FEATURE ARTICLE

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Dendrimers and gold nanoparticles as exo-receptors sensing biologically important anions†

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Dendrimers, alkylthiol-gold nanoparticles and gold-nanoparticle-cored dendrimers containing tethers terminated by a redox group (typically an iron sandwich) attached to a hydrogen-bonding group (amido, amino, silyl) are selective and efficient exo-receptors for the recognition, sensing and titration of oxo-anions, including ATP^{2-}, or halogens, mostly using cyclic voltammetry. Various positive dendritic effects were disclosed (in contrast to catalysis), and large gold-nanoparticle-cored redox dendrimers of this type that contain several hundred equivalent ferrocenyl groups readily adsorb on Pt electrodes, providing useful regenerable electrochemical sensors.

Introduction

As recalled by Lehn, molecular recognition is relevant to what can be called molecular sociology.[1] Since the enunciation of the "Lock-and-key" principle by Emil Fisher in 1894, selectivity in chemical binding has been a "Holy Trail" for chemists and biologists.[2] The concept of molecular recognition, introduced a century ago by Ehrlich,[3] has culminated only recently, however, especially in connection to life sciences, with the explosion of supramolecular chemistry.[1,4–11] Both electrochemical and optical properties (in particular fluorescence methods) of hosts have proven to be valuable for the design of sensory devices devoted to the recognition of cations, anions and neutral molecules.[4–11] The selective binding of guest ions by endo-receptor hosts coupled with an electrochemical response is a powerful method of paramount interest, and amperometric devices can be built on this principle.[4,5,8–11] A remarkable example is illustrated by the use of the ferrocene/ferrocenium redox mediator to fabricate an electrochemical glucose sensor.[7] The facility to switch on and off electrochemically using ferrocene has been first utilized by Saiji to transport alkali-metal cations across a liquid membrane containing a ferrocene-crown carrier.[8] (Fig. 1).

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Anions, the subject of this Feature Article, play many important roles in biology (for instance adenosine mono-, di- and triphosphate, AMP, ADP, ATP, DNA itself, RNA *etc.*)[1,4,5,9] and environmental problems (nitrate, phosphate, radioactive pertechnetate) and their recognition by endo-receptors has been extensively studied.[1,4,5,9,10] The use of metallocene switches to sense anions electrochemically has been in particular remarkably developed by Beer through elegant studies with the design of a variety of endo-receptors (chelates, tripods, crowns, porphyrins, calixarenes).[9] The interactions of anions with these metallocene-type endo-receptors are most often based on hydrogen-bonding interactions between the anion and a functional group nearby the redox center, so that the redox potential of this redox center is shifted upon interaction with the anion.[9] Moutet's group has also published several interesting reports along this line, especially with the biologically important ATP anion.[10] Supramolecular aspects of electrochemistry are relevant to this area and have been highlighted by Kaifer.[11]

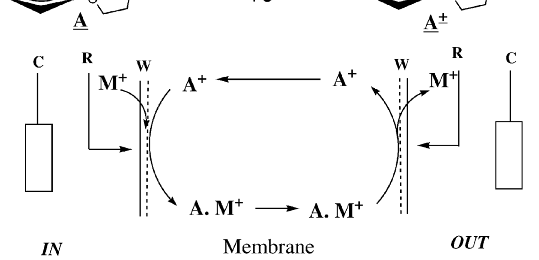

Fig. 1 Electrochemical ion transport using a redox-active crown-ether. W: minigrid platinum working electrodes; C: platinum plate counter electrodes; R: saturated calomel reference electrodes. Adapted from Saji and Kinoshita's report (ref. 8).

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† This feature article is dedicated to the memory of Professor Jean-Marc Kern, our distinguished colleague from the Louis Pasteur University (Strasbourg) deceased in the tragic plane crash of Charm-El-Cheik on January 2, 2004.

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Ferrocenyl dendrimers as electrochemical exo-receptors

Ferrocenyl dendrimers[12–25] whose first examples appeared in the early 90's[25] are well suited to function as electrochemical sensors, when all the ferrocenyl termini are equivalent, because they show a single wave in cyclic voltammetry (CV).[26] It seemingly means that the redox potentials of all these redox centers are the same. This is not exactly true because of the electrostatic factor. For instance, the oxidation of the second redox center is more difficult than the first one because of the repulsion between the two positive charges upon oxidation of a monocation.[27] This factor appears to be extremely weak in ferrocenyl-terminated dendrimers, however, because the ferrocenyl termini are separated by many bonds, and the through-space coulombic interaction is also apparently too weak to be detected even in large ferrocenyl dendrimers. Dendrimers with receptor sites at the periphery are exo-receptors in contrast with the above endo-receptors. The specificities of dendritic exo-receptors are the fractality of their surfaces that recalls that of viruses and cancer cells and their nanometer dimensions that allow recovery as for polymers and nano-sized biomolecules. They can also adsorb much more easily on surfaces than small endo-receptors, which leads to their use for the modification of electrodes and their function as re-usable sensors on metal surfaces.

The first examples of ferrocenyl dendrimers functioning for the recognition of anions were 9- and 18-amidoferrocenyldendrimers that were formed by reaction of chlorocarbonylferrocene with polyamine dendrimers.[28] Titration of these metallodendrimers were carried out using n-Bu$_4$N$^+$ salts of $H_2PO_4^-$, HSO_4^-, Cl^-, and NO_3^- and monitored by CV in CH_2Cl_2 (Fig. 2) and ^{1}H NMR. In CV, two types of behavior were recorded: (i) appearance of a new CV wave at less positive potentials for $H_2PO_4^-$ while the intensity of the initial CV wave decreases (for one equiv. anion, $\Delta E°$ was 220 mV with 9-Fc and 315 mV with 18-Fc), and (ii) progressive anodic shift of the initial wave for the HSO_4^-, Cl^- and NO_3^- (for one equiv. anion, $\Delta E°$ was respectively 65 mV, 20 mV and negligible with 9-Fc and 130 mV, 45 mV and 30 mV with 18-Fc).

The dichotomy of CV behavior between strongly and weakly interacting anions had been rationalized in the seminal article by Echegoyen and Kaifer's group with the square Scheme 1:[30] when the strength of the interaction between the anion and the reduced redox form (here ferrocenyl) is significant, a new wave appears, and the variation of ferrocenyl potential between the free and bound forms of Scheme 1 is related to the ratio of apparent association constants as follows: $E°_{\text{free}} - E°_{\text{bound}} = \Delta E°(\text{V}) = 0.059 \log (K_+/K_0)$ at 25 °C. $E°_{\text{bound}}$ corresponds to the addition of one equiv. anion per ferrocenyl branch, or throughout the article, the stoichiometric amount determined from the break points, for instance in Fig. 2.

Although only the ratio of apparent association constants is

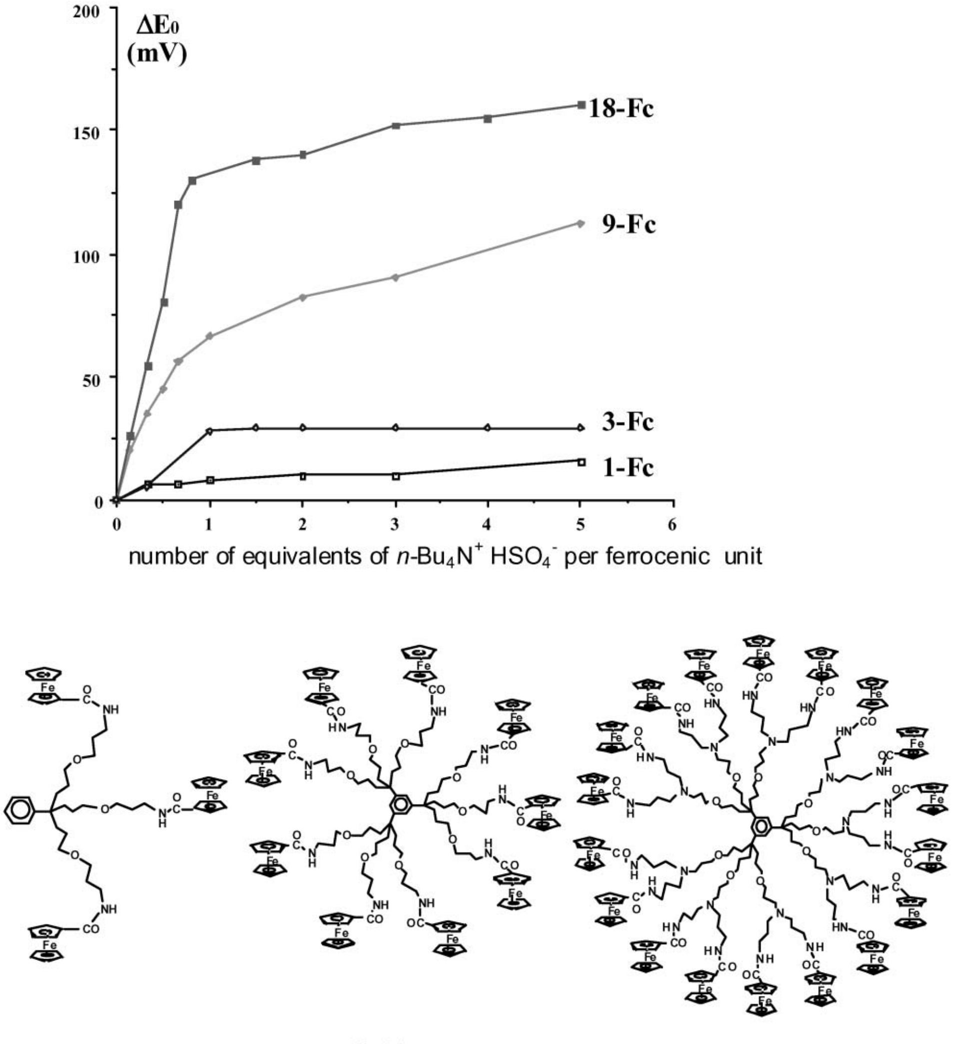
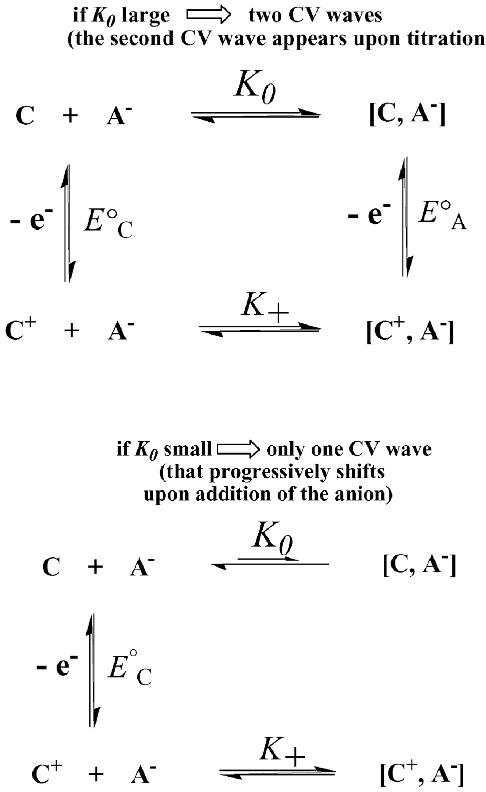


