Design of tailored multi-charged phosphorus surface-block dendrimers†

Valérie Maraval,[a] Alexandrine Maraval,[a] Grégory Spataro,[a] Anne-Marie Caminade,*[a] Jean-Pierre Majoral,*[a] Dong Ha Kim[bc] and Wolfgang Knoll*[c]

Received (in Montpellier, France) 21st July 2006, Accepted 31st August 2006
First published as an Advance Article on the web 20th September 2006
DOI: 10.1039/b610632n

Polycationic or neutral dendrons of generation 1 to 3 bearing protonated (or not) amino end groups and a vinyl group at the focal point as well as polyanionic or neutral dendrons of generation 1 to 3 decorated with carboxylate or carboxylic groups on their surface and exhibiting a vinyl group at the core were prepared. Addition of ethylenediamine to the vinyl core of dendrons having amino end groups allowed the synthesis of uniquely tailored water-soluble phosphorus bis-dendrons *via* core to core assembling of dendrons having a vinyl core. In preliminary experiments layer-by-layer deposition of bis-dendrons on silica surface was demonstrated.

Introduction

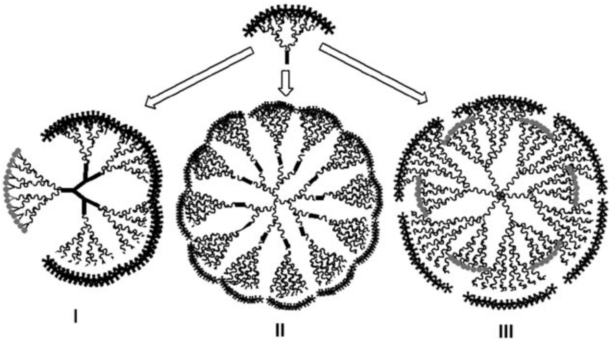
Dendrimers are symmetrical and spherical macromolecules, comprising a relative dense shell and composed of a core, branching sites, and terminal groups that usually form a well-defined structure.[1] Dendrons, also called dendritic wedges differ from dendrimers by the presence of one (or more) functional group(s) located at the core, these functional groups being generally different from the end groups located at the surface. Such a diversity in the nature and the location of functional groups offers many possibilities to build original dendritic macromolecules as already exemplified by us[2,3] and by others,[1] therefore enhancing in principle the use of such nano-objects in different fields ranging from biology to material sciences.

Indeed core–core coupling reactions between phosphorus containing dendrons or core-surface couplings involving both dendrons and dendrimers led for example to the formation of surface-block dendrimers I,[3] or layer-block dendrimers II.[4] Direct grafting of dendrons within the cascade structure of dendrimers gives rise *via* "core–interior" coupling reactions to other unprecedented dendritic macromolecules III[5] (Scheme 1).

Aiming at proposing original properties and applications of dendrons and dendrimers we focused first our attention to the preparation of water soluble phosphorus dendrimers which were found suitable candidates for a number of applications in biology.[6] Polycationic and polyanionic dendrimers also proved in our hands to be useful for surface modification (silica, quartz...) *via* layer-by-layer deposition[7] as well as for obtaining nanotubes[8] and microcapsules,[9] walls of these unprecedented materials being constituted of alternate polycationic and polyanionic layers. Water soluble polycationic dendrons were also found very useful: they allow the formation of dendronized nanolatexes with remarkable properties.[10]

These results obtained with hydrosoluble phosphorus dendrimers or dendrons prompted us to try to design water soluble phosphorus bis-dendrons[11] (surface-block dendrimers[12]) with one of the two dendrons bearing anionic groups in order to ensure solubility in water and easy surface modification (glass, quartz, nanotubes, nanocapsules, nanoparticles...) *via* electrostatic interactions, the other one bearing easily quaternizable amino end groups or any type of functional groups which will bring new properties for the considered surfaces and/or nanomaterials.

We report here the preparation of multifunctionalized dendrons of generation 1 to 3, their core to core assembly giving rise to unique tailored water soluble phosphorus bis-dendrons and preliminary results concerning their use for layer by layer deposition.



Scheme 1 Some examples of dendritic architectures built from dendrons.

---

[a] *Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 4, France. E-mail: caminade@lcc-toulouse.fr, majoral@lcc-toulouse.fr; Fax: +33 (0)5 61 55 30 03*
[b] *Division of Nano-sciences and Department of Chemistry Ewha Womans University II-I Daehyun-Dong, Seodaemun-Gu, Seoul 120-750, Korea*
[c] *Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany. E-mail: knoll@mpip-mainz.mpg.de; Fax: +49 (0)6131 379 360*

† Electronic supplementary information (ESI) available: characterization of all compounds (^{31}P, ^{1}H and ^{13}C NMR data). See DOI: 10.1039/b610632n

