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Photoreactivity of Tetra-Substituted Anthracene Derivatives and Their Mesophases

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Novel tetra-substituted anthracene derivatives were synthesized, and their liquid crystallinities were characterized by using polarizing optical microscopy, DSC, and XRD. Although photodimerization of the anthracene derivatives proceed quantitatively upon irradiation with high-pressure mercury lamp in chloroform, the photoirradiation of the mesophases of these derivatives did not yield the corresponding photodimers. XRD analysis of the mesophases showed unusual stacking of anthracene moieties, which have insufficient orbital overlap. Structural analysis is consistent with the photoreactivity.

Dendrimers have received considerable attention during the past three decades due to both their interesting structural properties and promising applications.[1] In particular, introduction of fluorophores, or photoreactive units, into the dendritic macromolecules has enable the development of new functional materials,[2] such as holographic storage,[2c] optical switching,[2d,e] light harvesting, long-term energy storage,[2f,g] and nonlinear-optic devices.[2i] Meanwhile, mesomorphic dendrimers have been extensively investigated and become an object of academic and practical interest.[3–7] In this context, the introduction of liquid-crystalline properties into dendrimers has been achieved using several techniques, such as microphase separation,[4] introduction of mesogenic groups,[5] hydrogen bonding,[6] and self-assembling benzyl ether dendrons.[7] Recently, we reported that thermotropic liquid crystallinity can be introduced into an anthracene having dendritic substituents. The photodimerization reaction of the anthracene moiety in the liquid-crystalline phase (SmE) proceeded quantitatively and regioselectively to afford only the anti-photodimer.[8] Although several examples of dendrimers containing photoreactive mesogenic groups at the periphery have been reported,[9] much less is known about the photoreactivity of the core of dendromesogen. During our studies on the photoreactivity of anthryl dendrimers, which have a liquid-crystalline phase, we found that molecular arrangements in their mesophase were the key to controlling the intermolecular photodimerization of the anthracene moiety. This report describes the self-assembly and photoreactivity of tetra-substituted anthryl dendrimers. Especially, a comparison of their photoreactivity in different phases, i.e., in solutions and in mesophases, is presented.

Results and Discussion

Anthryl dendrimers **1–4** were synthesized as shown in Scheme 1. Amidations of 2,3,6,7-tetrakis(methoxycarbonyl)-anthracene (**5**)[10] with diamines **6–8** afforded the cores of dendrimers **9–11**, and subsequent Michael additions with acrylates **12** and **13** gave the dendrimers **1–4**. In a typical run, compound **9** was obtained by the reaction of compound **5** with 1,6-hexanediamine (**6**). Subsequently, the treatment of **9** with methyl acrylate (**12**) produced dendrimer **1** in 36% yield. The dendrimers **1–4** are soft waxy materials at room temperature. Dendrimers **1–4** were characterized by ^{1}H NMR, ^{13}C NMR, and MALDI-TOF-Mass. The MALDI-TOF-Mass spectra of **1**, **2**, **3**, and **4** have parent peaks at m/z 1436.31, 1570.12, 1660.11, and 1772.12, respectively, which are consistent with the molecular weights of the dendrimers ([MH$^+$], calcd 1435.81, [MNa$^+$], calcd 1569.93, [MH$^+$], calcd 1660.07, and [MH$^+$], calcd 1772.19). The ^{1}H NMR spectra of **1–4** in $CDCl_3$ did not show signals for protons of the anthracene skeleton and amide groups, and only broad peaks for the protons of the dendritic substituents were observed. In the ^{13}C NMR spectra, definite signals for the aromatic carbons were also not observed. This phenomenon may be because of long relaxation times caused by aggregation of the anthryl dendrimers **1–4** in $CDCl_3$. To avoid aggregation by hydrogen bonding, NMR measurements of **1–4** in CD_3OD were attempted. In the case of dendrimer **1** in CD_3OD, a reasonable spectrum was obtained from which the structure could be determined. However, reliable ^{1}H NMR spectra and ^{13}C NMR spectra for **2–4** were not obtained because of their low solubility in CD_3OD. Nevertheless, a combination of MALDI-TOF-Mass spectroscopy, ^{1}H NMR spectroscopy of dendrimer **1**, thin layer chromatography (TLC), and gel permeation chromatography (GPC) was used to confirm the formation of dendrimers **1–4**.