Fig. 2 Variation (shift, cf. Scheme 1, bottom) $\Delta E°$ of the redox potential of the ferrocenyl system recorded by CV along the titration of [n-Bu$_4$N][HSO$_4$] by mono- (1-Fc), tri- (3-Fc), nona- (9-Fc) and octadeca-amidoferrocenyl (18-Fc) compounds showing the marked dendritic effect (1-Fc is the monoamidoferrocenyl derivative [FeCp(η^5-C$_5$H$_4$CONHCH$_2$CH$_2$OPh)]).[28,29]



Scheme 1 Square scheme in the cases where (i) the host–guest interaction is strong even in the reduced redox form of the host (top) and (ii) this interaction is negligible (bottom).[38]

accessible in this way, measurement of K_0 by ^{1}H NMR (using the shifting NH signal) can lead to K_+ as well. For instance, with 9-Fc and $K_+ = (2.2 \pm 0.2) \times 10^5$ in CH_2Cl_2. When the interaction between the ferrocenyl dendrimer and the anion is weak, only a CV wave shift is observed. The value of K_+, the apparent association constant between the oxidized (ferrocenium) form of the dendrimer and the anion, is then directly accessible using the value of the concentration c using the equation:

$\Delta E°(\text{V}) = 0.059 \log cK_+$ at 25 °C, which gives $K_+ = 544 \pm 50$, 8500 ± 500 and $61\,000 \pm 3000$ for respectively 1-Fc, 9-Fc and 18-Fc with HSO_4^- in CH_2Cl_2.

The equivalent point was found by CV to correspond to the interaction of one ferrocenyl branch *per* equiv. anion in this dendrimer series, but other stoichiometries were observed with other dendrimer series for some anions (*vide infra*).[28,29]

The positive dendritic effect in anion recognition

The 9- and 18-amidoferrocenyl dendrimers (respectively 9-Fc and 18-Fc) were compared to monomeric (1-Fc) and tripodal trimetallic (3-Fc) amidoferrocenyl derivatives (Fig. 1), and, as indicated by the above numbers, a strongly positive dendritic effect (*i.e.* the strength of the interaction characterized by $\Delta E°$ and K_+ is all the larger as the dendrimer generation is higher) was characterized by the values of $\Delta E°$ and apparent association constants for the anions: $\Delta E°$ (1-Fc) < $\Delta E°$ (3-Fc) < $\Delta E°$ (9-Fc) < $\Delta E°$ (18-Fc). The combined hydrogen bonding and electrostatic factors (attraction between the anion and the ferrocenium cation) alone cannot explain the high $\Delta E°$ values obtained with the 9-Fc and 18-Fc dendrimers, since the values found for the mono-amidoferrocenyl derivative 1-Fc are very weak (a few tens of mV). The synergy between these factors and the topology factor in endo-receptors (as pointed out by Beer)[9] or exo-receptors is required to provide large $\Delta E°$ and association constant values (Chart 1). This feature is to be compared with the positive dendritic effect. Indeed, not only do dendrimers give a better recognition of the anions than the monomer and tripod, but this recognition is easily quantified by the increase of the $\Delta E°$ values from 9-Fc to 18-Fc, *i.e.* when the dendrimer generation increases. This can tentatively be taken into account by the narrowing of the channels between the exo-receptor redox sites that forces a tighter hydrogen-bonding interaction when the dendrimer generation increases (as shown by molecular models). This positive dendritic effect in molecular recognition contrasts with the negative dendritic effect usually observed in catalysis whereby the reaction kinetics is lowered by the enforced steric constraints around the catalytic metal center inhibiting its approach by substrates when the dendrimer generation increases.[31]

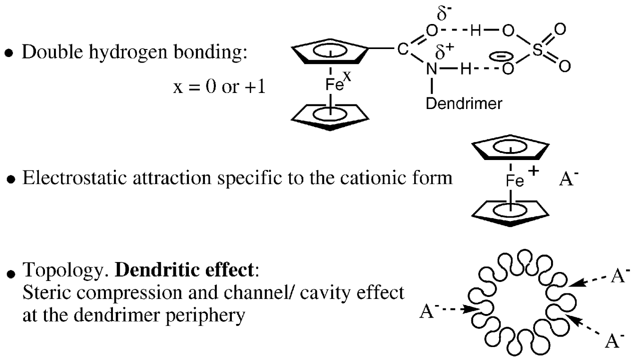


Chart 1 Factors responsible for the recognition of oxo-anions HSO_4^-, $H_2PO_4^-$ and ATP^{2-} by polyamidoferrocenyl dendrimers.

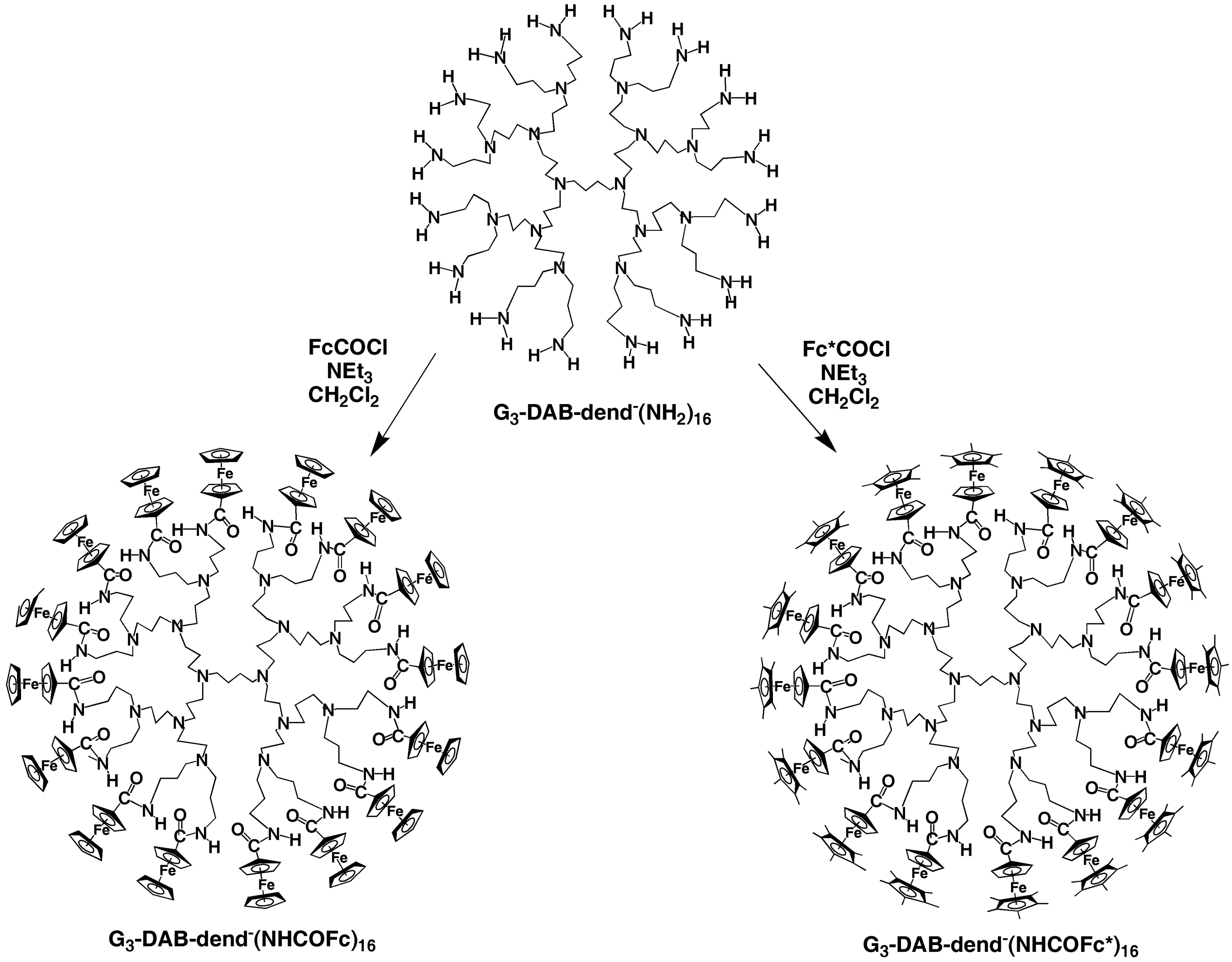
With the diaminobutane (DAB) dendrimers formulated G_n-DAB-dend-$(NH_2)_m$, amidoferrocenyl[32] and pentamethyl-amidoferrocenyl[33,34] dendrimers have been synthesized (Scheme 2) for the five generations from G_1 (4 branches) to G_5 (theoretical number: 64 branches).