Results and discussion

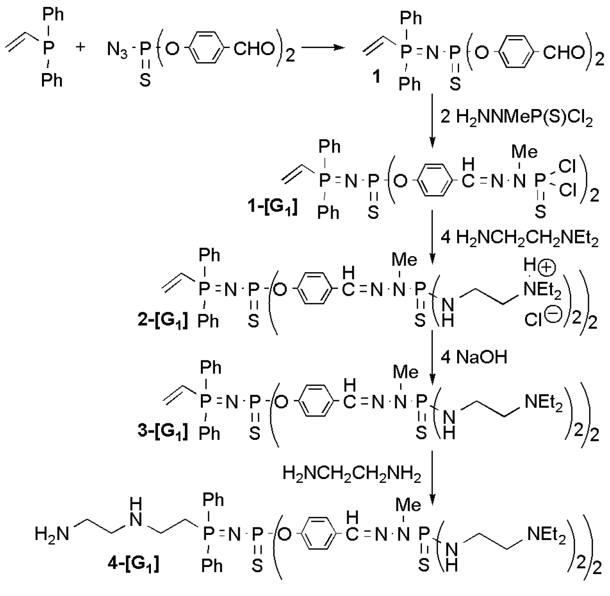
Synthesis of dendrons having amine/ammonium end groups

The first reaction carried out to synthesize these dendrons is a Staudinger reaction between diphenylvinylphosphine and the azide $N_3P(S)(OC_6H_4CHO)_2$ leading to the dialdehyde **1** (Scheme 2). Condensation of **1** with the phosphorhydrazide $H_2NN(CH_3)P(S)Cl_2$ affords the first generation dendron **1-[G$_1$]**^{4} which is further condensed with the diamine $H_2N(CH_2)_2NEt_2$ to give directly the tetraammonium dendron **2-[G$_1$]**. Hydrogen chloride formed during this process is quantitatively trapped by the terminal tertiary amines. Such an experiment can be easily followed by ^{31}P NMR, the grafting of four equivalents of diamine onto **1-[G$_1$]** inducing a large modification of the chemical shift corresponding to the terminal phosphorus groups (from 63.5 to 73.4 ppm). It must be emphasized that the use of a stoichiometric amount of amine prevents Michael type additions at the vinyl core, as shown by the absence of modification of the chemical shift corresponding to the P=N group at the core (see later). Addition of sodium hydroxide 1 M to **2-[G$_1$]** led to the neutral dendron **3-[G$_1$]**. This reaction is characterized in ^{31}P NMR by a signal corresponding to external P=S groups at 71.4 ppm. The last step leading to the targeted dendron **4-[G$_1$]** suitable for the synthesis of bis-dendrons *via* core–core coupling reactions, is a Michael type addition involving the vinyl group located at the core of **3-[G$_1$]** and a large excess of ethylenediamine $H_2N(CH_2)_2NH_2$. The formation of the dendron **4-[G$_1$]** is monitored by NMR: ^{31}P NMR shows two doublets at 21.0 and 55.8 ppm ($^2J_{PP}$ = 32.3 Hz) and one singlet (external $P(S)(NH(CH_2)_2NEt_2)_2$ groups) at 71.5 ppm while disappearance of the signals due to the vinyl groups is easily observed in ^{1}H NMR.

Such a strategy of synthesis of dendron **4-[G$_1$]** of generation 1 was applied for the obtaining of dendrons of higher generations, *i.e.* 2 and 3, incorporating also a primary amine at the core and tertiary amines on the surface. This implies first the preparation of dendrons of generation 2, **1-[G$_2$]** and 3, **1-[G$_3$]** bearing respectively, 4 and 8 terminal $P(S)Cl_2$ groups. For this purpose the growing of **1-[G$_1$]** is pursued using our classical method of synthesis of dendrimers whose first steps are described above, *i.e.* nucleophilic substitution of P–Cl bonds of **1-[G$_1$]** with 4-hydroxybenzaldehyde followed by condensation reaction with the phosphorhydrazide $H_2NN(CH_3)P(S)Cl_2$ leading to the dendron **1-[G$_2$]**, which in turn is treated with hydroxybenzaldehyde and $H_2NN(CH_3)P(S)Cl_2$ to give **1-[G$_3$]**.

The formation of the dendritic wedge **2-[G$_2$]** from **1-[G$_2$]** involves first the addition of 8 equiv. of the diamine $H_2N(CH_2)_2NEt_2$ which leads directly to the expected polycation bearing 8 terminal protonated amino groups on the surface. A marked shielding effect is observed in ^{31}P NMR for the signal of the phosphorus which undergoes the reaction, from 63.3 to 73.3 ppm. The presence of the unreacted vinyl group is indicated by ^{1}H NMR (ABCX system) and by ^{13}C NMR (δ = 138.1 ppm for CH_2=). The next step consists of the treatment of **2-[G$_2$]** with sodium hydroxide giving the neutral dendron **3-[G$_2$]** which in turn is treated with a large excess of ethylenediamine to afford, *via* a Michael type reaction, the dendron **4-[G$_2$]**, bearing a primary amine at the focal point and 8 tertiary amino groups on the outer shell (Scheme 3).

Similarly dendrons **2-[G$_3$]**, **3-[G$_3$]**, and **4-[G$_3$]** are grown from **1-[G$_3$]** using the above method. All the steps are monitored by ^{31}P, ^{1}H, and ^{13}C NMR. As an example the formation of **4-[G$_3$]** from **3-[G$_3$]** is indicated in ^{31}P NMR by a slight deshielding effect for the signal due to the P=S unit of the P=N–P=S linkage from 56.4 (**3-[G$_3$]**) to 55.9 (**4-[G$_3$]**) ppm, and a deshielding effect from 15.0 to 21.2 ppm for the signal due to the P=N unit. A marked shielding is also observed for the CH_2= transformed in NCH_2– in ^{13}C NMR from 136.8 to 42.3 ppm.

