

Novel Synthesis of Surface-Block Dendrimer Using [4+4] Photocycloaddition of Anthryl Dendrons

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ABSTRACT: Novel surface-block dendrimer was synthesized *via* a divergent/convergent approach using [4+4] photocycloaddition of two different anthracenes bearing a newly designed dendritic substituent, of which terminal groups are long alkyl chains for one hemisphere and oligo(ethylene oxide) chains for the other hemisphere. A solution of the two different anthryl dendrons was irradiated with a high-pressure mercury lamp to afford a hetero-dimer, which consists of the two different dendrons. The surface-block dendrimer was isolated by the use of size exclusion chromatography (SEC) and well characterized by NMR spectrum, SEC, and MALDI-TOF-Mass spectrum. Furthermore, this paper describes a ratio of the photoproducts (the hetero-dimer and two homo-dimers) that were obtained from the photocycloaddition reactions carried out in neat and an emulsion condition, along with the solution.

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KEY WORDS Surface-Block Dendrimer / Photodimerization / Anthracene / Emulsion / Divergent/Convergent Approach /

Dendritic macromolecules (dendrimers) have received considerable attention during the past three decades.^{1–5} Since the physicochemical properties of dendrimers depend remarkably on their structural characteristics, there is an increasing emphasis on syntheses of surface-block dendrimers, which have a spherical shape where the surface character of one hemisphere is different from that of the other, in order to provide future development of dendrimer-based smart materials.^{6–15} Recently, Percec and co-workers reported a new concept to provide bilayered supramolecular architectures; the Janus-dendritic system.¹⁶ Several methods of preparation of surface-block dendrimers have already been developed: a convergent approach,^{7–9} a divergent/convergent approach,^{10,11} and a divergent/divergent approach.^{12–15} Although the divergent/convergent approach is quite useful for combinatorial synthesis of surface-block dendrimers, only a few examples have been reported so far. Furthermore, the formation of surface-block dendrimer by the use of photoreaction of the focal point of two different hemispherical dendrons has never been described. Recently, we have reported the synthesis and photodimerization of a poly(amidoamine) dendron having an anthracene moiety at the focal point.^{17–23} During our studies on photoreactivities of anthracene bearing the dendritic substituent, we found that [4+4] photocycloaddition of anthracene moieties of two different dendrons gave the surface-block dendrimer. This paper describes the facile synthesis of surface-block dendrimer by the use of photocycloaddition of two different anthryl dendrons, of which

terminal groups are long alkyl chains for one hemisphere and oligo(ethylene oxide) chains for the other hemisphere.

EXPERIMENTAL

NMR spectra were measured on a Bruker AVANCE400 spectrometer. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-Mass) was performed on a Voyager Elite mass spectrometer using dithranol (1,8-dihydroxy-9[10H]-anthracenone) as a matrix. Size-exclusion chromatography (SEC) experiments were performed on a Japan Analytical Industry Co. model LC-918V with GS-320 columns (eluent: methanol) or JAIGEL 1H, 2.5H (eluent: chloroform). Photoirradiation was carried out in a Pyrex reactor. A 500 W high-pressure mercury lamp was used as the light source.

Reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., Kanto Kagaku Co., Ltd., or Aldrich Chemical Co. Inc. Dimethylformamide (DMF), acetonitrile, and ethanol used in reactions were further purified by general methods. Other solvents and reagents were used as received without further purification. Dendrons **1** and **2** were synthesized according to a previously reported method.¹⁷

Preparation of Hydrophobic Dendron 3

A mixture of thionyl chloride (2.09 g, 17.6 mmol) and octadecanoic acid (500 mg, 1.76 mmol) was stirred for 3 h at 80 °C. The excess reagent was removed

