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Dendrimers

Metalation of Polyamine Dendrimers with Ethynylcobalticenium for the Construction of Mono- and Heterobimetallic Polycationic Metallodendrimers

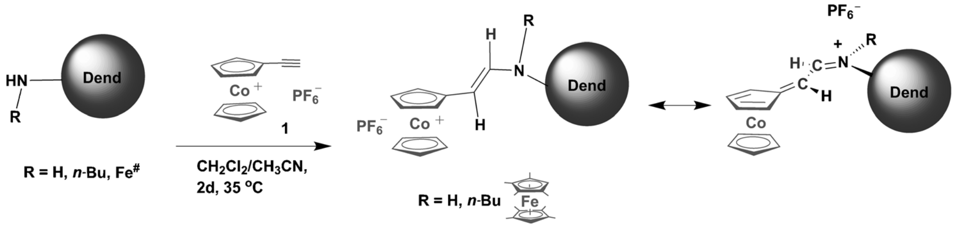
Yanlan Wang, Amalia Rapakousiou, Jaime Ruiz, and Didier Astruc*[a]

Abstract: The introduction of robust redox groups at the periphery of common amine-terminated dendrimers is of interest in the design of dendritic nanobatteries, sensors, and redox catalysts. Here we are applying the recently discovered uncatalyzed hydroamination of ethynylcobalticenium, a mild "green" reaction that quantitatively yields *trans*-enamines without the formation of any byproduct, to functionalize dendrimers that are terminated with primary or secondary amino groups. Poly(amido amine) (PAMAM) dendrimers terminated by primary amino groups and arene-centered dendrimers terminated by secondary amino groups yield dendrimers that contain up to 81 *trans*-enamine-cobalticenium termini using this reaction. The hydroamination reaction was also conducted with dendrimers that contained ferrocenylmethylamino groups, which yielded dendrimers that contained both ferrocenyl and cobalticenium termini. The size of the dendrimers was investigated using both dynamic light scattering and diffusion-ordered spectroscopy (DOSY) ^{1}H NMR spectroscopy, and the number of electrons involved in heterogeneous multielectron transfers at electrodes was searched by cyclic voltammetry. The latter works well up to the 27-branch dendrimer, whereas the 81-dendrimer yielded a result in an excess amount (110 electrons) owing to adsorption onto the cathode that becomes all the more significant as the metallodendrimer size increases.

Introduction

Metallodendrimers[1] are a class of well-defined metal-containing macromolecules[2] that show applications in sensing, catalysis, and materials science[1,3] in which the metal fragments are located inside the dendrimers[4] or at the periphery.[5] Metallodendrimers that contain stable redox centers are by and large ferrocene-terminated dendrimers.[6] Cobalticenium dendrimers[7,8] are of interest because of the robustness of the Co$^{III/II}$ redox center[9,10] and their complementarity with ferrocene dendrimers and other iron complexes[11] for electrochemical investigations of anion recognition and sensing and as nanobatteries.

Although cobalticenium branching relied for a long time on tedious synthesis and the functionalization of cobalticenium carboxylic acid,[10] recently the functionalization of ethynylcobalticenium using either click chemistry[12] or uncatalyzed mild hydroamination[13] opened new avenues for the derivatization of cobalticenium on nanomaterials. This latter reaction of readily available ethynylcobalticenium hexafluorophosphate[14,15] with primary and secondary amines is facile, quantitative, and does not form byproducts. It yields air-stable, strongly colored push–pull conjugated cobalticenium *trans*-enamines and thus appears to be an ideal "green" reaction for the efficient and facile functionalization of a variety of aminated dendrimers. These dendrimer functionalizations are illustrated and developed in this article [Eq. (1)].



(1)

Results and Discussion

Hydroamination of ethynylcobalticenium 1 with a PAMAM dendrimer

Ethynylcobalticenium **1** was easily synthesized as previously described in 60% overall yield from cobalticenium hexafluorophosphate.[14] The reaction between **1** and the commercially available first-generation poly(amido amine) (PAMAM) dendri-

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[a] Dr. Y. Wang, Dr. A. Rapakousiou, Dr. J. Ruiz, Prof. D. Astruc
ISM, UMR CNRS No. 5255, Université Bordeaux
33405 Talence Cedex (France)
E-mail: d.astruc@ism.u-bordeaux1.fr

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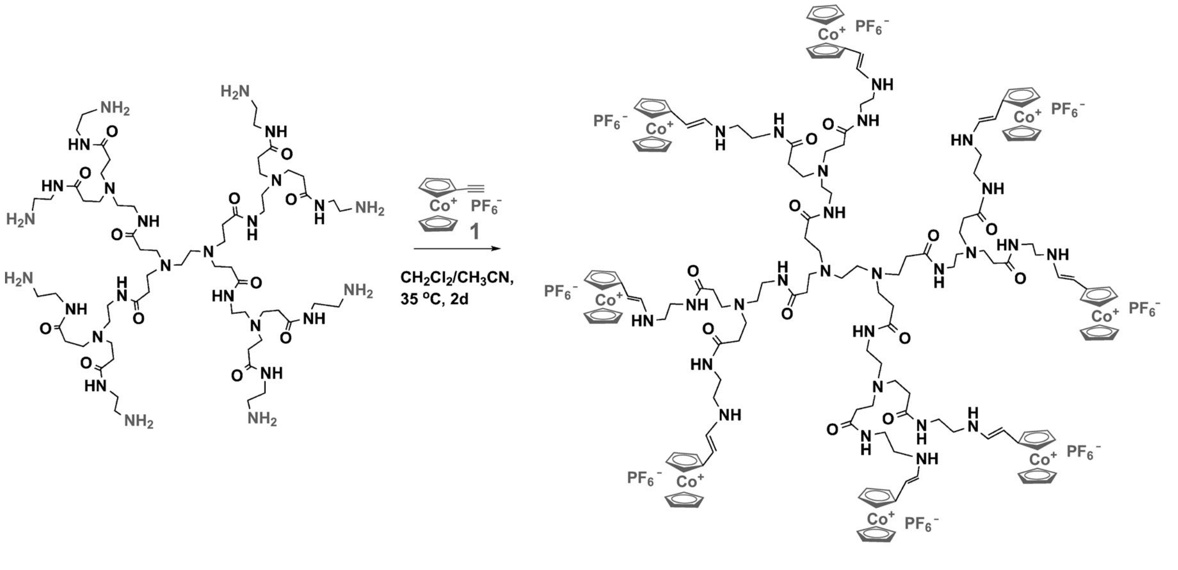


Scheme 1. Reaction of **1** with the first-generation PAMAM dendrimer yielding the all-*trans*-enamine-cobalticenium dendrimer **2**.

mer that contained eight terminal NH_2 groups (20 wt% solution in MeOH) in CH_3CN/CH_2Cl_2 (1:1) at 35 °C for two days yields the all-*trans*-enamine-cobalticenium dendrimer **2** (Scheme 1). The color of the mixture changed from yellow to deep red while stirring the reaction mixture, which indicates the formation of the enamine product. The workup gave a dark red solid that was washed with dry THF to remove the excess amount of complex **1** by using the solubility differences between dendrimer **2** and complex **1** in THF (yield 90%). Dendrimer **2** was fully characterized by ^1H (including diffusion-ordered spectroscopy (DOSY)), ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopy; elemental analysis; IR and UV/Vis spectroscopy; and cyclic voltammetry in DMF.