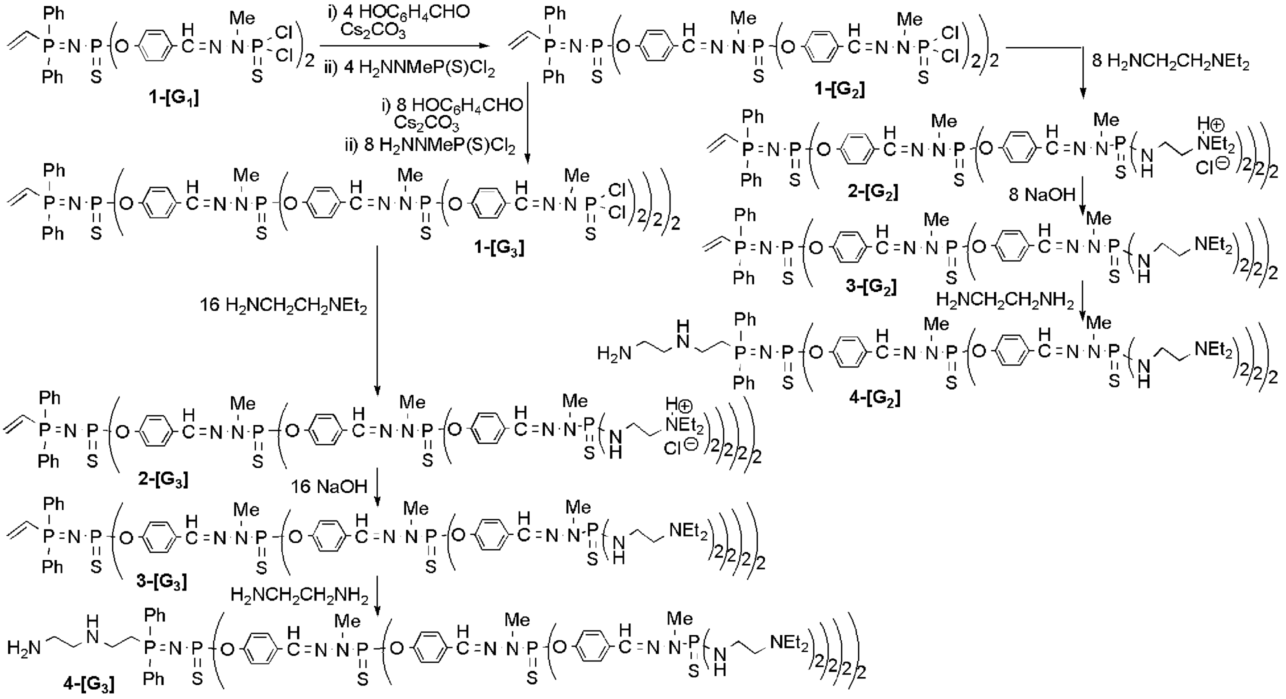


Scheme 2 Synthesis of the dendrons **4-[G$_1$]** bearing a primary amine at the focal point and 4 tertiary amino end groups.

Synthesis of dendrons having carboxylic acid/carboxylate end groups

Having in hand dendrons of generation 1, 2, and 3 with terminal amino groups and a primary amine at the core we further investigated the possibility to prepare dendrons keeping a vinyl group on the focal point and presenting carboxylic or carboxylate end groups.

The preparation of the simplest dendron of this type *i.e.* **5-[G$_1$]** involves first the treatment of **1-[G$_1$]** with 4-hydroxybenzaldehyde in the presence of caesium carbonate then a condensation reaction with hydrazine benzoic acid $H_2NNH\ C_6H_4COOH$ leading to the dendron **5-[G$_1$]** decorated with 4 carboxylic end groups. Such a grafting reaction is characterized by the disappearance of the signal corresponding to the CHO groups in ^{1}H NMR and IR on behalf of new signals due to the incorporation of both hydrazine and carboxylic groups. The most characteristic data is the presence of a singlet at 10.86 ppm in ^{1}H NMR and at 167.2 ppm in ^{13}C NMR, due to the presence of carboxylic groups. Further addition of sodium hydride leads to the salt **6-[G$_1$]**, a water soluble dendron of generation 1 (Scheme 4).



Scheme 3 Synthesis of dendrons of generation 2 (**2-[G$_2$]**, **3-[G$_2$]**, **4-[G$_2$]**) and 3 (**2-[G$_3$]**, **3-[G$_3$]**, **4-[G$_3$]**).

