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Electron flow in large metallomacromolecules and electronic switch of nanoparticle stabilization: new click ferrocenyl dentromers that reduce Au(III) to Au nanoparticles

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Dedication ((optional))

Abstract: Click ferrocenyl-terminal dentromers, a family of arenecored dendrimers with triple branching (9-Fc, 27-Fc, 81-Fc and 243-Fc) reduce Au(III) to ferricinium dentromer-stabilized Au nanoparticles (AuNPs). Cvclic voltammetry studies in CH₂Cl₂ show reversible CV waves with some adsorption for the 243-Fc dentromer and a number of redox groups found. 255 ± 25, using the Bard-Anson method, close to the theoretical number of 243. The dentromers reduce aqueous HAuCl₄ to water-soluble ferricinium chloride dentromer-stabilized gold nanoparticles (AuNPs) with core sizes between 30 and 47 nm. These triazolylferricinium dentromerstabilized AuNPs are reduced by cobaltocene to cobalticinium chloride and ferrocene dentromer-weakly stabilized AuNPs together with red shift of the AuNP plasmon. The weakness of the AuNP stabilization is characterized by dentromer extraction with CH₂Cl₂ along with irreversible AuNP agglomeration for the 9, 27 and 81ferrocenyl dentromer, only the 243-ferrocenyl dentromer-AuNP withstanding this process. Altogether this demonstrates the electronic switch of the dentromer-mediated AuNP stabilization.

Introduction

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Electron flow mechanisms in nanoscale materials has recently been a subject of scrutiny in physics, chemistry and biology.^[1] Metallomacromolecules containing precisely-localized redox relay centers are especially appropriate for such investigations.^[2] Ferrocenyl-terminated dendrimers are among the most precise metal-containing polymers and have attracted the attention of organometallic, electrochemistry and macromolecular communities for more than two decades.^[3-5] This interest is due

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to both their reversible cyclic voltammetry and the useful redox and functional chemistry of ferrocene^[6] that have applications as catalysts,^[7] nanoreactors,^[8] sensors,^[9] electrochemical mediators.^[10] molecular electrodes^[11] and biomedical vectors.^[12] In spite of many electrochemical studies, however, ferrocenylterminated dendrimers have not been used so far as redox agents for chemical transformations. Here we introduce the first use of ferrocenvl-terminated dendrimers as electron reservoirs to reduce Au(III) to Au nanoparticles that become stabilized by ferricinium chloride dendrimers. Therefore we have synthesized a new third-generation ferrocenyl (Fc)-terminated dendrimer containing a theoretical number of 243 terminal 1,2,3triazolylferrocenyl tethers (243-Fc) using Cu-catalyzed azide alkyne cycloaddition (CuAAC-type "click" chemistry^[13] as well as other known smaller Fc-terminated dendrimers of zeroth- (9-Fc), first- (27-Fc) and second generation (81-Fc).^[14]

In the present article the synthetic redox chemistry of Fcterminated redox dendrimers and dendrimer-stabilized large Au nanoparticles is presented. Indeed the reaction of Au(III) with the Fc-triazolyl-terminated dendrimer produces large water-soluble AuNPs in a size range useful in biomedical applications. In order to rapidly produce a large number of ferrocenyl groups at the dendrimer periphery we are using mesitylene as a starting arene core. The CpFe⁺-induced nona-allylation of mesitylene is known to burst the core methyl groups into nine branches. Further triple branching, involving Williamson and hydrosilylation reactions, provides 3^m branches, n = m-2 being the dendrimer generation number n in Gn. Whereas most dendrimers such as the PAMAM dendrimers^[3e,15] involve a construction based on double branching,^[16] the triple branching^[17] starting from the 1,3,5 tribranched arene core presented here provides super dendrimers that have been called "dentromer" [in Greek dentro (δεντρο) = tree, and meros (μεροσ) = part of $J^{[18]}$ a term that will be further used in this article.

Results and Discussion

Synthesis and characterizations of the ferrocenyl dentromers.

