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New Polyalkynyl Dendrons and Dendrimers: "Click" Chemistry with Azidomethylferrocene and Specific Anion and Cation Electrochemical Sensing Properties of the 1,2,3-Triazole-Containing Dendrimers

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Abstract: The synthesis and use of the new tris-alkynyl dendrons **2** to **5** are reported, including the Williamson reaction of **5** with 9-iodo (**9**), 27-iodo (**11**), and 81-iodo (**12**) dendritic cores to yield 27-alkynyl (**13**), 81-alkynyl (**14**), and 243-alkynyl (**15**) dendrimers. So-called "click" reactions of these three dendrimers with azidomethylferrocene (**20**) give 27-ferrocenyl (**16**), 81-ferrocenyl (**17**), and 243-ferrocenyl (**18**) dendrimers. Electrochemical recognition of oxo-anions ($H_2PO_4^-$ and ATP^{2-}) and Pd^{2+} cation has been compared using the three polyferrocenyl dendrimers. Derivatization of Pt electrodes with the dendrimers for recognition becomes more facile with increasing size of the dendrimer. This first "click" dendrimer bearing 243-ferrocenyl groups is the best one in the series to obtain robust, recyclable modified Pt electrodes, whereas previous "click" ferrocenyl dendrimers have not been suitable for this purpose.

Keywords: alkynes · click chemistry · dendrimers · ferrocenes · redox chemistry

Introduction

The multifaceted supramolecular properties of dendrimers[1] can be applied to various fields of nanoscience, such as vectors,[2] sensors,[3] and green catalysts.[4] The terminal alkyne function has high potential for chemical properties[5] (as exemplified by the recently reported catalysis of 1,3-dipolar cycloadditions by "click" reaction).[6] Alkynyl functions have previously been used by Newkome et al.[7] and Moore et al.[8] for dendritic construction. Various syntheses of dendrimers with alkynyl termini have also been reported.[9] We have now synthesized the new dendrons **2** to **5** containing three propargyl groups, and have used **5** to open the way to a set of larger polyalkynyl dendrimers containing 27, 81, and 243 alkynyl termini. Indeed, polyiodomethyl dendrimers, used here as dendritic cores, are known for up to nine generations (more than 10^5 branches).[10]

The good overall yield of the synthesis reported here and the easily performed steps used to obtain this Percec-type dendron[11] make it a good tool for obtaining dendronized polyalkynyl molecules. The phenol function located at the focal point of the dendron also allows its introduction onto materials using the classical Williamson reaction.

The reactivity of the three alkynyl dendrimers **13**, **14**, and **15** has now been tested in the "click" reaction with azidomethylferrocene (**20**), a substrate that has not previously been used for this reaction. Our previous "click" dendrimer synthesis involved azido-terminated dendrimers and terminal alkyne substrates. We now report "inverse click" reactions, that is, click dendrimer synthesis in which the terminal alkyne is located on the dendrimer branch termini.[9d,e] Finally, electrochemical recognition of ATP^{2-}, $H_2PO_4^-$, and Pd^{2+} has been probed using the new ferrocenyl dendrimers **16**, **17**, and **18** (containing 27, 81, and 243 ferrocenyl groups, respectively).[12] We recently reported[12d] syntheses of polyferrocenyl dendrimers, along with their redox recognition abilities. We now describe "inverse click" reactions using polyalkynyl cores. The resulting "inverse click" dendrimers display electrochemical properties that differ from those of the previously reported "normal click" dendrimer series. The large size of the dendrimers synthesized here has allowed the preparation of modified Pt electrodes that could not be ob-

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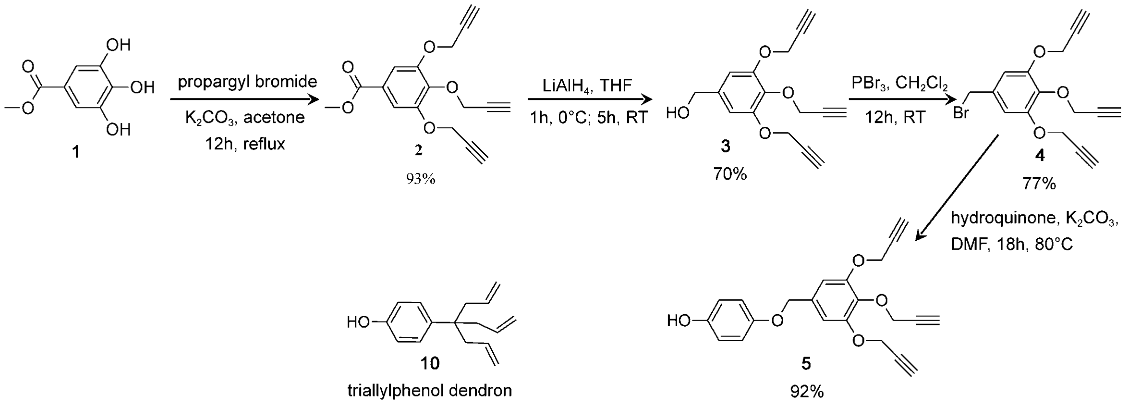
tained with the previously reported “normal click” dendrimers. The resulting dendritic effects are discussed.

Results and Discussion

Dendrimer synthesis: The tris-alkynyl dendron **5** was synthesized from commercially available methyl 3,4,5-trihydroxybenzoate **1** (Scheme 1). Four classical organic chemistry steps were performed to obtain the desired dendron **5** in 45 % overall yield. This synthesis only requires a purification step at the end of the process. The three first steps could be easily accomplished on a wide range of scales (from 100 mg to 10 g). The last step proved to be very sensitive to the dilution and addition time, and it was important to remove DMF prior to column chromatographic work-up. The dendron **5** was characterized by classical spectroscopic and analytical means, including mass spectrometry (molecular peak $+ Na^+$ at m/z 385.1050, calcd for $[M+Na]^+$ 385.1046; see the Supporting Information).

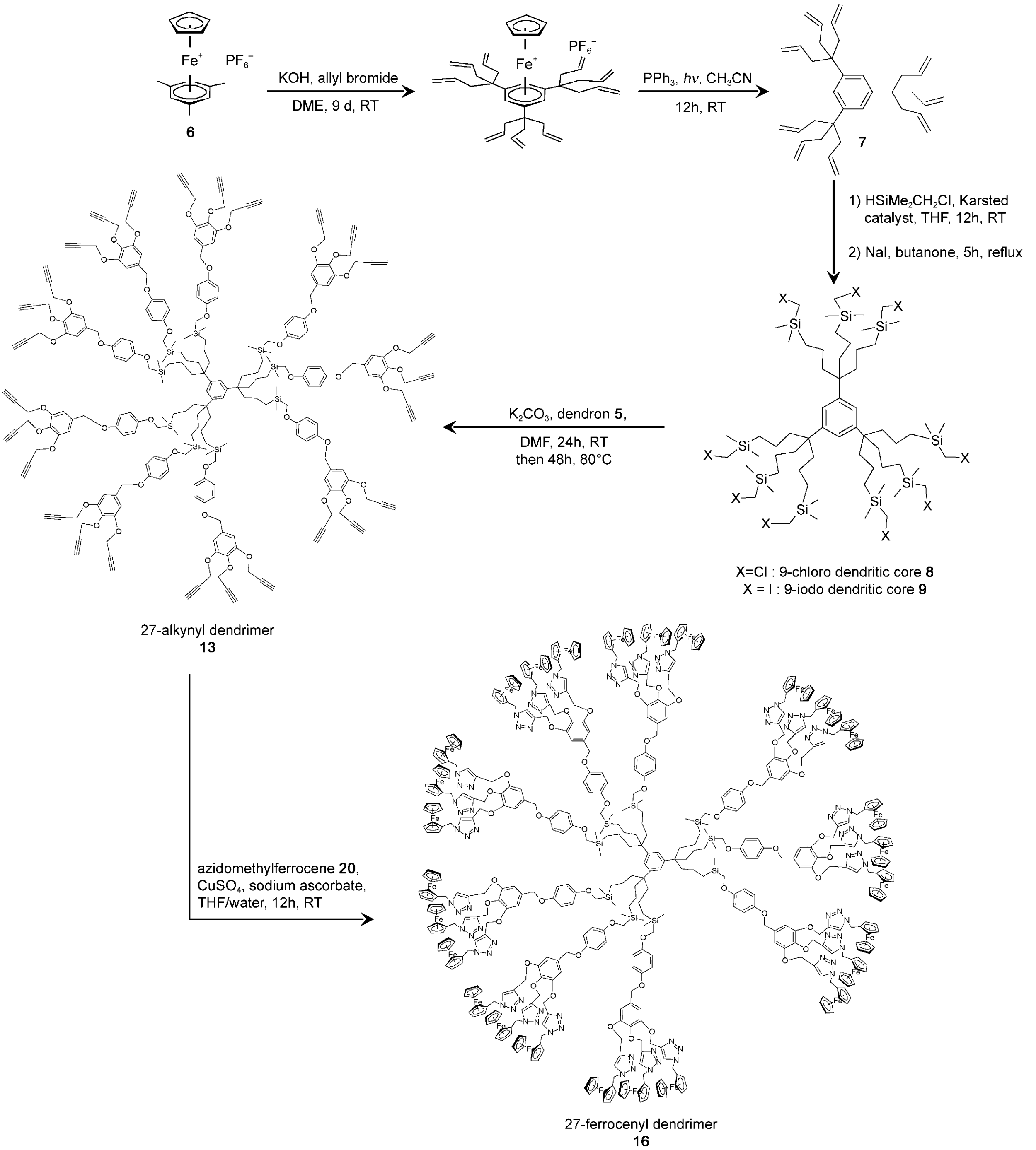
The known nona-allylation of $[FeCp(\eta^6\text{-mesitylene})][PF_6]$ **6** ($Cp = \eta^5\text{-}C_5H_5$) quantitatively furnished the 9-allyl dendritic core, **7**, on a large scale after visible-light photolysis to remove the metal moiety (Scheme 2).[10] Hydrosilylation of the terminal olefinic bonds of **7**, a reaction pioneered in dendrimer synthesis by van Leeuwen et al.,[13] was carried out as previously reported, using $HSiMe_2(CH_2Cl)$ and the Karsted catalyst, to regioselectively afford the known 9-chloromethyl(dimethyl)silyl intermediate **8**. Compound **8** was then stirred for 5 h with sodium iodide in refluxing butanone, which quantitatively afforded the known 9-iodomethyl(dimethyl)silyl dendritic core **9** (Scheme 2). Williamson reaction of **9** with the known triallyl-phenol dendron, **10**, has previously been reported to give the polyallyl dendritic core of the next higher generation. Repetition of the hydrosilylation and halogen-exchange steps is known to yield the 27-iodo dendritic core, **11**, and the last three steps have previously been used on the latter to yield the 81-iodo dendritic core **12**.[10b]

Coupling between the phenol dendron **5** and the dendritic core, using either of two methods, proceeded with similar yields. The first method involved reaction between the 9-iodomethyl(dimethyl)silyl dendritic core **9** and the phenol dendron **5** in the presence of K_2CO_3 (Scheme 2). The second involved the 9-chloromethyl(dimethyl)silyl dendritic core **8**, together with a stoichiometric amount of NaI, the phenol dendron **5**, and K_2CO_3. Both methods gave the 27-propargyl dendrimer **13** in 65–70 % yield. The MALDI-TOF mass spectrum showed the $[M+Na]^+$ peak at m/z 4415.1 (calcd for $[M+Na]^+$ 4415.7; see the Supporting Information). The first method was used with the 27-iodo dendritic core **11** to yield the 81-alkynyl dendrimer **14** (Scheme 3), and with the 81-iodo dendritic core **12** to yield the 243-alkynyl dendrimer **15** (Scheme 4). The only difference was in the reaction time, which was higher for each added generation. This set of dendrimers was characterized by dynamic light scattering (DLS) for the two larger dendrimers (6.2 ± 0.2 nm for **14**



Scheme 1. Tris-alkynyl and tris-allyl dendrons.

