 (s, P_1), 62.2 (s, P_2); ^1H NMR ($CDCl_3$/CFC113, 1/1) δ 3.33 (bd, $^3J_{HP}$=10.0 Hz, 63H, N–CH_3), 7.1–7.7 (m, 201H, Ar, CH=N); ^{19}F NMR ($CDCl_3$/CFC113, 1/1) δ −50.3 (br s, 48F, C^7F_2), −46.9 (br s, 48F, C^6F_2), −46.0 (br s, 72F, $C^{2,3,4}F_2$), −45.5 (br s, 48F, C^5F_2), −34.5 (br s, 48F, C^1F_2), −4.9 (br s, 72F, C^8F_3). Calcd for $C_{504}H_{264}F_{408}N_{42}O_{45}P_{22}S_{22}$ (16766): C, 36.11; H, 1.59; H, 3.51. Found: C, 36.23; H, 1.49; N, 3.42.

4.2.4. Fourth generation 1b-G_4. 96% Yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$/CFC113, 1/1) δ 53.0 (s, P_0), 61.3 (s, P_4), 62.2 (s, P_1), 62.5 (s, P_3), 62.6 (s, P_2); ^1H NMR ($CDCl_3$/CFC113, 1/1) δ 3.30 (br s, 135H, N–CH_3), 7.2–7.8 (m, 417H, Ar, CH=N); ^{19}F NMR ($CDCl_3$/CFC113, 1/1) δ −50.7 (br s, 96F, C^7F_2), -47.2 (br s, 96F, C^6F_2), −46.2 (br s, 144F, $C^{2,3,4}F_2$), −45.7 (br s, 96F, C^5F_2), −34.8 (br s, 96F, C^1F_2), −5.5 (br s, 144F, C^8F_3). Calcd for $C_{1032}H_{552}F_{816}N_{90}O_{93}P_{46}S_{46}$ (34102): C, 36.35; H, 1.63; N, 3.70. Found: C, 36.42; H, 1.71; N, 3.80.

4.2.5. Fifth generation 1b-G_5. 95% Yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$/CFC113, 1/1) δ 52.9 (s, P_0), 61.4 (s, P_5), 62.4 (s, $P_{1,2,3,4}$); ^1H NMR ($CDCl_3$/CFC113, 1/1) δ 3.27 (br s, 279H, N-CH_3), 7.1–7.8 (m, 849H, Ar, CH=N); ^{19}F NMR ($CDCl_3$/CFC113, 1/1) δ −50.8 (br s, 192F, C^7F_2), −47.3 (br s, 192F, C^6F_2), −46.4 (br s, 288F, $C^{2,3,4}F_2$), −45.8 (br s, 192F, C^5F_2), −34.8 (br s, 192F, C^1F_2), −5.7 (br s, 288F, C^8F_3). Calcd for $C_{2088}H_{1128}F_{1632}N_{186}O_{189}P_{94}S_{94}$ (68776): C, 36.46; H, 1.65; N, 3.79. Found: C, 36.51; H, 1.72; N, 3.82.

4.3. Synthesis and characterization of dendrimer 1g-G_5

To 0.200 g (8.655 μmol) of **1a-G_5** in 5 mL of freshly distilled THF was added 0.106 g (0.091 mmol) of the sodium salt of phenol. The resulting mixture was stirred overnight at room temperature. Then, the sodium chloride formed was removed by centrifugation. The resulting solution was evaporated under vacuum and the residue was washed three times with ether to give **1g-G_5** as a white powder in 95% yield.

