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Synthesis and characterization of water-soluble ferrocene-dendrimers

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ABSTRACT

The synthesis of two new families of water-soluble phosphorus dendrimers of type Poly(PhosphorHydrazone) (PPH) incorporating ferrocene(s) in their internal structure is reported. In the first series, the ferrocene is located at the core and the dendrimers (first and second generations) are ended either by ammonium groups or carboxylate groups, both ensuring the solubility in water. The electrochemical properties of one of them are reported. A new difunctional ferrocene suitable to be used as component of the branches of dendrimers has been synthesized and characterized by X-ray diffraction. It has been used for the synthesis of a second series of dendrimers incorporating 24 ferrocenes, located in the branches at the level of the second generation. The synthesis of these dendrimers is carried out up to the third generation ended by ammoniums or carboxylates.

1. Introduction

Ferrocene-containing dendrimers have attracted a great interest since a long time [1], mainly due to their particular electrochemical properties. Indeed, ferrocene derivatives undergo fast one-electron oxidation to the ferrocenium form, which is positively charged; such oxidation is frequently fully reversible. These properties, combined with those of dendrimers [2], have led to various uses, for instance as redox sensors for molecular recognition [3], or as mediators in amperometric biosensors [4], or as electron reservoir [5], and also as catalysts [6,7]. Most of these properties are studied in organic solvents; only few water-soluble dendrimeric ferrocenes have been already described. They include in particular one ferrocene at the core of the dendrimer ended by carbohydrate [8] or by carboxylic acids [9,10]. In other cases, the solubility in water is due to an hydrophilic interior generally based on Poly(PropylenImine) (PPI) dendrimers [11].

In this paper, we report new water-soluble ferrocene-dendrimers based on Poly(PhosphorHydrazone) (PPH) dendrimers [12], in which the ferrocene group(s) is(are) either located at the core, or at one layer of the internal structure, whereas the solubility in water is afforded either by ammoniums, or carboxylates as terminal groups [13].

2. Results and discussion

2.1. Ferrocene as core of water-soluble phosphorus dendrimers

We have already published the synthesis of dendrimers having a ferrocene as core, based either on the reactivity of ferrocene bis(diphenylphosphine) with azides [14], or of ferrocene dicarbaldehyde with phosphorhydrazide [15]. The P═N–P═S linkages generated in the first case are poorly stable when left in water for several days, whereas the phosphorhydrazones generated in the second case are stable; thus, we chose as core the ferrocene dicarbaldehyde. The resulting dendrimers have either $P(S)Cl_2$ (**1-G_n**) or aldehyde (**$1 - G'_n$**) terminal groups, thus they are soluble in organic solvents, but not in water. However, we have already demonstrated the use of both types of functional groups to obtain

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water-soluble dendrimers, either by reacting N,N-diethylethylenediamine with $P(S)Cl_2$ terminal groups to afford ammonium end groups [16], or by reacting malonic acid with aldehyde terminal groups, to afford carboxylate end groups after reaction with NaOH [17]. Here we have applied both reactions to generation 1 (**1-G$_1$**, $\mathbf{1-G_1'}$) and generation 2 (**1-G$_2$**, $\mathbf{1-G_2'}$) of the dendrimers built from ferrocene dicarbaldehyde as core. Such reactions afford dendrimers bearing charged terminal functions **2-G$_1^+$** (4 ammoniums), **3-G$_1^-$** (4 carboxylates), **2-G$_2^+$** (8 ammoniums), **3-G$_2^-$** (8 carboxylates) respectively, as shown in Scheme 1.

All these dendrimers are water-soluble, but due to the hydrophobic character of the internal structure, they are shrunk in water, and the NMR signals of the internal structure are frequently not detected in water, as we have already demonstrated for another type of water-soluble phosphorus dendrimer [18]. Thus the characterization by multinucleus NMR was done in methanol in the case of the ammonium terminations, and in dimethylsulfoxide in the case of the carboxylate terminations. The presence of the cyclopentadienyl rings at the core is detected in all cases in particular by the presence of two singlets in ^1H NMR at 4.3–4.4 ppm and 4.6–4.7 ppm. The grafting of the amines induces a deshielding of the signal in ^{31}P NMR, on going from the $P(S)Cl_2$ terminations ($\delta = 62–63$ ppm) to the $P(S)(NHR)_2$ terminations ($\delta = 69–70$ ppm). The grafting of the carboxylate is mainly demonstrated by the disappearance of the aldehyde signal in ^1H NMR ($\delta = 9.9$ ppm) on behalf of the appearance of two doublets ($^3J_{HH} = 15.9$ Hz) corresponding to the AB system generated by the $Ar{-}\underline{H}C{=}C\underline{H}{-}CO_2H$ linkage.

2.2. *Ferrocenes in the branches of water-soluble dendrimers*

2.2.1. *Synthesis of the difunctional ferrocene building block*

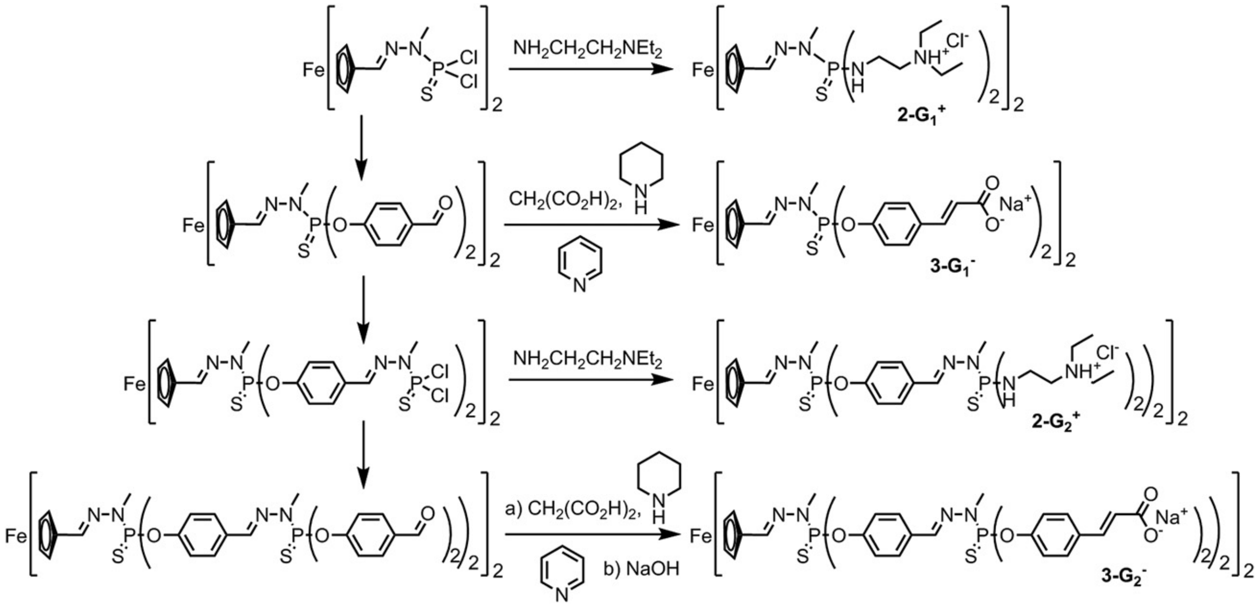
One of the main building blocks when synthesizing phosphorus dendrimers is hydroxybenzaldehyde. Thus the easiest way to incorporate a precise function (such as a ferrocene) in the branches of these dendrimers consists in synthesizing an analog of hydroxybenzaldehyde, it means a compound having both a phenol and an aldehyde. We have already used a chiral ferrocene possessing both functions for studying the influence of the branches on the chirality, depending on the location of the ferrocene [19], and also a phenol directly linked to the cyclopentadienyl (Cp) ring [15]. We report here the synthesis of a new ferrocene derivative in which the phenol group is linked to the Cp ring via a CH_2 linkage, to ensure a greater flexibility.