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under reduced pressure and the residue was dried at 60 °C under vacuum to give octadecanoyl chloride as thick oil (550 mg), which was used for the next step without further purification. The octadecanoyl chloride was added to a solution of **1** (364 mg, 0.320 mmol), DMF (3.0 mL), and triethylamine (176 mg, 1.74 mmol) at 0 °C, and the solution was stirred for 24 h at 45 °C under a nitrogen atmosphere. Water (3.0 mL) was added and the solution was stirred for 10 min. After removal of the solvent under reduced pressure at 45 °C, the residue was triturated with boiling THF (10 mL) and aqueous Na₂CO₃ (2.0 g/20 mL). After drying under reduced pressure, the crude product was purified by silica gel column chromatography (eluent, chloroform/methanol = 10/1) to afford dendron **3** (92 mg, 0.0443 mmol) in 12% yield: ¹H NMR (400 MHz, CDCl₃/CD₃OD = 10/1) δ 0.94 (t, *J* = 7.6 Hz, 12H), 1.21–1.29 (m, 120H), 2.16 (t, *J* = 7.6 Hz, 8H), 2.31–2.35 (m, 12H), 2.52–2.55 (m, 6H), 2.69–2.81 (m, 12H), 3.22–3.30 (m, 22H), 5.48 (s, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 8.29 (d, *J* = 8.0 Hz, 2H), 8.52 (s, 1H); MALDI-TOF-Mass for C₁₂₁H₂₁₅N₁₅O₁₂: *m/z* calcd., 2073.11 [MH⁺], 2095.09 [MNa⁺]; found: 2073.50, 2095.79.

Preparation of Hydrophobic Dendrion 4

A mixture of thionyl chloride (1.19 g, 10.0 mmol) and octadecanoic acid (284 mg, 1.00 mmol) was stirred for 3 h at 80 °C. The excess reagent was removed under reduced pressure, and the residue was dried at 60 °C under vacuum to give octadecanoyl chloride as thick oil (303 mg), which was used for the next step without further purification. The octadecanoyl chloride was added to a solution of **2** (150 mg, 0.0780 mmol), DMF (2.0 mL), and triethylamine (100 mg, 0.990 mmol) at 0 °C, and the solution was stirred for 24 h at 45 °C under a nitrogen atmosphere. Water (2.0 mL) was added, and the solution was stirred for 10 min. After removal of the solvent under reduced pressure at 45 °C, the residue was triturated with boiling THF (5 mL) and aqueous Na₂CO₃ (500 mg/12.5 mL). After drying under reduced pressure, the crude product was purified by silica gel column chromatography (eluent, chloroform/methanol = 4/1) to afford the dendron **4** (10 mg, 0.00246 mmol) in 4% yield: ¹H NMR (400 MHz, CDCl₃/CD₃OD = 10/1) δ 0.89 (t, *J* = 7.6 Hz, 12H), 1.22–1.28 (m, 240H), 2.18 (t, *J* = 7.6 Hz, 16H), 2.20–2.30 (m, 28H), 2.52–2.57 (m, 14H), 2.71–2.90 (m, 28H), 3.25–3.35 (m, 46H), 5.47 (s, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 8.29 (d, *J* = 8.0 Hz, 2H), 8.52 (s, 1H); MALDI-TOF-Mass for C₂₃₄H₄₃₃N₃₁O₂₄: *m/z* calcd., 4051.11 [MH⁺], 4074.092 [MNa⁺]; found: 4052.18, 4074.10.

Preparation of Hydrophobic Dendrion 5

To a solution of dendron **1** (200 mg, 0.199 mmol) in EtOH/CH₃CN (1/1: 3 mL) was added DIPEA (*N,N*-diisopropylethylamine) (172 mg, 1.33 mmol), nonanoic acid (151 mg, 0.955 mmol), and HOBt (1-hydroxybenzotriazole) (180 mg, 1.33 mmol). After stirring for 5 min at room temperature under a nitrogen atmosphere, EDC (1-ethyl-3-(dimethylaminopropyl)carbodiimide) hydrochloride (255 mg, 1.33 mmol) was added. After stirring at room temperature for 24 h, the mixture was evaporated. The residue was dissolved in chloroform/methanol (10/1: 20 mL), washed with aqueous saturated NaCl (10 mL), and concentrated. The crude product was purified by silica gel column chromatography using eluent (chloroform/methanol = 10/1) to afford dendron **5** (182 mg, 0.116 mmol) in 58% yield: ¹H NMR (400 MHz, CDCl₃/CD₃OD = 10/1) δ 0.94 (t, *J* = 7.6 Hz, 12H), 1.21–1.29 (m, 48H), 2.16 (t, *J* = 7.6 Hz, 8H), 2.31–2.35 (m, 12H), 2.52–2.55 (m, 6H), 2.69–2.81 (m, 12H), 3.22–3.30 (m, 22H), 5.48 (s, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 8.29 (d, *J* = 8.0 Hz, 2H), 8.52 (s, 1H); MALDI-TOF-Mass for C₁₂₁H₂₁₅N₁₅O₁₂: *m/z* calcd., 1568.15 [MH⁺]; found: 1567.65.

