Dendrimers

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Click Syntheses of 1,2,3-Triazolylbiferrocenyl Dendrimers and the Selective Roles of the Inner and Outer Ferrocenyl Groups in the Redox Recognition of ATP^{2-} and Pd^{2+}**

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Ferrocenyl (Fc) dendrimers[1] and polymers[2] have attracted much attention owing to their multielectron redox properties and functions as biosensors,[3] virus-like receptors,[4a] models of molecular batteries,[4b] and colorimetric sensors.[2] Fc-terminated dendrimers belong to the large family of redox-active metallodendrimers that may eventually mimic related nanometer-sized biological processes and provide useful energy-relevant devices.[5]

In typical examples, Nishihara and co-workers have extensively studied the efficient electrodeposition of acylbiFc nanodevices in gold nanoparticles,[6] and recently, the group of Reinhoudt and Ravoo elegantly demonstrated that small acylbiFc dendrimers form inclusion complexes with self-assembled monolayered β-cyclodextrin as "molecular print-boards".[7] Biferrocene itself can be incorporated without covalent bonding as a biferrocenium charge-transfer complex with the arylimino groups of Yamamoto's arylazidomethine dendrimers.[8] From these studies, it has become clear that the redox properties of the biFc derivatives, which include three easily accessible oxidation states, are much richer than those of the Fc group.

We have envisaged taking advantage of the possibility of stabilizing class II mixed-valence biferrocenium cations and exploiting specific properties of the two Fc groups therein.[9,10] Herein we report 1) the Cu^I-catalyzed azide alkyne "click" cycloaddition (CuAAC)[11] of the knew alkyne ethynylbiferrocene **1** with five generations of azido-terminated dendrimers containing 3^n terminal tethers, from $n=2$ (G_0, 9 termini) to $n=6$ (G_4, 729 termini), leading to the formation of large 1,2,3-triazolylFc-terminated dendrimers, 2) the isolation and full characterization of the first mixed-valence dendrimer, 3) the redox recognition, with positive dendritic effects, of both the ATP^{2-} anion using the outer Fc groups of the dendrimer and Pd^{II} using the inner Fc groups of the dendrimers, and 4) the role of the mixed-valence metallodendrimers.

The new complex **1** was synthesized in 50% overall yield from acetylbiferrocene[12] in a reaction that parallels that known for the synthesis of ethynylferrocene[13] (see the Supporting Information). The CuAAC reaction (Scheme 1) was carried out using $CuSO_4$/sodium ascorbate as the Cu^I source between the terminal alkyne **1** and five generations G_0 to G_4 of arene-centered dendrimers dend-N_3 constructed according to 1→3 connectivity[14] and containing in theory respectively 9 (G_0), 27 (G_1), 81 (G_2), 243 (G_3), and 729 (G_4) azido termini.[15,16]

The five triazolylbiFc dendrimers of generations G_0–G_4 are yellow solids that are soluble in dichloromethane and THF but insoluble in hydrocarbons, diethyl ether, and acetonitrile. They are air-stable and thermally stable, except that G_3-243 slowly becomes insoluble in all solvents, which we tentatively attribute to supramolecular polymerization owing to interpenetration of the terminal tethers among dendrimers. This irreversible catenation is selective to the interbranch spacing for this precise dendritic generation, and remarkably this phenomenon is not observed when the interbranch spacing is larger (in G_2-81) or smaller (in G_4-729).

Besides standard ^1H and ^{13}C NMR spectroscopy, infrared spectroscopy (G_0–G_4), and MALDI TOF mass spectrometry (G_0-9: m/z calcd 5086.98; found 5087.11, M^+, 100%), these metallodendrimers were also characterized by elemental analysis, size exclusion chromatography (SEC, Figure 1), and dynamic light scattering (DLS); the latter two techniques show the mass and size progression (Table 1).