Recognition of HSO_4^- proceeds best in CH_2Cl_2 with the parent Cp series with, again, a positive dendritic effect (*i.e.* an increase of $\Delta E°$ when the generation number increases, Fig. 3).[33,34]

In DMF, however, recognition and titration are only possible with the permethylated dendrimer series. It is subjected to another dramatic dendritic effect: the shift of the initial CV wave upon titration (weak interaction) is only observed with G_1 and a new wave (strong interaction) is observed with G_2 and G_3.[34] With amido ferrocenyl dendrimers, the oxidized ferrocenium form is not very stable due to the electron-withdrawing property of the amido group, but the electron-releasing permethylation in the Cp* ligand fully stabilizes this 17-electron form. As a result of this stabilization and the increased hydrophobicity of the Cp* dendrimers, the recognition of $H_2PO_4^-$ and ATP^{2-} is also much cleaner in the Cp* series than in the parent Cp series even if the electron-releasing character of the permethylated groups causes a slight decrease of the $\Delta E°$ values. With ATP^{2-}, the CVs are also clean with the Cp* dendrimers along the titration, and stoichiometry of 0.5 equiv. ATP^{2-}/ferrocenyl branch was found, corresponding to the doubly negative phosphate charge (Fig. 4). It is noteworthy that the dendritic effect on $\Delta E°$ values in this family of dendrimers is considerably less marked and sometimes nil, a feature that was also noted with ferrocenyl–urea dendrimers of this family for the recognition of $H_2PO_4^-$.[35]

The specificity of dendritic cationic aminoarene–iron sandwich complexes for halides

With the above dendrimer series, the order of $\Delta E°$ values was: $H_2PO_4^- > HSO_4^- > Cl^- > NO_3^-$. This order can very much vary from one dendrimer series to the other, however, and the same can be said with the dendritic effect: some dendrimer families (as the above one) give a strong dendritic effect for a given anion, and some others do not. For instance, an amidoferrocenyl dendrimer



Scheme 2 Syntheses of third-generation amidoferrocenyl[32] and pentamethylamidoferrocenyl dendrimers[33] from the corresponding DSM polyamine dendrimer G$_3$-dend-(NH$_2$)$_{16}$. For analysis and comparison of their behaviors as hosts of anions, see refs. 33 and 34.

with an octabenzylated durene core and 24 redox termini underwent values of the order of what was found for 9-Fc (Fig. 2) of the above series, far less than 18-Fc.

The octasubstituted cored dendrimer 24-FeAr containing 24 cationic aminoarene iron moieties [dendr-(η^6–NHC$_6$H$_4$Me-FeCp*)$_{24}$] (Cp* = η^5–C$_5$Me$_5$), *i.e.* 8 tripods, was compared to the analogous mono- and trimetallic aminoarene cationic complexes (respectively 1-FeAr and 3-FeAr, Fig. 5) with the same aminoarene–iron sandwich structure for the recognition of a collection of anions using the NH signal in ^{1}H NMR.[36] The recognition of the oxo-anions that had been successful with the amidoferrocenyl dendrimers was not possible at this time. On the other hand, that of the halides Cl$^-$ and Br$^-$ gave noteworthy results whereas the 18- and 24-amidoferrocenyl dendrimers hardly

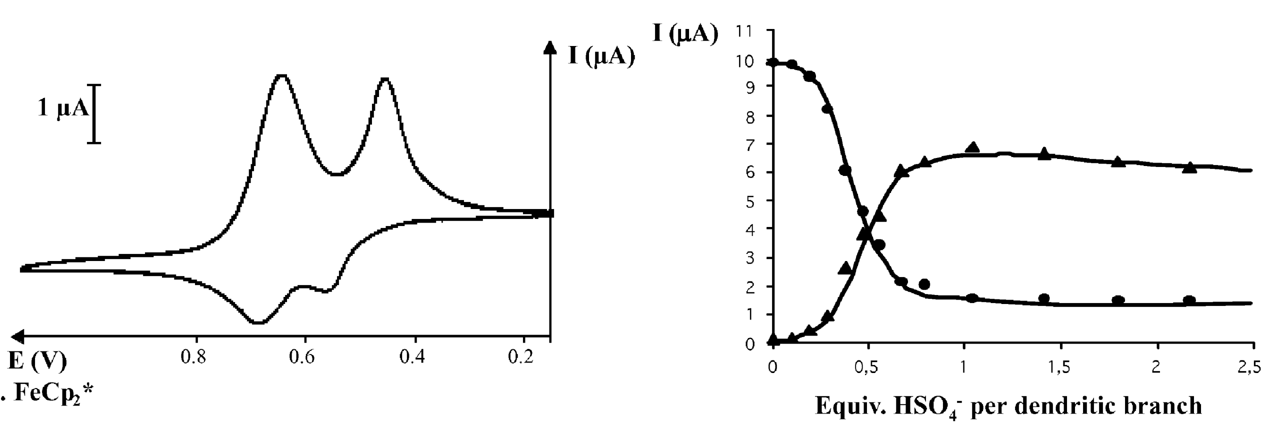


Fig. 3 Titration of a 3.3 × 10^{-4} M solution of the G$_3$–DAB-dend-(NHCOFc)$_{16}$ by a 10^{-3} M solution of [*n*-Bu$_4$N][HSO$_4$] in CH$_2$Cl$_2$ in the presence of 0.1 M [*n*-Bu$_4$N][PF$_6$], Pt anode, 20 °C. **A**: cyclovoltammogram obtained after addition of 0.5 equiv. [*n*-Bu$_4$N][HSO$_4$] per dendritic branch; **B**: variation of the intensities of the initial (●) and new (▲) waves along the titration.