The synthetic route to the difunctional ferrocene requires five steps from the commercially available ferrocenecarboxaldehyde **4**. The first step is the stannylation reaction of **4** which was carried out as published to afford **5** [20] with a selectivity of 95% to the 1′ position. The second step is a nucleophilic attack of lithiated bromoanisole on the carbonyl, which affords the ferrocene **6**. The third step is the reduction of the alcohol of **6** with BH_3,SMe_2 [21] or $TiCl_4/NaB(CN)H_3$ [22] to afford the ferrocene **7**. The fourth step is the substitution of the tributylstannyl group with nBuLi/DMF which leads to ferrocene **8**. The fifth and last step has to be carried out directly afterwards as **8** is not sufficiently stable for long term storage. This last step is the deprotection of the methoxy group with BBr_3, to afford the desired difunctional ferrocene **9** (Scheme 2) [23]. The overall yield for the synthesis of **9** is 17% from commercially available ferrocenecarboxaldehyde.

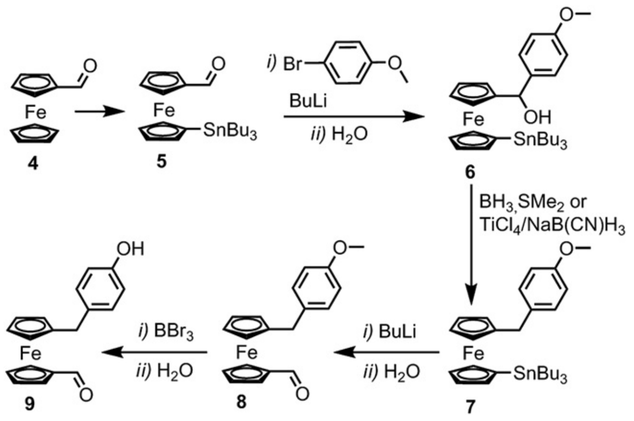
The structure of compound **9** has been confirmed by X-ray diffraction analysis on single crystals. The molecule displays a Z-like shape with the two Cp rings being slightly staggered with a twist angle of 12.8(2)° (Fig. 1). The two Cp rings are nearly parallel to each other with a centroid–Fe1–centroid angle of 178.23(3)°. The phenyl ring is exo with respect to the Cp ring to which it is attached and makes a dihedral angle of 85.57(16)° with it. The most interesting feature of the structure is the occurrence of the O–H…O hydrogen bond [O–H = 0.82 Å, H…O = 1.89 Å, O…O = 2.698(4) Å and O–H…O = 171.3°] between the hydroxyl O atom and the O atom of the aldehyde group of the symmetry related molecule ($-x + 1/2$, $y + 1/2$, $-z + 1/2$). These hydrogen bonds build up a zigzag-like chain developing parallel to the *b* axis (Fig. 2).

2.2.2. *Ferrocenes in the branches of dendrimers*

Despite the relatively low yield of the ferrocene **9**, the sodium salt of this compound was used for the grafting on the surface of a second generation dendrimer having $P(S)Cl_2$ terminations and built from cyclotriphosphazene as core (**10-G$_2$**) [24]. A small excess of ferrocene derivative was used, which was removed and recycled. The resulting dendrimer ended by ferrocene carbaldehyde $\mathbf{11-G_2'}$ was isolated in 74% yield after work-up. This dendrimer, as well as



Scheme 1. Synthesis of water-soluble dendrimers having a ferrocene as core.



Scheme 2. Synthesis of a difunctional ferrocene.

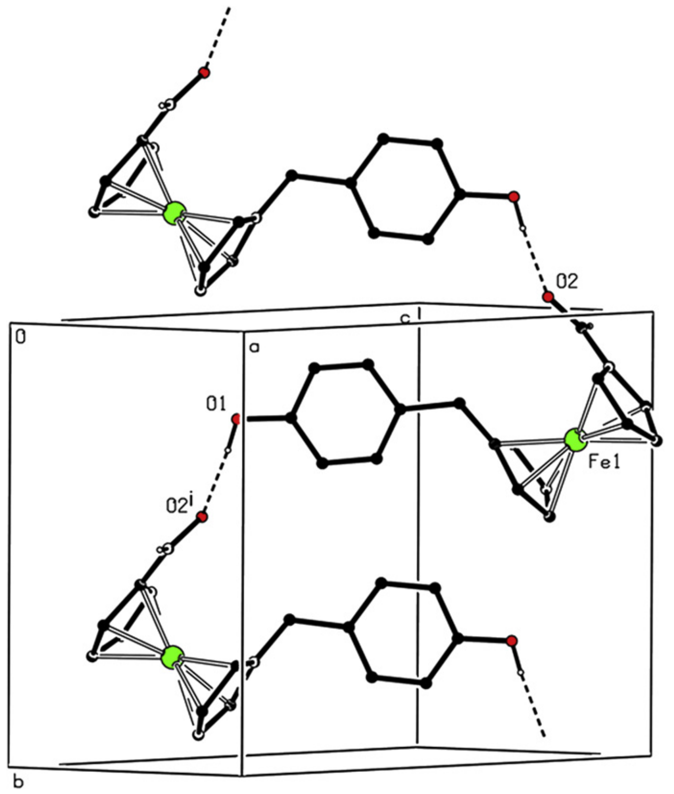


Fig. 2. Partial packing view showing the formation of the like zigzag chain through O—H…O hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted for clarity.

all the following ones, has 24 ferrocenes in its structure. In order to graft the same type of terminal groups to this dendrimer than in the case of the dendrimers having ferrocene as core, we needed first to have $P(S)Cl_2$, then hydroxybenzaldehyde as terminal groups. Thus, the next step consisted in reacting $H_2NNMeP(S)Cl_2$ for the condensation with the aldehydes of $\mathbf{11}-\mathbf{G}'_2$, to afford the dendrimer **11**-$\mathbf{G_3}$, ended by $P(S)Cl_2$ functions. Hydroxybenzaldehyde was then reacted in the presence of Cs_2CO_3, to afford dendrimer $\mathbf{11}-\mathbf{G}'_3$. Dendrimer **11**-$\mathbf{G_3}$ was also used for the reaction with N,N-diethylethylenediamine, which afforded the positively charged dendrimer **12**-$\mathbf{G}_3^+$. As in the case of the reaction **1**-$\mathbf{G_n}$ → **2**-$\mathbf{G}_n^+$, the reaction **11**-$\mathbf{G_3}$ → **12**-$\mathbf{G}_3^+$ is monitored by ^{31}P NMR, which displays the deshielding of the signal corresponding to the most external P(S) groups from 63.0 ppm to 69.5 ppm. Dendrimer **13**-$\mathbf{G}_3^-$ ended by carboxylate groups was also synthesized as previously, from dendrimer $\mathbf{11}-\mathbf{G}'_3$, using malonic acid (Scheme 3). Here also, the obtaining of dendrimer **13**-$\mathbf{G}_3^-$ is confirmed by the disappearance of the signal corresponding to the aldehydes, on behalf of the appearance of the system of two doublets due to the $Ar{-}\underline{H}C{=}C\underline{H}{-}CO_2H$ linkage in ^1H NMR.

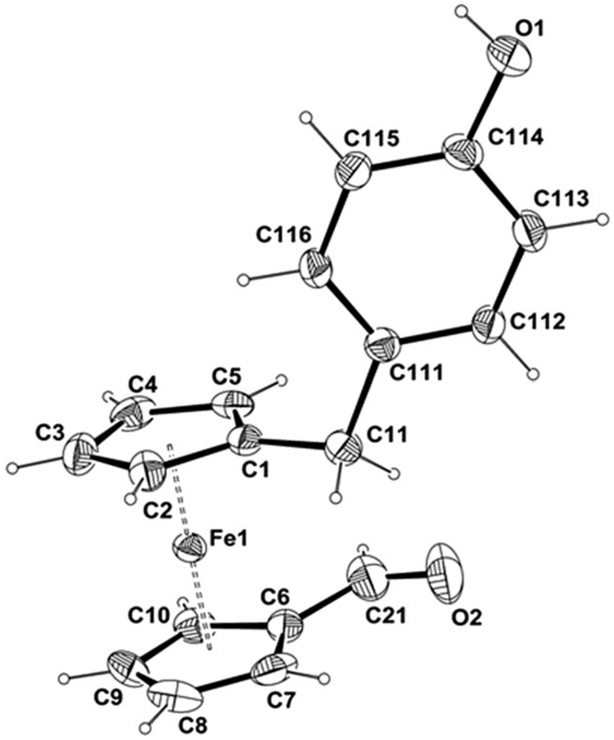


Fig. 1. Molecular view of compound **9**. Ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