The DLS measurements show that the size increase is reduced between G_3-243 and G_4-729 as compared to large size increases between the generations up to G_3, which must be due to steric congestion at the dendrimer surface in G_4-729 forcing extensive backfolding of the rather large triazolylbiFc termini inside the dendrimer.[17]

Cyclic voltammetry (CV) of the five metallodendrimers was recorded on Pt in CH_2Cl_2 using 0.1 M $[nBu_4N][PF_6]$ as the supporting electrolyte and decamethylferrocene (FcH*) as the internal reference. Each dendrimer shows two reversible waves at 0.43 and 0.75 V vs. $FcH^{*+/0}$ (Figure 2a), with the adsorption of the dendrimers on the electrode surface dramatically growing with increasing dendrimer generation. For instance, $\Delta(E_{pc}-E_{pa})$, which has a value of 60 mV for G_0-9

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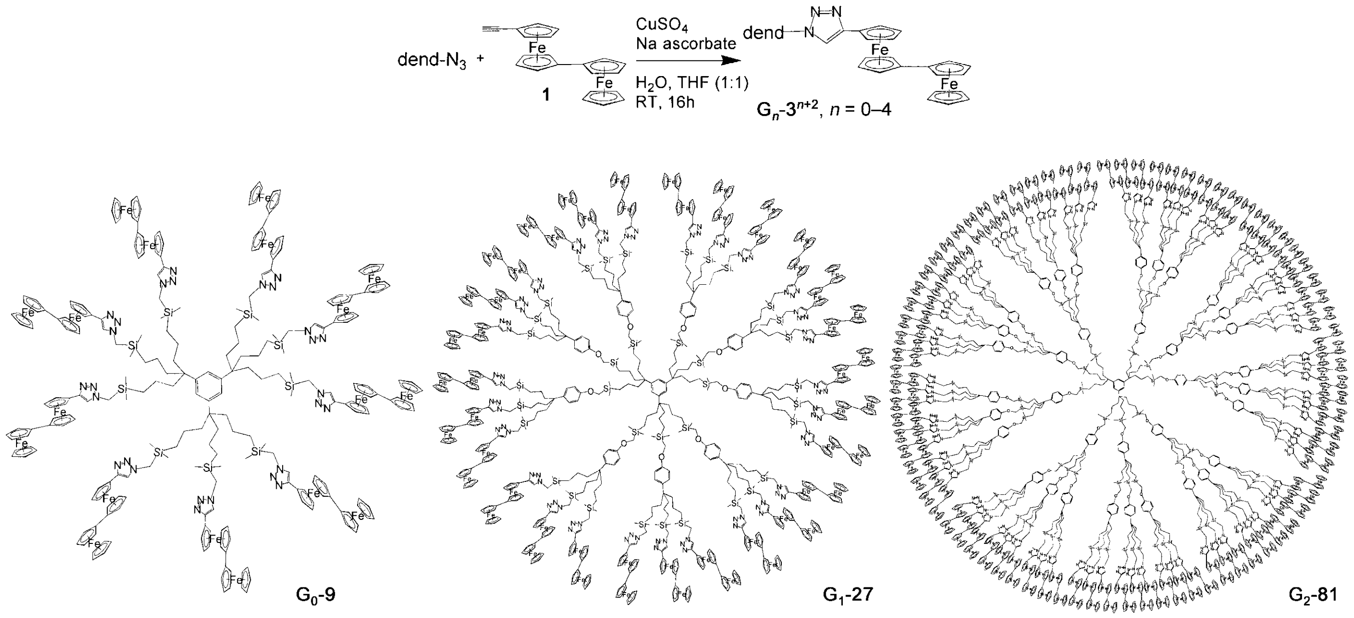


Scheme 1. The CuAAC reaction and structures of dendrimers G_0-9, G_1-27, and G_2-81.

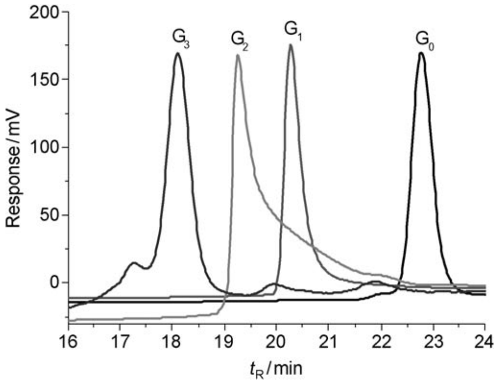


Figure 1. Size exclusion chromatograms of the triazolylbiferrocenyl dendrimers (t_R = retention time). The polydispersity indices (PDI) are 1.01 (G_0-9), 1.02 (G_1-27), 1.15 (G_2-81), and 1.08 (G_3-263). G_4-729 appeared to be too large for SEC analysis, but its chloromethylsilyl-terminated G_4 precursor provided a satisfactory SEC trace with PDI = 1.03 (see the Supporting Information).