Hydroamination of 1, with three generations of arene-centered dendrimers terminated with (9, 27, 81) secondary amine groups

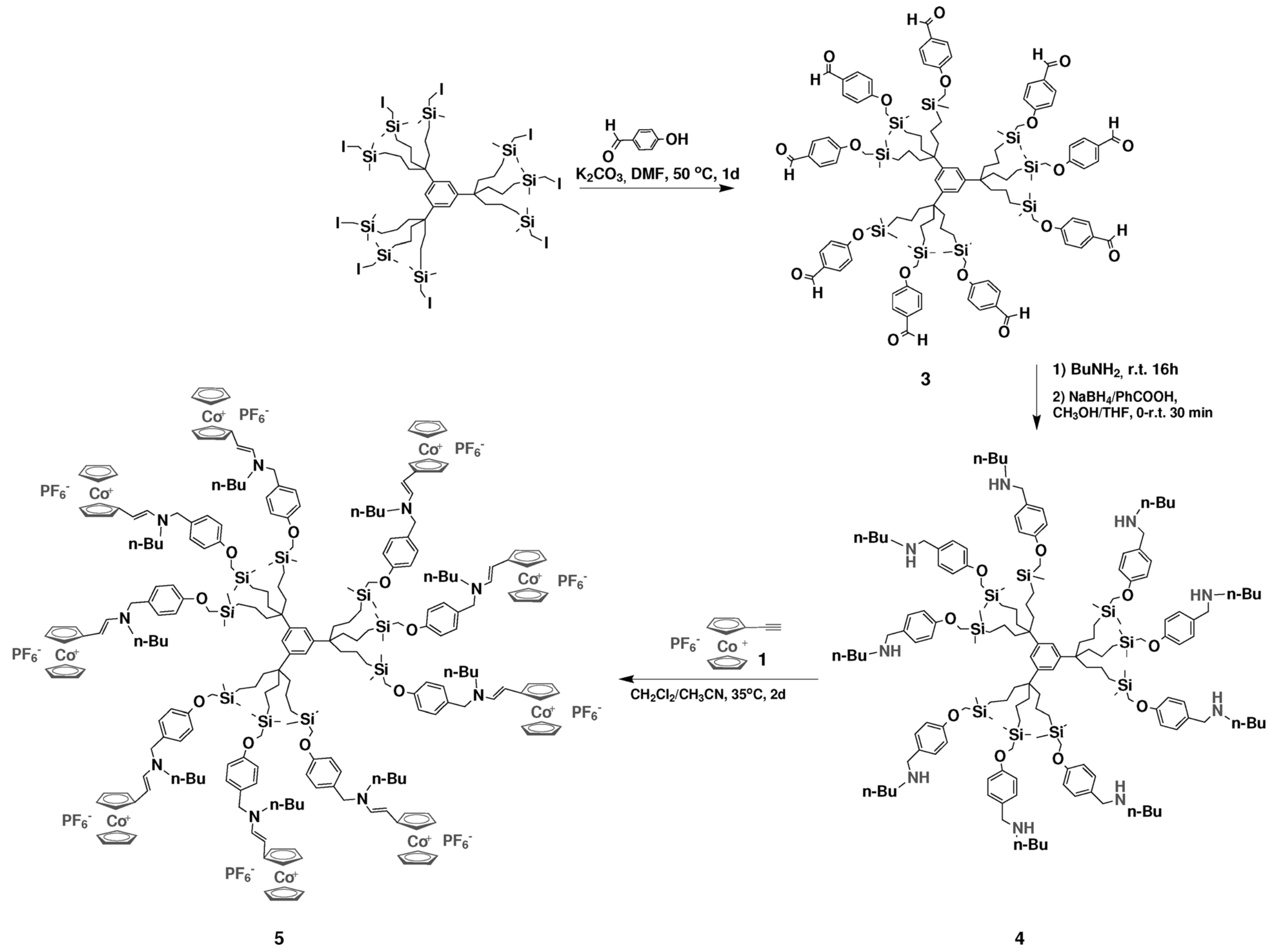
The hydroamination reaction to construct cobalticenium-functionalized nanomaterials was analogously extended to dendrimers terminated with secondary amine groups. Construction of the generations G0, G1, and G2 chloromethyl(dimethyl)silyl dendrimers with 1→3 connectivity[16] proceeded as described previously upon $CpFe^+$-induced (Cp = cyclopentadienyl) triallylation of mesitylene and *p*-methoxytoluene followed, after decomplexation, by hydrosilylation of the polyallyl dendritic cores and dendron using chloromethyldimethylsilane and iteration using a Williamson reaction with the tri-branched phenol dendron (phenol triallyl).[17] The terminal chloro groups were then substituted by iodo groups by reaction with sodium iodide to provide iodo-terminated dendrimers. Thus, the arene-cored dendrimer with terminal –NH*n*Bu groups (easily available upon Williamson reaction between the benzaldehyde dendrimer and butylamine followed by imine reduction) reacts with **1** to give the three generations of all-*trans*-enamine-cobalticenium dendrimers (Schemes 2, 3, and 4), which were fully characterized by ^1H (including DOSY), ^{13}C, ^{29}Si NMR spectroscopy; IR and UV/Vis spectroscopy; elemental analysis; and cyclic voltammetry.

Hydroamination of 1 with a nona-NHFc# dendrimer and synthesis of the bimetallic dendrimer 12

The convenience of the functionalization of nanomaterials with the ethynylcobalticenium PF_6 and the stability of the enamine-functionalized dendrimers encouraged the construction of heterobimetallic dendrimers **12** by this effective method (Scheme 5). The nona-NHFc# dendrimer terminated with nine octamethylferrocenylmethyl secondary amines was reported previously.[18] Its synthesis involves the reaction of FcCHO with the dendritic amine, a method that was pioneered by Casado's group.[18b] The reaction of this nona-NHFc# dendrimer with **1** leads to the heterobimetallic dendrimer **12** as a dark red solid (yield 90%) that was characterized by ^1H (including DOSY), ^{13}C, and ^{29}Si NMR spectroscopy; IR and UV/Vis spectroscopy; elemental analysis; and cyclic voltammetry.

Characterizations of the enamine cobalticenium dendrimers

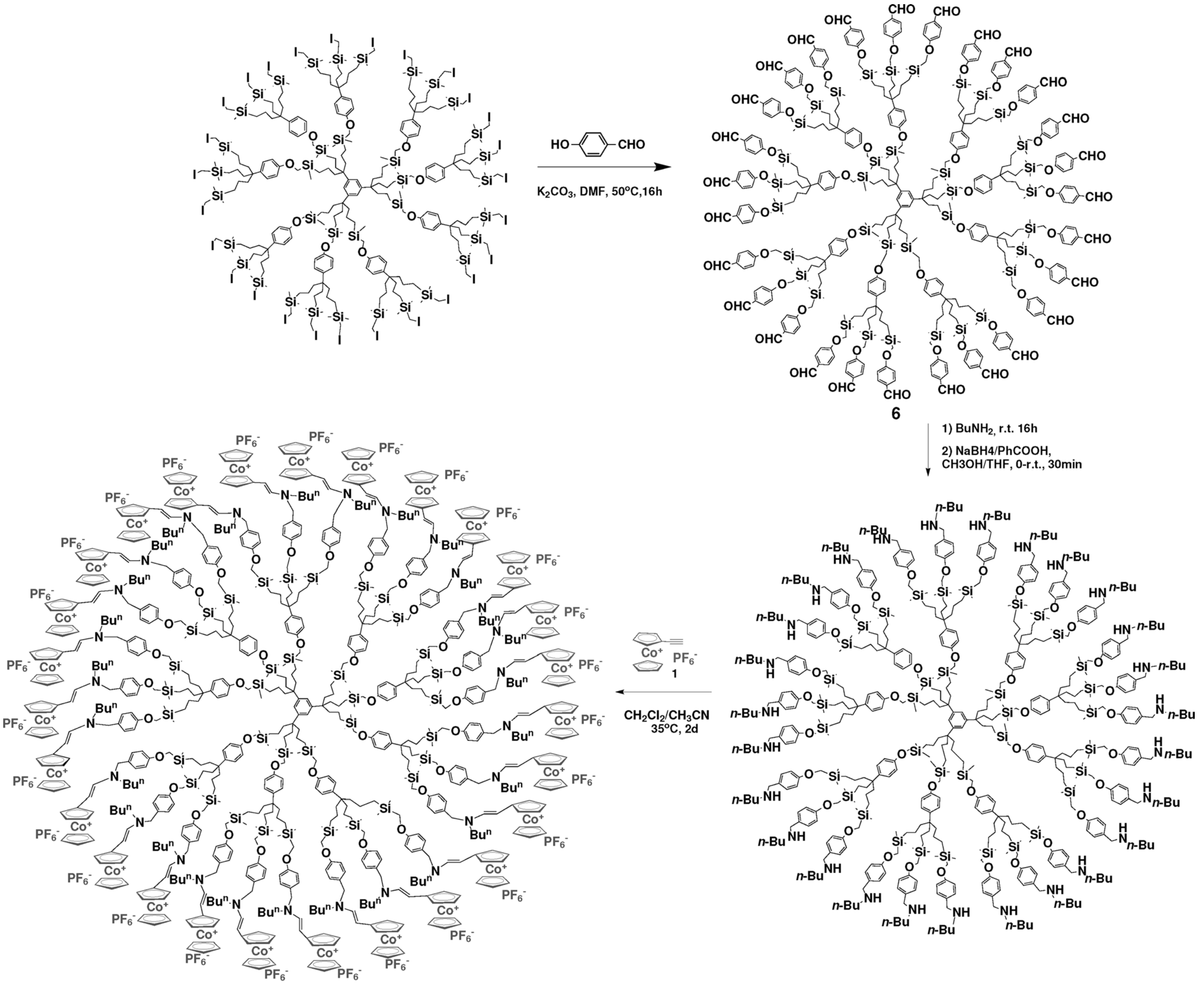
In the course of the synthesis of **5**, the new intermediate dendrimer **3** obtained by Williamson reaction was characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy; IR spectroscopy; MALDI-MS; and elemental analysis. The ^1H NMR spectrum showed the typical chemical shift of the proton on the CHO group at $\delta = 9.88$ ppm in $CDCl_3$, which corresponded to the peak at $\delta = 190.64$ ppm in the ^{13}C NMR spectrum assigned to the CHO carbon. The IR (KBr) spectrum also confirmed the structure with the strong absorbance at 1690 cm^{-1} ($\nu_{C=O}$) and 2750 cm^{-1} (ν_{CHO}), and the molecular ion in MALDI-TOF spectroscopy for