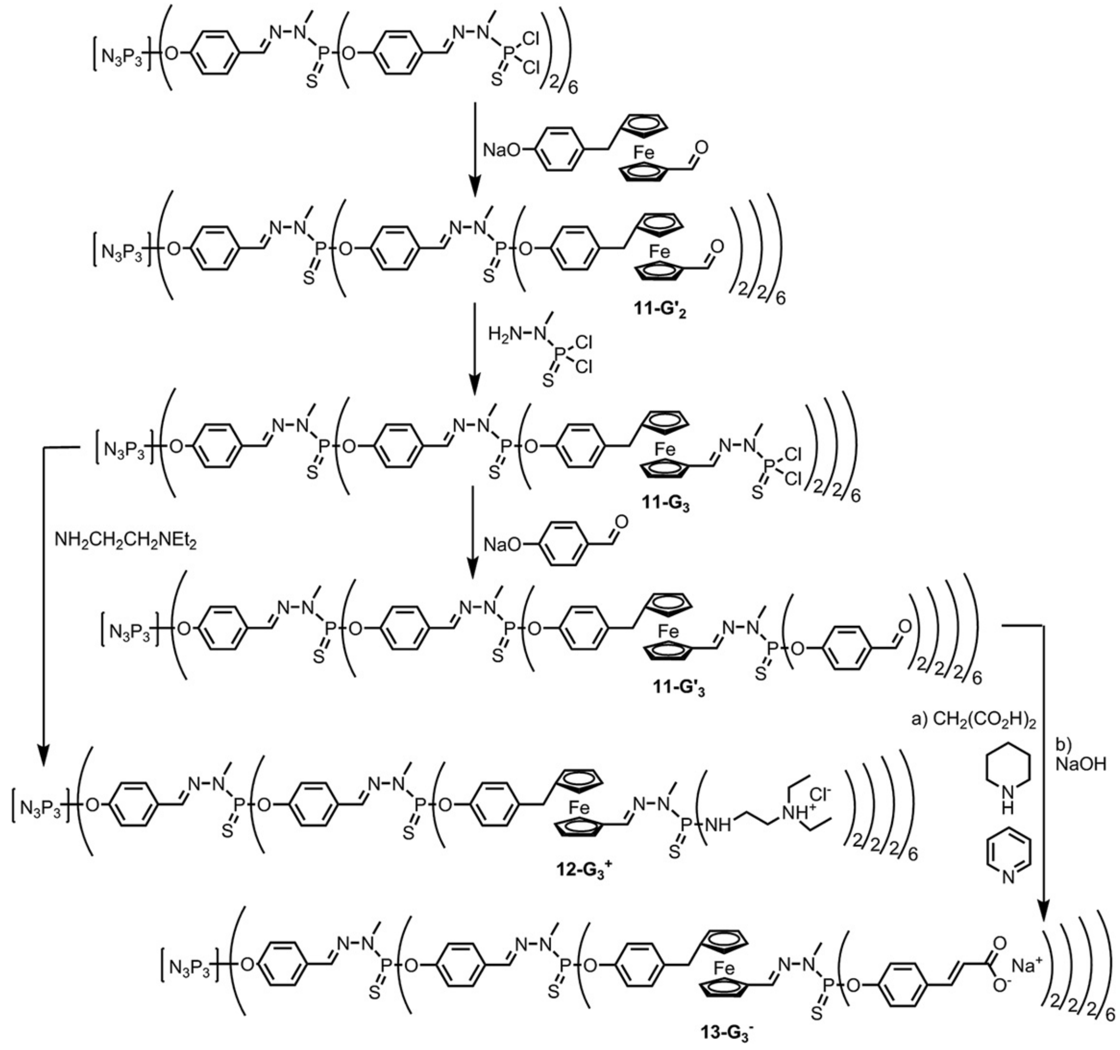
2.3. Preliminary electrochemical studies

We intended to study the dendrimers by Cyclic Voltammetry (CV) in water containing KCl as supporting electrolyte, but we observed a massive adsorption of the multicharged dendrimers onto the electrode. We tried to optimize the experiments on the small dendrimer **3**-$\mathbf{G}_1^-$. Fig. 3A displays the results of CV experiments on Gold, Glassy Carbon, and Platinum electrodes. The apparent larger resistivity of the solution observed in the case of the Au electrode is due to an important adsorption of **3**-$\mathbf{G}_1^-$ onto this electrode. As the adsorption is lower on the Pt electrode, the next experiments were all carried out with Pt electrodes. Cyclic voltammograms of dendrimer **3**-$\mathbf{G}_1^-$ in aqueous solution (see Fig. 3B) exhibit a single electrochemical process at +0.35 V/SCE attributed to ferrocene moiety [25].

Subsequently, the influence of the potential scan rate on the cyclic voltammograms was studied. The ratio between reduction peak current and oxidation peak current almost equals unity and anodic peak potential is independent of the logarithm of the scan rate; this confirms that the electrochemical oxidation process is reversible. The anodic peak intensity is correlated with the potential scanning rate (Fig. 4) by the following relationship (Randles–Sevcik equation) [26], valid for reversible systems:

$$I_\mathrm{p} = -0.4463nFSC\sqrt{\frac{nFD}{RT}\sqrt{\nu}}$$

where S is the electrode area (cm^2); C is the solute (dendrimer) concentration ($mol\ cm^{-3}$); D is the diffusion coefficient ($cm^2\ s^{-1}$); F



Scheme 3. Synthesis of water-soluble dendrimers having one layer of ferrocenes in the branches.

is the faraday (96,500 C); n is the number of exchanged electrons; v is the potential scanning rate (V s^{-1}) and T is the absolute temperature (K).

The dendrimer displays a linear relationship between peak current and the square root of the scan rate, which indicates a diffusion controlled process. In this condition, taking $n = 1$, we can deduce the diffusion coefficient [26,27] of **3-G_1^-** that is found to be equal to $5.6 \times 10^{-7} \pm 1 \times 10^{-7}$ cm^2 s^{-1}. Assuming the dendrimers adopt a spherical shape, the Stokes–Einstein relation provides the dendrimer radius: $D = k_BT/6\pi\eta r$, with k_B being the Boltzmann

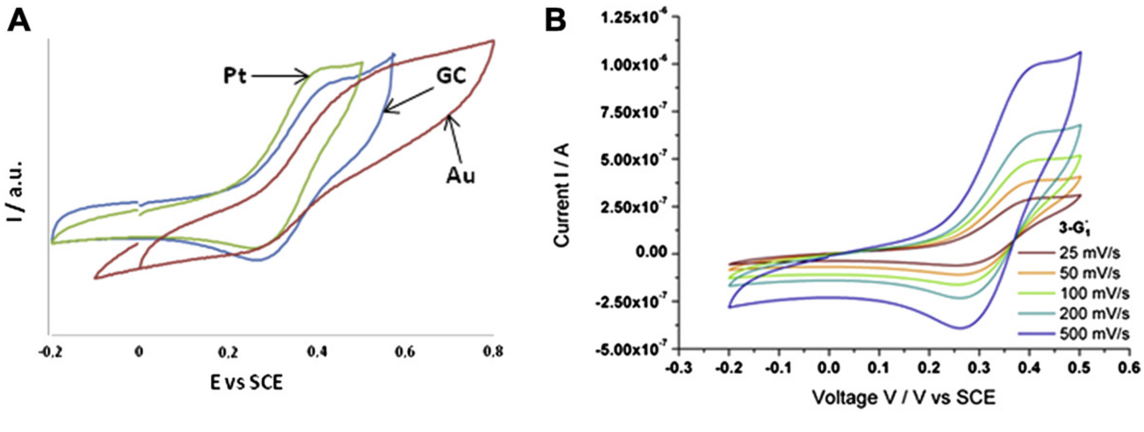


Fig. 3. A) Cyclic voltammograms of the **3-G_1^-** dendrimer in water with KCl as supporting electrolyte at 0.1 V s^{-1} at 23 ± 1 °C, on Pt electrode (Pt, $r = 0.25$ mm) (green line), on Glassy carbon electrode (GC, $r = 0.5$ mm) (blue line), on gold electrode (Au, $r = 10.12$ mm) (red line). B) Cyclic voltammograms of the **3-G_1^-** dendrimer that bear a ferrocene at the core on Pt microelectrode ($r = 0.25$ mm) in water with KCl as supporting electrolyte at different scan rate at 23 ± 1 °C. (For interpretation of color referred in this figure legend, the reader is referred to web version of the article.)