Table 1: Hydrodynamic diameters of the metallodendrimers (obtained by DLS), and calculated diffusion coefficient, volume, and density.

Product[a]	MM[b]	$2\times R_h$[c]	D[d] [m^{2}s^{-1}]	Volume[e] [m^3]	d[f] [kg m^{-3}]
G_1-27	16927	8.6	10.84×10^{-14}	3.33×10^{-25}	84
G_2-81	52522	14.7	6.34×10^{-14}	16.63×10^{-25}	52
G_3-243	159306	25.2	3.70×10^{-14}	83.79×10^{-25}	32
G_4-729	479928	27.2	3.43×10^{-14}	105.36×10^{-25}	76

[a] The hydrodynamic diameters of G_0-9 could not be obtained by DLS because it is below the lower limit of the technique. [b] MM: molecular mass (g mol^{-1}). [c] 2xR_h: hydrodynamic diameter (nm) measured in THF at 25 °C. [d] D: diffusion coefficient. [e] considering the globular shape of the dendrimer as a perfect sphere ($V = (4/3)\pi R_h^3$). [f] d: density.

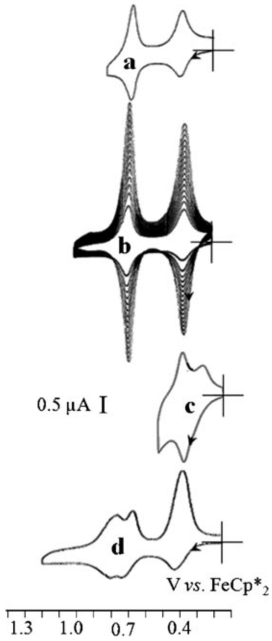


Figure 2. Cyclic voltammograms of G_2-81: a) in CH_2Cl_2, [nBu$_4$N][PF$_6$] 0.1 M; see Table 2 for data and conditions; b) progressive adsorption upon scanning around the biFc area; c) spitting of the first CV wave upon addition of ATP (the second wave is not represented, because its scanning destroys the first one); d) addition of Pd(OAc)$_2$ provoking the splitting of the second wave.

at 25 °C, progressively drops to 0 for G_3-243 and G_4-729 (Table 2), signifying complete adsorption at the first scan. This result is an advantage for the facile formation of robust metallodendrimer-modified electrodes (Figure 2 b) upon scanning around the biFc potential zone. The 1,2,3-triazolyl group is an electron-withdrawing substituent for the inner Fc

Table 2: Cyclic voltammetry data for the triazolylbiferrocenyl dendrimers.[a]

Product	$E_{1/2}$ [V][b]	Δ[b]	I_{pc}/I_{pa}[b]	$E_{1/2}$(V)[c]	Δ[c]	I_{pc}/I_{pa}[c]
G_0-9	0.430	0.060	1.25	0.740	0.060	3
G_1-27	0.430	0.045	1.6	0.745	0.030	3.2
G_2-81	0.430	0.005	1.8	0.745	0.010	1.3
G_3-243	0.430	0.000	1.9	0.750	0.000	1.5
G_4-729	0.430	0.000	2	0.740	0.000	1.8

[a] Solvent: CH_2Cl_2; electrolyte $[n\text{Bu}_4\text{N}][\text{PF}_6]$ 0.1 M; scan rate: 0.200 V s^{-1}; 25 °C; working and counter electrodes: Pt; quasi-reference electrode: Ag; all half-wave potentials $E_{1/2}$ are given versus the internal reference system $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2]^{+/0}$. [b] $(E_{pc}-E_{pa})$ for the first wave. [c] $(E_{pc}-E_{pa})$ for the second wave. See also Ref. [19b].

group, whereas the outer Fc group only bears the electron-releasing inner Fc group. Thus, if the mixed valence is localized (see below), the first oxidation wave at 0.43 V vs. FcH* can be assigned to the outer Fc groups that are easier to oxidize, whereas the second one at 0.74 V vs. FcH* can be assigned to the inner Fc groups. This assignment is confirmed by the remarkable selectivity of redox molecular recognition studies with the inner and the outer Fc groups.