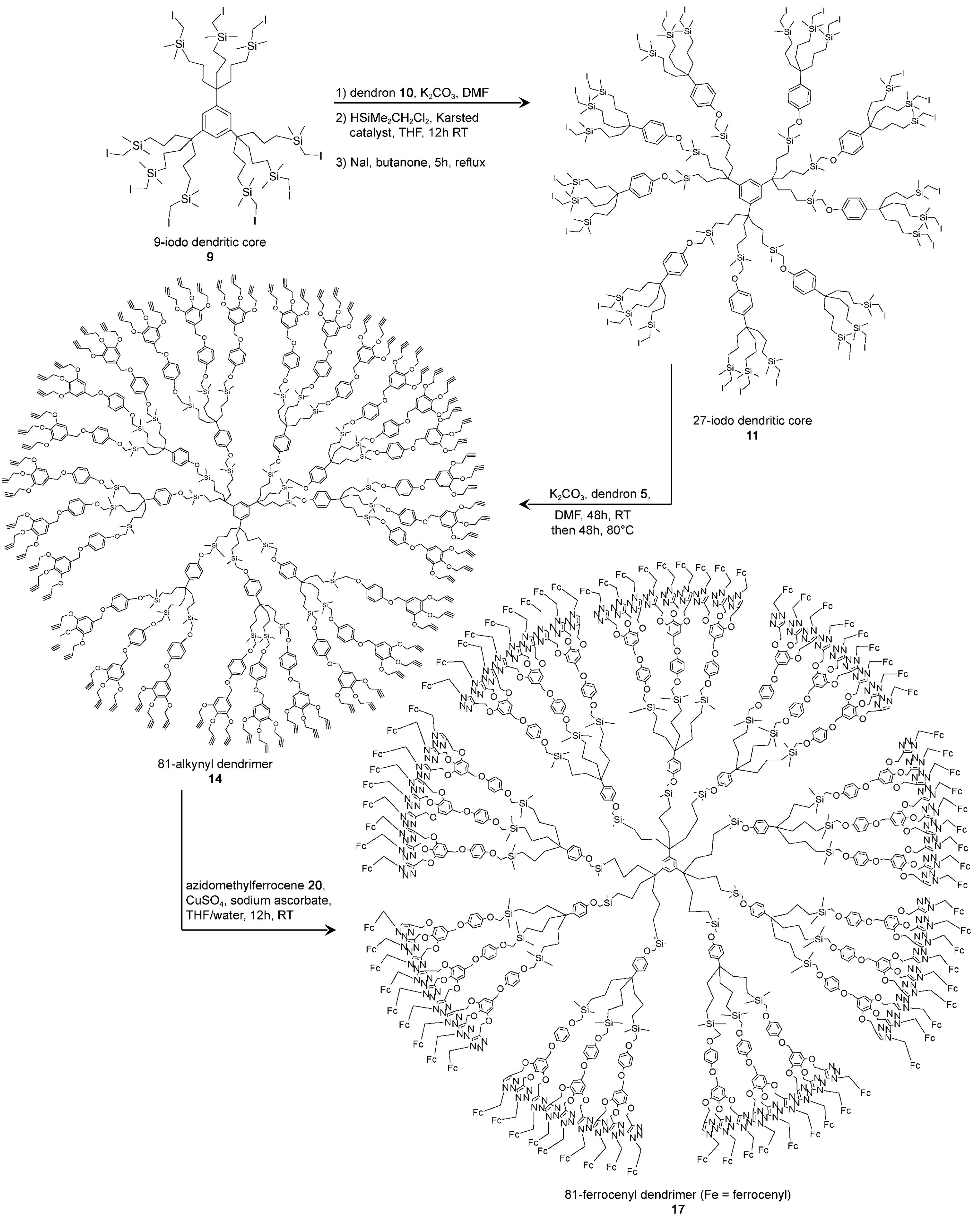
Abstract in French: *Nous reportons ici la synthèse et l’utilisation de nouveaux dendrons tris-alcynes (composés **2** à **5**). La réaction de Williamson entre **5** et les cœurs dendritiques polyiodés comportant 9, 27 ou 81 branches (composés **9**, **11** et **12**) conduit aux dendrimères poly-alcynes à 27, 81 et 243 branches respectivement (composés **13** à **15**). La réaction “click” de ces dendrimères avec l’azidométhylferrocène (**20**) permet d’obtenir des dendrimères polyferrocéniques à 27, 81 et 243 branches (composés **16** à **18**). La reconnaissance électrochimique d’oxo-anions ($H_2PO_4^-$ et ATP^{2-}) et du cation Pd^{2+} est comparée avec trois dendrimères polyferrocéniques, et l’obtention d’électrodes de Pt modifiées à l’aide de ces dendrimères pour cette reconnaissance est de plus en plus facile lorsque la taille du dendrimère augmente. Le premier dendrimère “click” comportant 243 ferrocènes est le meilleur de la série pour la modification d’électrodes de Pt. Ces électrodes sont robustes et recyclables avec ce dendrimère, alors que les dendrimères “click” précédemment publiés n’étaient pas utilisables pour cette fonction.*



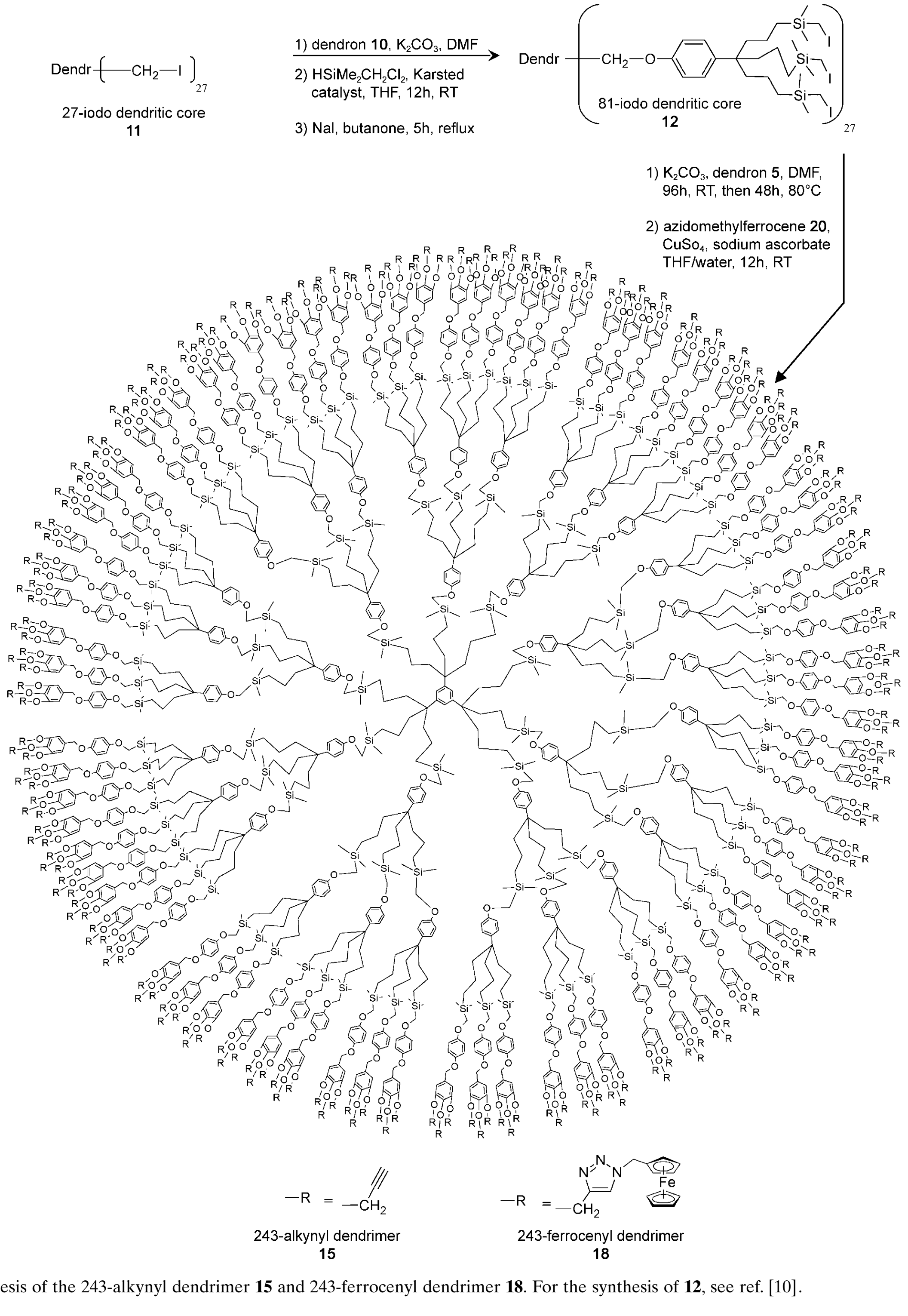
Scheme 2. Synthesis of the 27-alkynyl dendrimer **13** and 27-ferrocenyl dendrimer **16**. For the synthesis of **9**, see ref. [10].

and 6.6±0.2 nm for **15**), ^{1}H, ^{13}C, ^{29}Si, and DOSY NMR, IR, and elemental analysis (see the Experimental Section). Size-exclusion chromatography (SEC) showed the size progression from **13** to **15** (retention times of 20.53, 18.70, and 17.67 min, respectively) and the low polydispersities (1.02 for each compound). The size progression was also shown by the DOSY NMR data (4.1, 4.8, and 4.9 nm, respectively).