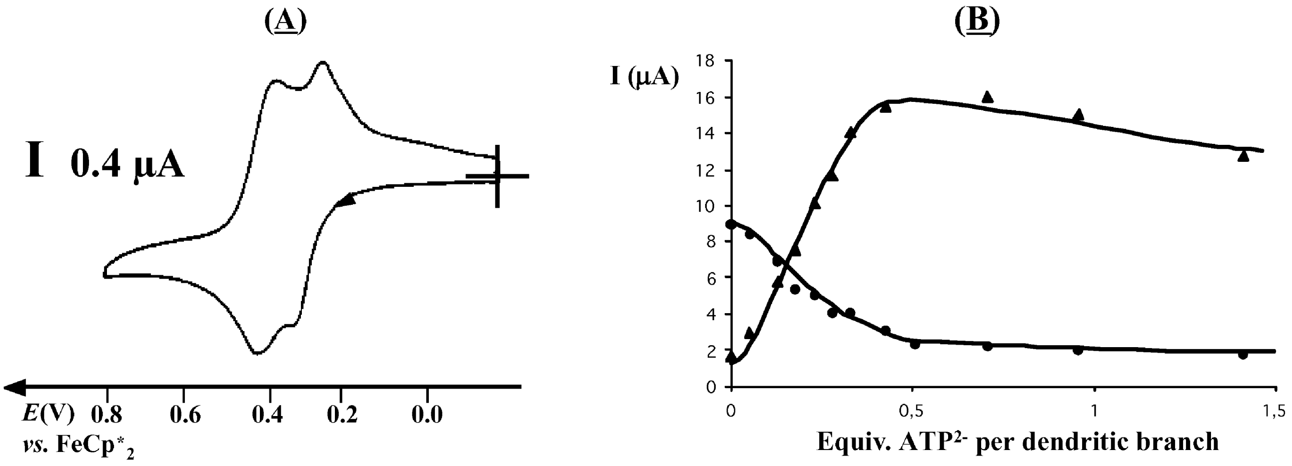
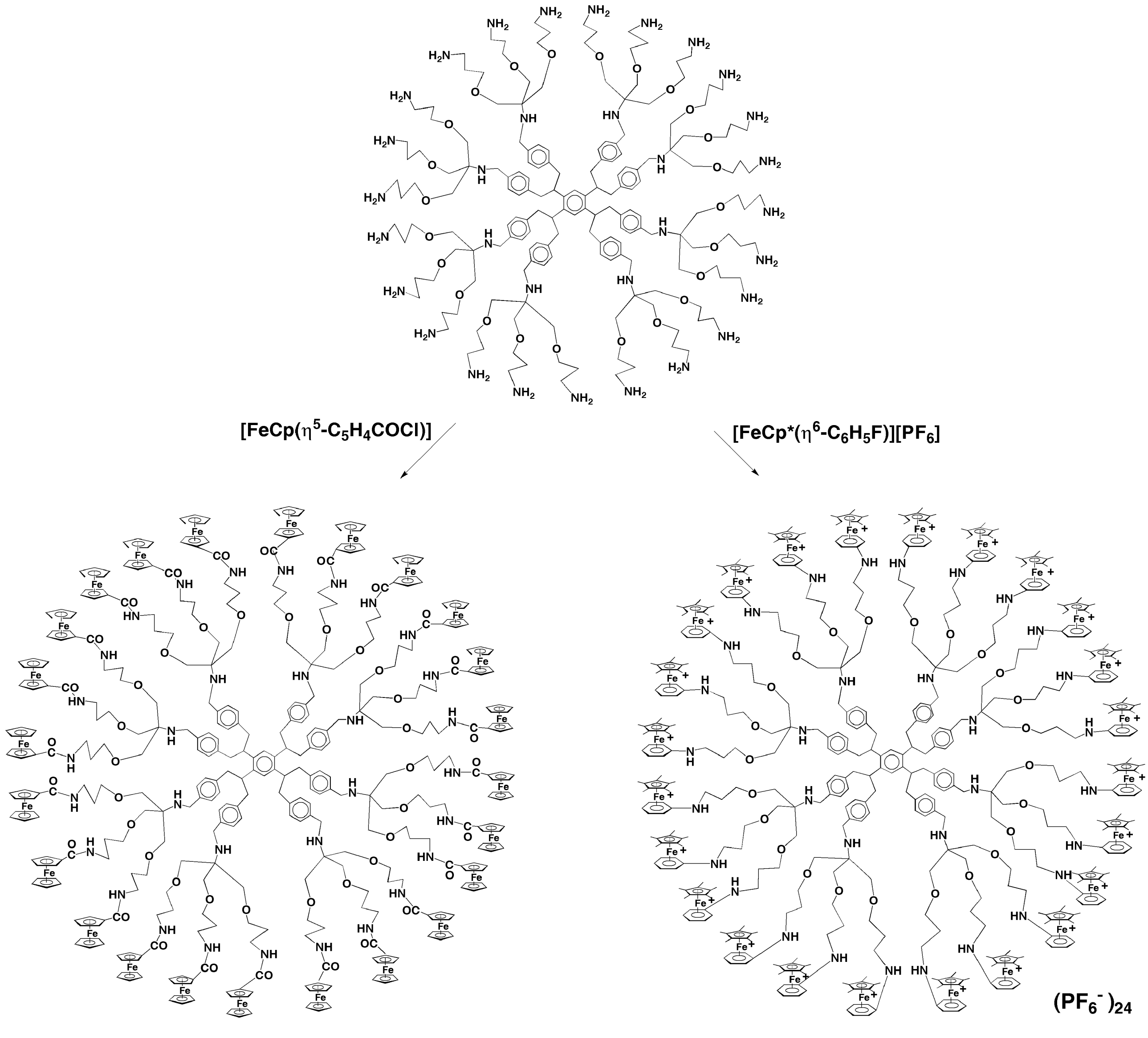


Fig. 4 Titration of a 1.25 × 10^{-4} M solution of G_4-DAB-dend-$(NHCOFc^*)_{32}$ (Scheme 2) by a 10^{-3} M solution of $[n\text{-}Bu_4N]_2[ATP]$ in CH_2Cl_2 in the presence of 0.1 M $[n\text{-}Bu_4N][PF_6]$, Pt anode, 20 °C. **A**: CV obtained after addition of 0.25 equiv. $[n\text{-}Bu_4N]_2[ATP]$ per dendritic branch; **B**: variation of the intensities of the initial (●) and new (▲) waves along the titration.



24-Fc

24-FeAr

Scheme 3 Syntheses of 24-amidoferrocenyl dendrimer (24-Fc) that recognizes oxo-anions (left) and cationic 24-arylFeCp* dendrimer (24-FeAr) that recognizes chloride and bromide (right).

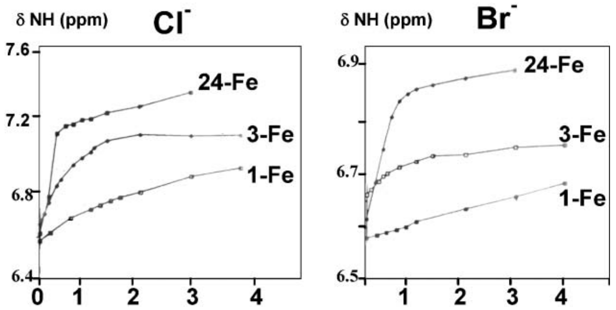


Fig. 5 Variation of δ_{NH} for the exocyclic amine proton of the 24-Fe dendrimer measured by ^{1}H NMR spectroscopy upon addition of *n*-Bu$_4$NCl or *n*-Bu$_4$NBr. Comparison with monometallic [FeCp*(η^6-C_3H_5NHPh)][PF$_6$] (1-Fe) and tripodal PhCH$_2$NHC{(CH$_2$)$_3$O(CH$_2$)$_3$NH-[η^6-PhFeCp*][PF$_6$]}$_3$ (3-Fe) showing the positive dendritic effect.

gave any significant ΔE° values for the recognition of these anions. The halides and the secondary amine groups of the dendrimer allow a single hydrogen bonding interaction due to the acidic amino group in constrast to amide groups with oxoanions forming a chelating double hydrogen bonding. For bromide, the titration showed an equivalent point also corresponding to a one-to-one interaction, and comparison with the mono- and tripodal compounds containing analogous redox sites indicated that only the dendrimer showed a clear equivalence point. With Cl$^-$, the equivalence point was even sharper and was found for 1/3 of chloride equiv. *per* branch, *i.e.* one Cl$^-$ per tripod. This unusual stoichiometry is remarkably specific for Cl$^-$ and shows that only Cl$^-$ fits in the cavity defined by a tripod at the dendrimer periphery.[35a] Ferrocenylaminosilane dendrimers reported by Cuadrado's group also showed recognition properties for the H$_2$PO$_4$$^-$ anion.[37] This example shows the importance of connectivity that was already shown for other dendrimer properties such as vapoconductivity.[35b]

Anion recognition by metallodendrimers assembled by hydrogen bonding between a redox-active dendronic phenol and dendritic primary amines

Supramolecular aspects of dendrimer chemistry, especially those involving hydrogen bonding have been the subject of interest in the last decade.[38,39] We were intrigued by the very simple possibility of hydrogen bonding between primary amines and phenols and by its potential use in dendrimer chemistry and molecular recognition. The tedious, time consuming dendritic syntheses often represent an obstacle for research and use of dendrimers. Therefore the advantage of forming dendrimers with redox-active termini by simply mixing a commercial polyamine core and a redox-active dendron is obvious. This is especially the case if a specific exo-receptor property with positive dendritic effect can be obtained as shown above in the covalently synthesized metallodendrimers. Indeed, there were precedents for hydrogen bonding between primary amines and alcohols with tetrahedral disposition of both O and N valences and 1 : 1 stoichiometry (*i.e.* minimal melting point for this stoichiometry), a property that had been used in crystal engineering and chiral recognition.[40]

Thus, mixing a DSM dendritic polyamine and a para-substituted phenol derivative leads to the replacement of the ^{1}H NMR signals of the OH protons at 5 ppm and NH$_2$ proton at 1.5 ppm by a common broad, concentration-dependent signal for these three protons located between 2.4 and 4.1 ppm. This means that supramolecular dendrimers involving reversible hydrogen bonding between the DSM polyamine and a phenol dendron form upon mixing these two components. The electrochemical timescale of the CV being much larger than that of the hydrogen-bond formation and breaking, the CV shows an average situation between the hydrogen-bonded and non-bonded dendrimer branches.[41]