Indeed, addition of the adenosyl triphosphate salt $[n\text{Bu}_4\text{N}]_2$[ATP] to the electrochemical cell containing G_2-81 provokes a splitting of the outer Fc CV wave at 0.43 V owing, to some extent, to ion-pairing interaction[18] between $[\text{ATP}]^{2-}$ and [outer Fc]$^+$, reflected by the new part of this CV wave (Figure 2c). Geiger and co-workers have shown that ion pairing can also have an important influence on the separation between the two CV waves of binuclear or multinuclear redox systems. For instance, these authors demonstrated that exchanging the ion-pairing BF_4 or PF_6 anion in the supporting electrolyte for the non-ion-pairing anions BAr_4 (Ar = C_6F_5 or *meta*-$C_6H_3(CF_3)_2$) provoked an increase of the splitting between the CV waves of biferrocene, oligoferrocenes, and other polynuclear complexes.[19a–c] We have compared the cyclic voltammograms of biferrocene[9,19d] and benzyltriazolylbiferrocene[20] with those of the triazolylbiFc dendrimers using both electrolytes $[n\text{Bu}_4\text{N}][\text{PF}_6]$ and $[n\text{Bu}_4\text{N}][\text{B}\{meta\text{-C}_6\text{H}_3(\text{CF}_3)_2\}_4]$, and we also observed a large increase of the E_2-E_1 value (480 mV) using the later. However, this enhancement is subjected to a negative dendritic effect,[19b] as opposed to the dramatic positive dendritic effect found in the recognition of the ATP anion described above, owing to synergistic additional supramolecular interactions that are enhanced by dendritic effects.

On the other hand, addition of $Pd(OAc)_2$ provokes the splitting of the CV wave at 0.74 V owing to coordination of the triazolyl ligand[20] attached to the inner Fc group, while the CV wave of the outer Fc group is left unchanged (Figure 2d). This splitting by 80 mV is due to the dendritic effect, because it is not observed at all with benzyltriazolylbiferrocene.[20] If the Pd^{II} cations are introduced as $[\text{Pd}(\text{MeCN})_4][\text{PF}_6]_2$, an analogous phenomenon is still observed, but a purple precipitate immediately forms, owing to the oxidized dendrimers that stabilize the Pd nanoparticles (PdNPs). The oxidized dendrimer and the PdNPs absorb in the UV/Vis spectrum around 600 nm (Figure 3), and these PdNPs stabilized by the G_0–G_2 biferrocenium dendrimers absorb at 530–550 nm (see the Supporting Information). The PdNPs formed in this way efficiently catalyze the Miyaura–Suzuki coupling of $PhB(OH)_2$ with PhI at 20 °C for 24 h at a concentration of 0.1 % Pd catalyst. These PdNPs are stable for a few hours. Although PdNPs did not form upon addition of $Pd(OAc)_2$ to the electrochemical cell, they formed upon further addition of methanol that reduced Pd^{II} to G_1-27-protected PdNPs. At 0.1 % Pd vs. substrates, yields of 33 % to 42 % of C–C coupling product were obtained in 24 h at 25 °C for PdNPs stabilized by G_0–G_2 dendrimers, and this yield reached 53 % of C–C coupled product upon diluting the G_1-PdNPs ten times to a concentration of 0.01 % Pd. Both the generation near-independency and the yield increase upon dilution are consistent with a leaching mechanism that generates catalytically active Pd atoms in solution,[21] which has already been observed with dendrimer-supported PdNPs.[21b,c]