Preparation of Hydrophilic Dendrion 6

A mixture of thionyl chloride (407 mg, 3.43 mmol) and [2-(2-methoxyethoxy)ethoxy]acetic acid (500 mg, 2.81 mmol) was stirred for 2 h at room temperature. The excess reagent was removed under reduced pressure, and the residue was dried at 60 °C under vacuum to give [2-(2-methoxyethoxy)ethoxy]acetyl chloride as light yellow oil (550 mg), which was used for the next step without further purification. The [2-(2-methoxyethoxy)ethoxy]acetyl chloride was added to a solution of **1** (320 mg, 0.318 mmol), DMF (2.0 mL), and triethylamine (180 mg, 1.78 mmol) at 0 °C, and the solution was stirred for 24 h at 45 °C under a nitrogen atmosphere. Water (2.0 mL) was added, and the solution was stirred for 10 min. Aqueous solution of sodium carbonate (2.0 g/50 mL) was added, and the solution was extracted with CH₂Cl₂ (6 × 30 mL). After removal of the solvent, the oily crude product was purified by SEC with methanol as eluent to afford dendron **6** (365 mg, 0.222 mmol) as a light-yellow oil in 70% yield: ¹H NMR (400 MHz, CDCl₃) δ 2.32–2.40 (m, 12H), 2.57–2.64 (m, 6H), 2.74–2.81 (m, 12H), 3.30–3.37 (m, 22H), 3.39 (s, 12H), 3.60–3.68 (m, 32H), 3.94 (s, 8H), 5.44 (d, *J* = 6.8 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H), 8.29 (d, *J* = 8.0 Hz, 2H), 8.48 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 32.5, 38.7, 51.6, 58.7, 58.8, 61.5, 68.4, 70.0, 70.1, 70.2, 70.3, 70.3, 70.4, 70.7, 71.6, 71.7, 125.0, 125.1, 125.4,

125.7, 127.0, 131.2, 133.3, 134.0, 170.7, 170.8, 173.0; MALDI-TOF-Mass for $C_{77}H_{127}N_{15}O_{24}$: m/z calcd., 1647.93 [MH^+]; found: 1648.31.

Preparation of Hydrophilic Dendron 7

To a solution of dendron **2** (150 mg, 0.0780 mmol) in EtOH/ CH_3CN (1/1: 4 mL) was added DIPEA (135 mg, 1.04 mmol), [2-(2-methoxyethoxy)ethoxy]-acetic acid (134 mg, 0.788 mmol), and HOBt (141 mg, 1.04 mmol). After stirring for 5 min at room temperature under a nitrogen atmosphere, EDC hydrochloride (200 mg, 1.04 mmol) was added. After stirring at room temperature for 24 h, the mixture was evaporated. The residue was purified by SEC with methanol as eluent to afford the dendron **7** (115 mg, 0.0359 mmol) as light-yellow oil in 58% yield: 1H NMR (400 MHz, $CDCl_3$) δ 2.25–2.40 (m, 28H), 2.45–2.65 (m, 14H), 2.64–2.82 (m, 28H), 3.30–3.37 (m, 46H), 3.56 (s, 24H), 3.60–3.69 (m, 64H), 3.96 (s, 16H), 5.45 (d, $J = 6.8$ Hz, 2H), 7.49 (t, $J = 8.0$ Hz, 2H), 7.59 (t, $J = 8.0$ Hz, 2H), 8.02 (d, $J = 8.0$ Hz, 2H), 8.29 (d, $J = 8.0$ Hz, 2H), 8.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.5, 33.9, 34.1, 36.3, 37.5, 39.0, 39.2, 39.3, 39.5, 50.0, 52.0, 52.6, 59.1, 70.4, 70.5, 71.1, 72.0, 77.4, 77.7, 78.1, 124.0, 125.0, 125.4, 127.0, 127.7, 129.4, 130.6, 131.7, 160.0, 160.1, 172.9, 173.1, 173.3; MALDI-TOF-Mass for $C_{145}H_{255}N_{31}O_{48}$: m/z calcd, 3200.76 [MH^+]; Found: 3201.15.