In order to compare the photoreactivities of the anthracene moieties in dendrimers **1–4** with the anthryl dendrons that we previously reported,[8,11] dendrimers **1–4** in chloroform (0.012 M) were irradiated with a high-pressure mercury lamp ($\lambda > 300$ nm) for 1 h at room temperature. The photodimerizations of the anthracene moiety occurred quantitatively to afford photodimers **14–17**, respectively (Scheme 2). The structures of the photodimers **14–17** were confirmed by ^{1}H and ^{13}C NMR

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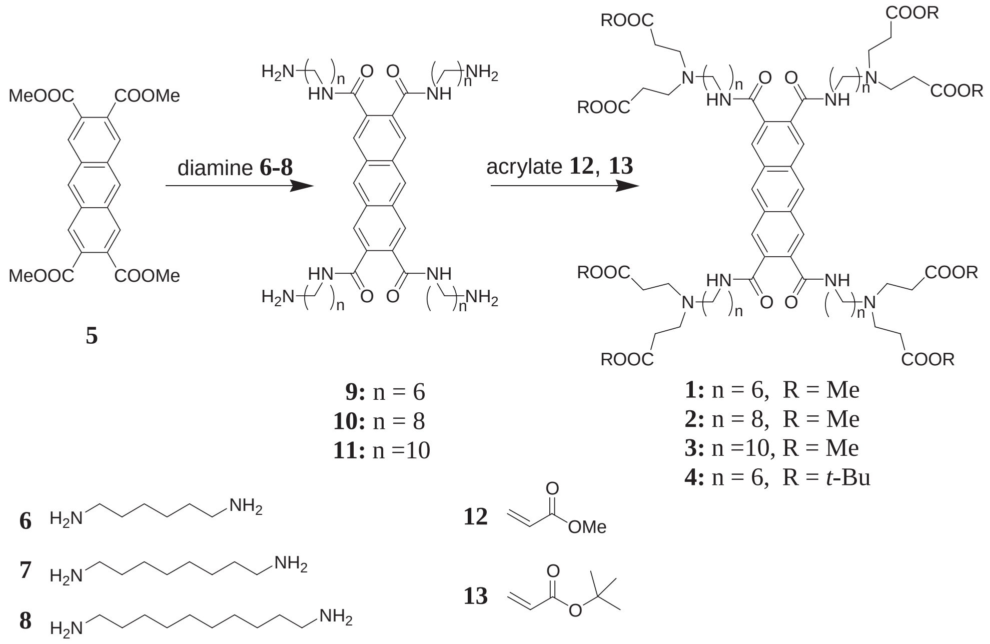
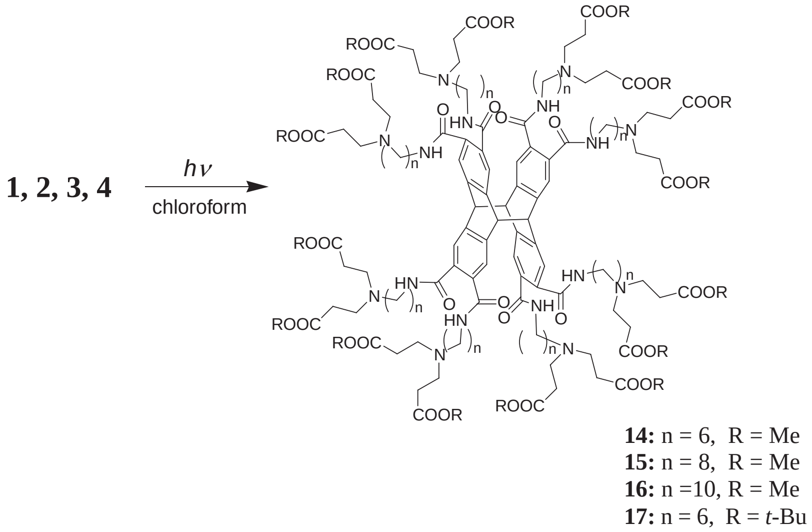


Scheme 1. Synthesis of anthryl dendrimers **1**–**4**.