Huisgen 1,3-dipolar cycloaddition reactions of **13**, **14**, and **15** with azidomethylferrocene, **20**, were "catalyzed" by Cu^{I} (used in stoichiometric amount)[12d] in a homogeneous THF/water medium yielding the 27-ferrocenyl dendrimer **16** (Scheme 2), the 81-ferrocenyl dendrimer **17** (Scheme 3), and the 243-ferrocenyl dendrimer **18** (Scheme 4), under the same reaction conditions (Scheme 5).[14] These functionalized dendrimers were characterized by DLS for the largest (5.3±1.0 nm for **18**), SEC, ^{1}H, ^{13}C, ^{29}Si, and DOSY NMR, IR, and cyclic voltammetry (see the Experimental Section and the Supporting Information). SEC showed the size pro-



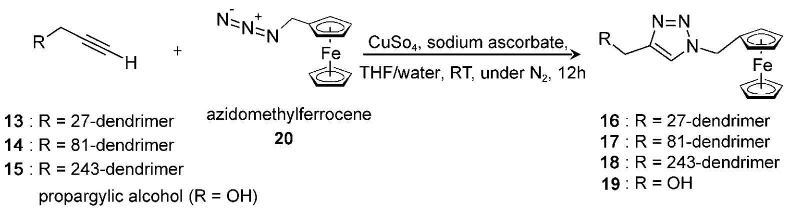
Scheme 3. Synthesis of the 81-alkynyl dendrimer **14** and 81-ferrocenyl dendrimer **17**. For the synthesis of **11**, see ref. [10].



Scheme 4. Synthesis of the 243-alkynyl dendrimer **15** and 243-ferrocenyl dendrimer **18**. For the synthesis of **12**, see ref. [10].

gression from **16** to **18** (retention times of 20.18, 18.70, and 17.82 min, respectively) and the low polydispersities (1.01 to 1.03). The size progression was also shown by the DOSY NMR data (3.2, 3.8, and 4.2 nm, respectively).

Cyclic voltammetry and electrochemical sensing: The cyclic voltammogram of **16** shows a single reversible wave at 0.61 V versus the internal reference redox system $[Fe(\eta^5\text{-}C_5Me_5)_2]^{+/0}$ (Table 1).[15] This wave corresponds to the oxido-reduction of the ferrocenyl group and shows that all of the ferrocenyl groups of the dendrimer are equivalent and independent on the electrochemical time scale. The number of ferrocenyl units was determined to be 30±3 for the 27-ferrocenyl dendrimer **16**, using the Bard–Anson



Scheme 5. “Click” reactions with azidomethylferrocene **20**.

Table 1. Electrochemical properties of the ferrocenyl CV waves for the three polyferrocenyl dendrimers **16**, **17**, and **18**.

	$E_{1/2}$ vs Fc*[a]	$E_{pa}-E_{pc}$ [mV]	I_{pc}/I_{pa}
27-Fc **16**[b]	0.610	30	3.80
81-Fc **17**[b]	0.600	0	1.90
243-Fc **18**[b]	0.595	0	2.00

[a] $E_{1/2}$ in V vs Fc* = $[Fe(\eta^5\text{-}C_5Me_5)_2]^{+/0}$ (average of the cathodic and anodic CV peaks). [b] Degassed solutions of the metallodendrimers in CH_2Cl_2; concentrations: 1.7×10^{-5} M for **16**, 5.8×10^{-6} M for **17**, and 1.9×10^{-6} M for **18**.

equation.[3b,16,17] This kind of calculation is precluded for compounds **17** and **18** by the adsorption of the dendrimers onto the electrode surface, because it yields excessively high results. Electrochemical recognition of both $H_2PO_4^-$ and ATP^{2-} was investigated. The interaction with HSO_4^- is much weaker than that with $H_2PO_4^-$, but the titration of HSO_4^- was nevertheless possible.[1]

Numerous studies by Beer et al. with endoreceptors[18] bearing one or more ferrocenyl groups have paved the way for the recognition of oxo-anions. Addition of $[n\text{Bu}_4\text{N}][H_2PO_4]$ to an electrochemical cell containing a solution of polyferrocenyl dendrimer (**16**, **17**, or **18**) in CH_2Cl_2 led to the appearance of a new wave at a potential less positive than the initial wave, the intensity of which decreased while that of the new wave increased (Figure 1). The equivalence point was reached when the initial wave was completely replaced by the new wave, as has previously been established for endoreceptors[18] and other ferrocenyl dendrimer structures.[12] Analysis of the CV waves using the square scheme has been rationalized by Echegoyen and Kaifer in a seminal article.[19]

We used this analysis to determine the ratio of apparent equilibrium constants $K_{(+)}$ and $K_{(0)}$ related to the strong interaction of the anion with the cationic ferrocenium form of the redox system, as well as with the neutral ferrocenyl form ($K \gg 1$). Only a rough estimate of $K_{(+)}/K_{(0)}$ and $K_{(+)}$ values could be obtained, because of the irreversible behaviour of the CVs of the dendrimers in the presence of $[n\text{Bu}_4\text{N}][H_2PO_4]$ and $[n\text{Bu}_4\text{N}]_2[\text{ATP}]$.

The electrochemical irreversibility is characterized by ($E_{pc}-E_{pa}$) values of 0.140 ± 0.010 V for compound **16**, under the conditions of Figure 2 at the end of the titration. This slow heterogeneous electron transfer between the electrode and the dendrimer redox sites is due to the very substantial structural transformation of the $H_2PO_4^-$/redox site ensemble in the course of electron transfer (in particular, tight ion pairs or

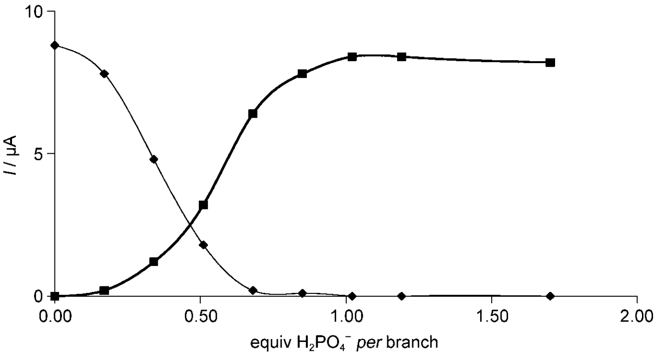


Figure 1. Titration of $[n\text{Bu}_4\text{N}][H_2PO_4]$ with the 81-alkynyl dendrimer **17** in CH_2Cl_2 at 20 °C by adding the salt of the ion to the dendrimer solution. Decrease of the intensity of the initial CV wave and increase of the intensity of the new CV wave vs. the number of equivalents of $[n\text{Bu}_4\text{N}][H_2PO_4]$ added per ferrocenyl branch. (See the supporting information for other titration curves).

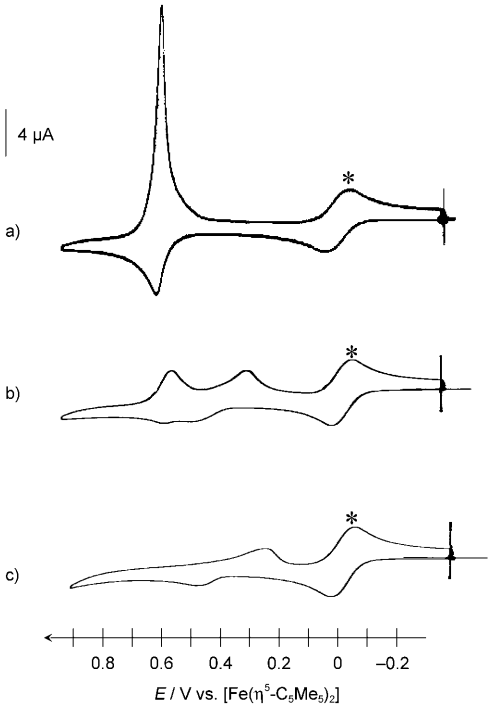


Figure 2. Cyclic voltammograms for the titration of $[n\text{Bu}_4\text{N}]_2[\text{ATP}]$ with the 27-ferrocenyl dendrimer **16** in CH_2Cl_2 at 20 °C by adding the salt of the ion to the dendrimer solution: a) before addition of $[n\text{Bu}_4\text{N}]_2[\text{ATP}]$, b) during titration of $[n\text{Bu}_4\text{N}]_2[\text{ATP}]$, and c) after addition of excess $[n\text{Bu}_4\text{N}]_2[\text{ATP}]$; * internal reference: $[Fe(\eta^5\text{-}C_5Me_5)_2]$.

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[1] A slightly positive dendritic effect (i.e., the variation in $E_{1/2}$ is larger for the dendrimer than for the monomer) is observed for the electrochemical recognition of the three oxo-anions by the dendrimer as compared to their recognition by the ferrocenyl monomer **19**.

aggregates are formed at the redox sites upon anodic oxidation in CH_2Cl_2; vide infra). The difference in $E_{1/2}$ values between the initial and the new wave (determined after addition of 0.5 equiv of $[nBu_4N][H_2PO_4]$, in order to observe both waves at the same time) was found to be 0.210 ± 0.010 V. This corresponds to a ratio of apparent association constants ($K_{(+)}/K_{(0)}$) of 4200 ± 400 according to the Echegoyen–Kaifer model.[19]

$$\log(K_{(+)}/K_{(0)}) = \Delta E_{1/2}/0.058 \text{ at } 20\,^{\circ}\text{C}$$

For ATP^{2-}, electrochemical recognition was also studied in CH_2Cl_2, and the observed trends closely followed those found for $H_2PO_4^-$. The addition of $[nBu_4N]_2[ATP]$ to an electrochemical cell containing a solution of the 27-ferrocenyl dendrimer **16** in CH_2Cl_2 caused, as in the case of $[nBu_4N][H_2PO_4]$, the appearance of a new wave at a potential less positive than the initial one. Indeed, the interaction of the anions with redox groups releases electron density, rendering oxidation of the ferrocene group easier. The intensity of the initial wave decreased, while that of the new wave increased (Figures 2 and 3). Thus, this is a case of a strong-type interaction that can be treated using the square scheme,[19] as with $[nBu_4N][H_2PO_4]$. The difference in ferrocenyl redox potential between the initial wave and the new wave is of the same order of magnitude as with $[nBu_4N][H_2PO_4]$, but slightly lower than for the latter (0.180 ± 0.010 V, i.e., 30 mV less than with $[nBu_4N][H_2PO_4]$). The corresponding ratio of apparent association constants is $K_{(+)}/K_{(0)} = 1300 \pm 150$. The equivalence point is reached when 0.5 equiv of $[nBu_4N]_2[ATP]$ has been added, which is in accord with the double negative charge of this anion. These strong interactions seen with $[nBu_4N][H_2PO_4]$ and $[nBu_4N]_2[ATP]$ are all the more remarkable as there is no conjugation between the triazole ring and the ferrocenyl group.

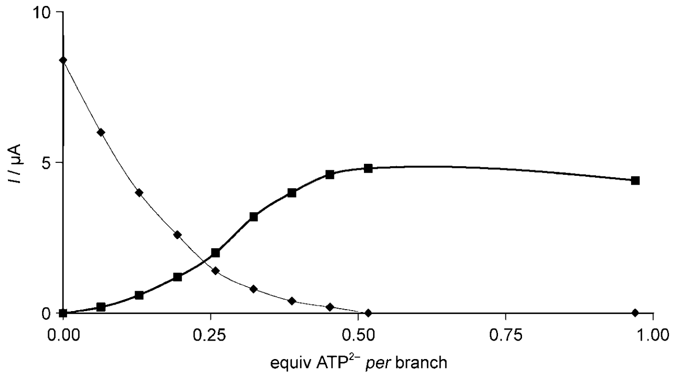


Figure 3. Titration of $[nBu_4N]_2[ATP]$ with the 81-ferrocenyl dendrimer **17** in CH_2Cl_2 at 20 °C by adding the salt of the ion to the dendrimer solution. Decrease of the intensity of the initial CV wave and increase of the intensity of the new CV wave vs. the number of equivalents of $[nBu_4N]_2[ATP]$ added per ferrocenyl branch (see Supporting Information for other titration curves).