Photodimerization of Hydrophobic Dendron 3

A solution of dendron **3** (25 mg, 0.012 mmol) in chloroform/methanol (5/1: 300 μ L) was irradiated with a high-pressure mercury lamp through a Pyrex filter for 6 h at room temperature. After removal of the solvent, the reaction mixture was dissolved in $CDCl_3/CD_3OD$ (10/1) for 1H NMR analysis.

Photodimerization of Hydrophilic Dendron 7

A solution of dendron **7** (50 mg, 0.015 mmol) in $CDCl_3$ (250 μ L) was irradiated with a high-pressure mercury lamp through a Pyrex filter for 4 h at room temperature. After removal of the solvent, the residue was purified by SEC with methanol as eluent to isolate the dendron **7** (4 mg, 0.0006 mmol) as light-yellow oil in 8% yield: 1H NMR (400 MHz, $CDCl_3$) δ 2.25–3.14 (m, 140H), 3.22–3.45 (m, 140H), 3.50–3.75 (m, 128H), 4.08 (s, 32H), 4.54 (s, 4H), 4.06 (s, 2H), 6.78–7.00 (m, 16H), 7.45–7.70 (m, 24H), 7.72–8.50 (m, 24H).

Preparation of Surface-Block Dendrimer 11

A mixture of **5** (19 mg, 0.012 mmol) and **7** (39 mg, 0.012 mmol) was dissolved in $CDCl_3/CD_3OD$ (5/1: 360 μ L) and irradiated with a high-pressure mercury lamp through a Pyrex filter for 4 h at room temperature. After removal of the solvent, the mixture was

purified by SEC with chloroform as eluent to afford dendrimer **11** (8.5 mg, 0.0018 mmol) in 22% yield: 1H NMR ($CDCl_3$) δ 0.81 (t, $J = 7.6$ Hz, 12H), 1.17–1.31 (m, 48H), 2.11 (t, $J = 7.6$ Hz, 8H), 2.29–2.35 (m, 40H), 2.40–2.58 (m, 20H), 2.61–2.78 (m, 40H), 3.24–3.30 (m, 68H), 3.30 (s, 24H), 3.57–3.61 (m, 64H), 3.64 (s, 2H), 3.91 (s, 16H), 4.05–4.12 (m, 2H), 4.53 (s, 4H), 6.77–6.86 (m, 16H); MALDI-TOF-Mass for $C_{230}H_{398}N_{46}O_{60}$: m/z calcd, 4768.90 [MH^+]; found: 4768.19.

Photo-irradiation of Mixture 5 and 7 without Solvent

A mixture of **5** (19 mg, 0.012 mmol) and **7** (39 mg, 0.012 mmol) was dissolved in chloroform/methanol (5/1). After removal of the solvent *in vacuo*, the residue was irradiated with a high-pressure mercury lamp through a Pyrex filter for 6 h at room temperature. The resulting mixture was analyzed by the use of SEC with chloroform as eluent.

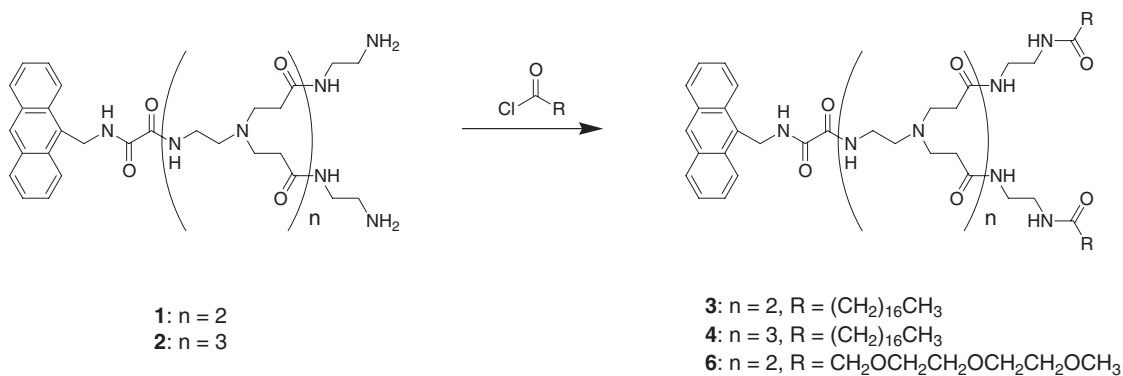
Photo-irradiation of Emulsion of a Mixture 5 and 7