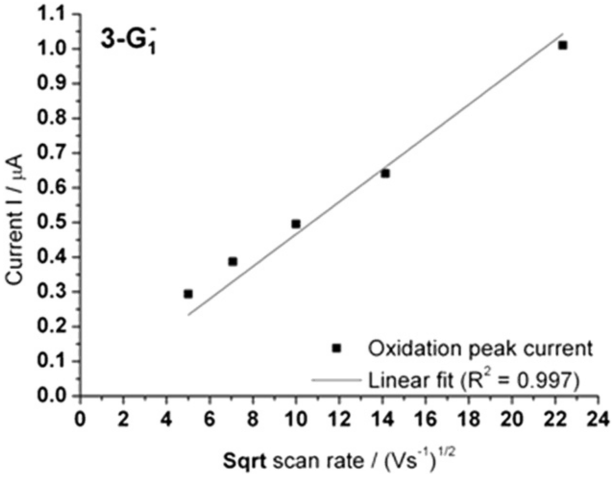


Fig. 4. Oxidation peak current of **3-G$_1^-$** plotted against the square root of the scan rate (**3-G$_1^-$** dendrimer (5×10^{-3} mol L^{-1}) on Pt microelectrode ($r = 0.5$ mm) in water with KCl as supporting electrolyte at different scan rates at 23 ± 1 °C).

constant, T the absolute temperature, η the solution viscosity and r the dendrimer radius. The diffusion coefficient D in water is 5.6×10^{-7} cm^2 s^{-1}, and the radius deduced from this value is 4 ± 2 nm (expected 2.5 nm).

The electrochemical behavior of the corresponding second generation dendrimers (**2-G$_2^+$** and **3-G$_2^-$**) was also studied. In both cases the oxidation was found not reversible, due to a high adsorption onto the electrodes, and presumably to the oxidation of the organic moieties of the dendrimer, inducing a drift of the current. In the case of dendrimers **12-G$_3^+$** and **13-G$_3^-$**, their solubility in the conditions used was not high enough to study their electrochemical behavior.

3. Conclusion

We have used two different types of difunctionalized ferrocenes for the synthesis of water-soluble Poly(PhosphorHydrazone) (PPH) dendrimers. The first one (ferrocene dicarbaldehyde) has two identical functions, and was used as core of the dendrimers. The second one was especially engineered to have two different functions (phenol and aldehyde) usable to be introduced in the branches of the dendrimers. All the water-soluble dendrimeric ferrocenes that we have synthesized possess a hydrophobic interior and a hydrophilic external layer. We have already demonstrated that other dendrimers having these properties are shrunk in water [18]. The consequence here is that it is difficult to perform electrochemical experiments, and only the smaller compound **3-G$_1^-$** affords a clean electrochemical response. When the dendrimers are larger, the ferrocene is buried inside the organic (hydrophobic) layer and cannot access easily to the electrode. The dendrimer ended by carboxylates **3-G$_1^-$** is practically non-aggregated in water, as shown by the measurement of the diffusion constant by electrochemistry. This might be related to the percentage of charged end groups at pH ~ 6 (more than 90% of charged terminal groups in the case of carboxylic acids), as measured for other dendrimers having the same terminal groups than here [28].

4. Experimental

All reactions are carried out under argon atmosphere and in freshly distilled solvents. All water used is demineralised using MilliQ equipment and the resistivity was 18 MΩ cm. All purifications by column chromatography were carried out with silicagel 60 as the static phase. All starting compounds were purchased from Aldrich, Merck or Fluka and used as received. Compounds **1-G$_1$**, **1 − G$_1'$**, **1-G$_2$**, **1 − G$_2'$** [15], **5** [20], and **10-G$_2$** [24] were synthesized as published. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and two-dimensional NMR spectra were recorded on a Bruker 300 (DPX300) and 200 (AC200) MHz spectrometers. Chemical shifts are reported in ppm relative to external standards (TMS for ^{1}H and ^{13}C and 85% H_3PO_4 for ^{31}P) and coupling constants are given in Hz. The numbering used for NMR assignment is shown in Fig. 5. Mass spectrometry experiments did not afford accurate information about the structure of these dendrimers, due to fragmentation and rearrangements [29].

4.1. Dendrimer *2-G$_1^+$*

A solution of 600 mg of dendrimer **1-G$_1$** (1.06 mmol, 1.0 eq) in 10 mL THF was cooled to 0 °C and to this 596 μL of N,N-diethylethylenediamine (4.24 mmol, 4.0 eq) was added dropwise. The reaction mixture was kept stirring overnight at room temperature. The solvent was evaporated and after two washing steps with ether, 472 mg (459 μmol, 43%) of dendrimer **2-G$_1^+$** was obtained as an orange powder.

^{1}H NMR (300 MHz, CD_3OD): 1.32 (m, 24H, N–CH$_2$–*CH$_3$*), 3.21 (m, 32H, CH$_2$), 3.35 (d, $^3J_{HP} = 10.2$ Hz, 6H, P$_1$–N–CH$_3$), 4.36 (s, 4H, Cp), 4.75 (s, 4H, Cp), 7.6 (s, 2H, CH=N–N–P$_1$). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): 69.8 (s, P$_1$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_3OD): 8.3 (N–CH$_2$*CH$_3$*), 31.2 (d, $^2J_{CP} = 9.9$ Hz, P$_1$–N–CH$_3$), 36.6 (CH$_2$–N–P$_1$), 49.2 (N*CH$_2$*CH$_3$) (CD_3OD), 52.6 (d, $^3J_{CP} = 6.6$ Hz, P$_1$–N–CH$_2$*CH$_2$*), 68.1 (Cp), 70.5 (Cp), 82.3 (Cp^{quat}), 138.8 (d, $^3J_{CP} = 14.1$ Hz, CH=N–N–P$_1$).

4.2. Dendrimer *2-G$_2^+$*

To a solution of 720 mg of dendrimer **1-G$_2$** (465 μmol, 1.0 eq) in 20 mL THF was added 523 μL of N,N-diethylethylenediamine (3.72 mmol, 8.0 eq) at 0 °C. This solution was kept stirring overnight at room temperature. The solvent volume was reduced and the dendrimer was precipitated from ether and washed several times with ether. A 1.00 g (403 μmol, 87%) of dendrimer **2-G$_2^+$** was obtained as an orange powder.

^{1}H NMR (300 MHz, CD_3OD): 1.31 (m, 48H, N–CH$_2$*CH$_3$*), 3.26 (d, $^3J_{HP} = 7.8$ Hz, 18H, P$_{1,2}$–N–CH$_3$), 3.33 (m, 64H, CH$_2$), 4.41 (s, 4H, Cp), 4.70 (s, 4H, Cp), 7.28 (d, $^3J_{HH} = 8.1$ Hz, 8H, CHarom), 7.65 (s, 2H,

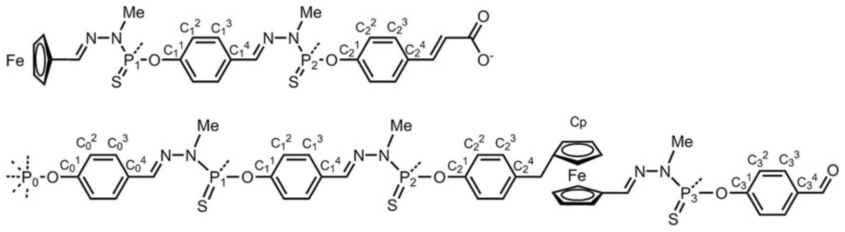


Fig. 5. Numbering used for NMR assignments.

