Synthesis of Ferrocene-Modified Phenylazomethine Dendrimers Possessing Redox Switching

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ABSTRACT: The phenylazomethine dendrimer (DPA) with amino groups at the terminal (end-amine dendrimer) was synthesized by the convergent method without protection from 4,4′-diamino-3,3′,5,5′-tetramethylbenzophenone (DTB) as the raw material. The amino groups enabled the periphery of the dendrimer (DPA) to be modified by functional molecules, and we succeeded in the synthesis of the end-ferrocene dendrimer (**A**), which was perfectly modified by the ferrocenes, in one step with high yields. The stepwise metal complexation from the core was also observed in **A** G2 and **A** G3. The equilibrium constant *K* of the terminal imine connected with ferrocnes was determined to be 10 times smaller than that of the *N*-diphenylmethylene imine (ca. 10^5 [M^{-1}]); however, it was strong enough for metal assembling. We found that **A** G3 showed redox switching by the addition of metal ions. The potential jump of the modified ferrocenes from 0.32 to 0.42 V was observed, when the complexation of $FeCl_3$, which started from the first layer, reached the third-layer imines next to the ferrocenes. This behavior was reversible based on the encapsulation reversibility and releasing of iron ions.

Introduction

Dendrimers, which are spherelike nanosized materials, have a perfectly hyperbranched structure.[1−7] This topology facilitates modification of the periphery of the dendrimers with a high density of functional molecules.[8−10] Its unique characteristics such as concentration of the chromophores in the uniform and symmetrical structures produce precisely controlled and amplified functions. Numerous dendrimers are now being developed as advanced functional nanomaterials for ion sensors,[11,12] catalysts,[13−15] drug delivery system (DDS),[16−19] etc. For instance, a prodrug for DDS, which is the dendrimer modified with drugs and enzyme substrates at the terminal, and sugar ball,[20] which is the dendrimer modified by a sugar-substrated amino acid and polymerized with them, and many other functions of dendrimers had been reported or under study. Ferrocene-modified dendrimers have also been reported by Astruc[21−26] and Kim et al.,[27−32] which exhibit an ion sensitivity. However, there is no report about the control of the functions in the terminal units using the unique inner space of the dendrimer, e.g., redox switching.[33−35] Thus, terminal modification is an important and effective approach to develop the functions of the dendrimers, even though there are some difficulties, for instance, low yields, etc.

We have already reported phenylazomethine dendrimers (DPA)[36−39] exhibiting a stepwise radial complexation with metal ions, which means fine control of the chemical environment in the interior of the dendrimer by metal assembling. Organic−inorganic materials of DPA have been developed using this complexation system.

Because of additional functions based on the modification of the periphery, we succeeded in synthesizing the end-amine phenylazomethine dendrimers by a novel synthetic method from 4,4′-diamino-3,3′,5,5′-tetramethylbenzophenone (DTB) as the raw material without protection, even though it is very difficult to synthesize the dendrimer with a functional group, such as the amino group, at the terminal by a convergent method without a protecting group. As a first attempt for terminal modification, ferrocenes were introduced to the end-amine DPA dendrimers. The amino group could be perfectly modified by the ferrocenes in one step, and novel end-ferrocene dendrimers (**A**) were isolated in high yields.

We showed the significant effect of the fine coordinated metals upon the redox potential of **A**. The redox potential switch of novel dendrimers with ferrocene units at the terminal was demonstrated by the fine-controlled metal assembling. This basic system of the redox potential control is believed to play an important role in redox probe or redox switching.

In this paper, we report the synthesis of the end-ferrocene dendrimer (**A**) following the new synthesis of an end-amine dendrimer, stepwise complexation behavior, and the significant effect of metals on the redox potential suggesting redox switching.

Experimental Section

4,4′-Diaminobenzophenone was purchased from Fluka. 4,4′-Methylenedi-2,6-xylidine (no special toxity) and tin(II) chloride were from Wako Pure Chemical Industries, Ltd. 2,6-Dimethylaniline was from Tokyo Kasei Kogyo Co, Ltd. Iron(III) chloride was from Merck. All other chemicals were purchased from Kantoh Kagaku Co.

The NMR spectra were recorded using a JEOL JMN400 FT-NMR spectrometer (400 MHz) in $CDCl_3$ + TMS (internal standard) solution. The MALDI-TOF-Mass spectra were obtained using a Shimadzu/Kratos KOMPACT MALDI mass spectrometer (positive mode; matrix: dithranol). The UV−vis spectra were obtained using a Shimadzu UV-3100PC spectrometer with a sealed quartz cell (optical path length: 1 cm). The cyclic voltammograms were recorded using an ALS 440 electrochemical analyzer. A glassy carbon electrode was used as the working electrode, which was polished with 0.05 mm alumina paste before the analysis. The counter and the reference electrodes were Pt wire and Ag/Ag^+, respectively. The Mössbauer spectra were measured using a Topologic systems model 222 constant-acceleration spectrometer at 293 K. The data were stored in a 1024-channel pulse height analyzer. The spectra were analyzed by fitting a Lorentzian line shape using MOSSWINN version 3 software.