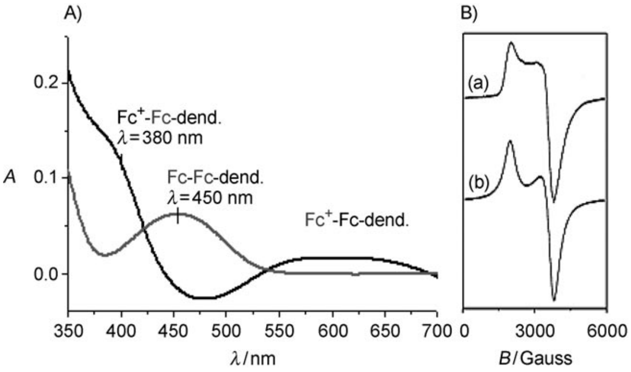
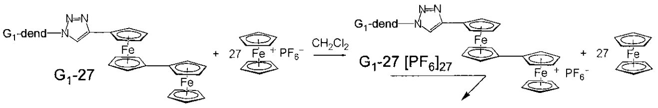


Figure 3. A) UV/Vis spectra of G_1-27 and $[G_1\text{-}27][\text{PF}_6]_{27}$. B) EPR spectra of $[G_1\text{-}27][\text{PF}_6]_{27}$ a) experimental; b) simulated; $g_{\parallel} = 3.413$, $g_{\perp} = 1.885$, $T = 4$ K; B = magnetic field.

In contrast to triazolylbiFc-terminated dendrimers, triazolylmonoFc-terminated dendrimers did not reduce $[\text{Pd}(\text{MeCN})_4][\text{PF}_6]_2$, thus showing the better efficiency of the outer Fc groups to reduce $[\text{Pd}(\text{MeCN})_4][\text{PF}_6]_2$ compared to triazolyl-substituted Fc groups either in triazolylmonoFc-terminated dendrimers or in triazolylbiFc-terminated dendrimers. This finding also shows that mixed-valence triazolylbiFc-terminated dendrimers stabilize catalytically active PdNPs.

To determine the electronic structure of these mixed-valence triazolylbiFc-terminated dendrimers, we oxidized G_1-27 with $[\text{FcH}][\text{PF}_6]$, which has a redox potential only slightly more positive (by 70 mV) than the redox potential of the outer Fc groups of the metallodendrimers. We therefore reasoned that precipitation of the mixed-valence polycationic metallodendrimer should completely drive the redox equilibrium toward its formation. Indeed, the addition of 27 equivalents $[\text{FcH}][\text{PF}_6]$ to G_1-27 in CH_2Cl_2 and subsequent addition of diethyl ether provided soluble ferrocene and the dark-blue dendritic complex $[G_1\text{-}27][\text{PF}_6]$ (Scheme 2), which was isolated as a powder subsequent to reprecipitation by addition of diethyl ether to a MeCN solution. $[G_1\text{-}27][\text{PF}_6]_{27}$ was soluble in MeCN but almost insoluble in CH_2Cl_2, and it was characterized by satisfactory elemental analysis and by UV/Vis and EPR spectroscopy (Figure 3), which showed the



Scheme 2.

classic spectrum of d^5 ferrocenium, and by Mössbauer spectroscopy under zero field at 77 K (Figure 4) and 293 K (see the Supporting Information). Both spectra show a localized mixed-valence state, as for parent biferrocenium itself[9] at this frequency (10^{-8} s).

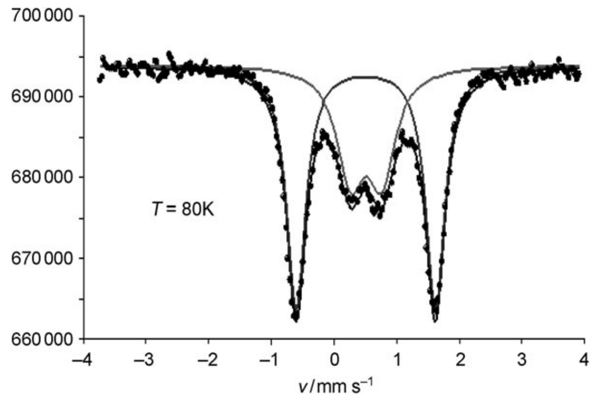


Figure 4. Mössbauer spectra of [G$_1$-27][PF$_6$]$_{27}$ at zero field and 80 K. Outer quadrupole doublet (inner Fc, Fe^{II}): isomer shift (IS) = 0.506(3), quadrupole splitting (QS) = 2.224(6). Central doublet (outer ferrocenium group): IS = 0.51(1); QS = 0.491(17). See the spectrum at 293 K in the Supporting Information, also showing localized mixed valence.