The known **9-allyl** core was synthesized using the CpFe⁺ induced nona-allylation of mesitylene followed by visible-light photolysis.^[19] Hydrosilylation reaction of this **9-allyl** core with chloromethyldimethylsilane catalyzed by the Karstedt catalyst in diethyl ether gives the **9-CI** intermediate, which upon reaction with NaN₃ provides **9-N₃** that reacts with ethynylferrocene by

click chemistry, generating the G0-triazolylferrocenyl dentromer **9-Fc** (Figure 1 and Scheme 1)^[14]

of the G0, G1, G2 The construction and G3 chloromethyl(dimethyl)silyl dentromers is carried out by iteration using Williamson reaction with the known triallyl phenol dendron,^[19] then hydrosilylation of the resulted allyl-terminated dentromer with chloromethyldimethylsilane.^[20] The terminal chloro groups are then substituted by azido groups using sodium azide providing azido-terminated dentromers that react further with ethynylferrocene, yielding the known G1 (27-Fc) and G2 (81-Fc) dentromers with 27 and 81 1,2,3-triazolylferrocenyl termini, respectively (Figure 1 and Scheme 1). The new dentromer 243-Fc has now been synthesized using the same iteration of reactions according to Scheme 1. These ferrocenyl dentromers are characterized by ¹H and ¹³C NMR; see the supporting information (SI), by their electrochemistry and electron-transfer chemistry (vide infra) and Size Exclusion Chromatography, SEC with PDI = 1.03 for 243-Fc (Figure S10).



Figure 1. Planar representation of the structures of the 1,2,3-triazolylferrocenyl dentromers 9-Fc, 27-Fc, 81-Fc and 243-Fc.

AFM studies.

Atomic force microscopy (AFM) studies of **243-Fc** have been conducted on a solid-state sample using glass surfaces that have a negative surface charge density for clean substrate imaging. A diluted THF solution of the dentromer is deposited on a glass surface by spin coating (800-1000 rpm for one minute, 0.1% w/w) followed by evaporation. The height of the dentromer layer that is quite uniform represents a monolayer of single-dentromer height of 10 nm for the **243-Fc** dentromer, whereas a width of 80 nm shows the formation of various dentromer aggregates on the glass surface (Figure 2).



Scheme 1. Synthesis of the Fc-dentromers 9-Fc, 27-Fc, 81-Fc and 243-Fc.



Figure 2. AFM images of **243-Fc** on glass support shown in (a) two dimensions and (b) three dimensions; (c) The diameters are 80 nm on average, and the height is 10 nm. AFM was operated in the tapping mode with a resonance frequency of around 200 MHz. The tip has a radius of 10 nm.

Cyclic voltammetry studies.

The 243-Fc dentromer was further studied by cyclic voltammetry^[21] using decamethylferrocene (FeCp*2) as the internal reference.^[22] The cyclic voltammograms (CVs) are recorded in CH₂Cl₂. This 1,2,3-triazolylferrocenyl dentromer shows, with some adsorption ($i_c/i_a = 1.7$), a single, chemically and electrochemically reversible CV wave ($\Delta E_p = 60 \text{ mV}$) at $E_{1/2}$ = 0.555 V vs. decamethylferrocene in CH₂Cl₂ for all the apparently equivalent ferrocenyl groups, which is the same E_{1/2} value as that of the 9-Fc, 27-Fc and 81-Fc dentromers.^[14] All the ferrocenyl redox potentials of the various redox groups appear equivalent, although a tiny difference among all of them is due to the extremely small electrostatic factor that distinguishes all these redox potentials. The distinction between these various redox potentials is so small that it is not apparent, and therefore only a single CV wave is observed.^[21,23] The electrochemical reversibility reflects fast electron transfers between the electrode and the dentromer within the electrochemical time scale.^[21] This is taken into account by fast rotation of the dentromer bringing all the redox centers in turn near the electrode within the electrochemical time scale and/or fast electron hopping among the redox sites (Figure 3a).[24]

Determination of the number of electrons included in this CV wave using the Bard-Anson equation^[23] with decamethyl-ferrocene as the internal reference yields a value of 255 ± 25 electrons for **243-Fc**, thus in good agreement with the theoretical number. The experimental value observed in slight excess is not due to adsorption that seems to selectively affect the cathodic wave, since the calculation of the number of redox centers was carried out using the anodic wave intensity that is not marred by the adsorption (*vide supra*). The ¹H and ¹³C NMR spectra are consistent along the dentromer construction; thus it is assumed that the number of lacking ferrocenyl redox centers, if any, is minimal.