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4,4′-Diamino-3,3′,5,5′-tetramethylbenzophenone (DTB, end-amine G1 dendron) was synthesized by a previously reported literature method. *N*-(Ferrocenylmethylene)-2,6-dimethylbenzenamine, the end-amine G2 and G3 dendrons, and all the dendrimers were synthesized by a previous method.

End-Amine G1 Dendron (4,4′-Diamino-3,3′,5,5′-tetramethylbenzophenone). 4,4′-Methylenedi-2,6′-xylidine (10 g, 39.3 mmol) and chloranil (20 g, 81.3 mmol) were dissolved in a 200 mL of ethanol/water = 4/1 solution. The reaction mixture was heated at 100 °C for 4 h under N_2. The precipitate was removed by filtration, and the solution was concentrated to dryness. The end-amine G1 dendron (8.4 g, 31.3 mmol, 81%) was isolated by silica gel (neutral) column chromatography (chloroform/ethyl acetate = 8:1 → 6:1 → 4:1) as a light brown powder. The end-amine G1 dendron: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 7.45 (s, 4H), 3.98 (s, 4H), 2.21 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ = 195.03, 146.53, 130.89, 128.10, 120.19, 17.59. IR (KBr, cm^{-1}): 3445, 3361 (N−H), 1647 (C═O), 1565 (phenyl), 1324, 1184, 770. MALDI-TOF-Mass (matrix: dithranol): Calcd: 268.35 $[M^+H]^+$. Found: 268.8.

End-Amine G2 Dendron. The end-amine G1 dendron (1.0 g, 3.72 mmol), 4,4′-diaminobenzophenone (158 mg, 0.744 mmol), and 1,4-diazabicyclo[2.2.2]octane (DABCO) (502 mg, 4.47 mmol) were dissolved in chlorobenzene (25 mL). Titanium(IV) chloride (212 mg, 1.12 mmol) was added through a dropping funnel under N_2. The reaction mixture was heated at 125 °C for 1 h. The precipitate was removed by filtration, and the solution was concentrated to dryness. The end-amine G2 dendron (199 mg, 0.279 mmol, 37%) was isolated and purified by preparative recycling GPC with chloroform as the eluent for the measurements. The end-amine G2 dendron: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 7.57 (d, J = 8.3 Hz, 4H), 7.34 (s, 4H), 6.78 (d, J = 8.3 Hz, 4H), 6.71 (s, 4H), 3.91 (s, 4H), 3.69 (s, 4H), 2.13 (s, 12H), 2.00 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ = 195.34, 169.09, 156.34, 145.50, 143.19, 131.55, 130.70, 130.05, 129.19, 125.08, 120.68, 120.30, 17.41. IR (KBr, cm^{-1}): 3473, 3387 (N−H), 1650 (C═O), 1620 (C═N), 1570 (phenyl), 1334, 1186, 1124. MALDI-TOF-Mass (matrix: dithranol): Calcd: 713.9 $[M^+H]^+$. Found: 712.6. Anal. Calcd for $C_{47}H_{48}N_6O$: C, 79.2; H, 6.79; N, 11.79. Found: C, 77.5; H, 6.56; N, 11.4.

End-Amine G3 Dendron. The end-amine G2 dendron (450 mg, 0.63 mmol), 4,4′-diaminobenzophenone (26.8 mg, 0.126 mmol), and 1,4-diazabicyclo[2.2.2]octane (DABCO) (246 mg, 2.19 mmol) were dissolved in chlorobenzene (25 mL). Titanium(IV) chloride (212 mg, 1.12 mmol) was added through a dropping funnel under N_2. The reaction mixture was heated at 125 °C for 1 h. The precipitate was removed by filtration, and the solution was concentrated to dryness. The end-amine G3 dendron (148 mg, 0.211 mmol, 73%) was isolated and purified by preparative recycling GPC with chloroform as the eluent for the measurements. The end-amine G3 dendron: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 7.58−7.27 (m, 16H), 6.89−6.58 (m, 24H), 3.86 (s, 8H), 3.68 (s, 8H), 2.16−1.90 (m, 48H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ = 194.99, 169.20, 168.95, 168.76, 156.50, 155.70, 155.00, 145.35, 143.10, 131.95, 131.55, 130.80, 130.38, 130.09, 129.97, 129.49, 129.17, 120.99, 120.81, 120.72, 120.67, 120.45, 120.08, 17.51. IR (KBr, cm^{-1}): 3469, 3390 (N−H), 1640 (C═O), 1620 (C═N), 1572 (phenyl), 1334, 1186, 1125. MALDI-TOF-Mass (matrix: dithranol): Calcd: 1602.06 $[M^+H]^+$. Found: 1602.6.

