Supporting Information

Novel Poly(amidoamine) Dendritic Polymer Analogue Bearing Redox—Active Spacers

Chih-Chien Chu, and Toyoko Imae*

Graduate School of Science and Technology, Keio University, Hiyoshi, Kohuku-ku,

Yokohama 223-8522, Japan

Experimental Section

Materials and Instruments. 1,3-diamino-2-propanol, methyl acrylate, oxalyl chloride, acetic anhydride, triethylamine, DMSO (anhydrous) were all obtained as high-purity reagent-grade chemicals (>99%) from either Aldrich or Wako Chemical Co. and used without further purification. All organic solvents were AR grade and purchased from either Wako or Junsei Chemical Co. Nuclear magnetic resonance (NMR) spectra were recorded using a Jeol JNM-CMX300 MHz spectrometer at room temperature using CDCl₃ as the solvents; the signal of additive trimethylsilane (TMS) was adopted as an internal standard. Fourier-transform infrared absorption (FT-IR) spectra were recorded on a Varian FT-60A/896 spectrometer. Elemental analysis was carried out by a PerkinElmer 2400 series II CHNS/O elemental analyzer. *N*-phenylacetamide was used as the calibration standard, and the measurement for each sample was repeated for three times. Scanning electron micrographs (SEM) were taken on Hitachi S-4700 FE-SEM, operating at 15 kV, and X-ray photoelectron spectroscopy (XPS) was carried out using Jeol JPS-9000MX X-ray photoelectron spectrometer with a monochromator Mg–Kα source (10 kV, 10 mA).

Synthesis. *Model Compound 1.* A methanol solution (6 cm³) of 1,3-diamino-2-propanol (181 mg, 2.01 mmol) was added dropwise into a round-bottomed flask that contained methyl acrylate (1.04 g,

12.1 mmol) and methanol (4 cm³) at 0 °C using an ice/water bath. The reaction mixture was allowed to warm to room temperature and stirred for 2 days under N₂. Then the volatiles were removed under reduced pressure using a rotary evaporator and vacuum to give the desired product in a quantitative yield. ¹H NMR (CDCl₃, 300 MHz): $\delta = 3.70$ (1H, –CHOH), 3.67 (12H, –COOCH₃), 2.82 (8H, – NCH₂CH₂), 2.46 (12H, –CH₂COOCH₃ and –NCH₂CHOH); ¹³C NMR (CDCl₃, 75 MHz): $\delta = 172.8$, 66.0, 58.6, 51.5, 49.8, 32.4.

Spacer-Modified Dendriemr 2. A methanol solution (3 cm³) of 1 (469 mg, 1.08 mmol) was added dropwise into a round-bottomed flask that contained 1,3-diamino-2-propanol (1.99 g, 22.1 mmol) and methanol (7 cm³) at 0 °C using an ice/water bath. The reaction mixture was allowed to warm to room temperature and stirred for 7 days until complete disappearance of terminal methyl ester groups on 1, monitored by NMR. The mixture was then diluted with methanol (60 cm³) and directly transferred dropwise to another round-bottomed flask that contained methyl acrylate (12.0 g, 0.140 mol) and methanol (40 cm³) at 0 °C using an ice/water bath. The reaction mixture was allowed to warm to room temperature and stirred for 2 days under N₂. The volatiles were removed under reduced pressure using a rotary evaporator and vacuum. The crude product was purified by flash column chromatography on SiO₂ and eluted with dichloromethane (CH₂Cl₂)/methanol, gradually increasing from 98:2 to 90:10, to yield dendrimer 2 as a pale yellowish gum (1.03 g, 70%).¹H NMR (CDCl₃, 300 MHz): $\delta = 7.6$ (4H, -NHCO), 3.81 (4H, -CHOH), 3.67 (24H, -COOCH₃), 3.48 (4H, -NHCH₂CHOH), 3.08 (4H, -NHCH₂CHOH), 2.83 (12H, -NCH₂CH₂), 2.73 (12H, -NCH₂CH₂), 2.46 (36H, -CH₂COOCH₃ and -CHOHCH₂N); ¹³C NMR (CDCl₃, 75 MHz): $\delta = 173.2$, 173.0, 67.7, 58.0, 51.7, 50.5, 49.6, 43.0, 33.9, 32.4; Elemental Anal. Calcd for C₅₉H₁₀₆N₁₀O₂₅: C, 52.28%; N, 10.33%; H, 7.88%. Found: C, 52.53%; N, 10.29%; H, 7.66%.

Spacer-Modified Dendriemr 3. Dendrimer 3 was synthesized from 2 (343 mg, 0.253 mmol) using the same method as successive amidation of terminal methyl ester with 1,3-diamino-2-propanol (927 mg, 10.3 mmol) and then Michael addition of terminal amines with methyl acrylate (5.80 g, 67.4 mmol). The crude product was purified by flash column chromatography on Al_2O_3 and eluted with

CH₂Cl₂/methanol, gradually increasing from 98:2 to 70:30, to yield dendrimer **3** as a pale yellowish gum (340 mg, 42%).¹H NMR (CDCl₃, 300 MHz): $\delta = 7.8$ (4H, –NHCO), 7.6 (8H, –NHCO), 3.81 (12H, –CHOH), 3.67 (48H, –COOCH₃), 3.45 (12H, –NHCH₂CHOH), 3.09 (12H, –NHCH₂CHOH), 2.84 (28H, –NCH₂CH₂), 2.74 (28H, –NCH₂CH₂), 2.46 (84H, –CH₂COOCH₃ and –CHOHCH₂N); ¹³C NMR (CDCl₃, 75 MHz): $\delta = 173.2$, 173.1, 67.7, 58.7, 58.0, 51.7, 50.9, 49.7, 43.2, 34.3, 32.5; Elemental Anal. Calcd for C₁₃₉H₂₅₀N₂₆O₅₇: C, 52.21%; N, 11.39%; H, 7.88%. Found: C, 52.25%; N, 11.39%; H, 7.61%.