$CH{=}N{-}N{-}P_1$), 7.74 (s, 4H, $CH{=}N{-}N{-}P_2$), 7.86 (d, $^3J_{HH} = 8.1$ Hz, 8H, CHarom.). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3OD): 62.4 (s, P_1), 70.2 (s, P_2). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3OD): 7.9 ($N{-}CH_2CH_3$), 31.1 (d, $^2J_{CP} = 10.0$ Hz, $P_{1,2}{-}N{-}CH_3$), 36.2 ($CH_2{-}N{-}P_2$), 49.6 ($N{-}CH_2CH_3$), 52.2 (d, $^3J_{CP} = 6.9$ Hz, $P_2{-}N{-}CH_2CH_2$), 68.5 (Cp), 71.1 (Cp), 81.2 (Cp^{quat}), 121.3 (d, $^3J_{CP\text{-}1} = 5.1$ Hz, C_1^2), 127.8 (C_1^3), 133.2 (C_1^4), 137.5 (d, $^3J_{CP} = 12.5$ Hz, $CH{=}N{-}N{-}P_1$), 151.1 (d, $^2J_{CP} = 6.9$ Hz, C_1^1).

4.3. Dendrimer **3-G_1^-**

A mixture of 486 mg of dendrimer **1** – $\mathbf{G_1'}$ (537 μmol, 1.0 eq), 895 mg of malonic acid (8.6 mmol, 16 eq) and 45 μL of piperidine (freshly distilled over CaH_2) were dissolved in 30 mL pyridine (freshly distilled over CaH_2) and kept under stirring overnight at 95 °C. The reaction mixture was refluxed for 15 min and precipitated with 37% HCl (in the dark). The precipitate was washed several times with water and ether and subsequently freeze-dried. The dendrimer was turned into a sodium salt with 9.08 mL of aqueous NaOH (0.1996 M, 4 eq). This quantitatively yielded 624 mg of dendrimer **3-G_1^-** as a dark red powder.

^1H NMR (300 MHz, DMSO-d_6): 3.22 (d, $^3J_{HP} = 11.4$ Hz, 6H, $P_1{-}N{-}CH_3$), 4.29 (s, 4H, Cp), 4.55 (s, 4H, Cp), 6.48 (d, $^3J_{HH} = 15.9$ Hz, 4H, $CH{=}CH$), 7.23 (d, $^3J_{HH} = 7.9$ Hz, 8H, CHarom.), 7.58 (d, $^3J_{HH} = 15.9$ Hz, 6H, $CH{=}CH$ and $CH{=}N{-}N{-}P_1$), 7.77 (d, $^3J_{HH} = 7.9$ Hz, 8H, CHarom.). $^{31}P\{^1H\}$ NMR (121.5 MHz, DMSO-d6): 61.5 (s, P_1). $^{13}C\{^1H\}$ NMR (75.5 MHz, DMSO-d_6): 33.2 (d, $^2J_{CP} = 12.3$ Hz, $P_1{-}N{-}CH_3$), 68.8 (Cp), 71.7 (Cp), 81.1 (Cp^{quat}), 119.8 ($Ar{-}CH{=}CH$), 121.7 (d, $^3J_{CP} = 5.1$ Hz, C_1^2), 130.3 (C_1^3), 132.1 (C_1^4), 142.2 ($CH{=}N{-}N{-}P_1$), 143.2 ($CH{=}CH{-}COOH$), 151.8 (d, $^2J_{CP} = 6.7$ Hz, C_1^1), 167.9 (COO).

4.4. Dendrimer **3-G_2^-**

In 50 mL of pyridine (freshly distilled over CaH_2) were dissolved 750 mg of dendrimer **1** – $\mathbf{G_2'}$ (335 μmol, 1.0 eq), 558 mg of malonic acid (5.36 mmol, 16 eq) and 70 μL of piperidine (freshly distilled over CaH_2). This solution was stirred overnight at 95 °C. The mixture was refluxed for 15 min; the dendrimers were precipitated from 37% HCl and washed several times with water and ether. The dendrimers were transformed into their sodium salt analog by means of ion exchange with 13.5 mL of NaOH (0.1996 M, 2.70 mmol, 8 eq), which yielded 868 mg (338 μmol, 100%) of dendrimer **3-G_2^-** as an orange powder.

^1H NMR (300 MHz, DMSO-d_6): 3.23 (d, $^3J_{HP} = 10.8$ Hz, 6H, $P_1{-}N{-}CH_3$), 3.31 (d, $^3J_{HP} = 10.5$ Hz, 12H, $P_2{-}N{-}CH_3$), 4.28 (s, 4H, Cp), 4.58 (s, 4H, Cp), 6.45 (d, $^3J_{HH} = 15.9$ Hz, 8H, $CH{=}CH$), 7.22 (m, 24H, CHarom.), 7.53 (d, $^3J_{HH} = 15.9$ Hz, 8H, $CH{=}CH$), 7.68 (m, 24H, CHarom.), 7.93 (s, 6H, $CH{=}N{-}N{-}P_{1,2}$). $^{31}P\{^1H\}$ NMR (121.5 MHz, DMSO-d_6): 61.8 (2s, $P_{1,2}$). $^{13}C\{^1H\}$ NMR (75.5 MHz, DMSO-d_6): 33.2 (d, $^2J_{CP} = 12.4$ Hz, $P_1{-}N{-}CH_3$), 33.4 (d, $^2J_{CP} = 12.2$ Hz, $P_2{-}N{-}CH_3$), 68.7 (Cp), 71.7 (Cp), 81.2 (Cp^{quat}), 120.0 (C_1^2), 121.8 (d, $^3J_{CP} = 3.2$ Hz, C_2^2), 128.8 (C_1^3), 130.3 (C_2^3), 132.2 (C_2^4), 132.4 (C_1^4), 141.3 (d, $^3J_{CP} = 16.4$ Hz, $CH{=}N{-}N{-}P_{1,2}$), 143.0 ($CH{=}CH{-}COOH$), 151.3 (d, $^2J_{CP} = 6.6$ Hz, C_2^1), 151.6 (d, $^2J_{CP} = 4.8$ Hz, C_1^1), 168.0 (COO).

4.5. (4-Methoxyphenyl)-(1′-tributylstannylferrocenyl)-methanol **6**

In a Schlenk tube, a solution of 325 μL of bromoanisole (2.6 mmol) in 7.5 mL of THF was cooled down to −64 °C. To this solution, 1.5 mL of a *n*-butyl lithium solution (1.6 M in pentane, 2.4 mmol) were slowly added and the mixture was stirred for 1 h at this temperature. At −64 °C a 20 mL THF solution containing 1.19 g of ferrocene **5** (2.36 mmol) was added. This mixture was stirred for 15 min at −64 °C and was allowed to stir for 2 h at room temperature. The THF was evaporated and the product was dissolved in DCM and washed several times with distilled water till both phases were clear. The organic phase was dried over Na_2SO_4 and evaporated. The crude material was purified by column chromatography (several percent of ethyl acetate in hexane, increasing to 10%, with few drops of triethylamine) yielding 1.04 g of compound **6** as an orange oil (1.70 mmol, 72%).