For $[nBu_4N][HSO_4]$ in CH_2Cl_2, the interaction with the 27-ferrocenyl dendrimer **16** was indeed weak, but the titration and the recognition could nevertheless be carried out. The addition of $[nBu_4N][HSO_4]$ to an electrochemical cell containing a solution of the dendrimer **16** in CH_2Cl_2 did not, however, lead to the appearance of a new wave, and only a shift of the CV wave towards a less positive potential was observed (Figures 4 and 5). The maximum shifts of 75 mV for the anodic wave potential and 70 mV for the cathodic one were reached around the equivalence point, which allowed the titration of $[nBu_4N][HSO_4]$. A further noteworthy feature was that a rather strong adsorption was observed throughout the titration. With $[nBu_4N][H_2PO_4]$ and $[nBu_4N]_2[ATP]$, the wave was clearly electrochemically irreversible during the titration. The absolute apparent associa-

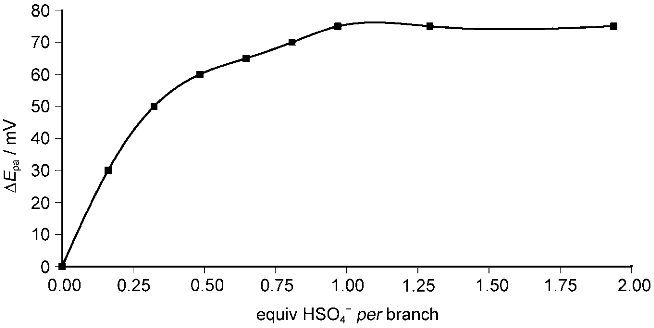


Figure 4. Titration of $[nBu_4N][HSO_4]$ with the 27-ferrocenyl dendrimer **16** in CH_2Cl_2 at 20 °C by adding the salt of the ion to the dendrimer solution: shift of E_{pa} toward less positive potentials recorded by CV as a function of the number of equivalents of $[nBu_4N][HSO_4]$ added per ferrocenyl branch.

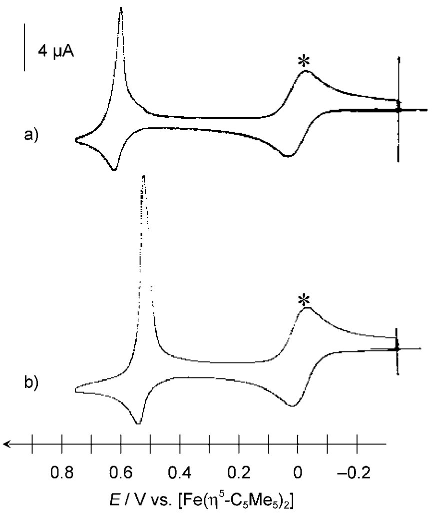


Figure 5. Cyclic voltammograms for the titration of $[nBu_4N][HSO_4]$ with the 27-ferrocenyl dendrimer **16** in CH_2Cl_2 at 20 °C by adding the salt of the ion to the dendrimer solution: a) before addition of $[nBu_4N][HSO_4]$, b) after addition of excess $[nBu_4N][HSO_4]$; * internal reference: $[Fe(\eta^5\text{-}C_5Me_5)_2]$.

tion constant $K_{(+)}$ between compound **16** and the anion HSO_4^- could then be defined by:

$$\log K_{(+)}c = \Delta E_{1/2}/0.058 \text{ at } 20\,^{\circ}\text{C}$$

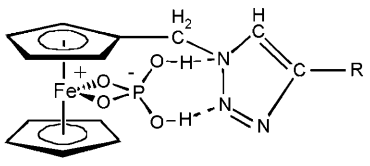
giving $K_{(+)} = (4 \pm 0.4) \times 10^4\ \text{L mol}^{-1}$. The same analyses with ATP^{2-} and $H_2PO_4^-$ were performed for the 81-ferrocenyl dendrimer **17** and for the 243-ferrocenyl dendrimer **18**. A slightly positive dendritic effect (i.e., an increase in the potential difference with increasing dendritic generation) was observed for $H_2PO_4^-$. The results are summarized in Table 2.

Table 2. Results of the electrochemical recognition of the oxo-anions using the three ferrocenyl dendrimers **16**, **17**, and **18** and the three modified Pt electrodes.

	$H_2PO_4^-$			ATP^{2-}		
	$E_{1/2}$[a] ($E_{pa}-E_{pc}$)	$\Delta E_{1/2}$[b]	$K_{(+)}/K_{(0)}$	$E_{1/2}$[a] ($E_{pa}-E_{pc}$)	$\Delta E_{1/2}$[b]	$K_{(+)}/K_{(0)}$
27-Fc **16** on Pt	–	–	–	0.410 (100)	0.200	2800
27-Fc **16**[c]	0.400 (140)	0.210	4200	0.430 (215)	0.180	1300
81-Fc **17** on Pt	–	–	–	0.390 (135)	0.210	4200
81-Fc **17**[c]	0.350 (75)	0.250	20400	0.420 (115)	0.180	1300
243-Fc **18** on Pt	–	–	–	0.375 (170)	0.220	6200
243-Fc **18**[c]	0.340 (85)	0.255	24900	0.415 (120)	0.180	1300

[a] $E_{1/2}$ in V vs $[Fe(\eta^5\text{-}C_5Me_5)_2]^{+/0}$ (average of the cathodic and anodic CV peaks), ($E_{pa}-E_{pc}$) in mV. [b] $\Delta E_{1/2}$ in V. [c] Degassed solutions of the metallodendrimers in CH_2Cl_2; concentrations: 1.7×10^{-5} M for **16**, 5.8×10^{-6} M for **17**, and 1.9×10^{-6} M for **18**.

It is important to notice that the recognition is as good here when the ferrocenyl unit is not conjugated with the triazolyl ring as when there is conjugation.[12d] A possible explanation is that the chelation of the positively charged iron atom in the oxidized ferrocenium form by the two $P{-}O^{-1/2}$ bonds of $H_2PO_4^-$ is stabilized by the chelating double H-bonding of the two dihydrogenphosphate $O{-}H^{\delta+}$ bonds with two neighboring nitrogen atoms of the triazole ring (see below). This discards the direct intramolecular ferrocenyl–triazole electronic interaction as being the most important factor of the oxo-anion–ferrocenium interaction in the case of the "normal click" ferrocenyl dendrimers.[12d] This chelating double H-bonding does not exist in the case of HSO_4^-, which is responsible for the difference in strength of the interactions with $H_2PO_4^-$ and HSO_4^-, and this difference is larger in the presence of the nearby triazole ring than in its absence.[3b]



Fabrication of electrodes modified with the "click" dendrimers: The accessibility of modified electrodes[20] has also been explored. Each generation of polyferrocenyl dendrimer allows the fabrication of Pt electrodes with adsorbed dendrimer, but the capacity for strong adsorption on a Pt electrode increases with increasing generation (Tables 3 and 4). The first-generation dendrimer with 27 ferrocenyl groups does not adsorb well, whereas that with 243 ferrocenyl groups adsorbs very strongly and is resistant to washing the salt of ATP^{2-} or Pd^{2+} with CH_2Cl_2 (Table 4 and Figure 6).

Table 3. Results of the electrochemical recognition of Pd^{2+} using the three ferrocenyl dendrimers **16**, **17**, and **18** and the three modified Pt electrodes.

	$E_{1/2}$ ($E_{pa}-E_{pc}$)[a] Before addition of Pd^{2+}	$E_{1/2}$ ($E_{pa}-E_{pc}$)[a] After addition of excess Pd^{2+}	$\Delta E_{1/2}$ [mV]	$K_{(+)}$
27-Fc **16** on Pt	0.610 (0)	0.645 (30)	−35	–
27-Fc **16**[b]	0.610 (30)	0.650 (35)	−40[c]	10700
81-Fc **17** on Pt	0.600 (0)	0.650 (30)	−50	–
81-Fc **17**[b]	0.600 (0)	0.650 (20)	−50	15500
243-Fc **18** on Pt	0.595 (0)	0.660 (40)	−65	–
243-Fc **18**[b]	0.595 (0)	0.660 (0)	−65	28600

[a] $E_{1/2}$ in V vs $[Fe(\eta^5\text{-}C_5Me_5)_2]^{+/0}$ (average of the cathodic and anodic CV peaks), ($E_{pa}-E_{pc}$) in mV. [b] Degassed solutions of the metallodendrimers in CH_2Cl_2; concentrations: 1.7×10^{-5} M for **16**, 5.8×10^{-6} M for **17**, and 1.9×10^{-6} M for **18**. [c] Shift of 40 mV toward more positive potential, in contrast to what is observed for $[nBu_4N][HSO_4]$ (shift toward less positive potential).

The modified electrodes were compared after 50 adsorption cycles and after 200 adsorption cycles (see the Experimental Section for details of the experimental procedure). The intensity obtained, the stability at various scan rates (Figure 6), and the recognition of $[Pd(MeCN)_4](BF_4)_2$[2] (Figure 7) and $[nBu_4N]_2[ATP]$ (Figure 8) were explored (Table 2 and Table 3). The robustness of the various modified electrodes was tested by measuring the intensity before and after operation for 30 min (about 200 cycles) with a fresh solution of 0.1 M $[nBu_4N][PF_6]$ in CH_2Cl_2 (Table 4). The electrode modified with **18** proved to be an excellent, re-usable redox sensor.

Finally, electrochemical recognition of $[Pd(MeCN)_4][BF_4]_2$ by the dendrimers (Figure 9) was also found to be possible but, as with $[nBu_4N][HSO_4]$, was weak with only a CV wave shift rather than the appearance of a new wave. Moreover, the CV waves remained fully chemically and electrochemi-

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[2] The addition of $[Pd(MeCN)_4](BF_4)_2$ to both the dendrimer solution and the modified Pt electrode provokes only a shift of the CV wave.

Table 4. Robustness of the various modified Pt electrodes.

	I [μA] after 200 cycles adsorption	I [μA] after 200 cycles in CH_2Cl_2[a]	I [μA] after 50 cycles adsorption	I [μA] after recycling[b]
27-Fc **16** on Pt	11.6	7.8	6.4	1.7
81-Fc **17** on Pt	26.6	18.5	11.6	7.4
243-Fc **18** on Pt	40.2	22.6	11.8	8.2

[a] On the modified Pt electrode obtained after 200 adsorption cycles (see Experimental Section). [b] Intensity obtained for the electrode after 50 adsorption cycles (see the Experimental Section) after titrating ATP^{2-} and washing with CH_2Cl_2.