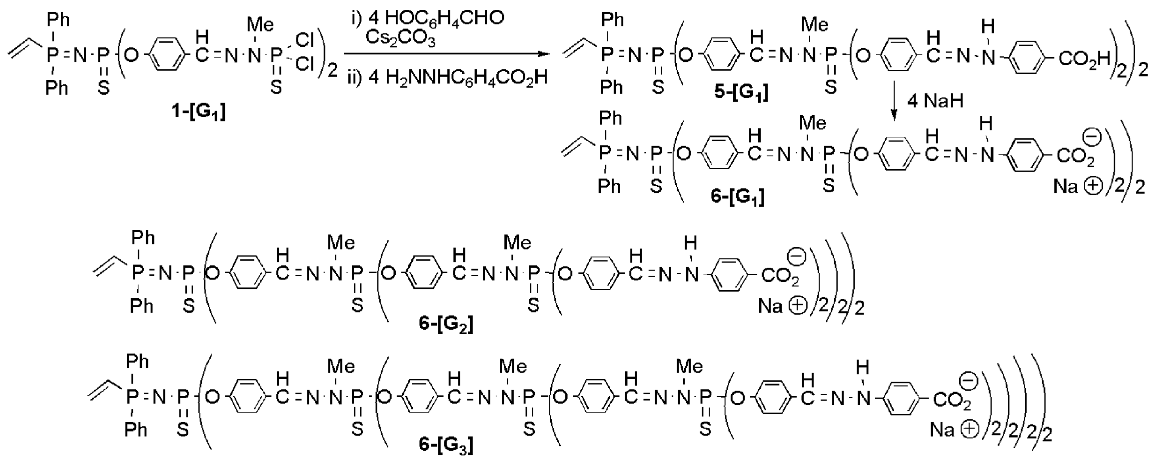
The same sequence of reactions was applied to dendrons of generation 2 bearing 8 aldehyde end groups and generation 3 (16 aldehyde end groups). Water-soluble dendrons **6-[G$_2$]** and **6-[G$_3$]**, respectively were thus obtained and fully characterized (see experimental section). In all of these experiments, reactions were monitored by ^{31}P, ^{1}H and ^{13}C NMR.

Synthesis of polyanionic bis-dendrons

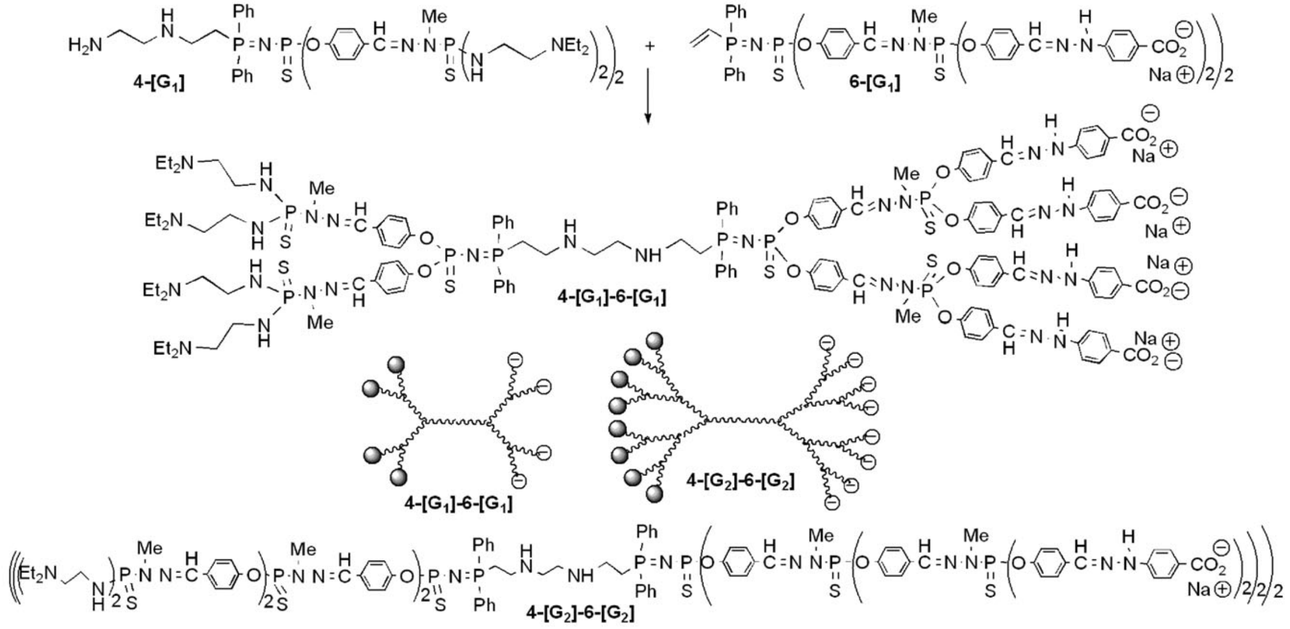
Cross coupling reactions between dendrons bearing vinyl groups and amino groups at the core were attempted with the goal to prepare tailored water-soluble phosphorus surface-block dendrimers. Such a coupling involves a Michael type addition as shown in Scheme 5.

Typically the reaction proceeds at 70 °C in a THF/water 1/1 solution containing each dendron partner. The first experiments were conducted with dendrons of similar generation *i.e.* **4-[G$_1$]**, and **6-[G$_1$]** (generation 1) on the one hand, and **4-[G$_2$]** and **6-[G$_2$]** (generation 2) on the other. Surface-block dendrimers **4-[G$_1$]-6-[G$_1$]**, and **4-[G$_2$]-6-[G$_2$]** were thus obtained in 90% yield.