Scheme 2. Synthesis of the dendrimer G0-**3** by Williamson reaction between G0-CH$_2$I (nine branches) and 4-hydroxybenzaldehyde; synthesis of the G0 dendrimer **4** terminated with nine secondary amine groups and uncatalyzed hydroamination of **1** with dendrimer **4** to give the all-*trans*-enamine-cobaltocenium dendrimer **5**.

$(C_{126}H_{174}O_{18}Si_9)Na^+$ was found at 2251.7 (see the Supporting Information).

The reaction between the 9-benzaldehyde dendrimer **3** and an excess amount of neat *n*-butylamine at RT under N_2 gave a light yellow oil as the intermediate imine complex that was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy; IR spectroscopy; MALDI-TOF MS; and elemental analysis. The ^{1}H NMR spectrum showed the disappearance of the CHO group at $\delta=9.88$ ppm (300 MHz, $CDCl_3$) and the appearance of the new chemical shift at $\delta=8.12$ ppm for the $-CH{=}N-$ proton, and the IR (KBr) showed the strong absorbance at 1645 cm^{-1} assigned to the C=N bond absorption. In the MALDI-TOF spectrum of the G0 nona-imine ($C_{162}H_{255}O_9Si_9N_9$), the molecular peak was found at 2725.4 (see Supporting Information). Then this G0-nona-imine was reduced by NaBH$_4$/PhCOOH at 0 °C in MeOH/THF (1:1),[19] thus giving the 9-NH*n*Bu dendrimer **4** as a light yellow oil (yield 90 %), which was characterized by ^{1}H, ^{13}C, ^{29}Si NMR spectroscopy; IR spectroscopy; MALDI-TOF MS; and elemental analysis. The ^{1}H NMR spectrum showed the disappearance of the chemical shift at $\delta=8.12$ ppm that belonged to the $-CH{=}N-$ group and the appearance of the new peak at $\delta=3.45$ ppm that was assigned to the two protons on the $-PhCH_2N-$ groups. The IR spectrum (KBr) showed the absorbance at 3300 cm^{-1} (ν_{N-H}), and the molecular ion in MALDI-TOF for **4** $(C_{116}H_{273}O_9Si_9N_9)Na^+$ was found at *m/z* 2765.4. Upon reaction between **1** and the 9-NH*n*Bu dendrimer **4** in CH_3CN/CH_2Cl_2 (1:1) at 35 °C, the color of the mixture changed from yellow to deep red, and after two days the reaction was completed, thus giving the quite air-stable all-*trans*-enamine-cobalticenium dendrimer **5** that was characterized by ^{1}H (including DOSY), ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopy; elemental analysis; IR and UV/Vis spectroscopy; MALDI-TOF MS; and cyclic voltammetry. The two protons on the $-CH{=}CH-$ groups appeared at $\delta=4.87$ ppm (d, $J=11.72$ Hz, 9 H) and 7.60 ppm (d, $J=11.72$ Hz, 9 H) of the ^{1}H NMR spectrum in $(CD_3)_2CO$ and showed the all *trans*-enamine cobalticenium structure, and the MALDI-TOF spectrum confirmed the structure of **5**: *m/z* calcd for $(C_{270}H_{363}O_9Si_9N_9Co_9)(PF_6)_9$: 5965.4; molecular ion found for $(C_{270}H_{363}O_9Si_9N_9Co_9)(PF_6)_8$ at *m/z* 5820.4, for $(C_{270}H_{363}O_9Si_9N_9Co_9)(PF_6)_7$ at *m/z* 5675.5, and for $(C_{270}H_{363}O_9Si_9N_9Co_9)(PF_6)_6$ at *m/z* 5530.7 (Figure 1). All these characterizations indicated that the hydroamination that yielded **5** was quantitative.



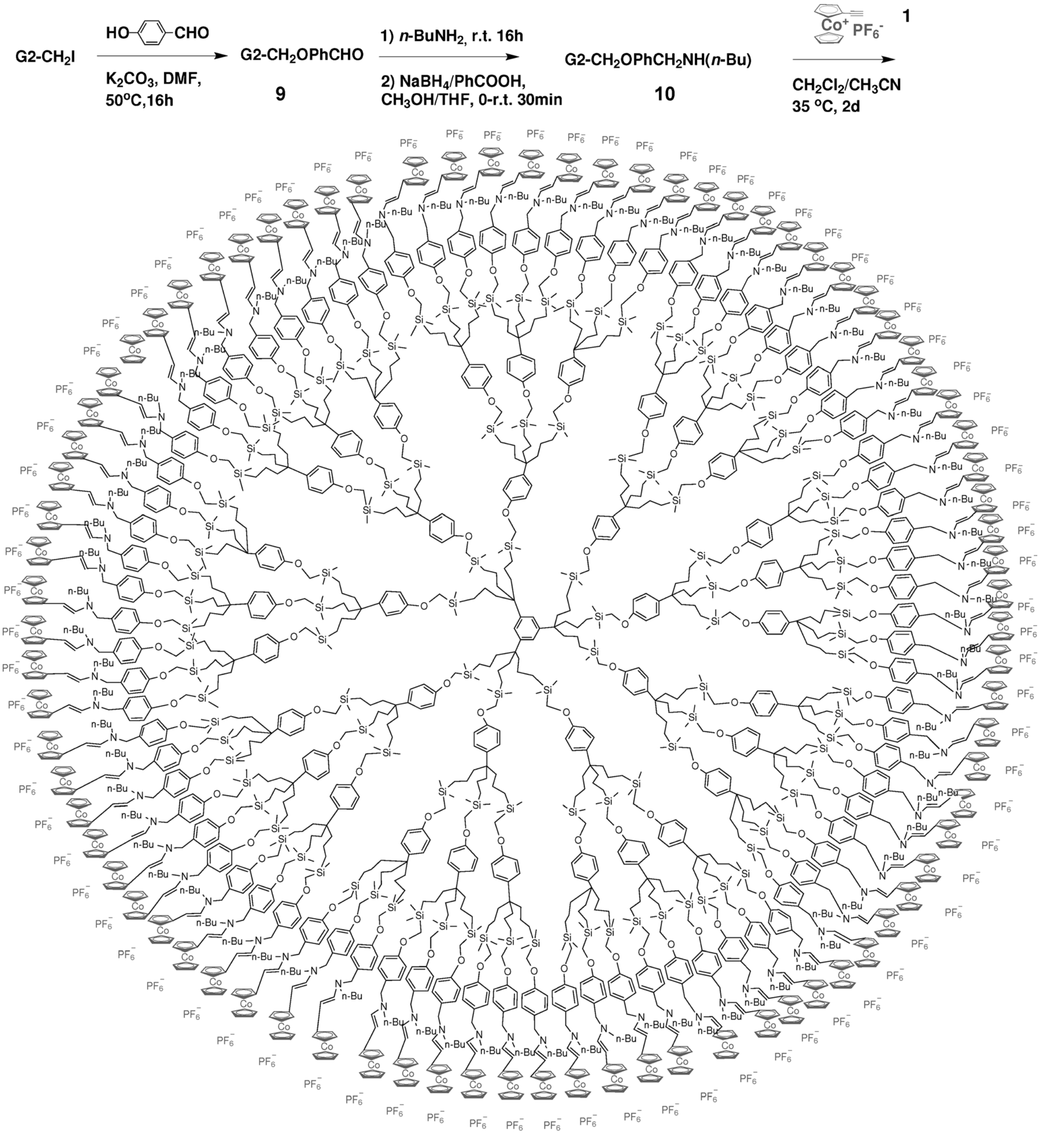
Scheme 3. Synthesis of dendrimer G1-**6** by Williamson reaction between G1-CH$_2$I (27 branches) and 4-hydroxybenzaldehyde; synthesis of the dendrimer **7** and hydroamination of **1** with dendrimer **7** giving the all-*trans*-enamine-cobalticenium dendrimer **8**.