A mixture of **5** (19 mg, 0.012 mmol) and **7** (39 mg, 0.012 mmol) was dissolved in toluene/methanol (5/1: 0.5 mL). The solution was mixed with 5 mL of dilute hydrochloric acid (pH 3) to give a lacteous emulsion. The emulsion was irradiated with a high-pressure mercury lamp through a Pyrex filter for 6 h at room temperature. After removal of the solvent, the residue was analyzed by the use of SEC with chloroform as eluent.

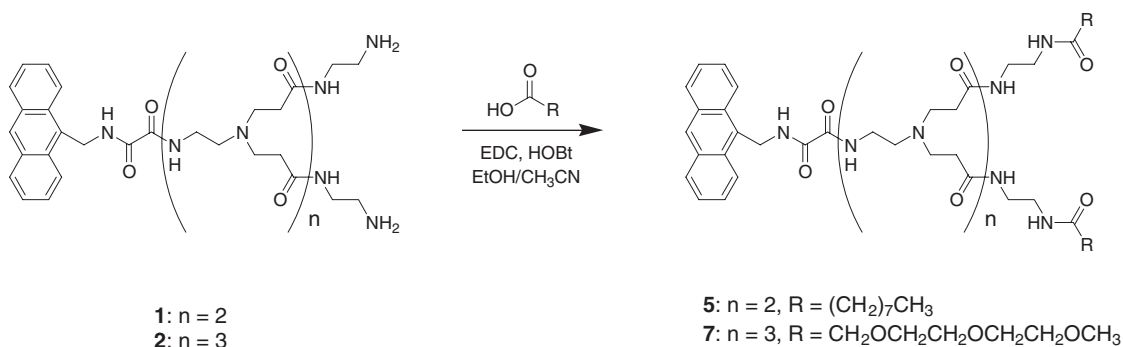
RESULTS AND DISCUSSION

In order to prepare the surface-block dendrimer *via* the divergent/convergent approach, various poly(amidoamine) dendrons were synthesized by the divergent method and subsequent modifications of terminal groups. As precursors, dendrons **1** and **2** possessing NH_2 groups at the terminals were prepared as described before.¹⁷ Hydrophobic alkyl arms were introduced by amidation of the surface NH_2 groups of dendrons **1** and **2** with octadecanoyl chloride to give dendrons **3** and **4** in 12% and 4% yield, respectively (Scheme 1). On the other hand, amidation of the surface NH_2 groups of dendron **1** with nonanoic acid was carried out in the presence of EDC, HOBt, and DIPEA for 1 d at room temperature in EtOH/ CH_3CN (1/1) to give dendron **5** in 58% yield (Scheme 2). Compounds **3–5** are insufficiently soluble in conventional solvents but are soluble in a mixed solvent (chloroform/methanol). Meanwhile, hydrophilic arms were introduced through amidation of the surface NH_2 groups of dendron **1** with [2-(2-methoxyethoxy)ethoxy] acetyl chloride to give dendron **6** in 70% yield (Scheme 1). Dendrimer **7** was obtained in 58% yield (Scheme 2) when