The complex [G$_1$-27][PF$_6$]$_{27}$ may be considered as belonging to class II of mixed-valence complexes according to the Robin–Day classification,[22] because the first coordination spheres of the two iron centers are identical with cyclopentadienyl rings, even if the ring substituents are different, provoking a dissymmetry of the two valence potential wells.

In conclusion, the first "click" synthesis, isolation, and characterization of five generations of triazolylbiFc dendrimers has been carried out. Their electronic structure and role as the first mixed-valence dendrimers have also been determined. The mixed-valence species can be considered to belong to class II from the Mössbauer data, despite a splitting of the CV waves that reaches 480 mV using the supporting electrolyte [nBu$_4$N][B{$meta$-C$_6$H$_3$(CF$_3$)$_2$)}$_4$]. Redox recognition is also remarkable, as it selectively involves the first CV wave for ATP^{2-} (outer Fc) and the second one for Pd^{II} in Pd(OAc)$_2$ and [Pd(MeCN)$_4$][PF$_6$]$_2$ (inner Fc) with dendritic effects, and both the neutral and mixed-valence dendrimers stabilize catalytically active Pd nanoparticles.

Experimental Section

"Click" synthesis of the 1,2,3-triazolylbiFc dendrimers G$_n$-3^{n+2}, (n = 0–4): Ethynylbiferrocene **1** (1.5 equiv per branch,) and the azido-terminated dendrimer were dissolved in oxygen-free THF (50 mL), and oxygen-free water (50 mL) was added. A solution of 1 M CuSO$_4$ (1 equiv per branch) was added at 0 °C, with subsequent dropwise addition of a freshly prepared solution of 1 M sodium ascorbate (2 equiv per branch). The brown solution at 0 °C changed to orange at room temperature. The reaction mixture was allowed to stir for 24 h under N$_2$ at room temperature. Then CH$_2$Cl$_2$ (100 mL) was added followed by the addition of an aqueous solution of ammonia. The mixture was allowed to stir for 10 min in order to remove all the copper salts trapped inside the dendrimer. The organic phase was washed twice with water, dried over sodium sulfate, and filtered, and the solvent was removed under vacuum. The product was then washed with methanol to remove the excess alkyne and precipitated from CH$_2$Cl$_2$ with methanol and then with pentane, giving a yellow powder. G$_0$-9: 0.134 g, yield 80 %. Elemental analysis calcd (%) for C$_{261}$H$_{291}$Fe$_{18}$N$_{27}$Si$_9$: C 61.56, H 5.72; found: C 60.58, H 7.91. The G$_1$–G$_4$ dendrimers were obtained analogously (see the Supporting Information).

Synthesis of the mixed-valence dendrimer [G$_1$-27][PF$_6$]: A solution of ferrocenium hexafluorophosphate (0.043 g, 0.128) in CH$_2$Cl$_2$ (50 mL) was added to a solution of G$_1$-27 (0.080 g, 0.005) in CH$_2$Cl$_2$ (5 mL) at room temperature, formation of a dark-blue precipitate was observed, and the mixture was allowed to stir under N$_2$ for 1 h at room temperature. Complete precipitation of the product was obtained by dropwise addition of diethyl ether (50 mL) to the reaction mixture. After filtration under N$_2$ on Celite, the solid was dried under vacuum to give [G$_1$-27][PF$_6$]$_{27}$ as a dark-blue powder (0.062 g, 66.3 % yield). Elemental analysis calcd (%) for C$_{882}$H$_{1029}$Fe$_{54}$N$_{81}$O$_9$Si$_{36}$P$_{27}$F$_{162}$: C 50.70, H 5.01; found: C 49.74, H 5.05. From the filtrate, 0.023 g (96 %) ferrocene was recovered.

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