The completion of the reaction was monitored mainly by ^{31}P NMR which pointed out significant shifts concerning P=N=P=S groups owing to dendron **6-[G$_n$]**. As an example the ^{31}P signal of the P=N group of P=N–P=S units in **4-[G$_2$]** (terminal amino groups) and **6-[G$_2$]** (terminal carboxylate groups) at 21.2 (d, $^2J_{PP}$ = 33.7 Hz) for **4-[G$_2$]** and 14.7 (d, $^2J_{PP}$ = 28.0 Hz) ppm for **6-[G$_2$]** disappears on behalf of new signals at 21.6 (d, $^2J_{PP}$ = 31.9 Hz) and 21.7 (d, $^2J_{PP}$ = 30.9 Hz), respectively. A slight change is observed for the two ^{31}P signals of the P=S group of the P=N=P=S units moving from 55.8 (d, $^2J_{PP}$ = 33.7 Hz) for **4-[G$_2$]** and 55.1 (d, $^2J_{PP}$ = 28.0 Hz) for **6-[G$_2$]** to 55.6 (d, $^2J_{PP}$ = 31.9 Hz),



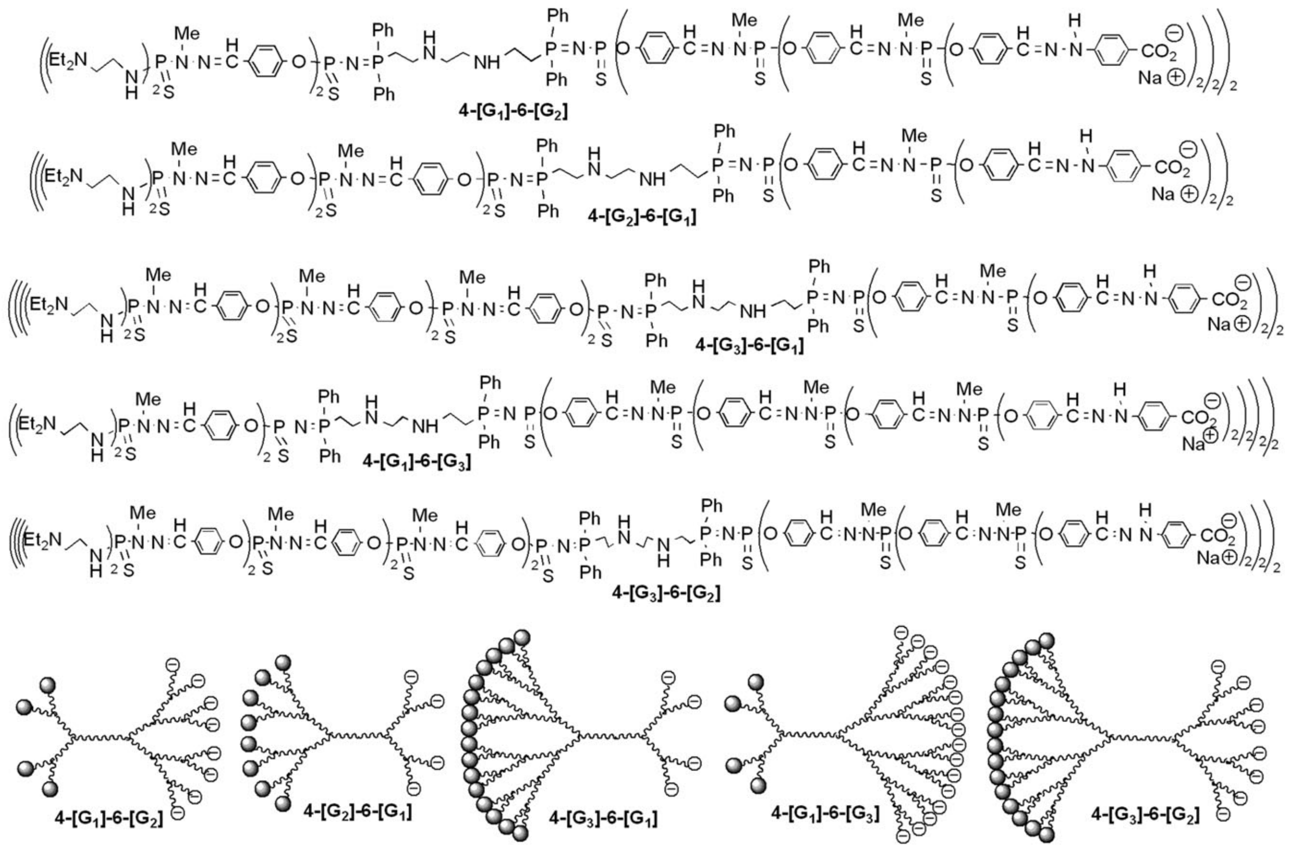
Scheme 4 Preparation of polyanionic dendrons of generation 1 to 3: **6-[G$_1$]**, **6-[G$_2$]**, **6-[G$_3$]**.



Scheme 5 Strategy of synthesis of symmetrical bis-dendrons (**4-[G$_1$]-6-[G$_1$]**, **4-[G$_2$]-6-[G$_2$]**).

and 56.1 (d, $^2J_{\mathrm{pp}} = 30.9$ Hz) ppm for **4-[G$_2$]-6-[G$_2$]**. Completion of the reaction is also monitored by ^{1}H and ^{13}C NMR which show the complete disappearance of the signals due to the vinyl groups.

Therefore such a strategy allowed us to couple dendrons of the same generation. Similarly this methodology was applied to the coupling of dendrons of different sizes and generation (Scheme 6). Unsymmetrical multi-charged phosphorus bis-



Scheme 6 Chemical structure of unsymmetrical bis-dendrons of generation 1, 2 or 3.