End-Amine G1 Dendrimer. The end-amine G1 dendron (710 mg, 2.65 mmol), *p*-phenylenediamine (43 mg, 1.32 mmol), and 1,4-diazabicyclo[2.2.2]octane (DABCO) (890 mg, 7.93 mmol) were dissolved in chlorobenzene (20 mL). Titanium(IV) chloride (1.32 g, 6.93 mmol) was added through a dropping funnel under N_2. The reaction mixture was heated at 125 °C for 1 h. The precipitate was removed by filtration, and the solution was concentrated to dryness. The end-amine G1 dendrimer (260 mg, 0.427 mmol, 32%) was isolated and purified by preparative recycling HPLC with chloroform as the eluent for the measurements. The end-amine G1 dendrimer: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 7.31 (s, 4H), 6.67 (s, 4H), 6.51 (s, 4H), 3.80 (s, 4H), 3.61 (s, 4H), 2.15 (s, 12H), 2.04 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ = 168.04, 146.84, 144.89, 142.52, 130.65, 130.00, 129.68, 126.45, 121.66, 120.56, 120.44, 17.68, 17.60. IR (KBr, cm^{-1}): 3457, 3397 (N−H), 1652 (C═O), 1620 (C═N), 1568 (phenyl), 1330, 1186, 862. MALDI-TOF-Mass (matrix: dithranol): Calcd: 609.8 $[M^+H]^+$. Found: 609.7.

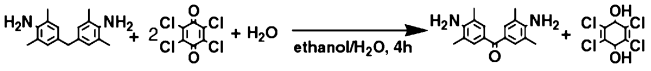
End-Amine G2 Dendrimer. The end-amine G2 dendron (191 mg, 0.268 mmol), *p*-phenylenediamine (14.5 mg, 0.134 mmol), and 1,4-diazabicyclo[2.2.2]octane (DABCO) (246 mg, 2.19 mmol) were dissolved in chlorobenzene (20 mL). Titanium(IV) chloride (104 mg, 0.548 mmol) was added through a dropping funnel under N_2. The reaction mixture was heated at 125 °C for 1 h. The precipitate was removed by filtration, and the solution was concentrated to dryness. The end-amine G2 dendrimer (126 mg, 0.0841 mmol, 63%) was isolated and purified by preparative recycling HPLC with chloroform as the eluent for the measurements. The end-amine G2 dendrimer: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 7.48 (d, J = 8.3 Hz, 4H), 7.38 (s, 4H), 7.33 (s, 4H), 6.74 (m, 8H), 6.61 (s, 4H), 6.55 (d, J = 8.3 Hz, 4H), 6.47 (d, J = 8.3 Hz, 4H), 6.34 (s, 4H), 3.87 (s, 4H), 3.84 (s, 4H), 3.67 (s, 4H), 3.48 (s, 4H), 2.17 (s, 12H), 2.14 (s, 12H), 2.06 (s, 12H), 1.88 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ = 169.15, 169.02, 167.89, 154.62, 152.99, 147.10, 145.36, 143.13, 134.27, 130.71, 130.28, 130.08, 129.77, 129.55, 125.71, 125.40, 121.51, 121.08, 120.59, 120.53, 120.43, 120.22, 17.64, 17.58, 17.50, 16.92. IR (KBr, cm^{-1}): 3457, 3374 (N−H), 1648 (C═O), 1620 (C═N), 1563 (phenyl), 1334, 1186, 1125. MALDI-TOF-Mass (matrix: dithranol): Calcd: 1497.96 $[M^+H]^+$. Found: 1497.7. Anal. Calcd for $C_{100}H_{100}N_{14}$: C, 80.2; H, 6.73; N, 13.09. Found: C, 78.7, H, 6.65; N, 12.8.

End-Amine G3 Dendrimer. The end-amine G3 dendron (100 mg, 0.062 mmol), *p*-phenylenediamine (3.4 mg, 0.0031 mmol), and 1,4-diazabicyclo[2.2.2]octane (DABCO) (409 mg, 3.64 mmol) were dissolved in chlorobenzene (20 mL). Titanium(IV) chloride (173 mg, 0.912 mmol) was added through a dropping funnel under N_2. The reaction mixture was heated at 125 °C for 19 h. The precipitate was removed by filtration, and the solution was concentrated to dryness. The end-amine G3 dendrimer (62 mg, 0.0189 mmol, 61%) was isolated and purified by preparative recycling HPLC with chloroform as the eluent for the measurements. The end-amine G3 dendrimer: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 7.58−7.30 (m, 28H), 6.89−6.61 (m, 56H), 3.85−3.45 (m, 32H), 2.17−1.90 (m, 96H). IR (KBr, cm^{-1}): 3423 (N−H), 1652 (C═O), 1633 (C═N), 1558 (phenyl), 1326, 1171, 1035. MALDI-TOF-Mass (matrix: dithranol): Calcd: 3276.2 $[M^+H]^+$. Found: 3276.1.