Generations G1 and G2 of all-*trans*-enamine cobalticenium dendrimers that contained 27 and 81 cobalticenium PF$_6$ at the periphery were constructed, respectively, by the method described above for the synthesis of the G0 dendrimer; these reactions were completed in two days at 35 °C (Scheme 3 and 4). The intermediate dendrimers **6**, **7**, **9**, and **10** were fully characterized by ^{1}H, ^{13}C, ^{29}Si NMR spectroscopy; IR spectroscopy; and elemental analysis. These large-generation dark red all *trans*-enamine cobalticenium dendrimers **8** and **11** were fully characterized by ^{1}H (including DOSY), ^{13}C, ^{29}Si, ^{31}P NMR spectroscopy; IR and UV/Vis spectroscopy; elemental analysis; and cyclic voltammetry in DMF and showed properties that were similar in all these characterizations to those of dendrimer **5** (see the Supporting Information).

As the numbers of cobalticenium hexafluorophosphate groups in the dendrimers increased, the solubility in THF decreased regularly. The smaller dendrimers **2**, **5**, and **12** showed good solubility in THF. However, the solubility of dendrimer **8** in THF was very limited, and the largest dendrimer **11** was not soluble in THF but only DMF. The IR (KBr) for all the cobalticenium-enamine dendrimers showed a strong absorbance at 1614 cm^{-1} for the C=C bond and 836 cm^{-1} for the PF$_6$ group (Table 1). In the UV/Vis spectra, the weak adsorption in the region of 410–422 nm was assigned to the d–d* transition of cobalticenium,[20] and the transitions in the area of 483–514 nm for all the dendrimers seem to be due to d–d* mixed

Table 1. IR and UV/Vis absorptions for dendrimers **2**, **5**, **8**, **11**, and **12**.

Dendrimer	UV/Vis [nm] λ_{max1}	λ_{max2}	IR [cm^{-1}] $\nu_{C=C}$	ν_{PF6}
2 (8 Co)	410	483	1621	840
5 (9 Co)	415	495	1614	836
8 (27 Co)	415	495	1614	838
11 (81 Co)	415	495	1814	838
12 (9 Co + 9 Fe$^{\#}$)	422	514	1607	838



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Scheme 4. Synthesis of dendrimer G2-**9** by Williamson reaction with G2-CH_2I (81 branches) and 4-hydroxybenzaldehyde; synthesis of the G2 dendrimer **10** terminated with 81 secondary amine groups and hydroamination of **1** with dendrimer **10** giving the all-*trans*-enamine-cobaltocenium dendrimer **11**.

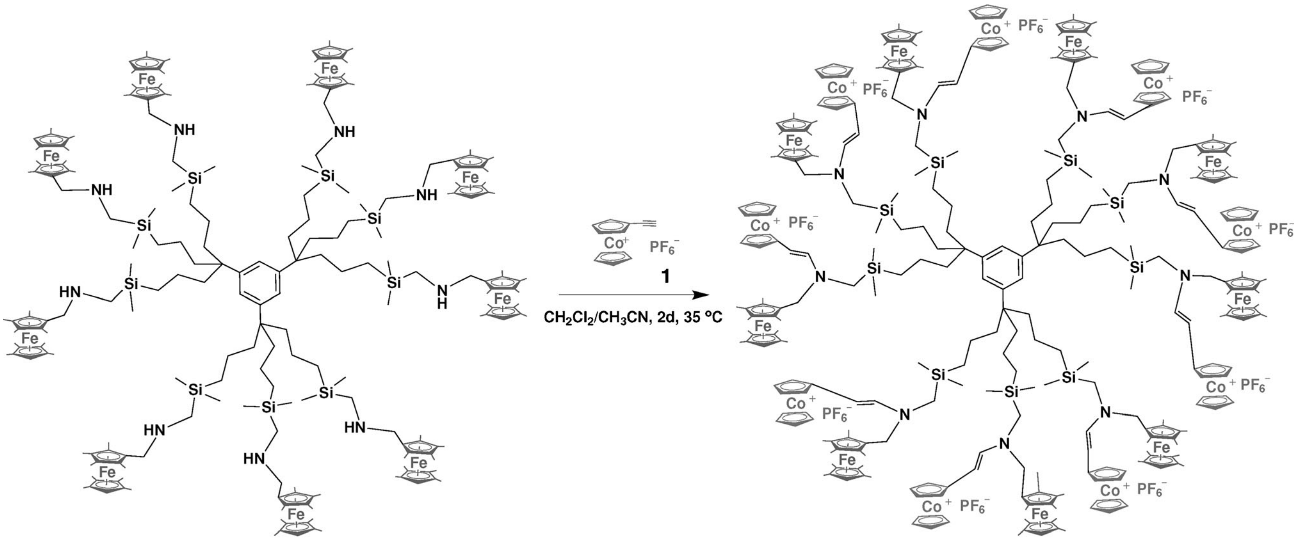
with charge transfer from the ligand to the metal (Figure 2, Table 1). The variation of λ_{max} within the group of dendrimers **2**, **5**, and **12** is probably caused by the variation of functional group on the enamine (Figure 2).

DOSY experiments were carried out for dendrimers **2**, **5**, **8**, **11**, and **12** in $CO(CD_3)_2$ at 25 °C (Table 2). The main goal of these

Table 2. DOSY and DLS experiments for dendrimers **2**, **5**, **8**, **11**, and **12**.

Compound	$D^{[a]}$ ($\pm$0.1) [$m^2 s^{-1}$]	$r_H^{[b]}$ ($\pm$0.1) [nm]	$r_H^{[c]}$ ($\pm$5) [nm]
2 (8 Co)	1.65×10^{-10}	4.13	–
5 (9 Co)	1.65×10^{-10}	4.13	–
8 (27 Co)	1.03×10^{-10}	6.64	–
11 (81 Co)	0.87×10^{-10}	7.86	35
12 (9 Co + 9 Fe#)	2.22×10^{-10}	3.09	–

[a] Diffusion coefficient measured in $CO(CD_3)_2$ at 25 °C. [b] Hydrodynamic radius from DOSY calculated using the Stokes–Einstein equation. [c] Hydrodynamic diameter from DLS. The values were obtained in acetone. The results are not reliably available for small dendrimers in DLS.



nona-NHFe#

12

Scheme 5. Synthesis of the bimetallic dendrimer **12** by hydroamination reaction of **1** with nona-NHFc# (Fc# = octamethylferrocenyl).