Adsorption on the platinum electrode is probed by scanning around the oxidation potentials of the peripheral ferrocenyl groups approximately 20 cycles and therefore modified the Pt electrode. The 243-Fc dentromer-modified electrode was produced in this way.^[25] The electrochemical behavior of this modified electrode in CH2Cl2 containing only the supporting electrolyte (Figure 3b,c) gave rise to a well-defined, symmetrical redox wave that was characteristic of a surface-confined redox couple, with the expected linear relationship of peak current with various scan rates: 50, 100, 200, 300 mV/s. The stability of the modified electrode towards electrochemical recycling was demonstrated by the fact that repeated scans did not change the shape and intensity of the CVs. By comparison, the quality of the modified electrodes increases with the increase of generation in the series: 9-Fc < 27-Fc < 81-Fc < 243-Fc (Figures S11-13 and Table S2). See the surface coverage and the full width data at half maximum for the surface wave of all the modified electrodes with the different Fc dentromers in the SI (Table S2).

Oxidation of the ferrocenyl dentromers by acetylferricinium hexafluorophosphate.

The weakly electron-withdrawing 1,2,3-triazolyl group shifts the redox potential of the ferrocenyl dentromers (0.555 V vs.

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Figure 3. CVs of the **243-Fc** dentromer in CH₂Cl₂ containing 0.1 M [*n*-Bu₄N][PF₆]: (a) CV of **243-Fc** (4 mg) in CH₂Cl₂: reversible wave at E_{1/2} = 0.555 V [vs. FeCp*₂ as an internal reference (Cp* = η^{5} -C₅Me₅), scan rate: 0.2 V·s⁻¹]; (b) modified Pt electrode at various scan rates in CH₂Cl₂ and (c) plot of the wave intensity as a function of scan rate (linearity showing the expected behavior of an adsorbed dentromer).

FeCp*₂) by 0.015 V towards anodic values compared to that of ferrocene (0.45 V vs. FeCp*₂), thus a ferricinium salt would not be the best to oxidize the ferrocenyl dentromers. Acetylferricinium hexafluorophosphate, a classic oxidant, was selected, because the oxidation potential of FcCOMe^{+/0} is 0.80 V vs. FeCp*₂, which would in principle insure exergonic, electron transfers by 0.245 V, thus favorable. Acetylferricinium hexafluorophosphate was synthesized according the Geiger's method and used to oxidize the **9-Fc** and **243-Fc** dentromers in CH₂Cl₂ at r.t. under nitrogen (see the experimental section). This finally resulted in the production of insoluble dark-blue solids, this color being characteristic of ferricinium, and the compounds were characterized by EPR and Mössbauer spectroscopies.

Mössbauer spectroscopy.

This technique is not very sensitive to the ferrocene substituents, but on the other hand it is very sensitive to the oxidation state, giving a QS value around 2.4 mm s⁻¹ for the doublet of ferrocene derivatives and a value near QS = 0 mm s⁻¹ (singlet or very narrow doublet) for ferricinium compounds.^[26] This distinction allows to easily recognize ferrocene-type and ferricinium-type components in the spectrum. The zero-field Mössbauer spectrum of dentromer **9-FcPF**₆ was recorded at 80K for a sample obtained according to the procedure described in the experimental section, leaving a dark-blue powder. The



Figure 4. Zero-field Mössbauer spectrum of the dentromer $9-Fc^+PF_6^-$ at 80K.