***N*-(Ferrocenylmethylene)-2,6-dimethylbenzenamine (Ferrocene-Modified Model Compound).** Ferrocenecarboxyaldehyde (200 mg, 0.934 mmol), 2,6-dimethylaniline (113 mg, 0.934 mmol), and 1,4-diazabicyclo[2.2.2]octane (DABCO) (629 mg, 5.61 mmol) were dissolved in chlorobenzene (10 mL). Titanium(IV) chloride (260 mg, 1.40 mmol) was added through a dropping funnel under N_2. The reaction mixture was heated at 125 °C for 5 h. The precipitate was removed by filtration, and the solution was concentrated to dryness. The ferrocene-modified model compound (289 mg, 0.911 mmol, 98%) was isolated by silica gel (neutral) column chromatography (hexane/ethyl acetate = 6:1 → 8:1). *N*-(ferrocenylmethylene)-2,6-dimethylbenzenamine: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 8.29 (s, H), 7.02 (d, H), 6.91 (dd, H), 4.76 (s, 2H), 4.43 (s, 2H), 4.22 (s, 5H), 2.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ = 162.68, 151.31, 127.74, 126.65, 124.96, 123.04, 122.57, 80.52, 72.97, 70.76, 69.44, 68.94, 31.47, 22.59, 18.37, 14.11. IR (KBr, cm^{-1}): 3084, 2940 (N−H), 1641 (C═N), 1481 (phenyl), 1382, 1181, 817. MALDI-TOF-Mass (matrix: dithranol): Calcd: 317.2 $[M^+H]^+$. Found: 318.1.

A G2 (End-Ferrocene Dendrimer G2). The end-amine G1 dendrimer (140 mg, 0.229 mmol), ferrocenecarboxyaldehyde (246 mg, 1.147 mmol), and 1,4-diazabicyclo[2.2.2]octane (DABCO) (309 mg, 2.75 mmol) were dissolved in chlorobenzene (40 mL). Titanium(IV) chloride (129 mg, 0.690 mmol) was added through a dropping funnel under N_2. The reaction mixture was heated at 125 °C for 10 h. The precipitate was removed by filtration, and

Scheme 1. Synthesis of End-Amine G1 Dendron (DTB)



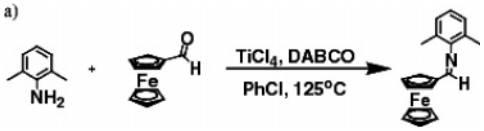
the solution was concentrated to dryness. The ferrocene-modified model compound (285 mg, 0.212 mmol, 92%) was isolated and purified by preparative recycling HPLC with chloroform as the eluent for the measurements. A G2: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 8.11 (d, 4H), 7.45 (s, 4H), 7.26 (s, 8H), 6.81 (s, 4H), 6.62 (s, 4H), 4.80 (s, 8H), 4.51 (s, 8H), 4.28 (d, 20H), 2.15 (s, 12H), 1.57 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ = 163.22, 162.84, 153.67, 151.24, 146.76, 135.49, 129.62, 126.70, 126.34, 80.57, 71.03, 69.29, 30.98; 18.63. IR (KBr, cm^{-1}): 3084, 2951 (N−H), 1631 (C═N), 1568 (phenyl), 1335, 1165, 823. MALDI-TOF-Mass (matrix: dithranol): Calcd: 1392.9 $[M^+H]^+$. Found: 1394.1.

A G3 (End-Ferrocene Dendrimer G3). The end-amine G2 dendrimer (150 mg, 0.100 mmol), ferrocenecarboxyaldehyde (214 mg, 1.002 mmol), and 1,4-diazabicyclo[2.2.2]octane (DABCO) (270 mg, 2.40 mmol) were dissolved in chlorobenzene (40 mL). Titanium(IV) chloride (112 mg, 0.60 mmol) was added using a dropping funnel under N_2. The reaction mixture was heated at 125 °C for 17 h. The precipitate was removed by filtration, and the solution was concentrated to dryness. The ferrocene-modified model compound (218 mg, 0.071 mmol, 71%) was isolated and purified by preparative recycling HPLC with chloroform as the eluent for the measurements. A G3: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 8.13 (m, 8H), 7.42 (m, 16H), 6.77 (m, 16H), 4.79 (m, 16H), 4.47 (m, 16H), 4.82−4.36 (m, 40H), 2.19−1.89 (m, 48H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ = 168.54, 167.52, 162.91, 153.96, 152.29, 151.58, 147.05, 135.00, 131.15, 130.85, 129.87, 126.70, 121.67, 120.64, 80.40, 71.09, 69.26, 47.20, 31.60, 18.45. IR (KBr, cm^{-1}): 3072, 2951 (N−H), 1629 (C═N), 1581 (phenyl), 1405, 1164, 820. MALDI-TOF-Mass (matrix: dithranol): Calcd: 3066.17 $[M^+H]^+$. Found: 3064.6.