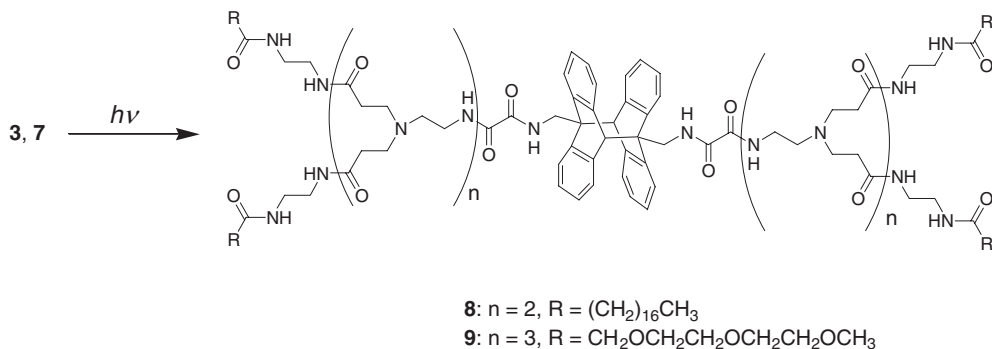
Synthesis of Surface-Block Dendrimer



Scheme 1. Synthesis of the dendrons **3**, **4** and **6**.



Scheme 2. Synthesis of the dendrons **5** and **7**.

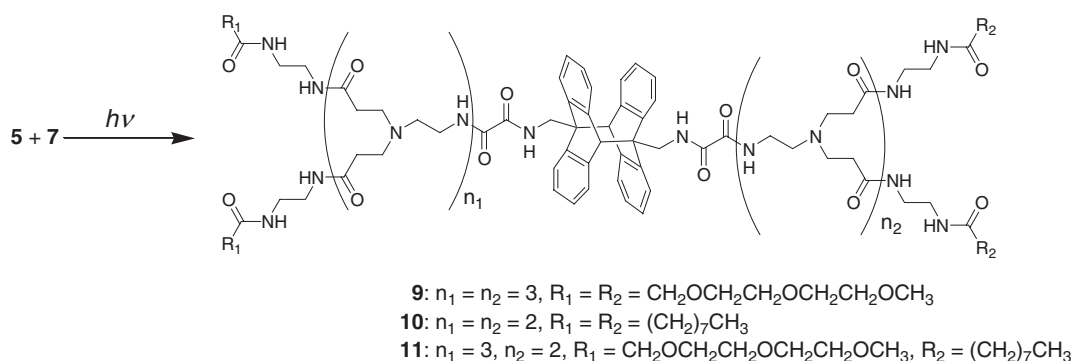


Scheme 3. Photodimerization of dendrons **3** and **7**.

dendron **2** was allowed to react with [2-(2-methoxyethoxy)ethoxy] acetic acid in the presence of EDC, HOBt, and DIPEA for 1 d at room temperature in EtOH/CH₃CN (1/1). The structures of dendrons **3–7** were confirmed by ¹H, ¹³C NMR spectroscopies, and MALDI-TOF-Mass. The MALDI-TOF spectra of dendrons **3–7** clearly showed the parent peaks at *m/z* 2073.50, 4052.18, 1567.65, 1648.31, and 3201.15, which are consistent with the molecular weights of the dendrons **3–7** ([MH⁺], calcd. 2073.11, 4051.11, 1568.15, 1647.93, and 3200.76), respectively.

In order to clarify the photoreactivity of the anthryl dendrons, photodimerizations of dendrons **3** and **7** were examined as shown in Scheme 3. A solution

(chloroform/methanol = 5/1) of dendron **3** was irradiated with a high-pressure mercury lamp ($\lambda > 300$ nm) for 6 h at room temperature under a nitrogen atmosphere to afford the corresponding photodimer **8** in 84% yield, which was estimated by ¹H NMR analysis of the reaction mixture. Unfortunately, the photodimer **8** could not be isolated by silica-gel column chromatography and size-exclusion chromatography (SEC) because of its poor solubility. On the other hand, a chloroform solution of dendron **7** was irradiated with the high-pressure mercury lamp ($\lambda > 300$ nm) for 4 h at room temperature under nitrogen atmosphere to afford photodimer **9**, which was isolated by the SEC, in 80% yield.



Scheme 4. Synthesis of surface-block dendrimer **11**.