main compound is represented by a doublet for 9-FcPF6 (IS = 0.564 mm \cdot s⁻¹; QS = 0.413 mm \cdot s⁻¹). Although this major complex in the spectrum is the awaited 9-ferricinium PF_6 dentromer (80 ± 5%), the presence of another minor component of the ferrocenyl-type (20 ± 3%) indicates that oxidation was not complete. In another similar reaction, a slight excess (5% vs. stoichiometry) of acetylferricinium hexafluorophosphate was used, and an analogous Mössbauer results was obtained with (15 ± 5%) of ferrocenyl-type signal. These % values are approximate, because absorption energy is not necessarily exactly the same for both oxidation states even at low temperature. This lack of complete oxidation is possibly due to insufficient driving force from the acetyl ferricinium oxidant resulting in the formation of random mixed-valent Fe(II)/Fe(III) dentromers with a small amount of Fe(II). Indeed the driving force between the acetylferricinium oxidant and the dentromer ferrocenyl groups, although exergonic, is only about 0.245 V. Thus electron-transfer sometimes occurs eventually with long distance, for instance if ferrocenyl groups back fold toward the dentromer center (but not only), which becomes difficult in the case of weak driving force. It is also possible that the electrostatic factor, that renders electron transfer more difficult along the increase of the positive charges in the dentromer, inhibits electron transfer with the last ferrocenyl branches. A similar phenomenon has been observed in the oxidation of redox groups in dendrimers by the Balzani and Stoddart groups.^[27]

Electron Paramagnetic Resonance (EPR).

The dentromers **9-FcPF**₆ and **243-FcPF**₆ are synthesized similarly by oxidation of the neutral ferrocenyl dentromers by $FcCOMe^{+}PF_{6}^{-}$ in CH_2Cl_2 at r.t. (see experimental section) for electron paramagnetic resonance (EPR) measurements as powders at 80K. The EPR spectra show a low spin Fe(III) signal that is classic for the orthorhombic distortion characteristic of the



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Figure 5. EPR spectra at 80K of dentromer as powders (a) 9-FcPF_6 and (b) 243-FcPF_6.

17-electron d⁵ ferricinium at g = 2.09 for **9-Fc⁺PF**₆ and g = 2.065 for **243-Fc⁺PF**₆^[28] A signal at g = 4.245 is also observed corresponding to high-spin Fe(III) that probably reflects some decomposition, but this signal is not observed for **9-FcPF**₆ which might signify a higher instability in several days at r.t. for **243-FcPF**₆ compared to **9-FcPF**₆.

Oxidation of the click ferrocenyl dentromers by Au(III) to click ferricinium dentromer-stabilized gold nanoparticles (AuNPs)

The reaction of the dentromer **9-Fc** with HAuCl₄ (stoichiometry: 1 equiv. Fc/1 equiv. HAuCl₄) occurs within 5 min at r.t. upon stirring in a homogeneous THF/H₂O solution (1/19 ml). A color change from light yellow to red-purple is observed, the reaction time becoming longer upon increasing the dentromer generation number. Finally a red-purple AuNP^[29,30] solution is obtained for each dentromer generation (Figure S15). These red-purple solutions are characterized by UV-vis. spectroscopy and transmission electron microscopy (TEM). The UV/vis. spectra show the characteristic surface plasmon band (SPB) of Fc dentromer-stabilized AuNP/Fc ranging from 536 to 549 nm, the SPB being progressively red-shifted as the generation number increases (Figure 6). The AuNP core sizes of these AuNPs determined by TEM are between 30 and 47 nm (Figures S16-19). The dynamic light scattering measurement for 81-Fc has been shown to reflect a diameter size of 9 nm, [8b] thus the AuNP cores appear to be larger than the dentromers. This means that the AuNPs are stabilized around their periphery by several dentromers.

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Figure 6. (a) UV-vis. absorption and (b) color of AuNPs stabilized by ${\sf Fc}^{*}{\sf Cl}^{-}$ dentromers.

Reactions of the ferricinium chloride dentromer-stabilized AuNPs with cobaltocene.