Results and Discussion

4,4′-Diamino-3,3′,5,5′-tetramethylbenzophenone (DTB, end-amine G1dendron) (**1**) was synthesized by the oxidation of 4,4′-methylenedi-2,6-xylidine using chloranil[40,41] (Scheme 1) and was isolated in an 81 wt % yield. The coupling of benzophenone with 4,4′-diaminobenzophenone easily took place; however, **1** does not allow a reaction with itself or benzophenone by dehydration in the presence of $TiCl_4$ (Scheme 2). This means that the methyl group at the 3,5-position retards the coupling reaction by steric hindrance.[42] By using **1** without protecting groups as the starting material, the G2 and G3 dendrons with an amino group at the terminal (end-amine G2 and G3 dendrons) were synthesized under previously reported dehydration conditions using $TiCl_4$ from **1** and diaminobenzophenone.[43,44] A series of end-amine dendrimers were synthesized through the coupling with *p*-phenylenediamine at the core (Scheme 2). These compounds were characterized by MALDI-TOF-Mass, IR, ^{1}H NMR, and ^{13}C NMR.

Scheme 3. Synthesis of End-Ferrocene Model Compound



Modification of the ferrocene at the terminal of the dendrimer occurred by dehydration with ferrocenecarboxyaldehyde and the end-amine dendrimers. As a control experiment, *N*-(ferrocenylmethylene)-2,6-dimethylbenzenamine (model compound) is produced in a 98 wt % yield through the reaction of ferrocenecarboxyaldehyde in the presence of an equimolar amount of 2,6-dimethylaniline for 5 h (Scheme 3). The steric hindrance of the aldehyde group is not sufficient to quantitatively react, although it takes more than 5 h. The end-ferrocene dendrimers (**A**) G2 and G3 (Chart 1) were obtained in 92 and 71% yields, respectively. Perfect modification at the terminal was revealed by the TOF-Mass spectra.

^{57}Fe Mössbauer spectroscopy showed the presence of ferrocene with a divalent iron, whose spectra included a symmetric doublet as shown in Figure 1. The Mössbauer parameter, isomer

Scheme 2. Synthesis of End-Amine G3 Dendrimer

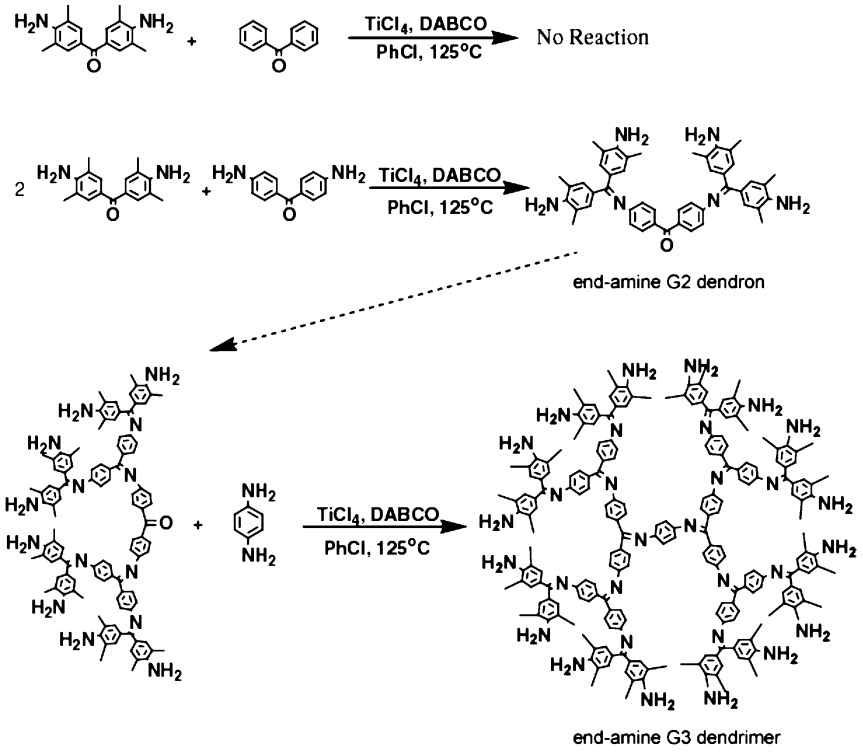


Chart 1. (a) End-Ferrocene G2 Dendrimer (A G2); (b) End-Ferrocene G3 Dendrimer (A G3)

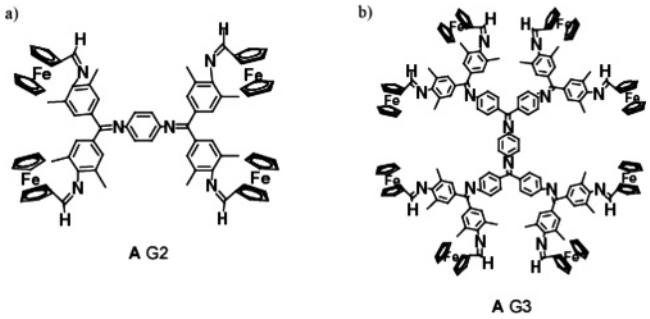


Table 1. Mössbauer Parameter, Isomer Shift, and QS of End-Ferrocene Model, G2 and G3 Dendrimers, and Ferrocene[a]

	A G2	**A** G3	ferrocene	model compd
IS (mm/s)	0.31	0.32	0.32	0.33
QS (mm/s)	2.21	2.26	2.39	2.29

[a] Ferrocene is for the comparison. Mössbauer spectra were measured at 293 K. IS and QS were determined by fitting a Lorentzian line shape to the measured spectra using MOSSWINN version 3 software.