$^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 65.8 (s, $P_{1\text{-}2\text{-}3\text{-}4}$), 66.0 (s, P_5); ^1H NMR ($CDCl_3$) δ 3.3 (br s, 279H, CH_3), 7.1–7.9 (m, 945H, Ar and CH=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 33.1 (d, $^2J_{CP}$=12.9 Hz, CH_3–N–$P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$), 121.4 (d, $^3J_{CP}$=3.5 Hz, C^2_5), 121.8 (s, $C^2_{0\text{-}1\text{-}2\text{-}3\text{-}4}$), 125.4 (s, C^4_5), 128.3 (s, $C^3_{0\text{-}1\text{-}2\text{-}3\text{-}4}$), 129.5 (s, C^3_5), 132.3 (s, $C^4_{0\text{-}1\text{-}2\text{-}3\text{-}4}$), 138.5 (d, $^3J_{CP}$=13.6 Hz, C^4_4–*CH*=N), 139.1 (d, $^3J_{CP}$=12.8 Hz, $C^4_{0\text{-}1\text{-}2\text{-}3}$–*CH*=N), 150.6 (d, $^2J_{CP}$=7.1 Hz, C^1_5), 151.2 (d, $^2J_{CP}$=6.3 Hz, $C^1_{0\text{-}1\text{-}2\text{-}3\text{-}4}$). Calcd for $C_{1320}H_{1224}N_{186}O_{189}P_{94}S_{94}$ (28643): C, 55.35; H, 4.31; N, 9.10. Found: C, 55.49; H, 4.42; N, 8.97.

4.4. Synthesis and characterization of dendrimer 1n-G_5

To a solution containing 100 mg of dendrimer **1a-G_5** (0.0045 mmol) in THF was added dropwise a solution of THF (10 mL) containing the sodium salt of 4-octylphenol (110 mg, 0.482 mmol). The reaction mixture was stirred overnight at room temperature and then centrifuged to remove sodium chloride. After solvent removal under reduced pressure the crude material was washed with pure pentane to afford the expected dendrimer **1n-G_5** as a white powder. 90% Yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$) 52.8 (s, P_0), 62.4 (s, $P_{1,2,3,4}$), 63.0 (s, P_5); ^1H NMR ($CDCl_3$) 0.88 (br s, 288H, CH_3), 1.27 (br s, 960H, CH_2), 1.56 (br s, 192H, CH_2), 2.54 (br s, 192H, CH_2), 3.31 (br s, 279H, N–CH_3), 7.1–7.8 (m, 849H, Ar, CH=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$) 14.4 (s, CH_3), 23.0 (s, CH_2), 29.6 (s, CH_2), 29.7 (s, CH_2), 29.8 (s, CH_2), 31.8 (s, CH_2), 32.3 (s, CH_2), 33.4 (d, $^2J_{CP}$=12.7 Hz, N–CH_3), 35.7 (s, *C*H_2–Ar), 121.5 (d, $^3J_{CP}$=4.3 Hz, C^2_5), 122.2 (br s, $C^2_{0,1,2,3,4}$), 128.6 (br s, C^3_4), 128.7 (br s, $C^3_{0,1,2,3}$), 129.7 (s, C^3_5), 132.6 (s, $C^4_{0,1,2,3}$), 132.8 (s, C^4_4), 138.7 (br d, $^3J_{CP}$=13.1 Hz, CH=N–N–P_5), 138.7 (br d, $^3J_{CP}$=13.1 Hz, CH=N–N–$P_{1,2,3,4}$), 140.4 (s, C^4_5), 148.9 (d, $^2J_{CP}$=7.2 Hz, C^1_5), 151.6 (br d, $^2J_{CP}$=7.1 Hz, $C^1_{0,1,2,3,4}$). Calcd for $C_{2088}H_{2760}N_{186}O_{189}P_{94}S_{94}$ (39415): C, 63.63; H, 7.06; N, 6.61. Found: C, 63.72; H, 7.13; N, 6.51.