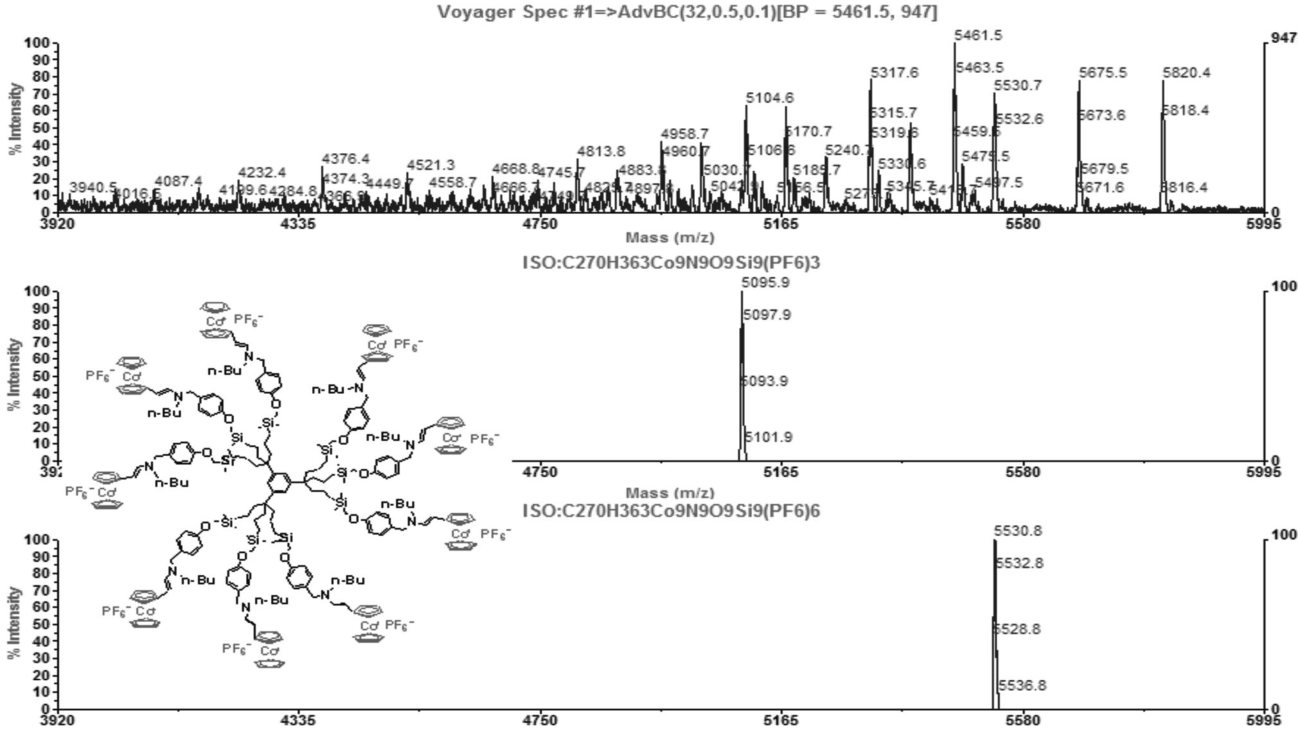


Figure 1. MALDI-TOF spectrum for dendrimer **5**.

experiments was to measure the diffusion coefficient D by ^{1}H NMR spectroscopy. In the ^{1}H NMR spectroscopic experiment, diffusion is mathematically treated as DOSY to obtain the equivalent of 'spectral' chromatography. The objective is thus double: to measure the diffusion coefficients of the molecules in solution and to obtain a DOSY spectrum that reflects the purity of the assembly (see the Supporting Information). For compound **2** (eight branches), the average diffusion coefficient value obtained was $D = (1.65 \pm 0.1) \times 10^{-10}$ m^2 s^{-1}. In the case of the G0 dendrimer **5** (nine branches), the calculated diffusion coefficient was $D = (1.65 \pm 0.1) \times 10^{-10}$ m^2 s^{-1}, and for the dimetallic G0 dendrimer **12** (nine branches) the calculated diffusion coefficient was $D = (2.22 \pm 0.1) \times 10^{-10}$ m^2 s^{-1}. These three small-sized dendrimers **2**, **5**, and **12** gave close hydrodynamic radii of 4.13, 4.13, and 3.09 nm, respectively, under identical conditions. In the case of G1 dendrimer **8** (27 branches), the calculated diffusion coefficient was $D = (1.03 \pm 0.1) \times 10^{-10}$ m^2 s^{-1}, and the hydrodynamic radius was 6.64 nm, whereas in the

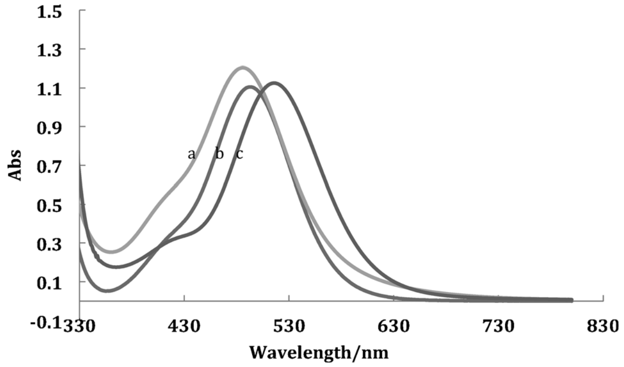


Figure 2. Compared UV/Vis absorptions for dendrimers a) **2**, b) **5**, and c) **12**.

case of the G2 dendrimer **11** (81 branches) the calculated diffusion coefficient was $D=(0.87\pm0.1)\times10^{-10}\ \mathrm{m^2\,s^{-1}}$, and the hydrodynamic radius was 7.86 nm. The DOSY experiment results give clear evidence of size progression as dendrimer generation increases. Otherwise, for the largest dendrimer **11**, the values obtained from dynamic light scattering (DLS) were larger than the sizes obtained from DOSY experiments, which is taken into account by the intermolecular associations. For dendrimers **2**, **5**, **8**, **12**, it was not possible to obtain reproducible sizes by DLS because of strong electrostatic intermolecular associations.[21]

Cyclic voltammograms of the dendrimers terminated with cobalticenium

Seminal electrochemical studies of cobalticenium and derivatives have been reported by Geiger, including a reversible $Co^{III/II}$ reduction that generated the neutral d^7 "19-electron" cobaltocene species and at much more negative potential another single-electron reduction to the d^8 "20-electron" Co^{I} anion.[9] Cobaltocenes are thermally stable, air-sensitive complexes, whereas the very-high-energy Co^{I} anion has never been isolated. In molecular nanomaterials such as large metallodendrimers, the second wave is marred by considerable adsorption and chemical irreversibility, therefore the attention here focuses on the first cyclic voltammetry wave that is very useful because its reversibility is still present. The cyclic voltammograms (CVs) of dendrimers **2**, **5**, **8**, **11**, and **12** were determined in DMF with $FeCp^*_2$ ($Cp^*=\eta^5\text{-}C_5Me_5)_2$)[22] as the reference. The $Co^{III/II}$ reduction wave was indeed found to be chemically and electrochemically reversible (Figure 2). The redox potential $E_{1/2}$ of this reversible $Co^{III/II}$ CV wave in dendrimers ranged from −1.03 to −1.07 V versus $FeCp^*_2$. For the comparatively small dendrimers **2**, **5**, **8**, and **12**, the CVs show an adsorption that is negligible for this reversible $Co^{III/II}$ wave ($i_a/i_c=1$), so that comparison with the internal reference $FeCp^*_2$ provides a good estimation, by using the Bard–Anson equation [Eq. (2)],[23] of the number of electrons n_d involved in the $Co^{III/II}$ redox process as a function of the monomer and dendrimer intensities (i), concentrations (c), and molecular weights (M).

$$n_d=(i_d c_m/i_m c_d)(M_m/M_d)^{0.275} \tag{2}$$

According to this equation, the number of electrons found to be transferred in the $Co^{III/II}$ wave are $n_d=(7.5\pm1)$, (8.2 ± 1), (28 ± 2), and (8.5 ± 1) when using this equation for dendrimers **2**, **5**, **8**, and **12**, respectively, which is in good agreement with the theoretical values of 8, 9, 27, and 9 redox groups in the dendrimers (Table 3). The CV of dendrimer **12** also showed the chemically and electrochemically reversible $Fe^{II/III}$ oxidation wave for the octamethylferrocenyl group. The redox potential $E_{1/2}$ of the $Fe^{II/III}$ wave was 0.20 V versus $FeCp^*_2$ and −0.27 V versus $FeCp_2$, respectively (Table 3, Figure 3C and D). However, for the largest dendrimer **11**, the adsorption during the electrochemistry measurements was more significant than with the smaller dendrimers (Figure 3B), and consequently a larger value $n_d=(110.5\pm5)$ than the theoretical number of redox groups was found.