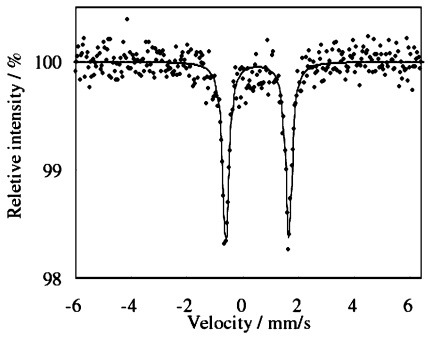


Figure 1. Mössbauer spectrum of end-ferrocene G3 dendrimer, which was measured at 293 K.

shift (IS), and quadrupole splitting (QS) of the ferrocene dendrimers were smaller than those of ferrocene, which indicates a decrease in the electron density by binding with the imine group as an electron-withdrawing group on the ferrocene ring (Table 1).

The metal assembling property of **A** was confirmed by a spectroscopic measurement. A Job plot was carried out for the model compound relative to the periphery imine units of **A**, (*N*-(ferrocenylmethylene)-2,6-dimethylbenzenamine), in chloroform/acetonitrile (1/1) solvent (see Supporting Information). It showed a maximum at the 0.5 mole fraction of the model compound, and the equilibrium constant of complexation, *K*, was determined to be ca. 10^5 [M^{-1}], which is 10 times smaller than that of the *N*-diphenylmethylenimine (cf. K = ca. 9.6 × 10^5 M^{-1}) by curve fitting, a theoretical simulation of the experimental data. The smaller *K* was based on the steric hindrance of the methyl groups located next to the imine; however, it was thought not to be the obstacle to complexation with metals.

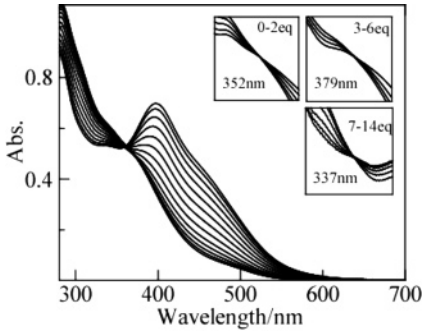


Figure 2. UV−vis spectra changes during the addition of $FeCl_3$ to the end-ferrocene G3 dendrimer in $CH_3CN/CHCl_3$ = 1/1 solvent. Isosbestic points were observed at 352 nm (0−2 equiv), 379 nm (3−6 equiv), and 337 nm (7−14 equiv), which indicate that complexation proceeds from the core imines to the terminal imines.

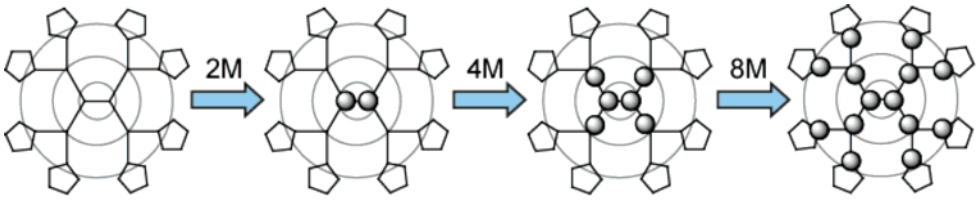
During the addition of $FeCl_3$, we found a similar complexation behavior of **A** G3 to that of DPA (Figure 2). Using UV−vis spectroscopy to monitor the titration until an equimolar amount of $FeCl_3$ had been added, three changes in the position of the isosbestic point were observed, indicating that the complexation proceeds not randomly but stepwise. The spectra of **A** G3 gradually changed with an isosbestic point at 352 nm due to the addition of 2 equiv of $FeCl_3$. The isosbestic point that shifted upon the further addition of $FeCl_3$ appeared at 379 nm between 3 and 6 equiv. While adding between 7 and 14 equiv of $FeCl_3$, an isosbestic point appeared at 337 nm. Overall, the number of added equivalents of $FeCl_3$ required to induce a shift was in agreement with the number of imine sites present in the different layers of **A** G3. The titration results suggest that the complex action proceeds in a stepwise fashion from the core imines to the terminal imines of **A** G3, as shown in Scheme 4.

A similar stepwise complexation was also observed with **A** G2. These results further supported the idea that metal ions are incorporated in a stepwise fashion, first filling the layers close to the dendrimer core and then progressively the more peripheral layers.