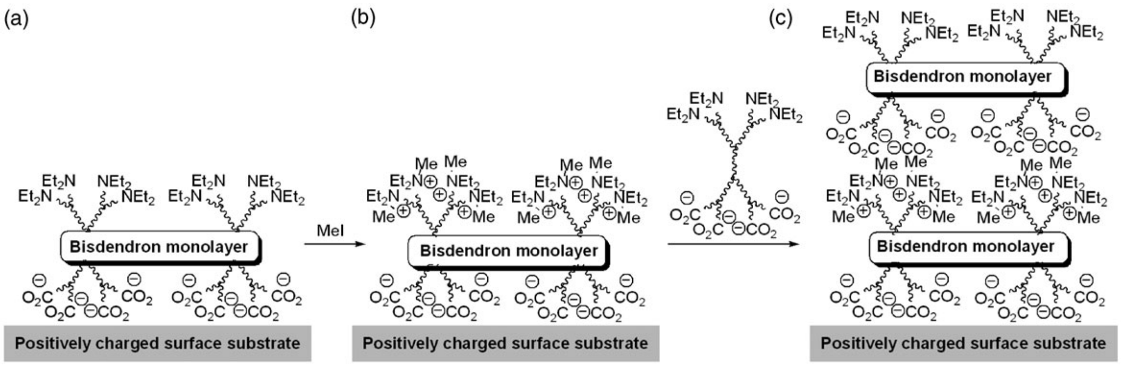


Fig. 1 Schematic diagram for the preparation of a bis-dendron multilayer on a silica surface.

dendrons **4-[G$_1$]-6-[G$_2$]**, **4-[G$_2$]-6-[G$_1$]**, **4-[G$_3$]-6-[G$_1$]**, **4-[G$_1$]-6-[G$_3$]**, and **4-[G$_3$]-6-[G$_2$]**, were thus prepared for the first time and fully characterized (see Supplementary Information†).

Layer by layer deposition

Layer by layer deposition of polycationic and polyanionic dendrimers allowed us to prepare well defined nanotubes and microcapsules with walls entirely formed with alternate layers of these dendrimers.[8,9] Electrostatic interactions play a key role in such a construction and allow for the formation of stable new nanomaterials. It was tempting to see if such a deposition could be performed using not two kinds of dendrimers (or polymers) but using only one kind of building block, that is to say the water-soluble bis-dendrons reported in this study. Of course, in a first approach experiments have to be done on a planar surface in order to facilitate the characterization of the deposition and to prove the feasibility of the concept.

In a preliminary experiment some of these symmetrical bis-dendrons were deposited on a silica surface precoated with a monolayer of 3-APDMES (3-aminopropyl dimethylethoxy silane) in order to ensure a positive surface. The schematic diagram of construction of multilayers starting from bis-dendrons **4-[G$_1$]-6-[G$_1$]** or **4-[G$_2$]-6-[G$_2$]** is shown in Fig. 1. Deposition of the first layer took place *via* strong electrostatic interaction between the positively charged silica surface and the polyanionic part (**6-[G$_1$]**) of bis-dendrons **4-[G$_1$]-6-[G$_1$]** (Fig. 1a). The neutral surface thus obtained was quaternized using methyl iodide as alkylating reagent (Fig. 1b). The resulting positive surface was then coated with the bis-dendron **4-[G$_1$]-6-[G$_1$]** (Fig. 1c). The bis-dendron thin film was built by reiteration of quaternization and adsorption sequences up to deposition of 4 layers. A similar process was used starting with bis-dendrons of generation 2, *i.e.* **4-[G$_2$]-6-[G$_2$]**. UV-visible absorbance, SPRS (surface plasmon resonance spectroscopy) measurements allowed characterization of these controlled associations of monolayers which were also characterized by AFM.[13]

Such preliminary results validate for the first time our assumption that these unique bis-dendrons can be advantageously used for layer-by-layer deposition on a surface instead of alternating between polycationic and polyanionic dendrimers.

Conclusion

Different neutral, cationic or anionic phosphorus-containing dendrons have been prepared. The nature of functional groups located at the core of these dendrons allows their grafting *via* a Michael type reaction and the formation of a large variety of original bis-dendrons constituted of dendrons of different size and generation and decorated with carboxylate groups and protonated (or not) or alkylated (or not) tertiary amino groups.

Preliminary experiments clearly indicate that these macromolecules are perfect nano-objects for attractive surface modification *via* layer-by-layer deposition. Work is in progress to study the properties of the multilayers formed in these conditions and to extend such a new strategy for various functionalisation of nanomaterials such as nanotubes, nanocapsules, nanoparticles, *etc*. Use of these amphiphilic surface-block dendrimers for the construction of a variety of supramolecular structures *via* self assembly is also under current investigation.

Experimental

General

All manipulations were carried out with standard high vacuum and dry-argon techniques. The solvents were freshly dried and distilled (THF and ether over sodium/benzophenone, pentane and CH_2Cl_2 over phosphorus pentoxide, toluene over sodium). Classical ^1H, ^{13}C, ^{31}P NMR 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 ^1H and ^{13}C NMR. The attribution of ^{13}C NMR signals has been done using J_{mod}, two-dimensional HMBC, and HMQC, Broad Band or CW ^{31}P decoupling experiments when necessary.