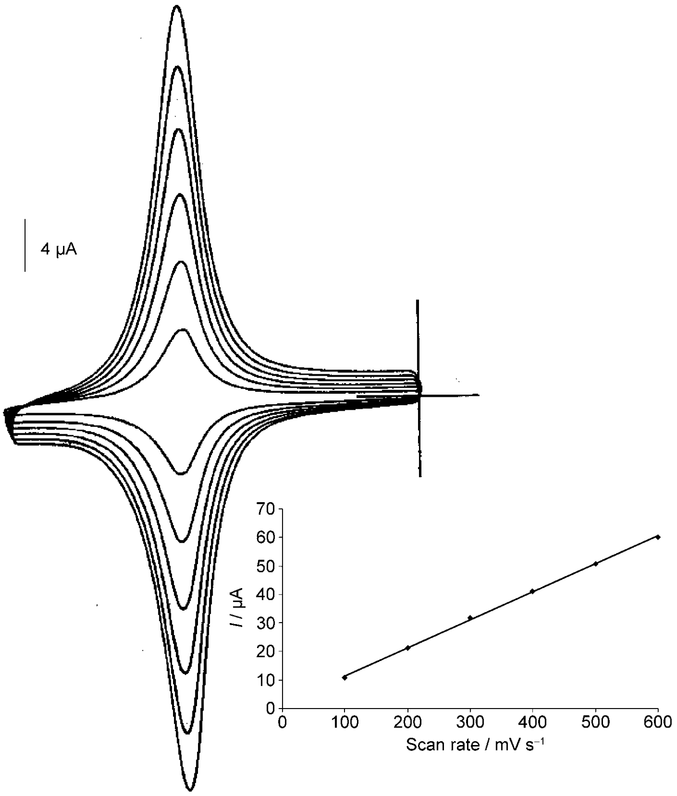

Figure 6. Stability of the Pt electrode with adsorbed 243-ferrocenyl dendrimer **18** for various scan rates (from smaller to larger at 100, 200, 300, 400, 500, and 600 $mV\,s^{-1}$) observed by cyclic voltammetry.

cally reversible without adsorption. This is most likely indicative of a weak ionic interaction. Interestingly, this is in sharp contrast with the previously reported "normal click" ferrocenyl dendrimers, which provided a strong interaction. This is obviously due to the fact that the previous click ferrocenyl dendrimers were conjugated whereas the present ones are not.

Conclusion

New, easily prepared tris-alkynyl dendrons have been synthesized from commercial precursors. The use of these dendrons in dendrimer synthesis has been exemplified by their efficient Williamson reactions with three polyiodo dendritic cores yielding a 27-alkynyl, an 81-alkynyl, and a 243-alkynyl dendrimer.

The "click" reaction of these dendrimers with azidomethylferrocene yields the new 27-ferrocenyl, 81-ferrocenyl, and 243-ferrocenyl dendrimers, which are capable of electrochemically recognizing oxo-anions such as HSO_4^-, $H_2PO_4^-$, and ATP^{2-} as well as the Pd^{2+} cation.

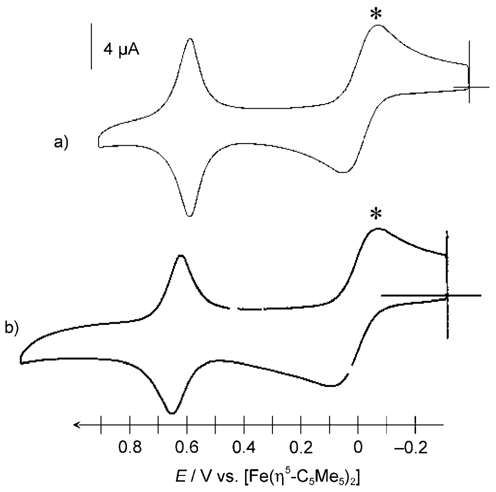

Figure 7. Cyclic voltammograms for the recognition of Pd^{2+} by the modified Pt electrode with adsorbed 243-ferrocenyl dendrimer **18** in CH_2Cl_2 at 20 °C: a) before addition of $[Pd(MeCN)_4](BF_4)_2$, b) after addition of excess $[Pd(MeCN)_4](BF_4)_2$; * internal reference: $[Fe(\eta^5\text{-}C_5Me_5)_2]$. Note the flattening of the CV of the internal reference (for discussion, see ref. [15b]).

Recognition of the phosphorus-containing oxo-anions results from a strong interaction with the ferrocenyl redox system that is accentuated by the presence of the triazole ring, probably due to double H-bonding to the N atoms. On the other hand, the interactions with HSO_4^- and Pd^{2+} are weak, but nevertheless allow titrations.

These three dendrimers form modified Pt electrodes, which are increasingly robust with increasing size of the dendrimer and allow the sensing of ATP^{2-} better than in solution. A positive dendritic effect is obtained with the modified electrodes, whereas this is not the case in solution. The described access to such large "click" dendrimers represents a significant advance, since it allows the preparation of modified electrodes that could not be prepared with the previous series of "click" ferrocenyl dendrimers.

Prospective uses include the possibility of applying this Williamson reaction to our larger polyiodo dendrimers and of using the 1,2,3-triazole dendritic rings as ligands for supramolecular catalysis applications using dendrimer-stabilized nanoparticles.

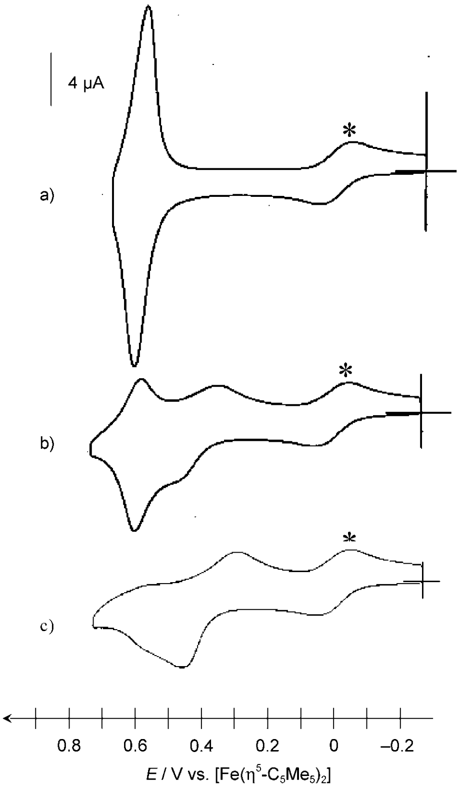

Figure 8. Cyclic voltammograms for the titration of $[nBu_4N]_2[ATP]$ by the modified Pt electrode with adsorbed 243-ferrocenyl dendrimer **18** in CH_2Cl_2 at 20 °C: a) before addition of $[nBu_4N]_2[ATP]$, b) during titration of $[nBu_4N]_2[ATP]$, and c) after addition of excess $[nBu_4N]_2[ATP]$; * internal reference: $[Fe(\eta^5\text{-}C_5Me_5)_2]$.

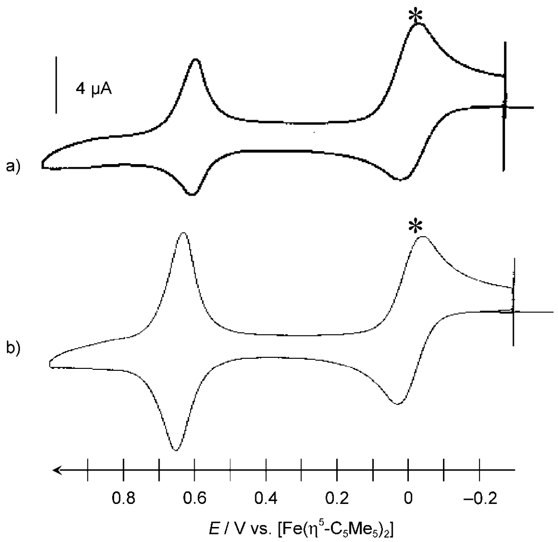

Figure 9. Cyclic voltammograms for the titration of $[Pd(MeCN)_4](BF_4)_2$ with the 81-ferrocenyl dendrimer **17** in CH_2Cl_2 at 20 °C by adding the salt of the ion to the dendrimer solution: a) before addition of $[Pd(MeCN)_4](BF_4)_2$, b) after addition of excess $[Pd(MeCN)_4](BF_4)_2$; * internal reference: $[Fe(\eta^5\text{-}C_5Me_5)_2]$.

Experimental Section

General: All operations were performed under nitrogen atmosphere using standard Schlenk techniques. Prior to use, THF was dried over sodium benzophenone ketyl and freshly distilled under a nitrogen atmosphere. Whenever mentioned, CH_2Cl_2 was dried over calcium hydride and freshly distilled under a nitrogen atmosphere. All other reagents were obtained from commercial sources and were used without further purification. All glassware was previously dried in an oven and cooled under a nitrogen flow.

Physical measurements: ^1H NMR spectra were recorded at 25 °C on a Bruker AC 250 (250 MHz), a Bruker Advance 300 (300 MHz), or a Bruker DPX 400 (400 MHz) spectrometer. ^{13}C NMR spectra were recorded in pulse FT mode on a Bruker AC 300 spectrometer at 75.50 MHz. ^{29}Si NMR spectra were recorded on a Bruker AC 300 spectrometer at 59.6 MHz. All chemical shifts are reported in parts per million (δ, ppm) with reference to $SiMe_4$ (TMS). Mass spectra were obtained at the CESAMO, Université Bordeaux I, on a PerSeptive Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. This instrument is equipped with a nitrogen laser (337 nm), a delayed extraction, and a reflector. It was operated at an accelerating potential of 20 kV in both linear and reflection modes. The mass spectra shown represent an average over 256 consecutive laser shots (3 Hz repetition rate). Peptides were used to calibrate the mass scale using the two-points calibration software 3.07.1 from PerSeptive Biosystems. Elemental analyses were performed at the Center of microanalysis of the CNRS, Lyon Villeurbanne, France. All electrochemical measurements were performed in degassed CH_2Cl_2 at 20 °C. Supporting electrolyte: 0.1 M $[nBu_4N][PF_6]$; working and counter electrode: Pt; quasi-reference electrode: Ag; internal reference: $[Fe(\eta^5\text{-}C_5Me_5)_2]^{+/0}$;[15] scan rate: 0.200 $V\,s^{-1}$.