^1H NMR (250 MHz, $CDCl_3$): 0.9–1.1 (m, 9H, $SnBu_3$), 1.6–1.1 (m, 18H, $SnBu_3$), 2.51 (d, $J = 2.7$ Hz, 1H, OH), 3.78 (s, 3H, OMe), 4.09 (m, 1H, Cp), 4.12 (s, 4H, Cp), 4.24 (t, $J = 1.6$ Hz, 1H, Cp), 4.40 (t, $J = 1$ Hz, 2H, Cp), 5.45 (d, $J = 2.7$ Hz, 1H, CH–O), 6.86 (m, 2H, CHarom), 7.31 (m, 2H, CHarom). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$): 10.3 (satellites: two doublets, $J119_{Sn}{-}13_C = 348$ Hz and $J117_{Sn}{-}13_C = 332$ Hz, $SnBu_3$), 13.9 ($SnBu_3$), 27.5 (satellites: two doublets, $J119_{Sn}{-}13_C = 58$ Hz and $J117_{Sn}{-}13_C = 55$ Hz, $SnBu_3$), 29.3 (satellites: one doublet, $J_{Sn}{-}13_C = 20$ Hz $SnBu_3$), 55.2 (OCH_3), 65.8 (quat Cp), 67.4 (Cp), 68.15 (Cp), 68.19 (Cp), 69.6 (satellites: two doublets, $J119_{Sn}{-}13_C = 394$ Hz and $J117_{Sn}{-}13_C = 377$ Hz, quat Cp), 71.01 (satellites: one doublet, $J_{Sn}{-}13_C = 33$ Hz, Cp), 70.98 (satellites: one doublet, $J_{Sn}{-}13_C = 33$ Hz, Cp), 71.9 (Cp), 74.92 (satellites: one doublet, $J_{Sn}{-}13_C = 41$ Hz, Cp), 74.95 (satellites: one doublet, $J_{Sn}{-}13_C = 41$ Hz, Cp),94.0 (CHOH), 113.8 (Ph), 127.6 (Ph)), 135.8 (quat Ph), 158.9 (quat Ph). $^{117}Sn\{^1H\}$ NMR ($CDCl_3$): −18.5. MS (DCI, NH_3): 611 (13%, M), 595 (100%, M−OH).

4.6. (4-Methoxyphenyl)-(1′-tributylstannylferrocenyl)-methane **7**

4.6.1. Method A

In a Schlenk tube, a 25 mL THF solution of compound **6** (3.91 mmol, 1.0 eq) was preheated to 90 °C to reflux conditions before 3.91 mL of a borane dimethylsulfide complex (1.0 M in DCM, 3.91 mmol, 1.0 eq) were added. The mixture was refluxed for 30 min and directly quenched with water. The product was extracted with pentane and the organic phase was dried over $MgSO_4$. The product was further purified on column chromatography using pentane as eluent. This procedure yielded 1.68 g of product **7** (2.83 mmol, 73%) as a red oil.

4.6.2. Method B

In a Schlenk tube, to 3 mL of THF, at 0 °C, were added 65 μl of titanium tetrachloride (0.6 mmol, 1 eq) and 189 mg of sodium cyanoborohydride (3 mmol, 5 eq). The reaction mixture, initially black, is kept stirring at 0 °C during 30 min to become gradually a clear yellow solution. To this solution was added a solution of 370 mg of compound **6** in 3 mL THF (0.6 mmol, 1.0 eq). After 5 min stirring at 0 °C, 50 mL of a 2 N aqueous ammonia solution was added. The reaction mixture was filtered on Büchner, washed three times with sodium hydroxide 2 N aqueous solution, then dried over Na_2SO_4 and evaporated to yield a yellow oil (370 mg). The product was further purified on silicagel by flash chromatography using a pentane/ether mixture (99/1) as eluent. This procedure yielded 0.329 g of product **7** (0.55 mmol, 92%) as a red oil.

^1H NMR (250 MHz, $CDCl_3$): 0.9–1.7 (m, 21H, $SnBu_3$), 1.74 (m, 6H, $SnBu_3$), 3.63 (s, 2H, CH_2), 3.77 (s, 3H, OMe), 3.97 (t, $J = 1.6$ Hz, 2H, Cp), 4.04–4.00 (s, 4H, Cp), 4.29 (t, $J = 1.6$ Hz, 1H, Cp), 6.80 (d, $J = 8.6$ Hz, 2H, CHarom), 7.09 (d, $J = 8.6$ Hz, 2H, CHarom). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$): 10.2 (satellites: two doublets, $J119_{Sn}{-}13_C = 347$ Hz and $J117_{Sn}{-}13_C = 332$ Hz, $SnBu_3$), 13.7 ($SnBu_3$), 27.4 (satellites: one doublets, $J_{Sn}{-}13_C = 57$ Hz, $SnBu_3$), 29.2 (satellites: one doublet, $J_{Sn}{-}13_C = 18.3$ Hz $SnBu_3$), 35.3 (CH_2), 55.2 (OCH_3), 67.5 (Cp), 68.5 (Cp), 68.7 (quat Cp), 71.3 (satellites: one doublet, $J_{Sn}{-}13_C = 34.6$ Hz, Cp), 75.0 (satellites: one doublet, J_{Sn}-$13_C = 42.2$ Hz, Cp), 88.1 (quat Cp), 113.3 (Ph), 129.2 (Ph), 133.9 (quat Ph), 157.8 (quat Ph). $^{117}Sn\{^1H\}$ NMR ($CDCl_3$): −18.3. MS (DCI, CH_4): 596 (100%, M + 1).

4.7. 1′-[(4-Methoxyphenyl)methyl]ferrocenecarboxaldehyde ***8***

In a Schlenk tube, a 20 mL THF solution of 0.84 g of compound **7** (1.41 mmol, 1.0 eq) was cooled to −78 °C before 791 μL of a *n*-butyl lithium solution (2.5 M in hexane, 1.98 mmol, 1.4 eq) were added. This mixture was stirred for 15 min at this temperature, and subsequently for 1 h at room temperature. Then it was cooled again to −78 °C and 593 μL of freshly distilled (on CaH_2) DMF (7.045 mmol, 5.5 eq) was added. This mixture was stirred at this temperature for 15 min and then stirred at room temperature overnight. The reaction was quenched by the addition of water followed by extraction with ether, washing with brine and drying on Na_2SO_4. After column purification (up to 30% ether in hexane) the product **8** was yielded as 0.363 g (1.09 mmol, 77%) of a red oil.

^{1}H NMR (250 MHz, $CDCl_3$): 3.52 (s, 2H, CH_2), 3.76 (s, 3H, OMe), 4.18 (m, 4H, Cp), 4.55 (t, J = 1.9 Hz, 2H, Cp), 4.73 (t, J = 1.9 Hz, 2H, Cp), 6.79 (m, 2H, CHarom), 7.05 (m, 2H, CHarom), 9.90 (s, 1H, CHO). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$): 34.4 (CH_2), 55.2 (OCH_3), 69.2 (Cp), 70.1 (Cp), 70.2 (Cp), 74.0 (Cp), 79.6 (quat Cp), 90.6 (quat Cp), 113.8 (Ph), 129.2 (Ph), 133.0 (quat Ph), 158.0 (quat Ph), 193.5 (CHO). MS (DCI, NH_3): 335 (100%, M + 1).

4.8. 1′-[(4-Hydroxyphenyl)methyl]ferrocenecarboxaldehyde ***9***

In a Schlenk tube, a 6 mL DCM solution of 207 mg of compound **8** (622 μmol, 1.0 eq) was cooled to −78 °C and 2.2 mL of boron tribromide (1.0 M in DCM, 2.2 mmol, 3.5 eq) were added. The reaction was stirred at room temperature and in the dark for 45 min. The reaction mixture was added to vigorously stirred ice water and stirred for 15 min. The product was extracted with DCM, washed three times with an aqueous 1.0 M $Na_2S_2O_3$ solution, three times with brine and finally dried over Na_2SO_4. After column chromatography (30% ether in pentane) the product **9** was yielded as a red powder (143 mg, 447 μmol, 72%). Monocrystals of **9** suitable for X-ray diffraction analysis have been obtained by slow diffusion of hexane in a dichloromethane solution of **9**.

^{1}H NMR (250 MHz, $CDCl_3$): 3.51 (s, 2H, CH_2), 4.18 (m, 4H, Cp), 4.55 (t, J = 1.9 Hz, 2H, Cp), 4.73 (t, J = 1.9 Hz, 2H, Cp), 6.72 (d, J = 8.5 Hz, 2H, CHarom), 6.99 (d, J = 8.5 Hz, 2H, CHarom), 9.90 (s, 1H, CHO). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$): 34.4 (CH_2), 69.1 (Cp), 70.1 (Cp), 70.2 (Cp), 73.8 (Cp), 80.5 (quat Cp), 91.2 (quat Cp), 115.2 (Ph), 129.5 (Ph), 132.4 (quat Ph), 155.9 (quat Ph), 193.5 (CHO). MS (DCI, NH_3): 321 (100%, M + 1).