In order to further characterize this macromolecular system we conducted reaction under nitrogen between $\mbox{cobaltocene}^{[31,32]}$ in THF and the purple THF/water (1/19 ml) solution of all the ferricinium dentromer-stabilized AuNPs (Scheme 2). The neutral 19-electron late transition-metal sandwich complexes of the first raw of the transition metals are known as strongly reducing electron-reservoir complexes.[32,33] This reaction process is shown on the UV-vis. spectra and on the pictures of the reaction media including after extraction with CH₂Cl₂ (Figures 7 and S20-23). The addition of cobaltocene to the 9, 27 and 81-ferricinium dentromer-stabilized AuNPs provokes the immediate formation of a purple precipitate and a slightly purple solution showing a much weaker SPB than before this reaction (Figures S21-23). For **9-Fc⁺Cl**⁻AuNP, this SPB is significantly red-shifted from 546 nm to 559 nm and is observed together with the band of cobalticinium at 400 nm (Figures S21, red curve b). Upon extraction with CH₂Cl₂ the purple precipitate and purple color of the solution disappear, which means decomposition of the AuNPs that also appear as a brown insoluble material at the interphase. Indeed the CH₂Cl₂ solution shows the ferrocenyl band at 430 nm in the UV-vis. spectrum (blue curve d), and its ¹H NMR spectrum confirms the presence of only the ferrocene dentromer (Figure S20). After this extraction, the aqueous solution still contains cobalticinium chloride as shown by its cobalticinium band at 398 nm in the UV-vis. spectrum (green curve c). This means that after the addition of cobaltocene to the 9-ferricinium dentromer-stabilized AuNPs, the precipitate shows the insolubility of the 9-ferrocenyl-dentromer-stabilized AuNPs, the ferrocenyl groups being hydrophobic contrary to the ferricinium groups. The facile extraction using CH2Cl2 also shows the weakness of the stabilization of the AuNPs by the 9-Fc dentromer contrasting with the robustness of the stabilization of these AuNPs by the 9-ferricinium dentromer, the latter benefiting from the electrostatic interaction. This series of experiments shows that upon reaction with HAuCl₄, the 9-Fc dentromer is oxidized to 9-ferricininium dentromer that electrostatically stabilizes AuNPs in THF/water, and that cobaltocene reduces the 9-ferricinium dentromer back to the 9-Fc dentromer.



Scheme 2. Synthesis of AuNP-243-Fc⁺Cl⁻ in THF/water and its reaction with cobaltocene. On the other hand for the other dentromer-stabilized AuNPs (9-Fc⁺Cl⁻, 27-Fc⁺Cl⁻ and 81-Fc⁺Cl⁻) extraction of **b** with CH₂Cl₂ (last step) leads to AuNP agglomeration and reformation of AuNP-free Fc dentromer (see SI).

The situation is very different in the case of the large 243ferricinium dentromer-stabilized AuNP. Following the reaction of AuNP-**243-Fc**⁺**CI**⁻ with cobaltocene, the clear homogeneous solution changes to a suspension that floculates to a red-purple precipitate. Upon shaking a few seconds it becomes a turbid red-purple solution for which the AuNP plasmon band in the UVvis. spectrum is observed at 548 nm, although it is less intense than before cobaltocene addition (Figure 7, red curve b). The cobalticinium band is observed therein around 400 nm. Then after addition of CH₂Cl₂ the cobaltocenium band is also observed at 402 nm in the UV-vis. spectrum of the aqueous phase (green curve **c**). The **243-Fc** dentromer is not extractable with CH₂Cl₂ from the AuNP with which it possibly forms a composite film because of its bulk (Scheme 2 and Figure 7) contrasting with the lower dentromer generations.