Modification of Pt electrodes with polyferrocenyl dendrimers 16, 17, and 18: A platinum electrode (Sodimel, Pt 30) was immersed in 10 % aqueous HNO_3 for 3 h, then rinsed with distilled water, dried in air, and polished using cerium oxide powder (5 MU). The dendrimers **16**, **17**, and **18** were electrodeposited onto such platinum-disk electrodes ($A = 0.0078\,cm^2$) from degassed solutions of metallodendrimer (1.7×10^{-5} M (**16**), 5.8×10^{-6} M (**17**), and 1.9×10^{-6} M (**18**), in order to obtain the same concentration in ferrocenyl groups) and $[nBu_4N][PF_6]$ (0.1 M) in CH_2Cl_2 by continuous scanning (0.20 $V\,s^{-1}$) up to 50 cycles or up to 200 cycles between 0.0 and 0.9 V versus $[Fe(\eta^5\text{-}C_5Me_5)_2]^{+/0}$. The coated electrodes were washed with CH_2Cl_2 in order to remove the solution of material and dried in air. The modified electrodes were characterized by CV in freshly distilled CH_2Cl_2 containing only the supporting electrolyte. They showed a single symmetrical CV wave, and the linear relationship between the peak current and the potential sweep rate was verified. The surface coverage Γ ($mol\,cm^{-2}$) by the ferrocenyl dendrimers **16**, **17**, and **18** was determined from the integrated charge of the CV wave, $\Gamma = Q/nFA$, where Q is the charge, n is the number of electrons transferred, F is the Faraday constant, and A is the area. For example, the surface coverage for the electrode modified with **16** was $3.62 \times 10^{-9}\,mol\,cm^{-2}$ (ferrocenyl sites), corresponding to $1.34 \times 10^{-10}\,mol\,cm^{-2}$ of **16** after 50 adsorption cycles, and $6.23 \times 10^{-9}\,mol\,cm^{-2}$ (ferrocenyl sites), corresponding to $2.31 \times 10^{-10}\,mol\,cm^{-2}$ of **16** after 200 cycles (Table 5).

Synthesis of methyl 3,4,5-tris(prop-2-yn-1-yloxy)benzoate (2): A mixture of methyl 3,4,5-trihydroxybenzoate **1** (10 g, 0.0543 mol) and propargyl bromide (80 % in toluene) (21 mL, 0.19 mol) was stirred for 10 min in degassed acetone. K_2CO_3 (50 g, 0.362 mol) was then added, and the reaction was carried out overnight under reflux. Thereafter, the solvent was removed from the resulting brown solution by rotary evaporation. The solid was redissolved in CH_2Cl_2 (200 mL), and this solution was dried over anhydrous magnesium sulfate and filtered. The solvent was removed by rotary evaporation. The product **2** was obtained as a slightly yellow oil that recrystallized (15.1 g, 93 %). M.p. 89.4 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.44$ (s, 2H; H_{Ar}), 4.80 (d, $^4J(H,H) = 2.3$ Hz, 2H; $p\text{-O-C}H_2\text{-C}{\equiv}C$), 4.78 (d, $^4J(H,H) = 2.3$ Hz, 4H; $m\text{-O-C}H_2\text{-C}{\equiv}C$), 3.89 (s, 3H; $CH_3\text{-O}$), 2.53 (t, $^4J(H,H) = 2.3$ Hz, 2H; $C{\equiv}C\text{-}H$), 2.45 ppm (t, $^4J(H,H) = 2.3$ Hz, 1H; $C{\equiv}C\text{-}H$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 166.23$, 151.27, 141.07, 125.74 (quat. C_{Ar}), 109.84 (C_{Ar}-H), 78.68, 77.94,

Table 5. Electrode surface coverage (Γ in mol cm^{-2}) for the various modified Pt electrodes.

	Γ [mol cm^{-2}][a] (ferrocenyl sites)	Γ [mol cm^{-2}][a]	Γ [mol cm^{-2}][b] (ferrocenyl sites)	Γ [mol cm^{-2}][b]
27-Fc **16** on Pt	3.62×10^{-9}	1.34×10^{-10}	6.23×10^{-9}	2.31×10^{-10}
81-Fc **17** on Pt	6.56×10^{-9}	8.10×10^{-11}	2.13×10^{-8}	2.63×10^{-10}
243-Fc **18** on Pt	7.46×10^{-9}	3.07×10^{-11}	3.75×10^{-8}	1.54×10^{-10}

[a] On the modified Pt electrode obtained after 50 adsorption cycles. [b] On the modified Pt electrode obtained after 200 adsorption cycles.

76.22, 75.60 (*C*≡C-H, C≡*C*-H), 60.30, 57.05 (O-*C*H$_2$-C≡C-H), 52.35 ppm (O-*C*H$_3$); IR: $\tilde{\nu}$=1724 (C=O), 2121 (C≡C), 3274 cm^{-1} (C≡C-H); MS: *m*/*z*: 619 [2*M*+Na$^+$], 321 [*M*+Na$^+$], 299 [*M*+H$^+$].

Synthesis of [3,4,5-tris(prop-2-yn-1-yloxy)phenyl]methanol (3): $LiAlH_4$ (19.3 g, 0.508 mol) was added to dry THF and this suspension was cooled to 0 °C. A solution of methyl 3,4,5-tris(prop-2-yn-1-yloxy)benzoate **2** (15.1 g, 0.0507 mol) in dry THF was then added dropwise. The mixture was stirred at 0 °C for 1 h, then at room temperature for a further 5 h. Thereafter, excess $LiAlH_4$ was quenched with water, and the solution was concentrated by rotary evaporation. The concentrate was extracted with CH_2Cl_2 (3×200 mL), and the combined organic layers were dried over anhydrous magnesium sulfate and filtered. The solvent was removed by rotary evaporation. The product **3** was obtained as a white powder (9.6 g, 70 %). M.p. 103.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=6.78 (s, 2H; *H*$_{Ar}$), 4.76 (d, ^4J(H,H)=2.4 Hz, 4H; *m*-O-C*H*$_2$-C≡C), 4.72 (d, ^4J(H,H)=2.1 Hz, 2H; *p*-O-C*H*$_2$-C≡C), 4.65 (s, ^3J(H,H)=6.1 Hz, 2H; HO-C*H*$_2$-C$_{Ar}$), 2.51 (t, ^4J(H,H)=2.4 Hz, 2H; C≡C-*H*), 2.46 (t, ^4J(H,H)=2.1 Hz, 1H; C≡C-*H*), 1.73 ppm (t, ^3J(H,H)=6.1 Hz, 1H; O*H*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=151.59, 145.31, 137.38 (quat. *C*$_{Ar}$), 106.88 (*C*$_{Ar}$-H), 79.17, 78.51, 75.91, 75.29 (*C*≡C-H, C≡*C*-H), 64.93 (HO-*C*H$_2$), 60.27, 56.94 ppm (O-*C*H$_2$-C≡C-H); IR: $\tilde{\nu}$=2121 (C≡C), 3294 (C≡C-H), 3538 cm^{-1} (O-H); MS: *m*/*z*: 563 [2*M*+Na$^+$], 293 [*M*+Na$^+$], 271 [*M*+H$^+$].

Synthesis of 5-(bromomethyl)-1,2,3-tris(prop-2-yn-1-yloxy)benzene (4): Compound **3** (9.6 g, 0.0356 mol) and PBr_3 (3.35 mL, 0.0356 mol) were stirred together in CH_2Cl_2 (dried over calcium hydride and freshly distilled) for 12 h at room temperature. Water was then added to quench the excess PBr_3. The mixture was concentrated by rotary evaporation and extracted with CH_2Cl_2 (3×200 mL). The combined organic layers were then dried over anhydrous magnesium sulfate and filtered. The solvent was removed by rotary evaporation to give compound **4** as a slightly yellow oil that recrystallized (9.2 g, 77 %). M.p. 63.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=6.75 (s, 2H; *H*$_{Ar}$), 4.71 (d, ^4J(H,H)=2.6 Hz, 4H; *m*-O-C*H*$_2$-C≡C), 4.67 (d, ^4J(H,H)=2.2 Hz, 2H; *p*-O-C*H*$_2$-C≡C), 4.41 (s, 2H; Br-C*H*$_2$-C$_{Ar}$), 2.52 (t, ^4J(H,H)=2.6 Hz, 2H; C≡C-*H*), 2.45 ppm (t, ^4J(H,H)=2.2 Hz, 1H; C≡C-*H*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=150.54, 136.16, 132.75 (quat. *C*$_{Ar}$), 108.42 (*C*$_{Ar}$-H), 78.06, 77.26, 75.19, 74.45 (*C*≡C-H, C≡*C*-H), 59.31, 56.04 (O-*C*H$_2$-C≡C-H), 52.61 ppm (*C*H$_2$-Br); IR: $\tilde{\nu}$=2120 cm^{-1} (C≡C), 3290.6 cm^{-1} (C≡C-H); MS: *m*/*z*: 355, 357 [*M*+Na$^+$], 333, 335 [*M*+H$^+$].

Synthesis of the “trialkyne-phenol” dendron 4-{[3,4,5-tris(prop-2-yn-1-yloxy)benzyl]oxy}phenol (5): Hydroquinone (0.99 g, 9 mmol) and K_2CO_3 (0.89 g, 6.5 mmol) were stirred together at 80 °C in dry dimethylformamide (DMF; 250 mL), and then a solution of compound **4** (0.5 g, 1.5 mmol) in DMF (100 mL) was added dropwise over a period of 1 h. The reaction was carried out for 18 h at 80 °C. The DMF was then removed in vacuo and the residue was partitioned between water and CH_2Cl_2. The organic layer was concentrated in vacuo and chromatographed on silica gel, eluting first with CH_2Cl_2 and then with CH_2Cl_2/MeOH 9:1. The obtained oil was dissolved in the minimum volume of CH_2Cl_2 and precipitated using excess pentane. The “trialkyne-phenol” dendron **5** was obtained as an off-white powder (0.5 g, 92 %). M.p. 76.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=6.87–6.74 (m, 6H; *H*$_{Ar}$), 4.95 (s, 2H; O-C*H*$_2$-C$_{Ar}$), 4.76 (d, ^4J(H,H)=1.9 Hz, 4H; *m*-O-C*H*$_2$-C≡C), 4.73 (d, ^4J(H,H)=1.9 Hz, 2H; *p*-O-C*H*$_2$-C≡C), 2.50–2.45 ppm (m, 3H; C≡C-*H*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=152.67, 151.67, 149.92, 136.63, 133.53 (quat. *C*$_{Ar}$), 116.14, 116.08, 107.74 (*C*$_{Ar}$-H), 79.14, 78.37, 75.98, 75.34 (*C*≡C-H, C≡*C*-H), 70.65 (C$_{Ar}$-*C*H$_2$-O), 60.36, 57.04 ppm (O-*C*H$_2$-C≡C-H); IR: $\tilde{\nu}$=2123 (C≡C), 3283 (C≡C-H), 3500 cm^{-1} (O-H); MS: *m*/*z*: 747 [2*M*+Na$^+$], 385 [*M*+Na$^+$]; elemental analysis calcd (%) for $C_{22}H_{18}O_5$: C 72.91, H 5.01, O 22.08; found: C 72.39, H 4.99, O 22.25.