4.9. Dendrimer **11** − $\mathbf{G}_2'$

To a suspension of 5.1 mg of NaH (215 μmol, 27 eq) in 5 mL of THF, a solution of 71.5 mg of compound **9** (223 μmol, 28 eq) in 5 mL THF was added at 0 °C. This mixture was stirred for 1 h at room temperature. Subsequently it was cooled again to 0 °C and a 5 ml THF solution of **10-G$_2$** (7.69 μmol, 1.0 eq) was added. The reaction was stirred overnight at room temperature. The solution volume was reduced and the dendrimer was precipitated from ether/pentane (1:3). A 66 mg (5.69 μmol, 74%) of dendrimer **11** − $\mathbf{G}_2'$ were obtained as an orange powder.

^{1}H NMR (300 MHz, $CDCl_3$): 3.22 (m, 54H, $P_{1,2}$—N—CH_3), 3.49 (s, 48H, CH_2Fc), 4.13 (s, 96H, Cp), 4.49 (s, 48H, Cp), 4.68 (s, 48H, Cp), 6.92–7.61 (m, 186H, CHarom + CH═N), 9.86 (s, 24H, CHO). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): 8.4 (s, P_0), 62.6 (s, P_1), 62.9 (s, P_2). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): 33.1 (d, $^2J_{CP}$ = 12.3 Hz, CH_3—N—$P_{1,2}$), 34.6 (CH_2), 69.4 (Cp), 70.2 (Cp), 70.3 (Cp), 74.0 (Cp), 79.6 (Cp^{quat}), 89.5 (Cp^{quat}), 121.2 (d, $^3J_{CP\text{-}2}$ = 4.5 Hz, C_2^2), 121.8 ($C_{0,1}^2$), 128.3 ($C_{0,1}^3$), 129.3 (C_2^3), 132.2 (C_0^4), 132.4 (C_1^4), 138.1 (C_2^4), 138.6 (m, CH═N—N—$P_{1,2}$), 148.9 (d, $^2J_{CP\text{-}2}$ = 7.1 Hz, C_2^1), 151.2 ($C_{0,1}^1$), 193.4 (CHO).

4.10. Dendrimer ***11-G$_3$***

To a solution of 100 mg (8.6 μmol, 1.0 eq) of dendrimer **11** − $\mathbf{G}_2'$ in 8 mL of chloroform were added 0.9 mL of a 0.24 M solution of $H_2NNMePSCl_2$ (265 μmol, 25 eq). After 45 min the product was precipitated from pentane twice. A 128 mg (8.3 μmol, 96%) of dendrimer **11-G$_3$** were obtained as an orange powder.

^{1}H NMR (300 MHz, $CDCl_3$): 3.23 (s, 48H, CH_2Fc), 3.35 (d, $^3J_{HP}$ = 15 Hz, 72H, CH_3N—P_3), 3.51 (m, 54H, CH_3N—$P_{1,2}$), 4.05 (2s, 96H, Cp), 4.31 (s, 48H, Cp), 4.59 (s, 48H, Cp), 6.95–7.62 (m, 212H, CHarom. + CH═N). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): 8.6 (s, P_0), 62.3 (s, $P_{1,2}$), 63.0 (s, P_3). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): 32.1 (d, $^2J_{CP}$ = 12.5 Hz, CH_3—N—P_3), 33.1 (d, $^2J_{CP}$ = 12.6 Hz, CH_3—N—$P_{0,1}$), 34.9 (CH_2), 68.7 (Cp), 69.0 (Cp), 70.1 (Cp), 71.0 (Cp), 79.0 (Cp^{quat}), 88.6 (Cp^{quat}), 121.2 (d, $^3J_{CP\text{-}2}$ = 4.5 Hz, C_2^2), 121.8 ($C_{0,1}^2$), 128.3 ($C_{0,1}^3$), 129.3 (C_2^3), 132.2 (C_0^4), 132.4 (C_1^4), 138.5 (C_2^4), 143.6 (d, $^3J_{CP1,2,3}$ = 18.9 Hz, CH═N—N—$P_{1,2,3}$), 148.8 (d, $^2J_{CP2}$ = 6.8 Hz, C_2^1), 151.2 (d, $^2J_{CP\text{-}0,1}$ = 6.0 Hz, $C_{0,1}^1$).

4.11. Dendrimer **11** − $\mathbf{G}_3'$

A solution of 71 mg of dendrimer **11-G$_3$** (4.59 μmol, 1.0 eq), 27.8 mg of p-hydroxybenzaldehyde (228 μmol, 50 eq) and 149 mg of Cs_2CO_3 (457 μmol, 100 eq) in 5 mL of THF was stirred overnight at room temperature. The product was precipitated from pentane yielding 91 mg (4.65 μmol, 100%) of dendrimer **11** − $\mathbf{G}_3'$ as an orange powder.

^{1}H NMR (300 MHz, $CDCl_3$): 3.24–3.32 (2s + d, $^3J_{HP}$ = 15 Hz, 48H + 72H, CH_2Fc + CH_3N—P_3), 3.41 (m, 54H, CH_3N—$P_{1,2}$), 3.95 (s, 96H, Cp), 4.26 (s, 48H, Cp), 4.52 (s, 48H, Cp), 6.95–7.82 (m, 402H, CHarom. + CH═N), 9.86 (s, 48H, CHO). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): 8.36 (s, P_0), 59.9 (s, P_3), 62.5 (s, P_1), 63.0 (s, P_2). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): 32.9 (d, $^2J_{CP}$ = 13.5 Hz, CH_3N—$P_{1,2,3}$), 34.8 (CH_2), 68.3 (Cp), 68.9 (Cp) 69.9 (Cp), 70.8 (Cp), 79.7 (Cp^{quat}), 88.3 (Cp^{quat}), 121.2 (d, $^3J_{CP\text{-}0,1,2}$ = 4.2 Hz, $C_{0,1,2}^2$), 121.8 (d, $^3J_{CP\text{-}3}$ = 5.1 Hz, C_3^2), 128.3 ($C_{0,1}^3$), 129.3 (C_2^3), 131.4 (C_3^3), 132.2 (C_0^4), 132.5 (C_3^4), 133.5 (C_4^4), 138.4 (C_2^4), 141.4 (d, $^3J_{CP\text{-}1,2,3}$ = 13.5 Hz, CH═N—N—$P_{1,2,3}$), 148.8 (d, $^2J_{CP\text{-}2}$ = 6.9 Hz, C_2^1), 151.2 ($C_{0,1}^1$), 155.2 (d, $^2J_{CP\text{-}3}$ = 6.7 Hz, C_3^1), 190.7 (CHO).

4.12. Dendrimer ***12-G$_3^+$***

To a 5 mL THF solution of 47 mg of dendrimer **11-G$_3$** (3.69 μmol, 1.0 eq) were added 25.4 μL of N,N-diethylethylenediamine (177 μmol, 48 eq) at 0 °C. It was washed twice with dry THF (partly soluble). 37 mg (1.76 μmol, 48%) of dendrimer **12-G$_3^+$** were obtained as an orange solid.

^{1}H NMR (300 MHz, CD_3OD): 1.23 (m, 24H, N—CH_2—*CH_3*), 3.21 (m, 32H, CH_2), 3.23 (2s, 48H, CH_2Fc), 3.35 (d, $^3J_{HP}$ = 15 Hz, 72H, CH_3N—P_3), 3.51 (m, 54H, CH_3N—$P_{1,2}$), 4.02 (2s, 96H, Cp), 4.21 (s, 48H, Cp), 4.58 (s, 48H, Cp), 6.98–7.63 (m, 212H, CHarom. + CH═N). ^{31}P{^{1}H} NMR (121.5 MHz, CD_3OD): 8.6 (s, P_0), 61.3 (s, P_1), 62.7 (s, P_2), 69.5 (s, P_3). ^{13}C{^{1}H} NMR (75.5 MHz, CD_3OD): 9.0 (*CH_3*CH_2—N), 32.1 (d, $^2J_{CP}$ = 12.5 Hz, CH_3N—P_3), 33.1 (d, $^2J_{CP}$ = 12.6 Hz, CH_3—N—$P_{1,2}$), 34.9 (CH_2), 36.3 (*CH_2*—N—P_3), 49.6 (CH_3*CH_2*—N), 52.2 (d, $^3J_{CP}$ = 6.9 Hz, *CH_2*CH_2—N—P_3), 68.7 (Cp), 69.0 (Cp), 70.1 (Cp), 71.0 (Cp), 79.0 (Cp^{quat}), 87.6 (s, Cp^{quat}), 121.2 (d, $^3J_{CP\text{-}2}$ = 4.5 Hz, C_2^2), 121.8 ($C_{0,1}^2$), 128.3 ($C_{0,1}^3$), 129.3 (C_2^3), 132.2 (C_0^4), 132.4 (C_1^4), 138.5 (C_2^4), 143.6 (d, $^3J_{CP\text{-}1,2,3}$ = 18.9 Hz, CH═N—N—$P_{1,2,3}$), 148.8 (d, $^2J_{CP\text{-}2}$ = 6.8 Hz, C_2^1), 151.2 (d, $^2J_{CP\text{-}0,1}$ = 6.0 Hz, $C_{0,1}^1$).