4.5. Synthesis and characterization of dendrimer 2d-G_3

To a warm solution (T=60°C) containing 1.00 g (67.5 μmol) of dendrimer **2c-G_3** in THF (15 mL) was added dropwise a small excess of aminoguanidinium chloride (359 mg, 3.25 mmol) in solution in warm methanol (5 mL). After addition, the system was stirred at 80°C under pressure for 48 h then concentrated under vacuum. The remaining oil was precipitated with cold pentane. After filtration, the white solid obtained was washed with Et_2O (3×20 mL). Removal of the small excess of aminoguanidinium hydrochloride was accomplished by redissolving the white solid in water and stirring the resulting solution overnight with Aldrich Scavengepore® 4-phenetoxybenzaldehyde-terminated resin. After filtration and evaporation of water, the guanidinium-terminated dendrimer **2d-G_3** was obtained as a white powder in 89% yield (1.16 g). $^{31}P\{^1H\}$ NMR (D_2O) δ 10.2 (s, P_0), 63.1 (br s, P_1, P_2, P_3); ^1H NMR (D_2O/CD_3CN) δ 3.28 (m, 126H, $CH_3NP_{1\text{-}3}$), 6.02 (br s, 240H, NH), 8.2–9.6 (m, 450H, ArH, CH=N); $^{13}C\{^1H\}$ NMR (D_2O/CD_3CN) δ 33.4 (m, CH_3NP), 122.4 (br s, C^2_0, C^2_1, C^2_2, C^2_3), 129.4 (s, C^3_0, C^3_1, C^3_2), 129.9 (s, C^3_3), 131.5 (m, C^4_0, C^4_1, C^4_2, C^4_3), 140.9 (m, CH=NNP), 148.5 (br s, CH=N), 152.7 (m, C^1_0, C^1_1, C^1_2, C^1_3), 157.0 (br s, CH=N). Calcd for $C_{720}H_{816}Cl_{48}N_{279}O_{90}P_{45}S_{42}$ (19260): C, 44.90; H, 4.27; N, 20.29. Found: C, 47.06; H, 4.33; N, 20.25.

4.6. General procedure for the synthesis of dendrimers 2e-G_x (x=2, 3)

To a solution of 200 mg of **2c-G_x** dendrimer (**x**=2, 29.2 μmol; **x**=3, 13.5 μmol) in distilled THF was added 2-hydrazinopyridine (**x**=2, 77.0 mg, 702 μmol; **x**=3, 72.0 mg, 648 μmol). The mixture was stirred at 40°C for 48 h, then concentrated and precipitated with pentane (20 mL) and filtered. The resulting solid was washed by ether (3×20 mL) and dried, leading to a pale yellow powder (**x**=2, 250 mg; **x**=3, 241 mg).

4.6.1. Second generation 2e-G_2. 95% Yield; $^{31}P\{^1H\}$ NMR (THF-d_8) δ 8.5 (s, P_0), 62.5 (s, P_2), 62.9 (s, P_1); ^1H NMR (THF-d_8) δ 3.33 (d, $^3J_{HP}$=13.8 Hz, 18H, CH_3NP_1), 3.35 (d, $^3J_{HP}$=11.4 Hz, 36H, CH_3NP_2), 6.66 ('t', $^3J_{HH}$=5.7 Hz, 24H, Pyr), 7.05 (d, $^3J_{HH}$=6.5 Hz, 12H, C^2_0H), 7.25 (m, 96H, C^2_1H, C^2_2H, Pyr), 7.52 (m, 24H, Pyr), 7.6–7.8 (m, 102H,

C_0^3H, C_1^3H, C_2^3H, CH═NNP), 7.96 (s, 24H, C*H*═NNH), 8.04 (m, 24H, Pyr), 10.64 (s, 24H, NH); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 32.19 (d, $^2J_{CP}$=12 Hz, CH_3NP_1), 32.24 (d, $^2J_{CP}$=12.1 Hz, CH_3NP_2), 106.0 (s, Pyr), 114.6 (s, Pyr), 120.6 (br s, C_0^2), 121.0 (br s, C_1^2, C_2^2), 126.8 (s, C_2^3), 127.9 (s, C_0^3, C_1^3), 132.08 (s, C_0^4), 132.1 (s, C_1^4), 132.8 (s, C_2^4), 137.2 and 137.3 (2s, Pyr and CH═NNPyr), 140.0 (m, CH═NNP), 147.3 (s, Pyr), 150.05 (d, $^2J_{CP}$=8 Hz, C_2^1), 150.6 (d, $^2J_{CP}$=8 Hz, C_0^1), 150.8 (d, $^2J_{CP}$=8 Hz, C_1^1), 156.9 (s, Pyr). Calcd for $C_{432}H_{384}N_{111}O_{42}P_{21}S_{18}$ (9030): C, 57.46; H, 4.29; N, 17.22. Found: C, 57.53; H, 4.35; N, 17.09.