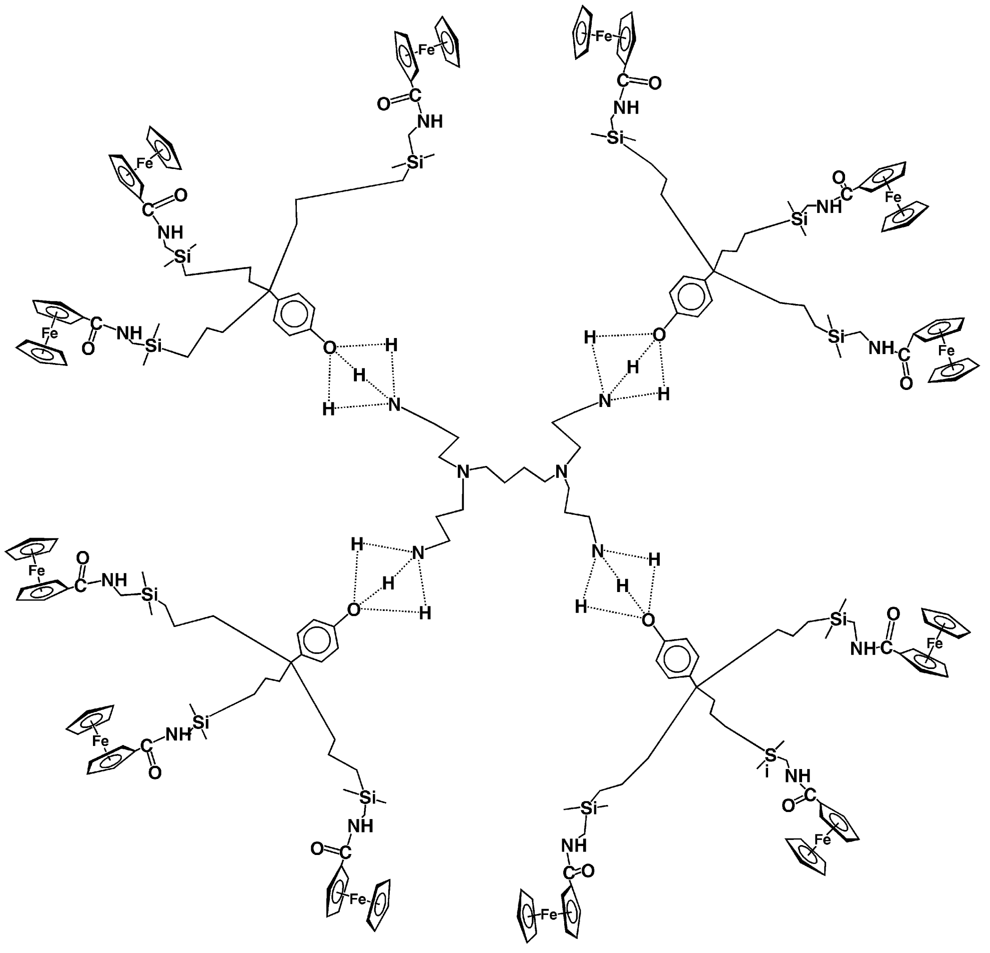
Upon titration of [*n*-Bu$_4$N][H$_2$PO$_4$] by FcCONHPr (Fc = ferrocenyl), the CV of this ferrocenyl group undergoes the appearance of a new, anodically shifted wave with ΔE° = 150 mV; this value reaches 210 mV with the dendron *p*-OH-C$_6$H$_4$C{(CH$_2$)$_3$SiMe$_2$-CH$_2$NHCOFc}$_3$ alone, and it is not changed in the presence of propylamine. It reaches 250 mV, however, with this dendron + G$_1$-DAB-dend-(NH$_2$)$_4$ and 280 mV with this dendron + G$_2$-DAB-dend-(NH$_2$)$_8$ or a higher generation polyamine dendrimer. This increase of the ΔE° value is the signature of a dendritic effect as shown previously with covalent redox metallodendrimers. With the monomer FcCONHPr + *n*-propylamine, it is necessary to add 2.5 equiv. [*n*-Bu$_4$N][H$_2$PO$_4$] to reach the equivalence point whereas one equiv. [*n*-Bu$_4$N][H$_2$PO$_4$] is enough with the covalent dendrimers, because the amine strongly competes with the amidoferrocenyl group in binding H$_2$PO$_4$$^-$. With G$_1$, only 0.5 equiv. [*n*-Bu$_4$N][H$_2$PO$_4$] is necessary, and a sudden disappearance of the initial CV wave is observed whereas the intensity of the new CV wave is much reduced. This can tentatively be taken into account by the formation of a rather stabilized dendritic supramolecular assembly in which the H$_2$PO$_4$$^-$ anion bridges two amidoferrocenyl units (Scheme 4).

The reduction of the diffusion coefficient responsible for the decrease of the CV wave intensity at the equivalence point can be taken into account by the sudden increase of the mass of this overall supramolecular assembly compared to the much smaller species present in solution before the equivalence point. For higher generations, the number of equivs. [*n*-Bu$_4$N] [H$_2$PO$_4$] necessary to reach the equivalence point progressively increases again (0.8 for G$_2$ and 2.0 for G$_3$ and G$_4$), probably due to the fact that the steric congestion around the dendrimer partly destabilizes, for high generations, the hydrogen bonds optimized in G$_1$ and G$_2$; this is also consistent with the limit of the ΔE° increase.[41] Finally, this strategy has also been applied to the recognition of [*n*-Bu$_4$N]$_2$[ATP] with success for G$_1$.[41b]

Amidoferrocenylalkanethiolate–gold nanoparticles (AFAT-AuNPs)

Gold nanoparticles have been known and used for centuries. Their interest lies on their biocompatibility, ease of fabrication under various forms and applications in nanotechnology including optics, electronics and even catalysis.[42] With alkylthiolate ligands, they are especially known from Mulvaney' seminal work[43] and the popular and practical Brust–Schiffrin biphasic method of synthesis.[44] They are very robust, quite monodisperse and easy to characterize by combining transmission electron microscopy (TEM), elemental analysis (Au : S ratio) and, as simple molecules, by standard spectroscopic methods (NMR, infrared, UV-Vis).[45] Thus, a variety of functional alkylthiolate ligands including ferrocenylalkylthiolates have been introduced either by direct synthesis or by ligand substitution of non-functional alkylthiolates with good control of the degree of substitution.[42,45,46] Variable proportion (7 to 38%) of amidoferrocenylundecanethiol (AFAT), a ligand deposited as self-assembled monolayers on gold surfaces by Creager,[47] was introduced into alkylthiolate–AuNPs using such reactions. The original core size of diameter around 2 nm with a number of ligands about 100 is unchanged in the course of these reactions.[48]

These AFAT–AuNPs show, as ferrocenyl-terminated dendrimers, a single CV wave in CH$_2$Cl$_2$ with a difference of potentials between the cathodic and anodic peaks that is lower than 60 mV (typically 20 mV). This indicates some adsorption due to the large size.[49,50] Addition of [*n*-Bu$_4$N][H$_2$PO$_4$] leads to the appearance of a new CV wave as with dendrimers, and the equivalence point is reached for a 1 : 1 stoichiometry (equiv. [*n*-Bu$_4$N][H$_2$PO$_4$] per AFAT branch) as with covalent dendrimers. It is remarkable that the ΔE° value is as large as 220 mV and constant whatever the



Scheme 4 Arbitrary representation of the reversible hydrogen bonding between G_1-DAB-dend-$(NH_2)_4$ and a triamidoferrocenyl dendron shown by the concentration-dependent average location of the (broad) NH_2 + OH signal in ^1H NMR between 2.4 and 4.1 ppm *vs.* TMS in $CDCl_3$.

proportion of AFAT ligands in the AFAT–AuNPs, corresponding to an apparent association constant ratio K_+/K_0 between $H_2PO_4^-$ and the AFAT–AuNPs of 5350 ± 550 (Fig. 6).

It is also possible to titrate [*n*-Bu_4N][H_2PO_4] selectively in the presence of both [*n*-Bu_4N][HSO_4] and [*n*-Bu_4N]Cl or to titrate [*n*-Bu_4N][HSO_4] alone, but the $\Delta E°$ value (cathodic shift) is only 40 mV with this latter anion (Fig. 7). The halides and nitrate cannot be recognized, however.

The alkyl chain length was varied without significant effect, but stereoelectronic effects of the AFAT ligand play a role: a Cp* analogue, and an heterodisubstituted 1-amido, 1′-acetyl-ferrocenyl derivative have been introduced onto AuNPs.[50] The electron-releasing Cp* ligand reduced the $\Delta E°$ value to 125 mV whereas the additional electron-withdrawing acetyl group enhances it to 275 mV (Fig. 8).

Similarly, for the recognition of [*n*-Bu_4N][HSO_4], the presence of the Cp* ligand reduces the $\Delta E°$ value to 25 mV whereas that of the withdrawing acetyl group enhances it to 170 mV. Interestingly, the introduction of the acetyl group also transforms the CV wave shift (weak-interaction case with the parent AFAT ligand) to the formation of a new wave (strong-interaction case). In summary, the AFAT nanoparticles and the amidoferrocenyl dendrimers show some similar trends, but detailed investigations indicate remarkable differences in the selectivity and some more flexibility in the design of the stereoelectronic feature around the ferrocenyl group.[50] Moreover, the AFAT–AuNPs are directly accessible whereas dendrimers require tedious multi-step syntheses. This ease of access will be further exploited with nanoparticle-cored ferrocenyl dendrimer.