The electrochemical properties of **A** were studied by cyclic voltammetry. **A** shows redox activity with the redox potential at 0.32 V vs Ag/Ag^+, which is 150 mV higher than that of the nonsubstituted ferrocene and 120 mV lower than that of ferrocenecarboxyaldehyde (Figure 3). The potential shift in the anodic peak potential is based on the electron-withdrawing nature of the imine, which is consistent with the Mössbauer spectra. The diffusion coefficients decrease with an increase in the generation number (G2: $D = 1.5 \times 10^{-5}$ [$cm^2\ s^{-1}$]; G3: $D = 9.6 \times 10^{-6}$ [$cm^2\ s^{-1}$]), which results in the decreased redox peak current (Table 2). The diffusion coefficients were calculated by the Cottrell equation based on experimental data using chronoampeometry, chronocoulometry, and HPPS (see Supporting Information).

We demonstrated the metal assembling effect on the redox reaction of ferrocene at the terminal. A significant effect upon the redox potential of the modified ferrocenes was observed. While sequentially adding 1 equiv of $FeCl_3$ solutions to the **A**

Scheme 4. Stepwise Complexation of End-Ferrocene G3 Dendrimer with $FeCl_3$



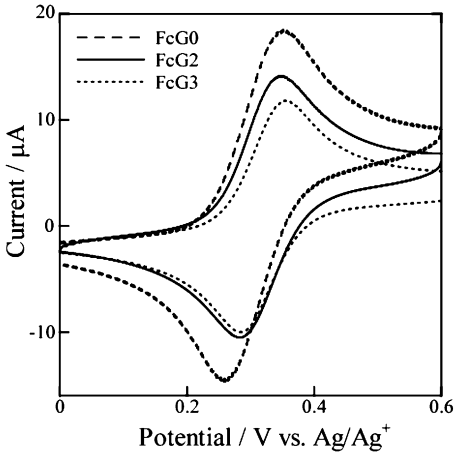


Figure 3. Cyclic voltammograms of (dash) end-ferrocene model, (solid) G2, and (dot) G3 dendrimers. Scan rate: 0.1 V/s. All measurements were performed on a glassy carbon disk electrode (diameter = 3 mm) in $CNCH_3/CHCl_3$ = 1/1 under a nitrogen atmosphere.

Table 2. Diffusion Coefficients D_0 of the End-Ferrocene Dendrimer (A) G*n* (*n* = 2, 3) and $FeCl_3$-Complexed A Gn Obtained from Chronoamperometry Experiments[a]

$D_0 \times 10^{-6}$ [$cm^2\ s^{-1}$]	*n* = 2	*n* = 3
end-ferrocene dendrimer (**A**) Gn	15	9.6
$(FeCl_3)_2$@**A** Gn	9.6	6.7
$(FeCl_3)_6$@**A** Gn	7.4	5.2
$(FeCl_3)_{14}$@**A** Gn		4.8

[a] The D_0 was calculated using the Cottrell equation.

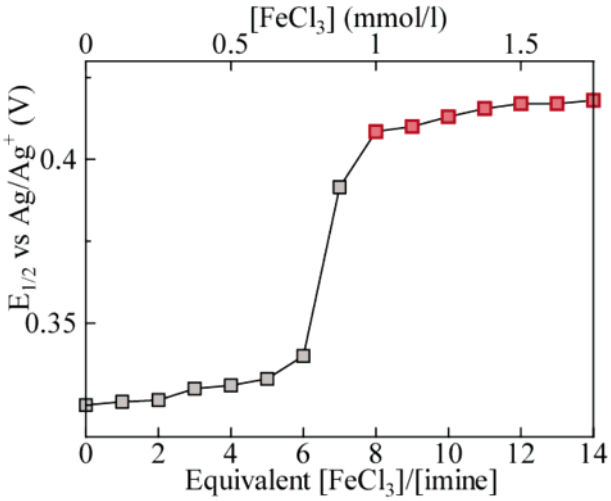


Figure 4. Redox potential changes in the terminal ferrocenes of the end-ferrocene G3 dendrimer due to the complexiation with $FeCl_3$. Scan rate: 0.1 V/s. All measurements were performed on a glassy carbon disk electrode (diameter = 3 mm) in $CNCH_3/CHCl_3$ = 1/1 under a nitrogen atmosphere.

G3 solution (1 mM), the redox potential was shifted from 0.32 to 0.42 V.

The shift in the anodic peak potential takes place due to the $FeCl_3$ assembly acting as an electron-withdrawing ion. It also supports, from an electrochemical aspect, the fact that metals form a complex with the imines next to the terminal ferrocenes.