The multi-electron transfer reactions are taken into account by the favorable driving force of the electron transfer from the 1,2,3-

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triazolylferrocenyl groups (E⁰ (Fe(II)/Fe(III) = 0.55 V) to Au(III) (E[°] Au(III)/Au(0) = 0.93 V) for the formation of ferricinium dentromer-stabilized AuNPs, then from $CoCp_2$ (E⁰ ($CoCp_2^{+/0}$) = -0.9 V) to the 1,2,3-triazolylferricinium dentromer-stabilized AuNPs. The formation of the AuNPs is essentially driven by the enormous electrostatic effect stabilizing the AuNPs. This strong effect is cancelled upon reaction with cobaltocene back reforming the neutral ferrocenyl dentromers. In summary the AuNP electrostatic stabilization is switched upon redox change.



Figure 7. (a) UV-vis. absorption of (a) AuNP-**243-Fc⁺CI**⁻, (b) AuNP-**243-Fc⁺CI**⁻ + cobaltocene giving AuNP-**243-Fc** and cobalticinium chloride, (c) H_2O phase after extraction of the solution **b** with CH₂Cl₂. Note that both solutions **a** and **b** show the purple color of the AuNPs with some variation illustrated by the SPB red shift of **b**).

Concluding remarks

A family of four Fc-terminated click metallodentromers, 9-Fc, 27-Fc, 81-Fc and 243-Fc was synthesized with a specific type of dentromers whose construction starts with the CpFe⁺-induced nona-allylation of mesitylene followed by successive triple branching at each generation. These syntheses include the new 243-Fc for which the AFM studies show a dentromer height of 10 nm and a width of 80 nm due to aggregation, whereas cyclic voltammetry studies show full chemical and electrochemical reversibility despite its large size. The modified Pt electrodes built with the ferrocenyl dentromers are all the more stable as the dentromer generation increases. Using the Bard-Anson equation the number of ferrocenyl redox centers was found experimentally to be close (255) to the theoretical one (243). The synthesis of this series of four dentromers with 3ⁿ ferrocenyl termini (n = m + 2, m being the generation number) allows to evaluate the variation of the dentromer properties from generation to generation in particular with respect to collective electron transfers to a strong oxidant such as Au(III). With a weaker oxidant such as an acetylferricinium salt, however, the oxidation reactions appear incomplete as shown by zero-field Mössbauer spectroscopy due to the weaker driving force of the reaction producing random mixed valent dentromer systems. The stabilization of AuNPs by ferricinium-terminated dentromers is achieved for all the dentromer generations, but the reaction is all the slower as the generation number increases. This results in the formation of large AuNP between 30 nm and 47 nm with progressive red shift of the SPB as the generation number increases. This range of sizes is that used in nanomedicine for

which dendrimers are known to largely contribute due to the encapsulation properties.^[34] Reaction of the ferricinium dentromer-stabilized AuNPs with cobaltocene provides a large driving force of about 1.5 V for reduction of the ferricinium groups back to ferrocenyl groups. This reaction considerably weakens the AuNP stabilization by cancellation of the electrostatic effect, as shown by the dentromer extraction with CH₂Cl₂ that destroys the AuNP ensemble. The AuNP are partly stabilized by the CI ligands provided by the precursor HAuCl₄ during their redox synthesis, but these experiments show that this stabilization is not sufficient, and that the electrostatic stabilization provided by the ferricinium-terminated dentromers is so efficient that these AuNPs are stable for months. On the other hand much AuNP destabilization occurs upon returning to the neutral Fc dentromers. The dentromer generation influences this destabilization that is achieved with the 9-, 27- and 81-Fc-AuNPs, whereas the 243-Fc dentromer withstands extraction and AuNP agglomeration. Multi-electron transfers from such ferrocenyl dentromers and their electronic consequences represent an impressive effect of the switch of the electrostatic factor; they are also reminiscent of multiple single-electron transfer processes in other nanomaterials such as fullerenes and nanoclusters.[35]

Experimental Section

General Data. For general data including solvents, apparatuses, compounds, reactions, spectroscopies, and CV, see the SI. Gn indicates the generation number n.