4.13. Dendrimer ***13*** − $\boldsymbol{G_3^-}$

In 2 mL of freshly distilled (on CaH_2) pyridine were dissolved 60 mg of dendrimer **11** − $\mathbf{G}_3'$ (3.07 μmol, 1.0 eq), 32 mg of malonic acid (307 μmol, 100 eq) and 1.5 mL of piperidine (freshly distilled

Table 1
Crystal data and structure refinement for compound **9**.

Identification code	**9**
Empirical formula	$C_{18}H_{16}FeO_2$
Formula weight	320.16
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 7.5652(10)$ Å $\alpha = 90°$
	$b = 11.0984(11)$ Å $\beta = 92.875(16)°$
	$c = 17.134(2)$ Å $\gamma = 90°$
Volume	1436.8(3) Å^3
Z	4
Density (calculated)	1.480 Mg/m^3
Absorption coefficient	1.050 mm^{-1}
F(000)	664
Crystal size	$0.64 \times 0.45 \times 0.1$ mm^3
Theta range for data collection	2.19–26.06°
Index ranges	$-9 \le h \le 9, -13 \le k \le 13, -21 \le l \le 21$
Reflections collected	10,984
Independent reflections	2804 [R(int) = 0.0702]
Completeness to theta = 26.06°	98.6%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2804/0/191
Goodness-of-fit on F^2	0.832
Final R indices [$I > 2$sigma(I)]	$R1 = 0.0367$, w$R2 = 0.0720$
R indices (all data)	$R1 = 0.0706$, w$R2 = 0.0788$
Largest diff. peak and hole	0.390 and −0.333 e.Å^{-3}

over CaH_2) and stirred overnight at 95 °C. The reaction mixture was refluxed for 15 min to remove the CO_2 and precipitated from HCl (37%). The precipitate was washed three times with water and twice with ether before it was freeze-dried. Ion exchange with 579 μL (0.1996 M, 116 μmol, 48 eq) of NaOH yielded 27 mg of dendrimer **13**-$\mathbf{G_3^-}$ (1.19 μmol, 39%) as an orange powder.

^{1}H NMR (300 MHz, DMSO-d$_6$): 3.22–3.41 (m, 102H, CH_3N–$P_{1,2,3}$), 3.90 (s, 48H, Cp), 3.97 (s, 48H, Cp), 4.21 (s, 48H, Cp), 4.48 (s, 48H, Cp), 6.39 (d, $^3J_{HH} = 15.6$ Hz, 48H, *CH*=CH–COO), 7.39 (d, $^3J_{HH} = 15.6$ Hz, 48H, CH=*CH*–COO), 6.95–7.82 (m, 402H, CHarom + CH=N). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): 8.17 (s, P_0), 60.8 (s, P_1), 61.4 (s, P_3), 62.9 (s, P_2).

A ^{13}C NMR spectrum could not be taken due to a limited solubility and low concentration.

4.14. *Cyclic Voltammetry*

The CV measurements of dendrimer $\mathbf{3} - \mathbf{G_1^-}$ were carried out with an Autolab PGSTAT100 controlled by GPES 4.09 software and performed in a homemade three electrode cell. The reference electrode was a saturated calomel electrode, separated from the aqueous solution by a bridge compartment. The counter electrode was a platinum wire with an approximate surface area of 1 cm^2. The working electrode was a platinum electrode (0.5 mm diameter). The dendrimer concentration was 3.73 mM and the supporting electrolyte (KCl) concentration was 100 mM in water. Before each measurement, the solution was degassed with argon and the working electrode was polished with a polishing machine (Presi P230).

4.15. *X-ray crystallography*

Single crystal of compound **9** was mounted and fixed at the tip of glass fibre on a Stoe IPDS diffractometer. Data were collected using the monochromatic MoKα radiation ($\lambda = 0.71073$). The Final unit cell parameters were obtained by the least-squares refinement of 5195 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collections.

Table 2
Bond lengths [Å] and angles [°] for compound **9**.

Fe(1)–CT1	1.6480(4)	Fe(1)–CT2	1.6432(4)
O(1)–C(114)	1.365(3)	C(7)–C(8)	1.390(5)
O(2)–C(21)	1.218(5)	C(8)–C(9)	1.401(5)
C(1)–C(5)	1.412(4)	C(9)–C(10)	1.399(5)
C(1)–C(2)	1.417(4)	C(11)–C(111)	1.521(3)
C(1)–C(11)	1.495(4)	C(111)–C(116)	1.376(4)
C(2)–C(3)	1.404(4)	C(111)–C(112)	1.380(4)
C(3)–C(4)	1.399(5)	C(112)–C(113)	1.370(4)
C(4)–C(5)	1.423(4)	C(113)–C(114)	1.380(4)
C(6)–C(7)	1.410(5)	C(114)–C(115)	1.382(4)
C(6)–C(10)	1.428(4)	C(115)–C(116)	1.385(4)
C(6)–C(21)	1.441(5)		
CT2–Fe(1)–CT1	178.23(3)	C(9)–C(10)–C(6)	106.9(3)
C(5)–C(1)–C(2)	106.7(3)	C(1)–C(11)–C(111)	114.6(2)
C(5)–C(1)–C(11)	127.1(3)	O(2)–C(21)–C(6)	123.9(4)
C(2)–C(1)–C(11)	126.2(3)	C(116)–C(111)–C(112)	117.9(2)
C(3)–C(2)–C(1)	108.9(3)	C(116)–C(111)–C(11)	122.1(3)
C(4)–C(3)–C(2)	108.3(3)	C(112)–C(111)–C(11)	120.0(3)
C(3)–C(4)–C(5)	107.6(3)	C(113)–C(112)–C(111)	121.8(3)
C(1)–C(5)–C(4)	108.5(3)	C(112)–C(113)–C(114)	120.0(3)
C(7)–C(6)–C(10)	107.8(3)	O(1)–C(114)–C(113)	117.4(3)
C(7)–C(6)–C(21)	126.0(3)	O(1)–C(114)–C(115)	123.3(3)
C(10)–C(6)–C(21)	125.4(3)	C(113)–C(114)–C(115)	119.3(3)
C(8)–C(7)–C(6)	107.9(3)	C(114)–C(115)–C(116)	119.8(3)
C(7)–C(8)–C(9)	108.6(3)	C(111)–C(116)–C(115)	121.3(3)
C(10)–C(9)–C(8)	108.7(3)		

The structure was solved by direct methods (SIR97 [30]) and refined by least-squares procedures on F^2 with the SHELXL-97 program [31] using the integrated system WINGX [32]. H attached to carbon or oxygen atoms were introduced at calculated positions and treated as riding on their parent atoms [d(CH) = 0.93–0.97 Å and d(OH) = 0.82 Å] with a displacement parameter equal to 1.2U$_{eq}$ (C_6H_5, C_5H_5, CH_2, OH) times that of the parent atom. The Molecular view was realised with the help of ORTEP-III [33] and the packing view was done using PLATON [34]. Crystal data and refinement parameters are shown in Table 1, bond lengths and angles in Table 2.

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Appendix A. Supplementary material

CCDC 842974 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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