Interestingly, as shown in Figures 4 and 5, a potential jump was observed in **A** G3 during the 6−8 equiv addition of $FeCl_3$. A similar shift was also observed in **A** G2 (Figure 6), but the behavior is emphasized with **A** G3. The shifted redox potential was separately observed better in **A** G3 than in **A** G2 because G3 underwent a bigger change in the potential. The equivalence

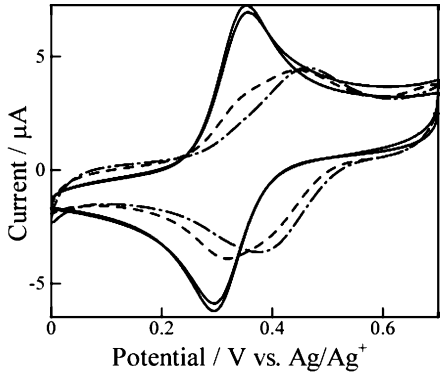


Figure 5. Cyclic voltammogram of the terminal ferrocenes during the addition of $FeCl_3$ to 1 mM end-ferrocene G3 solution (ferrocene units: 1 mM, dendrimer itself: 0.125 mM). Solid lines: 0, 2 equiv of $FeCl_3$; dash line: 8 equiv of $FeCl_3$; dash−dot line: 14 equiv of $FeCl_3$ Scan rate: 0.1 V/s. All measurements were performed on a glassy carbon disk electrode (diameter = 3 mm) in $CNCH_3/CHCl_3$ = 1/1 under a nitrogen atmosphere.

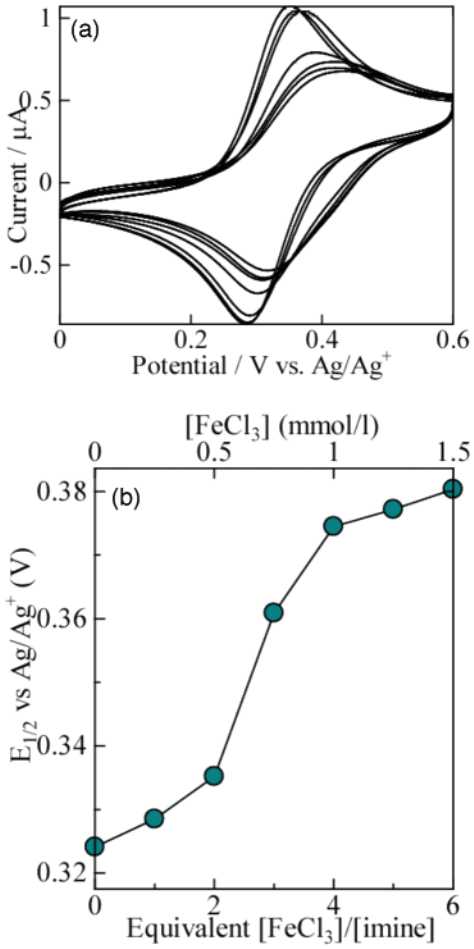


Figure 6. (a) Cyclic voltammogram of the terminal ferrocenes during the addition of $FeCl_3$ to 1 mM end-ferrocene G2 solution (ferrocene units: 1 mM, dendrimer itself: 0.25 mM). (b) Redox potential changes in the terminal ferrocenes of the end-ferrocene G2 dendrimer due to the complexation with $FeCl_3$. Scan rate: 0.1 V/s. All measurements were performed on a glassy carbon disk electrode (diameter = 3 mm) in $CNCH_3/CHCl_3$ = 1/1 under a nitrogen atmosphere.

of the switching point indicates that the $FeCl_3$ complexation in the first or second layer in the dendrimer does not affect the redox reaction of the terminal ferrocenes, and such a shift in the redox potential results from complexation in the third layer. A potential shift is observed by coordination of the iron ion on the imine sites in the third layer close to the ferrocene.

The potential change of **A** G2 was not drastic but gradual, though the increase with gradient was observed between 2 and 3 equiv, which means that the redox potential shift took place by the complexation at the terminal layer near the ferrocenes. The smaller potential change in **A** G2 did not cause separated wave but broad CV wave including the redox of both metal-complexed and free ferrocenes. The system will be applicable to ion sensing.

The peak current decreases during the complexation of the ion from the core as shown in Figures 5 and 6. The diffusion coefficient increased based on the dendrimer volume which got bigger after the encapsulation of metals (Table 2).

The reduction of Fe^{3+} occurred around −0.3 V (vs Ag/Ag^{+}). To reduce Fe^{3+}, the potential applied to the $FeCl_3$-complexed **A** G3 was swept to 0.0 V.[45] Right after the sweeping, the potential of ferrocene, which was shifted to 0.32 V by the complexation of $FeCl_3$, reverted back to the original redox potential of 0.42 V. Fe^{3+} changed to Fe^{2+} by sweeping to 0.0 V, and Fe^{2+} was released from the dendrimer imine due to the weak Lewis acidity. This result indicates that we reversibly switched the redox potential of ferrocene between 0.32 and 0.42 V by the control of the charge and amount of iron ions. End-ferrocene dendrimers with this basic system of redox potential control can be applied to materials for redox probe or redox switching.

In conclusion, we succeeded in the synthesis of an end-amine phenylazomethine G3 dendrimer, a functional dendrimer, without protecting groups using the steric hindrance of the 2,6-dimethyl groups. Efficient ferrocene modification is achieved using the functional dendrimer. We demonstrated for the first time the reversible redox potential switching of ferrocene by synchronizing metal assembling with the Fe ion redox in the dendrimer.

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Supporting Information Available: Job plot of **A** (Figure S1) and $t^{1/2}-Q$ curve transformed from $t-Q$ curve (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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