Gold nanoparticle-cored ferrocenyl dendrimers and modification of electrodes for useful sensors

Nanoparticle-cored dendrimers are new materials that have been reported for the first time in 2001.[51–53] With ferrocenyl termini, they combine the advantages of covalent ferrocenyl dendrimers and AFAT–AuNPs. Moreover, their large size (in our case) offers the possibility to easily derivatize electrodes with the redox ferrocenyl sensors, which makes them useful for sensing.[54] Thus, ferrocenyl AB_3 and AB_9 dendrons were synthesized with a monothiol for the ligand part A and three or nine amidoferrocenyl or silylferrocenyl groups for B_3[51] or B_9.[54] The AB_3 dendrons were assembled into AuNP-cored dendrimers either by direct synthesis using the Brust–Schiffrin method using a mixture of dodecanethiol and tripodal thiol ligands or by the ligand substitution method from dodecanethiol–AuNPs and a given amount of tripodal thiol ligand (Scheme 6). The numbers of AB_3 dendrons introduced in this way were between five and seven in 2.3-diameter AuNPs containing about 150 thiolate ligands overall. For the silylferrocenyl AB_9 dendrons, the ligand-substitution procedure no longer worked presumably for steric reasons, but the direct synthesis using a mixture of dodecanethiol and AB_9 thiol worked well (Scheme 7). Two closely related AB_9 dendrons were used leading to assemble about 10% respectively 20% AB_9 thiolate dendrons around 2.9 nm AuNPs bearing around 200 thiolate ligands overall. This means that these AuNPs contain about 180 respectively 360 equivalent silylferrocenyl groups at the periphery.[54]

The recognition experiments led to stoichiometries corresponding to a one equiv. [*n*-Bu_4N][H_2PO_4] per ferrocenyl branch with all

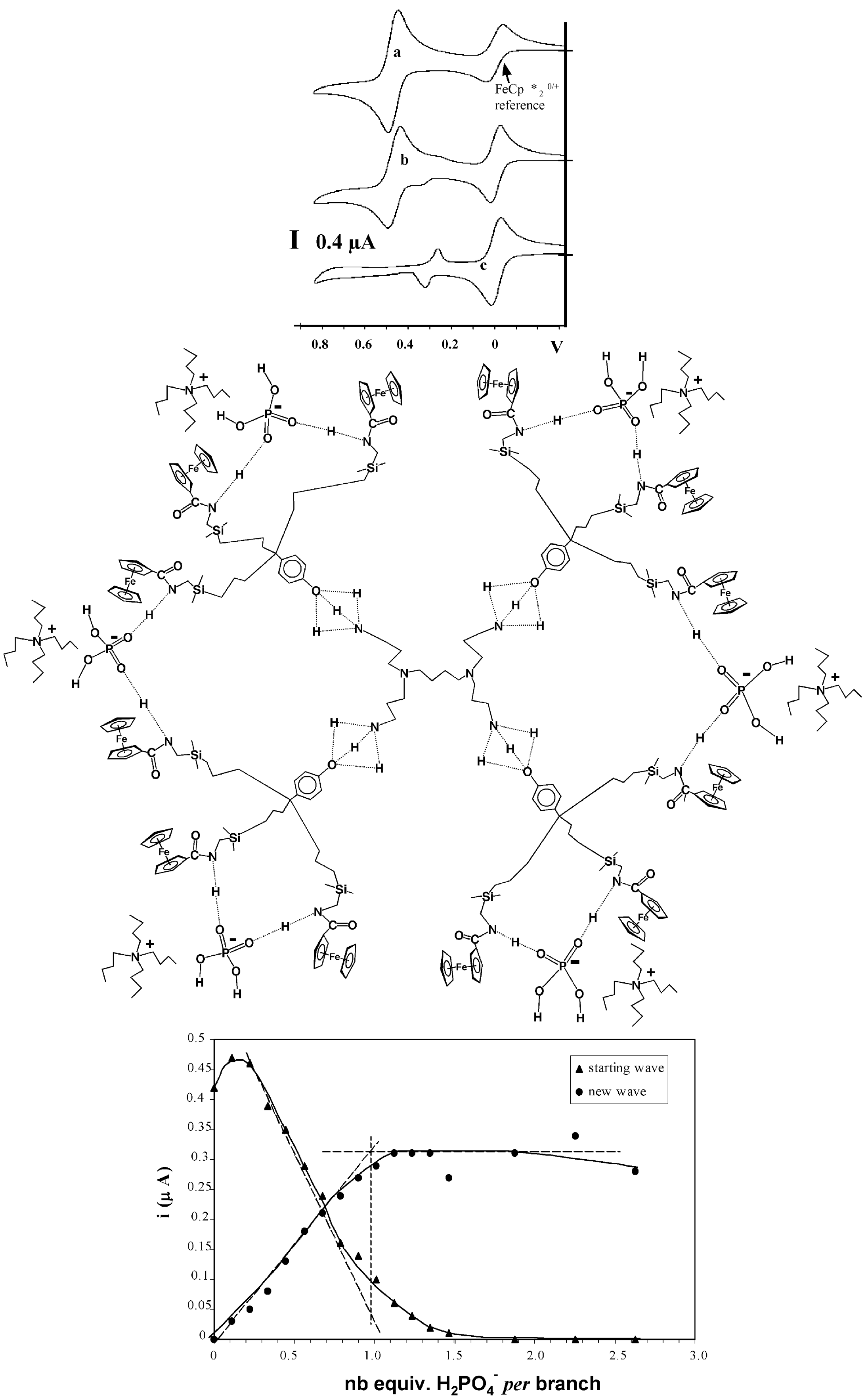
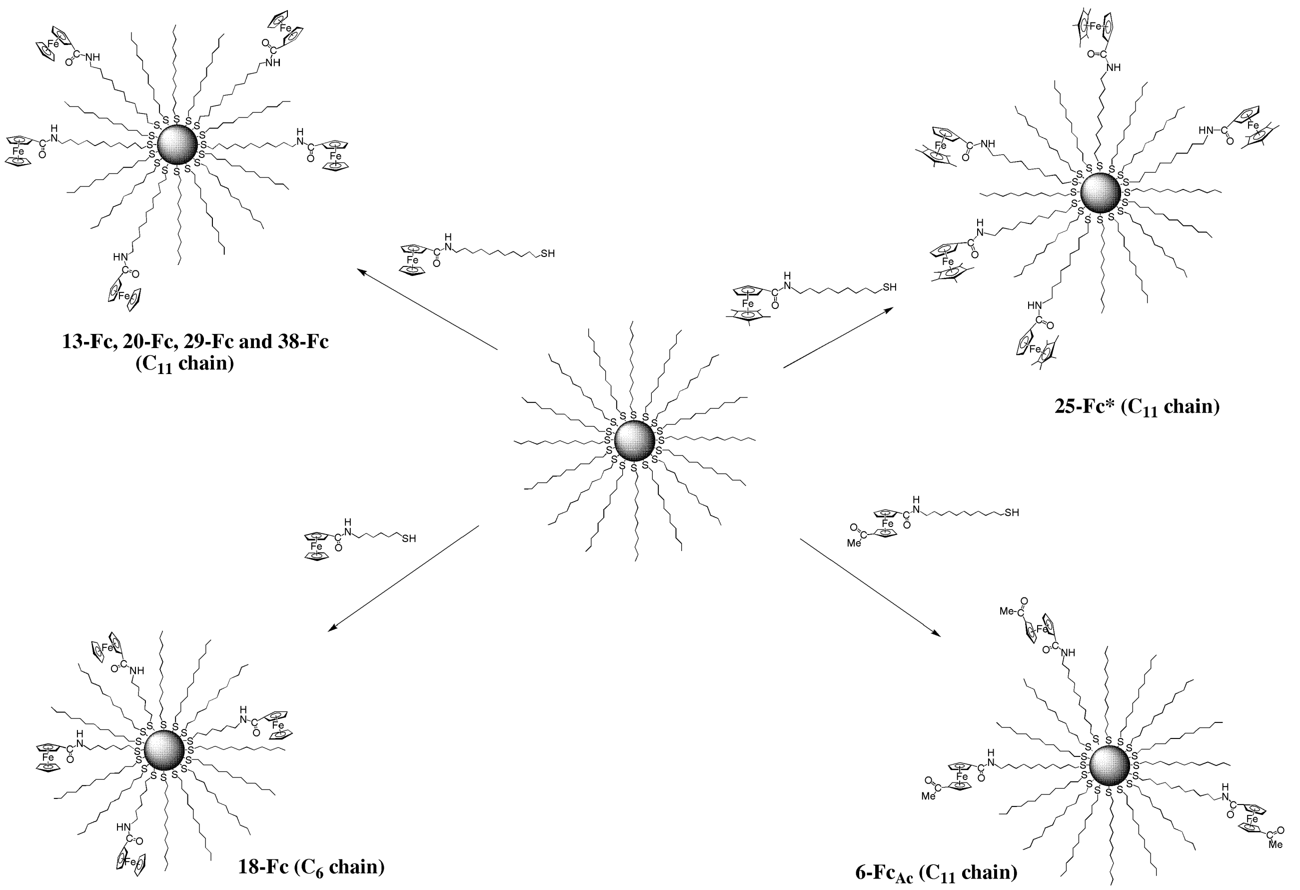


Fig. 6 Top: Titration of DAB-G_1 in CH_2Cl_2 (Pt, 0.1M [nBu$_4$N][PF$_6$], 20 °C, reference FeCp$^*_2$ = decamethylferrocene) by [nBu$_4$N][H_2PO_4]: (a) before addition; (b) 0.4 equiv.; (c) 0.5 equiv. Bottom: proposed supramolecular assembly between the triferrocenyl dendron + DAB-G_1 and 0.5 equiv. [n-Bu$_4$N][H_2PO_4] taking into account the sudden drop of CV wave intensity at the equivalent point (*i.e.* sudden drop of diffusion coefficient).