General procedure for the synthesis of the polyalkynyl dendrimers: A mixture of poly-iodomethyl(dimethyl)silyl dendritic core (1 equiv), phenol dendron **5** (2 equiv per branch), and K_2CO_3 (5 equiv per branch) was stirred in dry DMF at room temperature (1 d for the 27-iodo, 2 d for the 81-iodo, and 4 d for the 243-iodo dendritic core) under nitrogen atmosphere. The mixture was then stirred for a further 48 h at 80 °C. Thereafter, the solvent was removed in vacuo, and the residue was redissolved in CH_2Cl_2. This solution was filtered through silica and concentrated by rotary evaporation. The product was precipitated by treating the concentrated solution with excess MeOH three times to give the desired polyalkynyl dendrimer as an off-white gum in yields of 67, 61, and 59 %, respectively.

27-Alkynyl dendrimer 13: $C_{261}H_{282}O_{45}Si_9$; *M*$_W$ 4391.89 g mol^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.00–6.80 (m, 57H; *H*$_{Ar}$), 4.88 (s, 18H; O-C*H*$_2$-C$_{Ar}$), 4.74 (s, 54H; O-C*H*$_2$-C≡C), 3.46 (s, 18H; Si-C*H*$_2$-O), 2.49 (s, 18H; C≡C-*H*), 2.47 (s, 27H; C≡C-*H*), 1.66 (s, 18H; C*H*$_2$-CH$_2$-CH$_2$-Si), 1.15 (s, 18H; CH$_2$-C*H*$_2$-CH$_2$-Si), 0.60 (s, 18H; CH$_2$-CH$_2$-C*H*$_2$-Si), 0.05 ppm (s, 54H, Si-C*H*$_3$); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C, TMS): δ=156.46, 152.85, 152.03, 146.19, 136.98, 133.91 (quat. *C*$_{Ar}$), 116.45, 116.08, 115.14, 108.04 (*C*$_{Ar}$-H), 79.55, 78.83, 76.34, 75.69 (*C*≡C-H, C≡*C*-H), 70.91 (C$_{Ar}$-*C*H$_2$-O), 61.25 (Si-*C*H$_2$-O), 60.72, 57.37 (O-*C*H$_2$-C≡C-H), 44.29 (quat. *C*), 42.36 (*C*H$_2$-CH$_2$-CH$_2$-Si), 18.24 (CH$_2$-*C*H$_2$-CH$_2$-Si), 14.98 (CH$_2$-CH$_2$-*C*H$_2$-Si), −4.08 ppm (Si-*C*H$_3$); ^{29}Si NMR (60 MHz, $CDCl_3$, 25 °C, TMS): the spectrum showed only one peak at δ=0.85 ppm (all the branches had reacted); IR: $\tilde{\nu}$=2122 (C≡C), 3291 cm^{-1} (C≡C-H); MALDI-TOF: *m*/*z*: calcd for 4415.7; found: 4415.1 [*M*+Na$^+$]; elemental analysis calcd (%) for $C_{261}H_{282}O_{45}Si_9$: C 71.38, H 6.47; found: C 70.41, H 6.30; DOSY NMR gave $D=2.77\times10^{-10}$ m^2 s^{-1} in chloroform at 25 °C, which corresponds to a size of 4.1 nm; SEC showed the low polydispersity (1.02) and the size progression for the three alkynyl dendrimers.

81-Alkynyl dendrimer 14: $C_{882}H_{1002}O_{144}Si_{36}$; *M*$_W$ 14918.46 g mol^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.20–6.80 (m, 201H; *H*$_{Ar}$), 4.90 (s, 54H; O-C*H*$_2$-C$_{Ar}$), 4.74 (s, 162H; O-C*H*$_2$-C≡C), 3.57 (s, 18H; inner Si-C*H*$_2$-O), 3.48 (s, 54H; outer Si-C*H*$_2$-O), 2.50 (s, 81H; C≡C-*H*), 1.65 (s, 72H; C*H*$_2$-CH$_2$-CH$_2$-Si), 1.16 (s, 72H; CH$_2$-C*H*$_2$-CH$_2$-Si), 0.59 (s, 72H; CH$_2$-CH$_2$-C*H*$_2$-Si), 0.12 (s, 54H; inner Si-C*H*$_3$), 0.05 ppm (s, 162H; outer Si-C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=158.00, 155.04, 151.41, 150.60, 144.76, 138.26, 135.58, 132.53 (quat. *C*$_{Ar}$), 126.14, 117.01, 114.70, 113.76, 112.38, 106.68 (*C*$_{Ar}$-H), 78.17, 77.44, 74.98, 74.34 (*C*≡C-H, C≡*C*-H), 69.50 (C$_{Ar}$-*C*H$_2$-O), 59.89, 59.27, 59.07, 55.98 (O-*C*H$_2$-C≡C-H, Si-*C*H$_2$-O), 42.00 (*C*$_{quat}$), 40.98 (*C*H$_2$-CH$_2$-CH$_2$-Si), 16.61 (CH$_2$-*C*H$_2$-CH$_2$-Si), 13.53 (CH$_2$-CH$_2$-*C*H$_2$-Si), −5.44, −5.60 ppm (Si-*C*H$_3$); ^{29}Si NMR (60 MHz, $CDCl_3$, 25 °C, TMS): the spectrum showed only one peak at δ=0.793 ppm (all the branches had reacted); IR: $\tilde{\nu}$=2122 (C≡C), 3292 cm^{-1} (C≡C-H); elemental analysis calcd (%) for $C_{882}H_{1002}O_{144}Si_{36}$: C 71.01, H 6.77; found: C 70.51, H 7.28; DOSY NMR gave $D=2.41\times10^{-10}$ m^2 s^{-1} in chloroform at 25 °C, which corresponds to a size of 4.8 nm; DLS was indicative of only one population at a size of 6.2±0.2 nm; SEC showed the low polydispersity (1.02) and the size progression for the three alkynyl dendrimers.

243-Alkynyl dendrimer 15: $C_{2745}H_{3162}O_{441}Si_{117}$; *M*$_W$ 46498.43 g mol^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.14–6.75 (m, 633H; *H*$_{Ar}$) 4.84 (s, 162H; O-C*H*$_2$-C$_{Ar}$), 4.69 (s, 486H; O-C*H*$_2$-C≡C), 3.50 (s, 72H; inner Si-C*H*$_2$-O), 3.42 (s, 162H; outer Si-C*H*$_2$-O), 2.47–2.43 (m, 243H; C≡C-*H*), 1.61 (s, 234H; C*H*$_2$-CH$_2$-CH$_2$-Si), 1.11 (s, 234H; CH$_2$-C*H*$_2$-CH$_2$-Si), 0.54 (s, 234H; CH$_2$-CH$_2$-C*H*$_2$-Si), 0.06 (s, 216H; inner Si-C*H*$_3$), 0.01 ppm (s, 486H; outer Si-C*H*$_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, TMS): $\delta=159.05$, 156.10, 152.49, 151.69, 139.33, 136.69, 133.58 (quat. C_{Ar}), 127.21, 115.57, 114.83, 113.46, 107.76 (C_{Ar}-H), 79.24, 78.51, 76.04, 75.37 (C≡C-H, C≡C-H), 70.55 ($\mathrm{C_{Ar}}$-$C\mathrm{H_2}$-O), 60.92, 60.35, 60.15, 57.06 (O-$C\mathrm{H_2}$-C≡C-H, Si-$C\mathrm{H_2}$-O), 43.06 (quat. C), 42.09 ($C\mathrm{H_2}$-$\mathrm{CH_2}$-$\mathrm{CH_2}$-Si), 17.71 ($\mathrm{CH_2}$-$C\mathrm{H_2}$-$\mathrm{CH_2}$-Si), 14.62 ($\mathrm{CH_2}$-$\mathrm{CH_2}$-$C\mathrm{H_2}$-Si), −4.51 ppm (Si-$C\mathrm{H_3}$); ^{29}Si NMR (59.6 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): the spectrum showed only one peak at $\delta=0.792$ ppm (all the branches have reacted); IR: $\tilde{\nu}=2122$ (C≡C), 3293 cm^{-1} (C≡C-H); DOSY NMR gave $D=2.35\times10^{-10}\,\mathrm{m^2\,s^{-1}}$ in chloroform at 25 °C, which corresponds to a size of 4.9 nm; DLS was indicative of only one population at a size of 6.6 ± 0.2 nm; SEC showed the low polydispersity (1.02) and the size progression for the three alkynyl dendrimers.

Second procedure for the synthesis of the 27-alkynyl dendrimer 13: The nona-chloromethyl(dimethyl)silyl dendrimer **8** (0.1 g, 0.069 mmol), sodium iodide (0.1 g, 0.67 mmol), and the phenol dendron **5** (0.45 g, 1.24 mmol) were stirred in DMF at 80 °C for two days and then for a further day at room temperature. The DMF was then removed in vacuo. The residue was redissolved in $\mathrm{CH_2Cl_2}$ and the product was precipitated with excess MeOH to give the 27-propargyl dendrimer, **10**, as an off-white gum (0.21 g, 70 %). The spectroscopic data were identical to those obtained in the first synthesis (vide supra).

General procedure for the "click" coupling: The polyalkynyl dendrimer (1 equiv) and azidomethylferrocene **20** (2 equiv per branch) were dissolved in THF (30 mL). Copper(II) sulfate pentahydrate (4 equiv per branch) was then added with a small amount of water (20 mL), and the mixture was stirred and heated until complete dissolution. Sodium ascorbate (8 equiv per branch) was dissolved in water (10 mL) and this solution was added dropwise to the mixture. The resulting mixture was stirred overnight at room temperature under a nitrogen atmosphere. It was then concentrated by rotary evaporation and the residue was partitioned between $\mathrm{CH_2Cl_2}$ and aqueous ammonia solution. The organic layer was washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography, eluting first with $\mathrm{CH_2Cl_2}$ and then with $\mathrm{CH_2Cl_2}$/MeOH 9:1, to yield the desired dendrimers as yellow powders in yields of 72, 70, and 69 %, respectively.