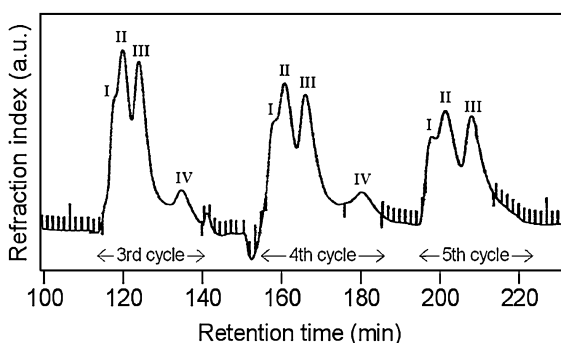


Figure 1. Chromatogram of recycling SEC of reaction mixture obtained by photocycloaddition reaction of mixture of **5** and **7** in solution. (Fraction corresponding to peak **IV** was removed from the recycling process in 4th cycle.)

For the purpose of formation of surface-block dendrimer, photocycloadditions of the hydrophobic dendrons **3–5** with the hydrophilic dendrons **6** and **7** were examined. Unfortunately, when hydrophobic dendron **3** was employed for the photocycloaddition with hydrophilic dendrons **6** and **7**, surface-block dendrimers were not isolated because of poor solubility. Formation of a surface-block dendrimer **11** was finally accomplished, as shown in Scheme 4. A solution (chloroform/methanol = 5/1) of dendrons **5** and **7** was irradiated with the high-pressure mercury lamp ($\lambda > 300\text{ nm}$) for 4 h at room temperature under a nitrogen atmosphere. Consequently, a mixture of three photodimers **9** (dimer of **5**), **10** (dimer of **7**), and heterodimer **11** were obtained in 70% yield that was estimated by $^1\text{H NMR}$ analysis of the reaction mixture. In order to separate the desired surface block dendrimer **11**, SEC experiment was performed on a HPLC (LC918, Japan Analytical Industry, Co. Ltd.) equipped with differential refractometer (RI-50) and gel permeation column (Jaigel 1H + 2.5H) with chloroform as eluent. Figure 1 shows a part of the typical recycling chromatogram of the reaction mixture. After four or more recycling processes (repeat passages through the columns), the chromatogram shows

four dominant peaks that were numbered **I**, **II**, **III**, and **IV**, in order of increasing retention time. These peaks were respectively assigned to **9**, **11**, **7/10** and **5** by $^1\text{H NMR}$ analysis of fractions collected from the several peaks. These assignments were supported by molecular weights of **9** (MW: 6400), **11** (MW: 4767), **7** (MW: 3200), **10** (MW: 3134), and **5** (MW: 1567), which are consistent with the retention times. To isolate the surface-block dendrimer **11**, fractions from **I**, **III** and **IV** were carefully removed from the recycling processes in each cycle. At last, fraction from **II** was collected and the dendrimer **11** was obtained in 22% yield. The structure of dendrimer **11** was confirmed by $^1\text{H NMR}$ spectroscopy and MALDI-TOF-Mass. The anthracenes proton signals [δ 7.51 (t, 2H), 7.57 (t, 2H), 8.07 (d, 2H), 8.29 (d, 2H), 8.52 (s, 1H); δ 7.49 (t, 2H), 7.59 (t, 2H), 8.02 (d, 2H), 8.29 (d, 2H), 8.48 (s, 1H)] of dendrons **5** and **7** in CDCl_3 disappeared and new multiplet peaks appeared at 6.77–6.86 ppm which consist with formation of the anthracene dimer. Two methylene proton signals [δ 5.48 (s, 2H), 5.45 (d, 2H)] of anthracenes' 9-positions of dendrons **5** and **7** disappeared and a new peak appeared at 4.53 ppm. The MALDI-TOF-Mass spectrum of **11** showed the parent peak at m/z 4768.19, which is consistent with the molecular weight of the dendrimer **11** ($[\text{MH}^+]$, calcd. 4768.90) as shown in Figure 2, although signals for the dendrons **5**, **7** generated by laser irradiation in the MALDI process *via* retro-cycloaddition reaction were much more strongly observed than the parent peak. The ratio of the photoproducts **11/10/9** was estimated to be 47%/29%/24% by means of area ratio of **I/II/III** of the chromatogram, which was obtained by Gaussian fitting, and $^1\text{H NMR}$ spectrum of the fraction from **III** (Table I).