Table 3. Compared $E_{1/2}$ values and numbers of electrons involved in the redox wave of the cyclic voltammogram for all the cobalticenium dendrimers.[a]

Compound	$E_{1/2}$ [V]	ΔE [mV]	n_d (number of electrons)
2 (8 Co)	−1.05	65	7.5 ± 1
5 (9 Co)	−1.04	60	8.2 ± 1
8 (27 Co)	−1.03	65	28.0 ± 2
11 (81 Co)	−1.03	50	110.5 ± 5
12 (9 Fe# + 9 Co)[b]	−1.07	70	8.5 ± 1

[a] Cyclic voltammetry of cobalticenium-enamine-terminated dendrimers (2 mM) obtained at a Pt electrode at 25 °C in DMF; supporting electrolyte: $[nBu_4N][PF_6]$, reversible $Co^{III/II}$ wave. Internal reference: $[FeCp^*_2]^{0/+}$. [b] The redox potential $E_{1/2}$ of the $Fe^{II/III}$ wave was 0.20 V versus $FeCp^*_2$ and −0.27 V versus $FeCp_2$, respectively.

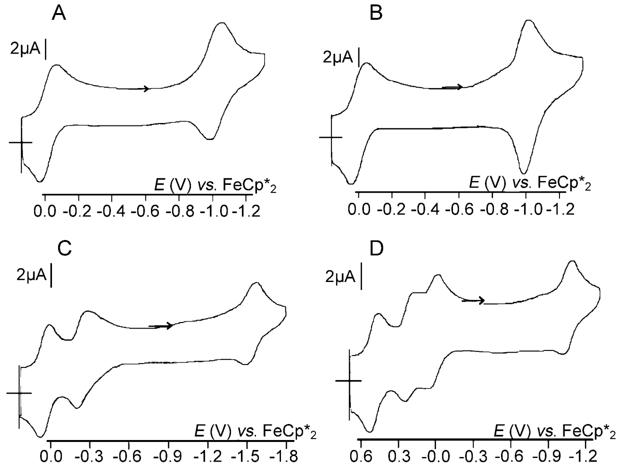


Figure 3. Cyclic voltammograms of A) **5**, B) **11**, and C,D) **12**.

Conclusion

With amine-terminated dendrimers, which are among the most common dendrimers (including the well-known PAMAM dendrimers), the addition of ethynylcobalticenium produces highly conjugated, deeply red-colored *trans*-enamine dendrimers and proceeds smoothly and quantitatively at 35 °C without the need of a catalyst (in contrast to the CuAAC "click" reaction) and without the formation of any byproduct. This uncatalyzed alkyne hydroamination is thus a "green" organometallic reaction that is very useful, because it is the most practical method of introducing the cobalticenium group onto dendrimers and thus also into a variety of other nanomaterials that are functionalized with a primary or secondary amine group. The ease and simplicity of the reaction allowed us to readily synthesize heterobimetallic dendrimers that contain both ferrocenyl and cobalticenium groups, which means that sophisticated nanomaterials become accessible using this method. The cobalticenium dendrimers are valuable since the $Co^{III/II}$ redox center is robust, as shown by the electrochemical studies reported in this article, and very complementary to the ferricenium/ferrocene redox couple. In spite of its robustness and utility, up to now it has been minimally employed owing to tedious synthetic methods, but the present modified procedure reported herein should greatly enhance its applications in the near future.

Experimental Section

General information

THF was dried over Na foil and distilled from the sodium benzophenone anion under nitrogen immediately prior to use. Dichloromethane (CH_2Cl_2) and CH_3CN were distilled from calcium hydride under nitrogen prior to use. All other solvents and chemicals were used as received. ^1H NMR spectra were recorded at 25 °C using a Bruker AC (200, 300, 400, 600 MHz) spectrometer. The ^{13}C NMR spectra were obtained in the pulsed FT mode at 75 MHz using a Bruker AC 300 spectrometer. All the chemical shifts (δ) are reported in parts per million with reference to Me_4Si for the ^1H and ^{13}C NMR spectra. All the ^1H, ^{13}C, ^{29}Si, and ^{31}P and DOSY NMR spectroscopic data and spectra are gathered in the Supporting Information. The mass spectra were recorded using an Applied Biosystems Voyager-DE STR-MALDI-TOF spectrometer (see the Supporting Information). The infrared spectra were recorded using an ATI Mattson Genesis series FTIR spectrophotometer. UV/Vis absorption spectra were measured using a Perkin–Elmer Lambda 19 UV/Vis spectrometer (see the Supporting Information). Electrochemical measurements (cyclic voltammetry) were recorded using a PAR 273 potentiostat under a nitrogen atmosphere at 293 K (see main text and the Supporting Information). The elemental analyses were performed at the Center of Microanalyses of CNRS at Lyon Solaize (France). DOSY NMR spectroscopic measurements were performed at 25 °C using a Bruker AVANCE II 600 MHz spectrometer. They were performed using ^1H NMR pulsed-gradient spectroscopic experiments, the simulated spin–echo sequence that leads to the measurement of the diffusion coefficient *D*, in which *D* is the slope of the straight line obtained when ln(*I*) is displayed against the square of the gradient-pulse power according to the following equation [Eq. (3)]:

$$\ln(I) = -\gamma^2 G^2 D \delta^2 (\Delta - \delta/3) \quad (3)$$

in which *I* is the relative intensity of a chosen resonance, γ is the proton gyromagnetic ratio, Δ is the intergradient delay (150 ms), δ is the gradient pulse duration (5 ms), and *G* is the gradient intensity. The diffusion constant of water ($2.3\times10^{9}\ m^2\,s^{-1}$) was used to calibrate the instrument (see the Supporting Information).

Dendrimer 2

Complex **1** (43.0 mg, 1.2×10^{-4} mol, 1.5 equiv for each branch) and the PAMAM dendrimer G1 (87 µL, 1×10^{-5} mol, 20 wt% solution in MeOH) were dissolved in CH_3CN/CH_2Cl_2 (1:1, 10 mL), then the mixture was stirred for 2 d under N_2 at 35 °C. The color of the mixture changed from yellow to deep red during the stirring. The solvent was removed under vacuum, and the residual solid was washed with dry THF three times, then the residual solid was dried under vacuum to give the all-*trans*-enamine-cobalticenium dendrimer **2** as a dark red solid (42.3 mg, yield 90%). UV/Vis: $\lambda_{max1} = 410$ nm, $\lambda_{max2} = 483$ nm, $\varepsilon = 1.00\times10^5\ L\,mol^{-1}$; IR (KBr): $\tilde{\nu} = 3430$ (ν_{N-H}), 1614 ($\nu_{CH=CH}$), 838 cm^{-1} (ν_{PF6}); CV = 2 mM, solvent: DMF, *T*: 20 °C, supporting electrolyte: $[nBu_4N][PF_6]$ (0.1 M), working and counter electrodes: Pt, reference electrode: Ag, scan rate: 0.200 $V\,s^{-1}$, internal reference: $FeCp^*_2$; $E_{1/2(rev)} = -1.05$ V, $\Delta E = 65$ mV; elemental analysis calcd (%) for $C_{158}H_{208}N_{26}O_{12}Co_8(PF_6)_8$: C 44.19, H 4.88, N 8.48; found: C 44.36, H 4.59, N 8.57.