Syntheses

Synthesis of dendrons bearing ammonium end groups. A stoichiometric amount of *N*,*N*-diethylethylenediamine (n = 1, 1.619 mmol, 232 μL; n = 2, 1.435 mmol, 205 μL; n = 3, 1.678 mmol, 240 μL) was added dropwise by syringe with strong stirring to a solution of dendron (n = 1, 0.410 mmol, 0.350 g; n = 2, 0.179 mmol, 0.330 g; n = 3, 0.105 mmol, 0.400 g) in distilled THF (15 mL). The solvent was removed by filtration after stirring overnight at room temperature. The residue was washed with distilled THF and evaporated to dryness to give the dendrons **2-[G$_n$]** as white powders. Yields: **2-[G$_1$]** 95%; **2-[G$_2$]** 98%; **2-[G$_3$]** 96%.

Synthesis of dendrons bearing amine end groups. A solution of NaOH 1 M ($n = 1$, 1.2 mL; $n = 2$, 1.15 mL; $n = 3$, 1.12 mL) was added dropwise to a stirred solution of 0.400 g of **2-[G$_n$]** ($n = 1$, 0.303 mmol; $n = 2$, 0.144 mmol; $n = 3$, 0.070 mmol) in distilled water (30 mL). The precipitate was recovered by centrifugation and dissolved in chloroform. Then, the organic solution obtained was dried over Na_2SO_4, filtered and evaporated to dryness to give **3-[G$_n$]** as white powders. Yields: **3-[G$_1$]** 90%; **3-[G$_2$]** 95%; **3-[G$_3$]** 97%.

Synthesis of dendrons bearing a diamine at the core. To a solution of 0.300 g of **3-[G$_n$]** ($n = 1$, 0.256 mmol; $n = 2$, 0.121 mmol; $n = 3$, 0.059 mmol) in THF (20 mL) was added a large excess of ethylenediamine ($n = 1$, 0.102 mol, 6.8 mL; $n = 2$, 48.426 mmol, 3.2 mL; $n = 3$, 23.579 mmol, 1.6 mL). The resulting mixture was stirred at room temperature for 3 hours. The solvent was then evaporated and the product was washed with mixtures THF/pentane to give **4-[G$_n$]** as white powders. Yields: **4-[G$_1$]** 95%; **4-[G$_2$]** 97%; **4-[G$_3$]** 98%.

Synthesis of dendrons bearing carboxylic acid end groups. To a solution of **1-[G′$_n$]** (n = 1–3) (obtained by reaction of hydroxybenzaldehyde on **1-[G$_n$]**) in THF were added 1.3x equiv. ($n = 1$, $x = 4$; $n = 2$, $x = 8$; $n = 3$, $x = 16$) of hydrazinobenzoic acid. A sufficient quantity of dry methanol to obtain a homogeneous solution was then added and the resulting solution was stirred overnight at room temperature. Then, 0.3x equiv. of ScavengePore polyphenylethyloxybenzaldehyde was added and the mixture was smoothly stirred at room temperature for 3 days. After filtration, the solution was evaporated to dryness and the new dendron was obtained as a pale orange powder. Yields: **5-[G$_1$]** 93%; **5-[G$_2$]** 95%; **5-[G$_3$]** 96%.

Synthesis of dendrons bearing carboxylate end groups. To a solution of **5-[G$_n$]** (n = 1–3) in THF was added a stoichiometric amount of sodium hydride ($n = 1$, 4 equiv.; $n = 2$, 8 equiv.; $n = 3$, 16 equiv.). This mixture was stirred overnight at room temperature. The solvent was then removed under vacuum, giving the polycarboxylate dendron **6-[G$_n$]** as a pink powder in quantitative yield.

Synthesis of bis-dendrons 4-[G$_n$]-6-[G$_{n'}$] ($n = n'$ or $n \neq n'$). To a solution of **4-[G$_n$]** in THF was added 0.5 equiv. of **6-[G$_{n'}$]**. Then, water was added to this mixture progressively until a homogeneous solution was obtained. This mixture was heated at 70 °C in a sealed flask during one week. Then, 0.5 equiv. of ScavengePore polyphenylethyloxybenzaldehyde was added and the resulting mixture was smoothly stirred during 2 days at room temperature. After filtration, the solution was evaporated to dryness, the bis-dendron was washed with ether : pentane mixtures to give pale orange powders. Yields: **4-[G$_1$]-6-[G$_1$]** 87%; **4-[G$_2$]-6-[G$_2$]** 90%; **4-[G$_1$]-6-[G$_2$]** 93%; **4-[G$_2$]-6-[G$_1$]** 90%; **4-[G$_3$]-6-[G$_1$]** 86%; **4-[G$_3$]-6-[G$_2$]** 92%; **4-[G$_1$]-6-[G$_3$]** 93%.

Acknowledgements

Thanks are due to the Fonds Social Européen (grant to G.S.) and to the CNRS-DFG program for financial support.

References

1 (*a*) *Dendrimers and dendrons*, ed. G. R. Newkome, F. Vögtle and C. N. Moorefield, John Wiley and Sons, Weinheim, Germany, 2001; (*b*) *Dendrimers and other dendritic polymers*, ed. J. M. J. Fréchet and D. A. Tomalia, John Wiley and Sons, Chichester, UK, 2001; (*c*) J. P. Majoral and A. M. Caminade, *Chem. Rev.*, 1999, **99**, 845–880.