Synthesis of dentromer 243-Fc: The syntheses of the different generations of Fc-dentromers are gathered in the SI. The 243-Fc dentromer is synthesized from 243-N₃ (0.3 g, 4.7×10⁻³ mmol, see SI.). The **243-N**₃ dentromer and ethynyl ferrocene (1.5 equiv. per branch) are dissolved in tetrahydrofuran (THF), then water is added (1:1 THF/water). CuSO₄ is added (1.2 equiv. per branch, 1M aqueous solution) to this reaction mixture, followed by dropwise addition of a freshly prepared solution of sodium ascorbate (2.4 equiv. per branch, 1M aqueous solution). The reaction mixture is stirred at r.t. for 16 h. After removing THF in vacuo, dichloromethane and an aqueous ammonia solution are added. The mixture is allowed to stir for 1 h in order to remove all Cu(I) trapped inside the dentromer. The organic phase is washed twice with water, dried with sodium sulfate, filtered over paper, and the solvent is removed in vacuo. The product is precipitated using dichloromethane/ pentane. The product 243-Fc is obtained as an orange-red powder in 77.9% yield (0.42 g, 3.7×10⁻³ mmol). ¹H NMR (300 MHz, CDCl₃): δ 7.31 (s, 243H), 7.15 (s, 234H), 6.89 (s, 234H), 4.73 (s, 486H), 4.27 (s, 486H), 4.07 (s, 1215H), 3.85 (s, 486H), 3.53 (s, 234H), 1.62 (s, 720H), 1.10 (s, 720H), 0.61 (s, 720H), 0.10 (s, 2160H); ¹³C NMR (76 MHz, CDCl₃): δ 159.13, 146.16, 138.71, 127.10, 119.68, 113.49, 75.73, 69.55, 68.56, 66.54, 60.29, 43.01, 41.86, 40.80, 17.45, 14.84, -3.80, -4.45; ²⁹Si NMR (CDCl₃, 59.6 MHz): δ 2.90 (SiCH₂N), 0.37 ppm (SiCH₂O).

Procedure for the preparation of 243-Fc⁺PF₆⁻: The **243-Fc** dentromer, dry dichloromethane and $CH_3COFc^+PF_6^-$ (1 equiv. per branch) are successively added into a Schlenk flask under nitrogen, then the solution is stirred for 16 h at r.t. Dichloromethane is removed *in vacuo*, then diethyl ether is added (3 x 10 mL) to wash the product 3 times, then dichloromethane is added (3 x 10 mL) to further wash the product 3 times

due to the poor solubility of the dentromer $Fc^+PF_6^-$. The product remains in the Schlenk flask as an insoluble dark-blue powder.

General procedure for the oxidation of the Fc-dentromers by Au(III) yielding Fc⁺CI⁻stabilized AuNPs: 18 mL of water is added into a Schlenk flask, and a solution of HAuCl₄·3H₂O (1mg in 1 mL H₂O) is added under stirring; then a solution of the Fc-dentromer (3 equiv. Fc branch per Au) dissolved in 1 mL THF is injected into the flask, and the solution is allowed to stir overnight at r.t. These AuNP solutions are further characterized by TEM (see the SI), the SPB recorded in the UV-vis. spectrum and their reaction with cobaltocene.

General procedure for the reaction of Fc⁺CI⁻stabilized AuNPs with cobaltocene: After the preparation of AuNPs stabilized by the ferricinium-terminated dentromers, the AuNP solution is degassed for 15 min, and the UV-vis. spectrum is recorded under N₂. Freshly prepared cobaltocene (1 equiv. per Fc) in THF (1 ml) is added to the AuNP solution under N₂, and the new UV-vis. spectrum is recorded after stirring for 3 min. Then CH₂Cl₂ is added to this mixture leading to the extraction the Fc-dentromer in the organic phase (in the cases of the 9-Fc, 21-Fc and 27-Fc dentromers, and the destabilized AuNPs aggregate), which is further characterized by ¹H NMR, whereas cobalticinium chloride is characterized in the aqueous phase **c** by its UV-vis. spectrum (in all cases). In the case of the 243-Fc-dentromer-stabilized AuNPs (**b**) in Scheme 2, no decomposition is observed.

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