4.6.2. Third generation 2e-G$_3$. 93% Yield; $^{31}P\{^1H\}$ NMR (THF-d_8) δ 9.4 (s, P_0), 63.6 (br s, P_1, P_2, P_3); ^1H NMR (THF-d_8) δ 3.32 (m, 126H, $CH_3NP_{1\text{-}3}$), 6.64 (m, 48H, Pyr), 7.1 (br s, 12H, C_0^2H), 7.25 (m, 228H, C_1^2H, C_2^2H, C_3^2H, Pyr), 7.49 (m, 48H, Pyr), 7.55–7.85 (m, 270H, C_0^3H, C_1^3H, C_2^3H, C_3^3H, CH═N), 8.04 (br s, 48H, Pyr), 10.01 (s, 48H, NH); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 32.8 (m, CH_3NP), 107.0 (s, Pyr), 115.2 (s, Pyr), 121.6 (br s, C_0^2), 121.9 (br s, C_1^2, C_2^2, C_3^2), 127.5 (s, C_3^3), 128.5 (s, C_0^3, C_1^3, C_2^3), 133.0 (s, C_0^4, C_1^4, C_2^4), 133.5 (s, C_3^4), 137.8 (br s, Pyr, CH═NNPyr), 139.9 (m, CH═NNP), 147.9 (s, Pyr), 151.1 (d, $^2J_{CP}$=8 Hz, C_3^1), 151.8 (m, C_0^1, C_1^1, C_2^1), 157.7 (s, Pyr). Calcd for $C_{912}H_{816}N_{231}O_{90}P_{45}S_{42}$ (19192): C, 57.08; H, 4.28; N, 16.86. Found: C, 57.21; H, 4.34; N, 16.78.

4.7. Synthesis and characterization of dendrimer 2f-G$_3$

To a solution containing 112 mg (5.8 μmol) of dendrimer **2e-G$_3$** in 2 mL of THF was added dropwise at 0°C, 2.80 mL of aqueous HCl 0.1 M. The mixture was stirred for one hour at 0°C, then concentrated and precipitated by addition of chloroform. After filtration, the resulting solid was washed with chloroform and ether and dried, leading to 117 mg of **2f-G$_3$** obtained as a pale yellow powder. 93% yield; $^{31}P\{^1H\}$ NMR (DMSO-d_6) δ 11.6 (s, P_0), 65.3 (s, P_3), 65.8 (br s, P_1, P_2); ^1H NMR (DMSO-d_6) δ 3.31 (m, 126H, $CH_3NP_{1\text{-}3}$), 6.96 (m, 48H, Pyr), 7.2 (br m, 240H, C_0^2H, C_1^2H, C_2^2H, C_3^2H, Pyr), 7.69 (m, 48H, Pyr), 7.96 (br m, 270H, C_0^3H, C_1^3H, C_2^3H, C_3^3H, CH═N), 8.32 (m, 48H, Pyr); $^{13}C\{^1H\}$ NMR (DMSO-d_6) δ 34.0 (m, CH_3NP), 112.7 (s, Pyr), 115.4 (s, Pyr), 122.1 (br s, C_0^2, C_1^2, C_2^2, C_3^2), 129.3 (br s, C_0^3, C_1^3, C_2^3), 130.3 (s, C_2^3) 131.8 (s, C_3^4), 132.9 (s, C_0^4, C_1^4, C_2^4), 137.9 (s, Pyr), 141.6 (br s, CH═NNPyr), 144,9 (m, CH═NNP), 147.1 (s, Pyr), 150.2 (br s, C_3^1), 151.6 (s, C_2^1), 152.3 (br s, C_1^1, C_0^1). Calcd for $C_{912}H_{864}Cl_{48}N_{231}O_{90}P_{45}S_{42}$ (20943): C, 52.31; H, 4.16; N, 15.45. Found: C, 52.25; H, 4.08; N, 15.37.

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