2 (*a*) J. P. Majoral, A. M. Caminade and V. Maraval, *Chem. Commun.*, 2002, 2929–2942; (*b*) A. M. Caminade and J. P. Majoral, *Acc. Chem. Res.*, 2004, **37**, 341–348.

3 A. M. Caminade, A. Maraval and J. P. Majoral, *Eur. J. Inorg. Chem.*, 2006, 887–901.

4 V. Maraval, R. Laurent, B. Donnadieu, M. Mauzac, A. M. Caminade and J. P. Majoral, *J. Am. Chem. Soc.*, 2000, **122**, 2499–2511.

5 (*a*) C. Galliot, C. Larré, A. M. Caminade and J. P. Majoral, *Science*, 1997, **277**, 1981–1984; (*b*) V. Maraval, R. Laurent, S. Merino, A. M. Caminade and J. P. Majoral, *Eur. J. Org. Chem.*, 2000, 3555–3568.

6 See for example: (*a*) A. M. Caminade and J. P. Majoral, *Prog. Polym. Sci.*, 2005, **30**, 4191–505; (*b*) M. Blanzat, C. O. Turrin, A. M. Aubertin, C. Vidal, A. M. Caminade, J. P. Majoral, I. Rico-Lattes and A. Lattes, *ChemBioChem*, 2005, **6**, 2207–2213; (*c*) J. Solassol, C. Crozet, V. Perrier, J. Leclaire, F. Béranger, A. M. Caminade, B. Meunier, D. Dormon, J. P. Majoral and S. Lehmann, *J. Gen. Virol.*, 2004, **85**, 1791–1799.

7 (*a*) S. Peleshanko, J. P. Majoral, A. M. Caminade, W. Knoll and V. V. Tsuruk, *Polym. Prep.*, 2002, **43**, 421; (*b*) J. L. Hernandez-Lopez, R. E. Bauer, W. S. Chang, G. Glasser, D. Grebel-Koehler, M. Klapper, M. Kreiter, J. Leclaire, J. P. Majoral, S. Mittler, K. Müllen, K. Vasilev, T. Weil, J. Wu, T. Zhu and W. Knoll, *Mater. Sci. Eng.*, 2003, **C23**, 267–274.

8 D. H. Kim, P. Karan, P. Göring, J. Leclaire, A. M. Caminade, J. P. Majoral, U. Gösele, M. Steinhart and W. Knoll, *Small*, 2005, **1**, 99–102.

9 B. S. Kim, O. V. Lebedeva, D. H. Kim, A. M. Caminade, J. P. Majoral, W. Knoll and O. I. Vinogradova, *Langmuir*, 2005, **21**, 7200–7206.

10 C. Larpent, C. Geniès, A. P. De Sousa Delgado, A. M. Caminade, J. P. Majoral, J. F. Sassi and F. Leising, *Chem. Commun.*, 2004, 1816–1817.

11 Charged bis-dendrons are rare. See in particular: (*a*) C. J. Hawker, K. L. Wooley and J. M. J. Fréchet, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1287–1297; (*b*) A. Ritzen and T. Frejd, *Eur. J. Org. Chem.*, 2000, **1**, 3771; (*c*) T. Ren, G. Zhang and D. Liu, *Tetrahedron Lett.*, 2001, **42**, 1007–1010.

12 Selected references about bis-dendrons: (*a*) K. L. Wooley, C. J. Hawker and J. M. J. Fréchet, *J. Chem. Soc., Perkin Trans. 1*, 1991, **1**, 1059–1076; (*b*) C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1992, **114**, 8405–8413; (*c*) K. L. Wooley, C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1993, **115**, 11496–11505; (*d*) D. J. Pesak and J. S. Moore, *Tetrahedron*, 1997, **53**, 15331–15347; (*e*) K. Aoi, K. Itoh and M. Okada, *Macromolecules*, 1997, **30**, 8072–8074; (*f*) S. M. Grayson and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2000, **122**, 10335–10344; (*g*) J. F. Nierengarten, J. F. Eckert, Y. Rio, M. P. Carreon, J. L. Gallani and D. Guillon, *J. Am. Chem. Soc.*, 2001, **123**, 9743–9748; (*h*) I. K. Martin and L. J. Twyman, *Tetrahedron Lett.*, 2001, **42**, 1119–1121; (*i*) E. R. Gillies and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2002, **124**, 14137–14146; (*j*) J. R. Morgan and M. J. Cloninger, *Curr. Opin. Drug Discovery Dev.*, 2002, **5**, 966–973; (*k*) S. Zhang, Y. Rio, F. Cardinali, C. Bourgogne, J. L. Gallani and J. F. Nierengarten, *J. Org. Chem.*, 2003, **68**, 9787–9797; (*l*) N. R. Luman and M. W. Grinstaff, *Org. Lett.*, 2005, **7**, 4863–4866; (*m*) P. Wu, M. Malkoch, J. N. Hunt, R. Vestberg, E. Kaltgrad, M. G. Finn, V. V. Fokin, K. B. Sharpless and C. J. Hawker, *Org. Lett.*, 2005, 5775–5777.

13 Full details will be reported in a forthcoming paper.