Acetylation of Dendrimer 3. A CH₂Cl₂ solution (3 cm³) of dendrimer 3 (40.0 mg, 12.5 µmol) was added dropwise into a round-bottomed flask that contained acetic anhydride (200 mm³) and triethylamine (3 cm³) at 0 °C using an ice/water bath. The reaction mixture was allowed to warm to room temperature and stirred for overnight. After the volatiles had been removed by rotary evaporation, the mixture was transferred to a separation funnel with 50 mL of CH₂Cl₂ and extracted using 3×50 mL of brine. The organic phase was dried over MgSO₄ and filtered; the solvent was evaporated to give acetylated dendriemr **3a** as a yellow gum in a quantitative yield. ¹H NMR (CDCl₃, 300 MHz): δ = 7.8 (4H, -NHCO), 7.38 (8H, -NHCO), 4.75 (12H, -CHOH), 3.43 (48H, -COOCH₃), 2.57 (56H, -NCH₂CH₂), 2.35 (28H, -CHOHCH₂N), 2.22 (56H, -CH₂COOCH₃), 1.89 (39H, -CH₃COOCH); ¹³C NMR (CDCl₃, 75 MHz): δ = 172.4, 170.3, 70.6, 54.6, 51.1, 49.3, 40.2, 32.0, 20.7.

Ketone 4. An anhydrous DMSO (1.60 g, 20.5 mmol) in CH₂Cl₂ (5 cm³) was then added to a reaction vessel that contained 2 M Oxalyl chloride (5 cm³, 10 mmol) at -78 °C. After stirred for 5 min, a CH₂Cl₂ (5 cm³) solution of **1** (865 mg, 1.99 mmol) was added dropwise into the mixture over 10 min. Keeping the temperature at -78 °C all the time, the turbid mixture was stirred for 2 h before triethylamine (2.05 g, 20.3 mmol) was added. The reaction mixture was allowed to warm to room temperature and further stirred for 2 h. After the volatiles had been removed by rotary evaporation, the mixture was transferred to a separation funnel with 50 mL of CH₂Cl₂ and extracted using 3×50 mL of water. The organic phase was dried over MgSO₄ and filtered; the solvent was evaporated. Vacuum distillation gave final ketone **4** as a yellowish oil in a quantitative yield. ¹H NMR (CDCl₃, 300 MHz): $\delta = 3.65$ (12H, -COOCH₃), 3.37

(4H, $-NCH_2CO$), 2.85 (8H, $-NCH_2CH_2$), 2.46 (8H, $-CH_2COOCH_3$); ¹³C NMR (CDCl₃, 75 MHz): $\delta = 208.8, 172.2, 61.2, 50.9, 49.5, 32.3$.

Spacer-Modified Dendrimer 5. Dendrimer 5 was prepared by chemical oxidation from 3 using the same method as the oxidation of model compound 1, and the spectroscopic data are as follows. ¹H NMR (CDCl₃, 300 MHz): $\delta = 4.14$ (24H, -NHCH₂CO), 3.67 (48H, -COOCH₃), 3.44 (28H, -COCH₂N), 2.86 (56H, -NCH₂CH₂), 2.47 (56H, -CH₂COOCH₃); ¹³C NMR (CDCl₃, 75 MHz): $\delta = 206.5$, 172.7, 61.9, 51.7, 50.1, 47.5, 32.8.

Electrochemistry. All electrochemical measurements were performed on a computerized electrochemical measurement system (HZ-3000, Hokuto Denko). A conventional three-electrode cell was used. A potassium chloride (KCl)-saturated Ag/AgCl electrode and a platinum (Pt) wire were used as the reference and counter electrodes, respectively. Electrodeposited Pt film with a geometric area of 1 cm² was employed as working electrode. A substrate of smooth Pt foil was immersed into an aqueous solution of H_2PtCl_6 ·6 H_2O (48 mM) in 1 M perchloric acid (HClO₄), and then a potentiostatic deposition was adopted for the preparation of the electrodeposited Pt electrode. As shown in Figure S4, this homemade working electrode was first characterized by XPS, revealing characteristic binding energy of Pt4d, Pt4f at 332/315, 74/71 eV, respectively. The SEM images (Figure S4, inset) also supported the successful electrodeposition of Pt catalyst onto Pt foil because of distinguishable changes of surface morphology before and after the electrodeposition. All solutions prepared in the electrochemical experiments were utilized with demineralized and filtered water of a resistivity not less than 18.2 M Ω cm taken from a Milli-Q water purification system (Milli-Q, USA). Prior to each study, the working electrode was subjected to a potential cycling program for 10 min with a scan rate of 50 mV/S in the potential range of 0–1.5 V.



Figure S1. ¹H (a) and ¹³C (b) NMR spectra for a 10 mg/cm³ CDCl₃ solution of dendrimer **2** at 25 °C.



Figure S2. ¹H (a) and ¹³C (b) NMR spectra for a 10 mg/cm³ CDCl₃ solution of dendrimer **3** at 25 °C.



Figure S3. ¹³C NMR spectra for a 10 mg/cm³ CDCl₃ solution of (a) dendrrimer **3** and (b) dendrimer **5** at 25 °C. The marked peaks were assigned to the carbon signals on the spacer before and after Swern oxidation.



Figure S4. XPS spectra and SEM images of (a) Pt foil and (b) electrodeposited Pt film.