27-Ferrocenyl dendrimer 16: $\mathrm{C_{558}Fe_{27}H_{579}N_{81}O_{45}Si_9}$; MW 10 900.88 g mol^{-1}; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta=7.62$, 7.60 (s, 27 H; H_{triazole}), 7.12–6.66 (m, 57 H; H_{Ar}), 5.24–5.05 (m, 108 H; $\mathrm{C_{triazole}}$-CH_2-$\mathrm{C_{ferrocene}}$, $\mathrm{C_{triazole}}$-CH_2-O), 4.72 (s, 18 H; $\mathrm{C_{Ar}}$-CH_2-O), 4.27–4.13 (m, 243 H; $\mathrm{C_{ferrocene}}$-H), 3.48 (s, 18 H; Si-CH_2-O), 1.68 (s, 18 H; CH_2-$\mathrm{CH_2}$-$\mathrm{CH_2}$-Si), 1.15 (s, 18 H; $\mathrm{CH_2}$-CH_2-$\mathrm{CH_2}$-Si), 0.60 (s, 18 H; $\mathrm{CH_2}$-$\mathrm{CH_2}$-CH_2-Si), 0.05 ppm (s, 54 H; Si-CH_3); ^{13}C NMR (63 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta=$ 156.44, 152.82, 152.58 (quat. C_{Ar}), 146.62 (core quat. C_{Ar}), 144.72, 143.98 (quat. C_{triazole}), 137.10, 133.84 (quat. C_{Ar}), 123.77, 123.28 (C_{triazole}-H), 116.38, 115.88 (C_{Ar}-H), 115.19 (core C_{Ar}-H), 107.26 (C_{Ar}-H), 81.80, 81.48 (quat. $C_{\mathrm{ferrocene}}$), 72.58, 70.73, 69.30, 69.14, 66.67, 66.01 ($C_{\mathrm{ferrocene}}$-H), 63.41, 63.36 ($\mathrm{C_{triazole}}$-$C\mathrm{H_2}$-O), 61.27 (Si-$C\mathrm{H_2}$-O), 50.40, 50.24 ($\mathrm{C_{ferrocene}}$-$C\mathrm{H_2}$-N), 44.31 (C_{quat}), 42.35 ($C\mathrm{H_2}$-$\mathrm{CH_2}$-$\mathrm{CH_2}$-Si), 18.24 ($\mathrm{CH_2}$-$C\mathrm{H_2}$-$\mathrm{CH_2}$-Si), 14.95 ($\mathrm{CH_2}$-$\mathrm{CH_2}$-$C\mathrm{H_2}$-Si), −4.04 ppm (Si-$C\mathrm{H_3}$); ^{29}Si NMR: the spectrum showed only one peak at $\delta=-0.388$ ppm; no azide or alkyne absorption was visible in the IR spectrum; MALDI-TOF MS: *m*/*z*: calcd for 10 924 [M+Na$^+$]; found: 10 927, side peaks: 10 686 [$M-$ferrocenyl$^+$], 10 444 [$M-2$ ferrocenyl$^+$], 9866 [$M-$dendron$^+$], 9632 [$M-$dendron$-$ferrocenyl$^+$]; DOSY NMR gave $D=3.65\times10^{-10}\,\mathrm{m^2\,s^{-1}}$ in chloroform, which corresponds to a size of 3.2 nm; SEC showed the low polydispersity (1.03) and the size progression for the three ferrocenyl dendrimers. Some signals appeared as doublets in the NMR spectra due to the difference between *meta* and *para* substituents (such as for the 81-ferrocenyl and the 243-ferrocenyl dendrimers).

81-Ferrocenyl dendrimer 17: $\mathrm{C_{1773}Fe_{81}H_{1893}N_{243}O_{144}Si_{36}}$; M_{W} 34 445.72 g mol^{-1}; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta=7.62$, 7.59 (s, 81 H; H_{triazole}), 7.16–6.66 (m, 201 H; H_{Ar}), 5.20–5.02 (m, 324 H; $\mathrm{C_{triazole}}$-CH_2-$\mathrm{C_{ferrocene}}$, $\mathrm{C_{triazole}}$-CH_2-O), 4.71 (s, 54 H; $\mathrm{C_{Ar}}$-CH_2-O), 4.25–4.11 (m, 729 H; $\mathrm{C_{ferrocene}}$-H), 3.54 (s, 18 H; inner Si-CH_2-O), 3.44 (s, 54 H; outer Si-CH_2-O), 1.63 (s, 72 H; CH_2-$\mathrm{CH_2}$-$\mathrm{CH_2}$-Si), 1.12 (s, 72 H; $\mathrm{CH_2}$-CH_2-$\mathrm{CH_2}$-Si), 0.56 (s, 72 H; $\mathrm{CH_2}$-$\mathrm{CH_2}$-CH_2-Si), 0.12 (s, 54 H; inner Si-CH_3), 0.02 ppm (s, 162 H; outer Si-CH_3); ^{13}C NMR (75.5 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta=$ 159.07 (inner quat. C_{Ar}), 156.10, 152.46, 152.22 (outer quat. C_{Ar}), 144.33, 143.60 (quat. C_{triazole}), 139.26 (inner quat. C_{Ar}), 136.84, 133.51 (outer quat. C_{Ar}), 127.18 (inner C_{Ar}-H), 123.48, 123.00 (C_{triazole}-H), 116.07, 115.56 (outer C_{Ar}-H), 114.87 (inner C_{Ar}-H), 107.00 (outer C_{Ar}-H), 81.49, 81.21 (quat. $C_{\mathrm{ferrocene}}$), 72.02, 70.41, 68.93, 68.75, 66.30, 65.94 ($C_{\mathrm{ferrocene}}$-H), 63.04 ($\mathrm{C_{triazole}}$-$C\mathrm{H_2}$-O), 60.97 (Si-$C\mathrm{H_2}$-O), 50.02, 49.88 ($\mathrm{C_{ferrocene}}$-$C\mathrm{H_2}$-N), 43.06 (C_{quat}), 42.00 ($C\mathrm{H_2}$-$\mathrm{CH_2}$-$\mathrm{CH_2}$-Si), 17.62 ($\mathrm{CH_2}$-$C\mathrm{H_2}$-$\mathrm{CH_2}$-Si), 14.57 ($\mathrm{CH_2}$-$\mathrm{CH_2}$-$C\mathrm{H_2}$-Si), −4.49 ppm (Si-$C\mathrm{H_3}$); ^{29}Si NMR: the spectrum showed only one peak at $\delta=-0.412$ ppm; no azide or alkyne absorption was visible in the IR spectrum; DOSY NMR gave $D=3.02\times10^{-10}\,\mathrm{m^2\,s^{-1}}$ in chloroform, which corresponds to a size of 3.8 nm; SEC showed the low polydispersity (1.01) and the size progression for the three ferrocenyl dendrimers.

243-Ferrocenyl dendrimer 18: $\mathrm{C_{5418}Fe_{243}H_{5835}N_{729}O_{441}Si_{117}}$; M_{W} 105 080.24 g mol^{-1}; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta=7.61$, 7.59 (s, 243 H; H_{triazole}), 7.16–6.64 (m, 633 H; H_{Ar}), 5.15–5.01 (m, 972 H; $\mathrm{C_{triazole}}$-CH_2-$\mathrm{C_{ferrocene}}$, $\mathrm{C_{triazole}}$-CH_2-O), 4.70 (s, 162 H; $\mathrm{C_{Ar}}$-CH_2-O), 4.22–4.08 (m, 2187 H; $\mathrm{C_{ferrocene}}$-H), 3.51 (s, 72 H; inner Si-CH_2-O), 3.43 (s, 162 H; outer Si-CH_2-O), 1.60 (s, 234 H; CH_2-$\mathrm{CH_2}$-$\mathrm{CH_2}$-Si), 1.10 (s, 234 H; $\mathrm{CH_2}$-CH_2-$\mathrm{CH_2}$-Si), 0.55 (s, 234 H; $\mathrm{CH_2}$-$\mathrm{CH_2}$-CH_2-Si), 0.07 (s, 216 H; inner Si-CH_3), 0.02 ppm (s, 486 H; outer Si-CH_3); ^{13}C NMR (75.5 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta=159.09$ (inner quat. C_{Ar}), 156.08, 152.46, 152.22 (outer quat. C_{Ar}), 144.33, 143.60 (quat. C_{triazole}), 138.92 (inner quat. C_{Ar}), 136.81, 133.48 (outer quat. C_{Ar}), 128.85, 127.17 (inner C_{Ar}-H), 123.42, 122.97 (C_{triazole}-H), 115.82, 115.55 (outer C_{Ar}-H), 114.87 (inner C_{Ar}-H), 106.99 (outer C_{Ar}-H), 81.56, 81.24 (quat. $C_{\mathrm{ferrocene}}$), 72.07, 70.41, 68.93, 68.61, 66.34, 65.94 ($C_{\mathrm{ferrocene}}$-H), 63.08 ($\mathrm{C_{triazole}}$-$C\mathrm{H_2}$-O), 60.95 (Si-$C\mathrm{H_2}$-O), 50.02, 49.87 ($\mathrm{C_{ferrocene}}$-$C\mathrm{H_2}$-N), 43.06 (C_{quat}), 42.54 ($C\mathrm{H_2}$-$\mathrm{CH_2}$-$\mathrm{CH_2}$-Si), 17.62 ($\mathrm{CH_2}$-$C\mathrm{H_2}$-$\mathrm{CH_2}$-Si), 14.66 ($\mathrm{CH_2}$-$\mathrm{CH_2}$-$C\mathrm{H_2}$-Si), −4.44 ppm (Si-$C\mathrm{H_3}$); ^{29}Si NMR: the spectrum showed only one peak at $\delta=-0.425$ ppm; no azide or alkynyl absorption was visible in the IR spectrum. DOSY NMR gave $\mathrm{D}=2.74\times10^{-10}\,\mathrm{m^2\,s^{-1}}$ in chloroform, which corresponds to a size of 4.2 nm. DLS was indicative of only one population with a size of 5.3 ± 1.0 nm. SEC showed the low polydispersity (1.1) and the size progression for the three ferrocenyl dendrimers.

Synthesis of the triazolylferrocenyl monomer 19: Propargyl alcohol (50 µL, 0.86 mol) and azidomethylferrocene **20** (0.1 g, 0.42 mmol) were dissolved in THF (20 mL). Copper(II) sulfate pentahydrate (0.42 g, 1.7 mmol) was then added with a small amount of water (15 mL), and the mixture was stirred and heated until complete dissolution. Sodium ascorbate (0.66 g, 3.3 mmol) was dissolved in water (5 mL) and this solution was added dropwise to the mixture. The resulting mixture was stirred at room temperature overnight. It was then concentrated by rotary evaporation and the residue was partitioned between $\mathrm{CH_2Cl_2}$ and aqueous ammonia solution. The organic layer was washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated by rotary evaporation. The desired click-ferrocenyl monomer was precipitated with excess pentane. It was recovered in quantitative yield as a yellow powder (0.12 g). M.p. 161.2 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta=7.42$ (s, 1 H; H_{triazole}), 5.29 (s, 2 H; N-CH_2-$\mathrm{C_{ferrocene}}$), 4.74 (d, ^3J(H,H) = 6.1 Hz, 2 H; $\mathrm{C_{triazole}}$-CH_2-OH), 4.29–4.19 (m, 9 H; $\mathrm{C_{ferrocene}}$-H), 2.31 ppm (t, ^3J(H,H) = 6.1 Hz, 1 H; O-H); ^{13}C NMR (75.5 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta=147.43$ (quat. C_{triazole}), 120.91 (C_{triazole}-H), 80.65 (quat. $C_{\mathrm{ferrocene}}$), 69.12, 68.95, 68.91 ($C_{\mathrm{ferrocene}}$-H), 56.70 ($\mathrm{C_{ferrocene}}$-$C\mathrm{H_2}$-N), 50.09 ppm ($C\mathrm{H_2}$-OH); IR: no alkyne or azide absorption was visible; MS: *m*/*z*: 617 [2M+Na$^+$], 320.05 [M+Na$^+$], 298 [M+H$^+$]; elemental analysis calcd (%) for $\mathrm{C_{14}H_{15}ON_3Fe}$: C 56.59, H 5.09; found: C 56.82, H 5.34.

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