Scheme 5 Syntheses of various AFAT-AuNPs (using the ligand substitution procedure) for the selective recognition and titration of oxo-anions (for instance, 18-Fc means AuNPs with 18% AFAT ligand and 82% dodecanethiolate ligand).

the AuNP-cored ferrocenyl dendrimers. The $\Delta E°$ values for this anion were 200 mV with the amidoferrocenyl AB_3 dendron–AuNPs, 115 mV for the silylferrocenyl AB_3 dendron–AuNPs and 125 mV for the AB_9 dendron–AuNPs. Recognition studies with $[n\text{-}Bu_4N]_2[ATP]$ gave results that were similar to those obtained with $[n\text{-}Bu_4N][H_2PO_4]$ except that the stoichiometry was reached for only 0.5 equiv. $[n\text{-}Bu_4N]_2[ATP]$ per ferrocenyl branch because of the double negative charge of ATP^{2-} (Fig. 9). The $\Delta E°$ values were usually only slightly lower for $[n\text{-}Bu_4N]_2[ATP]$ than for $[n\text{-}Bu_4N][H_2PO_4]$.

The silylferrocenyl AuNP-cored dendrimers are thus efficient sensors, because the silylferrocenium species is stable unlike the parent amidoferrocenium species. The silicon atom attached to the ferrocenyl group plays the role of a Lewis acid that interacts with the $H_2PO_4^-$ anion by hydrogen bonding. With $[n\text{-}Bu_4N][HSO_4]$, however, the silylferrocenyl dendrimers do not provide recognition. A $\Delta E°$ value of 42 mV with $K_+ = (18 \pm 4) \times 10^3$ L mol^{-1} was obtained with this anion using the tris-amidoferrocenyl dendron-AuNPs with the same stoichiometry. The weaker interaction of the amidoferrocenyl dendrimers with $[n\text{-}Bu_4N][HSO_4]$ than with $[n\text{-}Bu_4N][H_2PO_4]$ is due to the fact that NH–oxo anion hydrogen bonding is dominant, and the negative charge on the oxygen atoms is smaller in HSO_4^- than in $H_2PO_4^-$ (sulfur being more electronegative than phosphorus).

Electrodes modified by ferrocenyl polymers have been known for a long time.[54] More recently, Cuadrado *et al.* have extensively studied the derivatization of silylferrocenyl dendrimers.[12] Nishihara's group has reported the first example of modified electrodes with AuNPs containing ferrocenyl thiol ligands, in which the stabilization of the modified electrodes is provided by the biferrocenyl units whereas monoferrocenyl units do not afford stabilization.[55] We have noticed that the larger the ferrocenyl dendrimers, the more strongly they tend to adsorb on Pt electrodes in CH_2Cl_2 solutions, and the easier it is to prepare modified Pt electrodes with ferrocenyl dendrimers by scanning around the

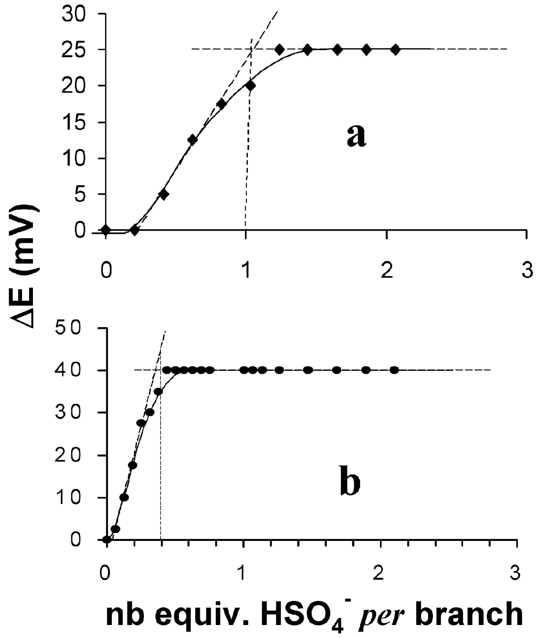


Fig. 7 Titration of $[n\text{-}Bu_4N][HSO_4]$ by gold nanoparticles containing AFAT ligands in CH_2Cl_2. Shift of $E_{1/2}$ towards positive potentials as a function of the number of equiv. $[n\text{-}Bu_4N][HSO_4]$ added *per* amidoferrocenyl branch of the colloids. (a) titration by 13-Fc-AFAT-AuNPs: the equivalence point is 1 equiv. $[n\text{-}Bu_4N][HSO_4]$ *per* amidoferrocenyl branch; (b) titration by 38-Fc: the equivalence point is only 0.4 equiv. $[n\text{-}Bu_4N][HSO_4]$ *per* amidoferrocenyl branch, possibly due to preferred amide–amide interactions of neighbor branches at high ligand load.

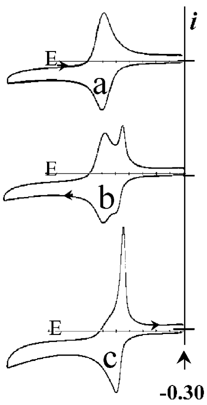
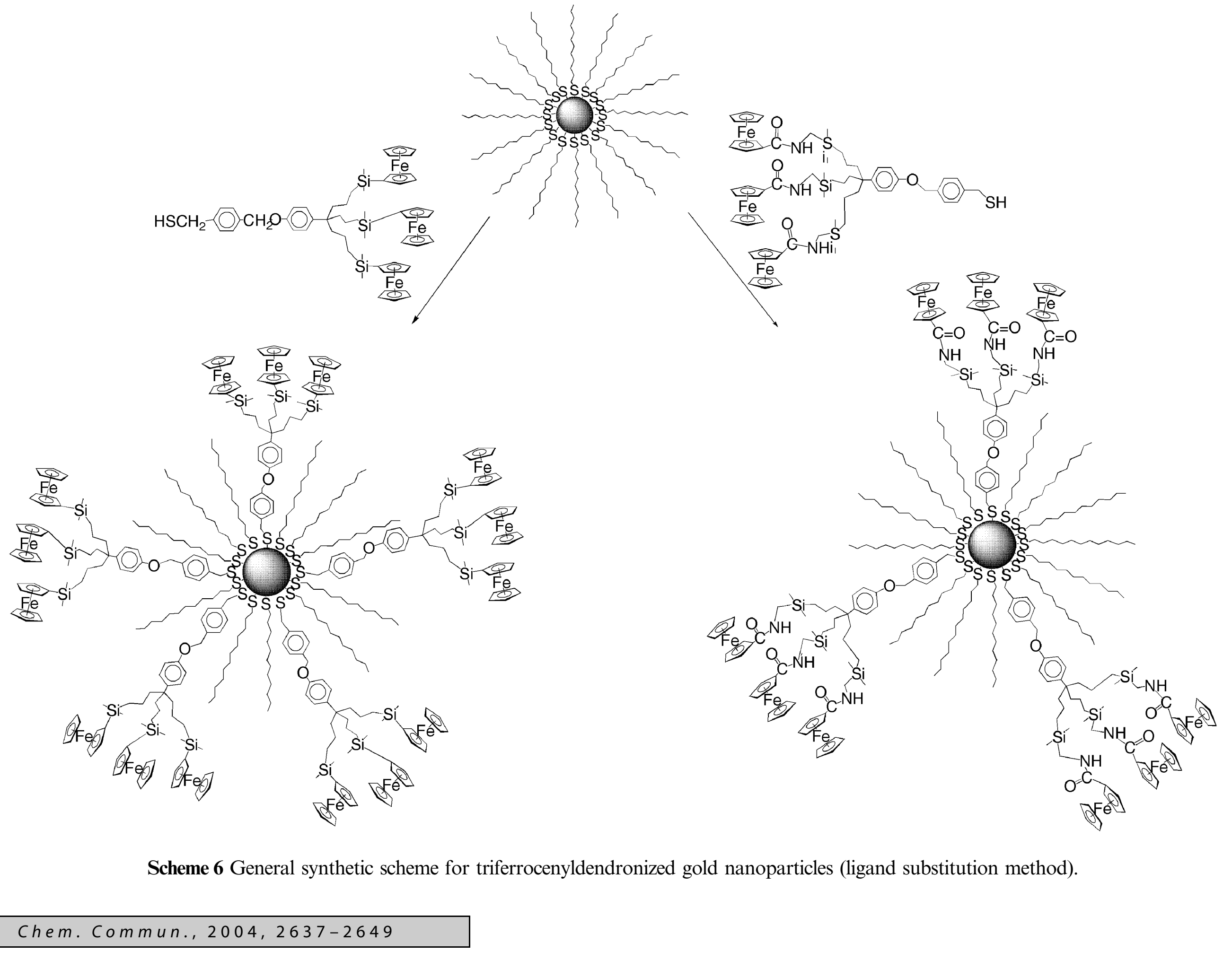


Fig. 8 Cyclic voltammograms of the 25-Fc*–AuNPs (Fc* = Cp*FeCp-). Solvent: CH_2Cl_2; reference electrode: aqueous SCE; working and counter electrode: Pt; supporting electrolyte: 0.1 M n-Bu_4NBF_4; scan rate: 200 mV.s^{-1} (a) without [n-Bu_4N][H_2PO_4], (b) with 0.75 equiv. [n-Bu_4N][H_2PO_4] per 1-amido, 1′-pentamethyl-ferrocenyl branch, (c) with excess [n-Bu_4N][H_2PO_4].