Dendrimer 3

The nona-CH_2I dendrimer (228.1 mg, 1×10^{-4} mol, 1 equiv), 4-hydroxybenzaldehyde (1.098 g, 9×10^{-3} mol, 10 equiv for each branch), and K_2CO_3 (2.484 g, 1.8×10^{-2} mol, 20 equiv for each branch) were mixed in one flask under N_2. DMF (10 mL) was added into the mixture with a syringe needle, the solution was stirred at 50 °C under N_2 for 24 h. The color of the solution changed from light yellow to light violet. Distilled H_2O (100 mL) was added to this mixture, a white precipitate formed, and the mixture was kept stirring for 10 min. After filtration, the filtrate was violet, and the residual white solid was on the surface of the Celite. This white solid was washed with H_2O (100 mL four times) to remove the DMF, 4-hydroxybenzaldehyde, and K_2CO_3. The white product was dissolved in CH_2Cl_2 to give a colorless solution. This solution was dried with anhydrous Na_2SO_4, the solvent was evaporated, and the dendrimer was obtained as a colorless gel (200 mg, yield 89%). IR (KBr): $\tilde{\nu} = 1690$ ($\nu_{C=O}$), 2750 cm^{-1} (ν_{CHO}); MALDI-TOF: *m/z* calcd for $(C_{126}H_{174}O_{18}Si_9)Na^+$: 2252.0; found: 2251.7; elemental analysis calcd (%) for $C_{126}H_{174}O_{18}Si_9$: C 67.88, H, 7.87; found: C 67.93, H 7.77.

Dendrimer 4

The 9-benzaldehyde dendrimer (223 mg, 10^{-4} mol) was dissolved in dry *n*-butylamine (10 mL), and this mixture was stirred at RT under N_2 for 16 h. The excess amount of *n*-butylamine was removed under vacuum to give a light yellow oil as the intermediate imine. IR (KBr): $\tilde{\nu} = 1645\ cm^{-1}$ ($\nu_{C=N}$); MALDI-TOF: *m/z* calcd for $(C_{162}H_{255}O_9Si_9N_9)$: 2725.6; found: 2725.4; elemental analysis calcd (%) for $C_{162}H_{255}O_9Si_9N_9$: C 71.39, H 9.43, N 4.63; found: C 71.50, H 9.55, N 4.67.

The G0-imine dendrimer (824 mg, 3×10^{-4} mol) was dissolved in MeOH/THF (1:1, 10 mL), then the mixed powder of $NaBH_4$ (306.4 mg, 8.1×10^{-3} mol, 3 equiv for each branch) and PhCOOH (998.5 mg, 8.1×10^{-3} mol, 3 equiv for each branch) was added to the solution slowly at 0 °C, and the mixture was left stirring under 0 °C for 30 min. The solvent was removed under vacuum, then dry

CH_2Cl_2 (30 mL) was added to the residual white solid. After separation, the organic solution was washed three times with a saturated $NaHCO_3$ solution and three times with distilled H_2O. The organic phase was dried with anhydrous Na_2SO_4, and the solvent was removed under vacuum to give the 9-NH*n*Bu dendrimer as a light yellow oil (746 mg, yield 90%). IR (KBr): $\tilde{\nu} = 3300\,cm^{-1}$ (ν_{N-H}); MALDI-TOF: *m/z* calcd for $(C_{162}H_{273}O_9Si_9N_9)Na^+$: 2764.9; found: 2765.4; elemental analysis calcd (%) for $C_{162}H_{273}O_9Si_9N_9$: C 70.92, H 10.03, N 4.59; found: C 70.67, H 10.12, N 4.65.

Dendrimer 5

Complex **1** (87 mg, 0.23 mmol, 2.63 equiv for each branch) and the 9-NH*n*Bu dendrimer **4** (27.43 mg, 0.01 mmol) were dissolved in CH_3CN/CH_2Cl_2 (1:1, 10 mL), then the mixture was stirred for 2 d under N_2 at 35 °C, and the color of the mixture changed from yellow to deep red during the stirring. The solvent was removed under vacuum, the dark red solid was washed three times with dry THF, then the residual dark red solid was dried under vacuum to give **5** as a dark red solid (53.7 mg, yield 90%). IR (KBr): $\tilde{\nu} = 1614$ ($\nu_{C=C}$), 836 cm^{-1} (ν_{PF6}); UV/Vis: $\lambda_{max1} = 415$ nm, $\lambda_{max2} = 495$ nm, $\varepsilon = 1.12\times10^5\,L\,mol^{-1}\,cm$; CV = 2 mM, solvent: DMF, *T*: 20 °C, supporting electrolyte: $[nBu_4N][PF_6]$ (0.1 M), working and counter electrodes: Pt, reference electrode: Ag, scan rate: 0.200 $V\,s^{-1}$, internal reference: $FeCp^*_2$; $E_{1/2(rev)} = -1.03$ V, $\Delta E = 65$ mV; MALDI-TOF: *m/z* calcd for $(C_{270}H_{363}O_9Si_9N_9Co_9)(PF_6)_9$: 5965.4; found $(C_{270}H_{363}O_9Si_9N_9Co_9)(PF_6)_8$: 5820.4; elemental analysis calcd for $(C_{270}H_{363}O_9Si_9N_9Co_9)(PF_6)_9$: C 54.35, H 6.13, N 2.11; found: C 53.40, H 6.18, N 2.23.

Dendrimer 6

The G1-CH_2I dendrimer (228.1 mg, 1×10^{-4} mol, 1 equiv), 4-hydroxybenzaldehyde (1.098 g, 9×10^{-3} mol, 10 equiv for each branch), and K_2CO_3 (2.484 g, 1.8×10^{-2} mol, 20 equiv for each branch) were mixed in a flask under N_2. DMF (10 mL) was added into the mixture with a syringe needle, and the solution was stirred at 50 °C under N_2 for 24 h. The color of the solution changed from light yellow to light violet. H_2O (100 mL) was added to this mixture, a white precipitate formed, and the mixture was kept stirring for 10 min. After filtration, the filtrate was violet, and the residual white solid was left on the surface of the Celite. The white solid was washed with H_2O (100 mL four times) to remove the DMF, 4-hydroxybenzaldehyde, and K_2CO_3. The white product was dissolved in CH_2Cl_2 to give a colorless solution. The solution was dried with anhydrous Na_2SO_4 and evaporated, and the compound was obtained as a colorless gel (200 mg, yield 89%). IR (KBr): $\tilde{\nu} = 1691\,cm^{-1}$ ($\nu_{CH=O}$); MALDI-TOF: *m/z* calcd for $(C_{477}H_{678}O_{63}Si_{36}Na^+)$: 8454.5; found: 8454.3; elemental analysis calcd (%) for $C_{477}H_{678}O_{63}Si_{36}$: C 67.95 H 8.11; found: C 67.58, H 8.01.

Dendrimer 7

The 27-benzaldehyde dendrimer **6** (843.2 mg, 1×10^{-4} mol) was dissolved in dry *n*-butylamine (10 mL), and this mixture was stirred at RT under N_2 for 16 h. The excess amount of *n*-butylamine was removed under vacuum, which gave the G1-imine as a light yellow oil. This compound was dissolved in MeOH/THF (1:1, 10 mL), then the mixed powder of $NaBH_4$ (306.4 mg, 8.1×10^{-3} mol, 3 equiv for each branch) and PhCOOH (998.5 mg, 8.1×10^{-3} mol, 3 equiv for each branch) was slowly added to the solution at 0 °C, then the mixture was left stirring under 0 °C for one hour. The solvent was removed under vacuum, dry CH_2Cl_2 (30 mL) was added to the residual white solid, and after filtration the organic solution was washed three times with saturated $NaHCO_3$ and three times with distilled H_2O. The organic phase was dried with anhydrous Na_2SO_4, and the solvent was removed under vacuum to give the 27-NH*n*Bu dendrimer **7** as a light yellow oil (897 mg, yield 90%). For G1-imine: IR (KBr): $\tilde{\nu} = 1645\,cm^{-1}$ ($\nu_{CH=N}$); elemental analysis calcd (%) for $C_{585}H_{921}N_{27}O_{36}Si_{36}$: C 70.83, H 9.36, N 3.81; found: C 70.65, H 9.46, N 3.67. For **7**: MALDI-TOF: *m/z* calcd for $(C_{585}H_{975}N_{27}O_{36}Si_{36}Na^+)$: 9997.2; found: 9998.2; elemental analysis calcd (%) for $C_{585}H_{975}N_{27}O_{36}Si_{36}$: C 70.44, H 9.85, N 3.79; found: C 70.61, H 9.62, N 3.68.