Recently, we reported regio-selective photodimerizations of anthracenes bearing a dendritic substituent, which proceed in their liquid crystalline phase²² or micellar aggregates,²³ and revealed that the regio-selectivities are reflected in unique molecular orienta-

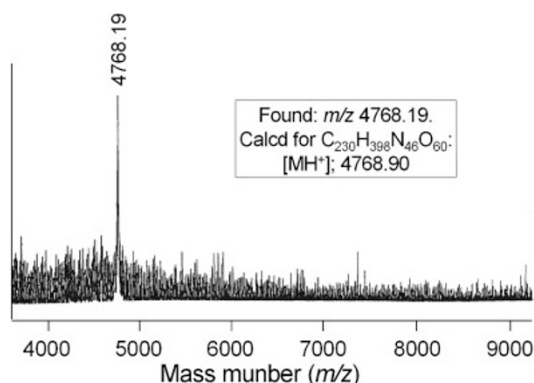


Figure 2. MALDI-TOF spectrum of surface-block dendrimer **11**.

Table I. Ratio of the photoproducts **11/10/9**

	11	10	9
solution	47%	29%	24%
neat	50%	32%	18%
emulsion	—	—	100%

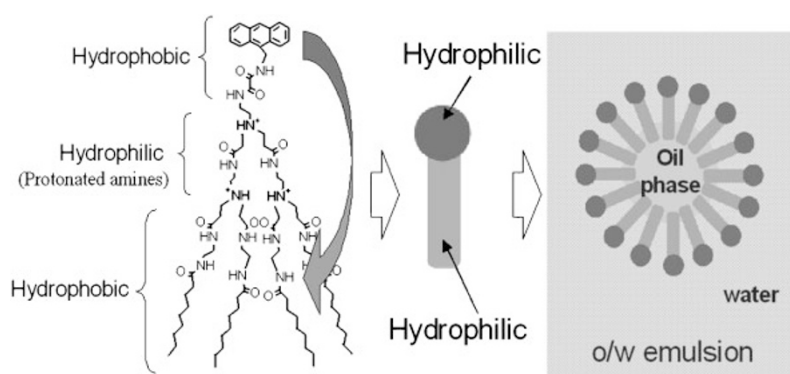


Figure 3. Schematic representation of the micelle formation of dendron **5** in o/w emulsion.

tions in such conditions. For the sake of development of a methodology that can more efficiently produce surface-block dendrimer *via* divergent/convergent approach, the photocycloadditions were attempted in solvent free and an emulsion condition where the molecular orientations might be different from in the case of the solution. The evaporated mixture of dendrons **5** and **7** was irradiated with the high-pressure mercury lamp for 6 h under a nitrogen atmosphere to afford photodimers **9–11** in 39% yield; the ratio of the photoproducts **11/10/9** was estimated to be 50%/32%/18%. (Table I). Meanwhile, the o/w emulsion was prepared by mixing a solution of dendrons **5** and **7** in toluene/MeOH (100/1) and dilute hydrochloric acid (pH 3). The emulsion was irradiated with the high-pressure mercury lamp ($\lambda > 300$ nm) for 6 h under a nitrogen atmosphere to afford only photodimer **9** in 28% yield. Interestingly, the formations of photoproducts **10** and **11** were not detected implying that photoreaction of dendron **5** was hampered when the o/w emulsion was used as a reaction medium. This might have occurred because dendron **5** at oil-water interface of the emulsion was folded up into a compact form, *i.e.*, the hydrophobic anthracene moiety and the alkyl chains will orient toward the oil phase, whereas hydrophilic protonated poly(amidoamine)

building block will orient toward the polar phase, as shown in Figure 3. Thus, we could not succeed in selective formation of the surface block dendrimer, but we found the example of collecting information about molecular orientation in emulsion by the use of photoreaction.

CONCLUSION

The results described herein show the first example of a surface-block dendrimer formed by photoreaction. The divergent/convergent approach to synthesis of surface-block dendrimer was achieved by the use of [4+4] photocycloaddition of anthracenes bearing two different dendritic substituents, of which terminal groups are long alkyl chains for one hemisphere and oligo(ethylene oxide) chains for the other hemisphere. Further work is in progress to explore the applications and advantages of this novel approach for synthesis of surface-block dendrimer.

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