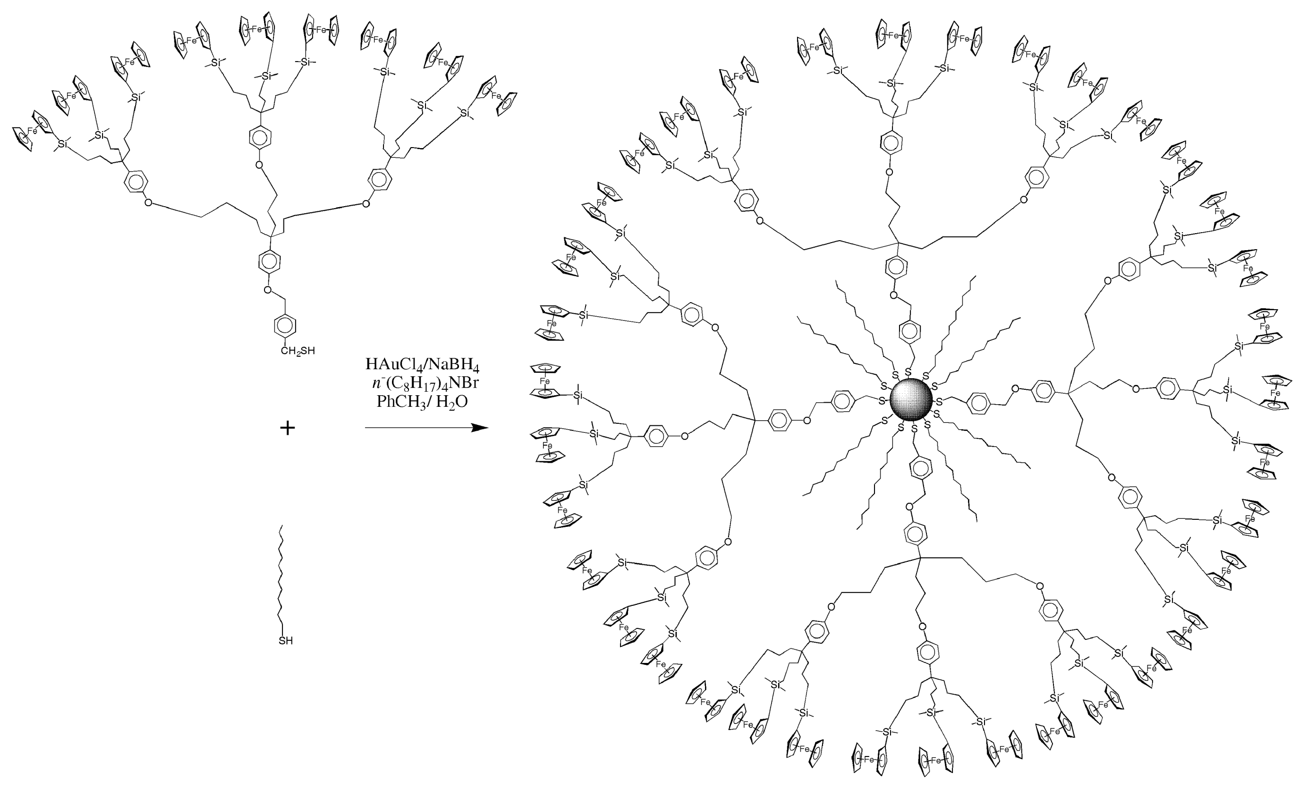
region of the ferrocenyl potential.[56] Thus, AuNP-cored ferrocenyl dendrimers discussed above are large and readily adsorb on Pt electrodes, forming perfectly stable derivatized electrodes upon scanning about 50 times (for saturation) around the ferrocenyl potential region. These modified Pt electrodes show remarkable changes upon introduction of a solution of [n-Bu_4N]$_2$[ATP]. The new CV wave observed has undergone a shift of potential; the anodic and cathodic peaks are no longer identical showing that a structural rearrangement, due to changes in hydrogen bonding and electrostatic interaction, occurs in the course of the heterogeneous electron transfer. [n-Bu_4N][H_2PO_4] and [n-Bu_4N]$_2$[ATP] are selectively recognized in the presence of other anions such as HSO_4^- and Cl^-; [n-Bu_4N][HSO_4] alone can also be recognized. The recognized salts can be washed from the electrode using CH_2Cl_2, but the AuN-cored ferrocenyl dendrimers are not removed and can serve again for further analogous experiments. Such recycling can be performed several times (Fig. 10).[53]

Conclusion and prospects

In this article, we have reviewed anion exoreceptors including metallodendrimers, gold nanoparticles and nanoparticle-cored ferrocenyl dendrimers, most often using cyclovoltammetry that monitors the redox switch. The comparison between mononuclear compounds, tripod derivatives and dendrimers shows that the variation of potential upon titration of anions is larger with dendrimers and increases with the dendrimer generation. This is what was called the positive "dendritic effect"[28,29] and was taken into account by the narrowing of the channels at the dendrimer periphery allowing a tighter interaction with the anionic guest. This contrasts with the negative dendritic effect found in catalysis whereby the catalytic efficiency decreases upon increasing the dendrimer generation.[31] We have also indicated that the dendritic effect depends on the nature of the anion and dendrimer. Thus amidoferrocenyl dendrimers, gold nanoparticles and gold nanoparticle-cored amidoferrocenyl dendrimers can be excellent sensors with large dendritic effect for oxo-anions whereas no significant recognition is found for halides whereas the opposite was found with cationic aminoarene–iron–Cp* dendrimers. Gold nanoparticles also showed a specific behavior including the possibility to selectively recognize some oxo-anions. Gold nanoparticle-cored ferrocenyl dendrimers are very large (nano-sized) ensembles, containing several hundred equivalent ferrocenyl groups at the dendrimer periphery, that readily adsorb on Pt electrodes, a property that we have used to prepare modified electrodes with



Scheme 6 General synthetic scheme for triferrocenyldendronized gold nanoparticles (ligand substitution method).



Scheme 7 Synthesis of a AuNP-cored silylferrocenyl dendrimer (direct method).

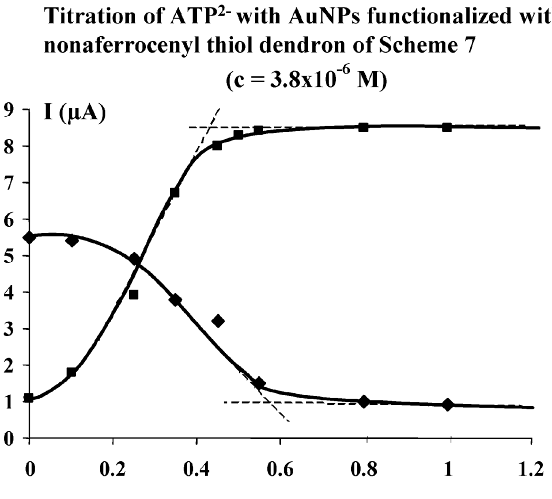


Fig. 9 Titration of ATP^{2-} with 9-Fc-thiolate dendron–AuNPs (Scheme 7). Decrease of the intensity of the initial CV wave; (◆) increase of the intensity of the new CV wave (■) *vs.* the number of equivs. of [n-Bu$_4$N]$_2$[ATP] added per ferrocenyl branch. Nanoparticles: 3.8 × 10^{-6} M in CH$_2$Cl$_2$.

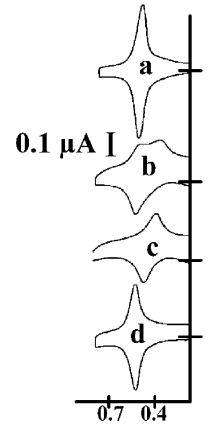


Fig. 10 Recognition of ATP^{2-} with AuNP functionalized with a non-asilylferrocenyl dendron shown in Scheme 7. CV: (a) modified electrode alone; (b) in the course of titration; (c) with excess of [n-Bu$_4$N]$_2$[ATP]; (d) after removal of [n-Bu$_4$N]$_2$[ATP] upon washing the modified electrode with CH$_2$Cl$_2$.

these sensors. Selective recognition involving the relatively low-energy hydrogen bonding can be followed by washing the oxo-anion and re-use of the robust modified electrode several times for further experiments. This contrasts with sensors based on coordination chemistry for which recognition involves the stronger coordination bonds that do not allow re-use of those sensors.

Some challenges remain: for instance chiral recognition and simultaneous recognition of both cations and anions (for instance with cobaltocenyl dendrimers[9,57] and others[58]); the approach of biologically important anions in water have still not been successfully solved despite interesting recent attempts.[59] It is probable that the combination of the present knowledge with a biomimetic approach or at least a sensor design taking into account principles used by Mother Nature will lead to significant progress in this challenging direction. Thus, some sophistication of the molecular design of the potential receptors and sensors is now clearly called for. Finally, the advantages of exo-receptors, such as dendritic effects and easy electrode modification, can potentially be applied to sense other substrates such as biologically important amino-acids. Work along these lines is currently underway in our laboratory.

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