Dendrimer 8

Complex **1** (90 mg, 2.43×10^{-4} mmol, 1.5 equiv for each branch) and the 27-NH*n*Bu dendrimer **7** (60 mg, 6×10^{-6} mol) were dissolved in CH_3CN/CH_2Cl_2 (1:1, 10 mL), then the mixture was stirred for 2 d under N_2 at 35 °C; the color of the mixture changed from yellow to deep red during the stirring. The solvent was removed under vacuum, the dark red solid was washed with dry THF and filtered three times, and the residual dark red solid was dried under vacuum to give compound **8** as a dark red solid (108 mg, yield 90%). UV/Vis: $\lambda_{max1} = 415$ nm, $\lambda_{max2} = 495$ nm, $\varepsilon = 3.38\times10^5\,L\,mol^{-1}$; IR (KBr): $\tilde{\nu} = 1614$ ($\nu_{CH=CH}$), 838 cm^{-1} (ν_{PF6-}); CV = 2 mM, solvent: DMF, *T*: 20 °C; supporting electrolyte: $[nBu_4N][PF_6]$ (0.1 M), working and counter electrodes: Pt, reference electrode: Ag, scan rate: 0.200 $V\,s^{-1}$; internal reference: $FeCp^*_2$; $E_{1/2(rev)} = -1.03$ V, $\Delta E = 65$ mV; elemental analysis calcd (%) for $C_{909}H_{1245}N_{27}O_{36}Si_{36}Co_{27}(PF_6)_{27}$: C 55.58, H 6.39, N 1.93; found: C 55.95, H 6.64, N 1.81.

Dendrimer 9

The G2-CH_2I dendrimer (145 mg, 5.27×10^{-3} mmol, 1 equiv), 4-hydroxybenzaldehyde (521 mg, 4.27×10^{-3} mmol, 10 equiv for each branch), and K_2CO_3 (1.178 g, 8.54×10^{-3} mmol, 20 equiv for each branch) were mixed in a flask under N_2. DMF (10 mL) was added into the mixture with a syringe needle, the solution was stirred at 50 °C under N_2 for 24 h and the color of the solution changed from light yellow to light violet. H_2O (100 mL) was added to this mixture, a white precipitate formed, and the mixture was kept stirring for 10 min. After filtration, the filtrate was violet and the residual white solid was on the surface of the Celite. The white solid was washed with H_2O (100 mL four times) to remove the DMF, the excess amount 4-hydroxybenzaldehyde, and K_2CO_3, and the white product was dissolved in CH_2Cl_2 to give a colorless solution. After drying with anhydrous Na_2SO_4, and under vacuum, compound **9** was obtained as a colorless gel (128 mg, yield 90%). IR (KBr): $\tilde{\nu} = 1688\,cm^{-1}$ ($\nu_{CH=O}$); elemental analysis calcd (%) for $C_{1530}H_{2190}O_{198}Si_{117}$: C 67.97, H 8.16; found: C 67.65, H 8.32.

Dendrimer 10

The 81-benzaldehyde dendrimer **9** (142 mg, 5.27×10^{-3} mmol) was dissolved in dry *n*-butylamine (10 mL), this mixture was stirred at RT under N_2 for 16 h, the excess amount of *n*-butylamine was removed under vacuum, and the residual light yellow oil was dissolved in MeOH/THF (1:1, 10 mL). The mixed powder of $NaBH_4$ (80.8 mg, 2.135×10^{-3} mol, 5 equiv for each branch) and PhCOOH (260.5 mg, 2.135×10^{-3} mol, 5 equiv for each branch) was slowly added to the solution at 0 °C. The mixture was left stirring under 0 °C for 30 min, the solvent was removed under vacuum, and dry CH_2Cl_2 (30 mL) was added to the residual white solid. After filtration, the organic solution was washed three times with saturated $NaHCO_3$ solution and three times with distilled H_2O. The organic phase was dried with anhydrous Na_2SO_4, and the solvent was removed under vacuum to give the 81-NH*n*Bu dendrimer as light yellow oil (137.5 mg, yield 90%). For G2-imine: IR (KBr): $\tilde{\nu}=1645\,cm^{-1}$ ($\nu_{CH=N}$); elemental analysis calcd (%) for $C_{1854}H_{2919}O_{117}Si_{117}N_{81}$: C 70.69, H 9.34, N 3.60; found: C 70.65, H 9.32, N 3.35. For **10**: elemental analysis calcd (%) for $C_{1854}H_{3081}O_{117}Si_{117}N_{81}$: C 70.32, H 9.81, N 3.58; found: C 70.60, H 9.64, N 3.69.

Dendrimer 11

Complex **1** (27.9 mg, 7.8×10^{-2} mmol, 1.5 equiv for each branch) and the 81-NH*n*Bu dendrimer **10** (20 mg, 6.4×10^{-4} mmol) were dissolved in CH_3CN/CH_2Cl_2 (1:1, 10 mL), the mixture was stirred for 2 d under N_2 at 35 °C, and the color of the mixture changed from yellow to deep red during the stirring. The solvent was removed under vacuum, the dark red solid was washed three times with dry THF, then the residual solid was dried under vacuum to give **11** as a dark red solid (34.7 mg, yield 90%). UV/Vis: $\lambda_{max1}=410$ nm, $\lambda_{max2}=496$ nm ($\varepsilon=1.12\times10^6\,L\,mol^{-1}\,cm^{-1}$); IR (KBr): $\tilde{\nu}=1614$ ($\nu_{CH=CH}$), 838 cm^{-1} (ν_{PF6}); CV = 2 mM, solvent: DMF, *T*: 20 °C, supporting electrolyte: $[nBu_4N][PF_6]$ (0.1 M), working and counter electrodes: Pt, reference electrode: Ag, scan rate: 0.200 $V\,s^{-1}$, internal reference: $FeCp^*_2$; $E_{1/2(rev)}=-1.03$ V, $\Delta E=50$ mV; elemental analysis calcd (%) for $C_{2826}H_{3891}O_{117}Si_{117}N_{81}Co_{81}(PF_6)_{81}$: C 55.94, H 6.46, N 1.87; found: C 56.30, H 6.64, N 1.69.

Dendrimer 12

Complex **1** (27.8 mg, 7.8×10^{-2} mmol, 1.5 equiv for each branch) and the nona-NHFc$^{\#}$ dendrimer (25 mg, 5.75×10^{-3} mmol) were dissolved in a mixture of CH_3CN (10 mL) and CH_2Cl_2 (10 mL). This solution was stirred for 2 d under N_2 at 35 °C. The color of the mixture changed from yellow to deep red during the stirring, dibutylamine (5 mL) was added, and the mixture was stirred for 30 min at RT. The solvent was removed under vacuum, the residual dark red solid was washed with dry diethyl ether and filtered three times, and it was dried under vacuum to give **12** as a dark red solid (38.8 mg, yield 90%). UV/Vis: $\lambda_{max1}=322$ nm, $\lambda_{max2}=422$ nm, $\lambda_{max3}=514$ nm ($\varepsilon=1.15\times10^5\,L\,mol^{-1}\,cm^{-1}$); IR (KBr): 1607 ($\nu_{C=C}$), 838 cm^{-1} (ν_{PF6}); CV 2 mM, solvent: DMF, *T*: 20 °C, supporting electrolyte: $[nBu_4N][PF_6]$ 0.1 M, working and counter electrodes: Pt, reference electrode: Ag, scan rate: 0.200 $V\,s^{-1}$, internal reference: $FeCp^*_2$; $E_{1/2(rev)}=0.20$ V, $\Delta E=70$ mV; $E_{1/2(rev)}=-1.07$ V, $\Delta E=70$ mV; elemental analysis calcd (%) for $C_{360}H_{525}Si_9N_9Co_9Fe_9(PF_6)_9$: C 57.12, H 6.99, N 1.67; found: C 57.30, H 6.74, N 1.69.

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