Scheme 2. Photodimerizations of anthryl dendrimers **1**–**4** in $CHCl_3$.

and MALDI-TOF-Mass spectroscopies. The structures of monomers **1**–**4** were also confirmed by these spectroscopies. In a typical analysis, the anthracene proton signals of dendrimer **1** [δ 8.15 (s, 4H), 8.56 (s, 2H)] disappeared, and a new singlet appeared at 7.00 ppm, which is consistent with the formation of photodimer **14**. In addition, the new singlet at δ 4.72, which corresponds to bridgehead protons of the photodimer **14**, confirms the [4 + 4] photocycloaddition reaction of the anthracene moiety (Fig. 1). Compared to anthryl dendrons reported so far,[8,11] these new anthracene derivatives show significantly high reactivity. For example, quantitative photodimerization easily occurred under fluorescent lighting. This high reactivity might be caused by aggregation in chloroform as discussed above, which is supported by a red-shift ($\approx$10 nm) in the absorption originating from the anthracene moiety as compared to methanol solution.

The liquid-crystalline behavior of dendrimers **1**–**4** was proven by observation with a polarized microscope. The optical textures showed birefringent and viscous domains (Fig. 2). A mesophase could not be assigned because typical optical textures were not observed. Although the thermal behavior of dendrimers **1**–**4** was investigated by using differential scanning calorimeter (DSC) and a polarizing optical microscope equipped with a hot-stage, a phase transition was not observed until decomposition began around 240 °C. As well, the photoreactivity of the mesophases were examined as follows. The liquid-crystalline dendrimers **1**–**4** were placed between Pyrex plates and irradiated with a high-pressure mercury lamp (λ > 300 nm). Surprisingly, photodimerization of dendrimers **1**–**4** did not occur at either room temperature or 200 °C, and the starting materials were recovered.

In order to investigate the effect of molecular arrangements

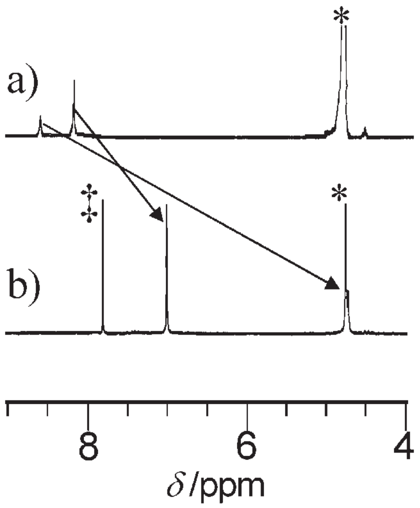


Fig. 1. ^{1}H NMR spectra of **1** in CD$_3$OD before and after photoirradiation: a) initial spectrum of **1** and b) spectrum after photoirradiation for 1 h, photodimer **14** was observed. The asterisks indicate solvent peaks. The double dagger indicates chloroform, which was used as the solvent in this reaction.

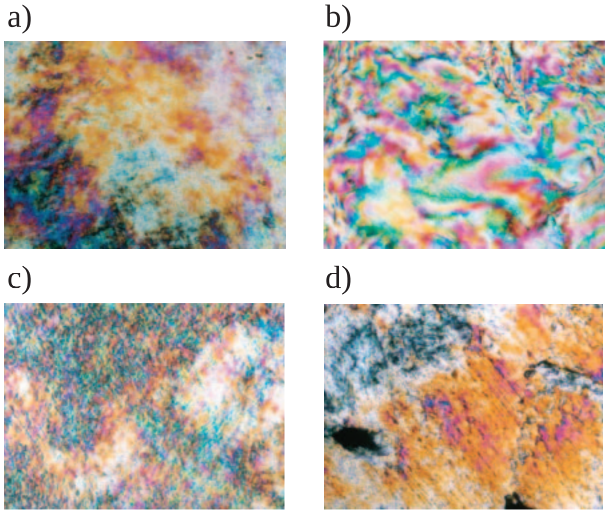
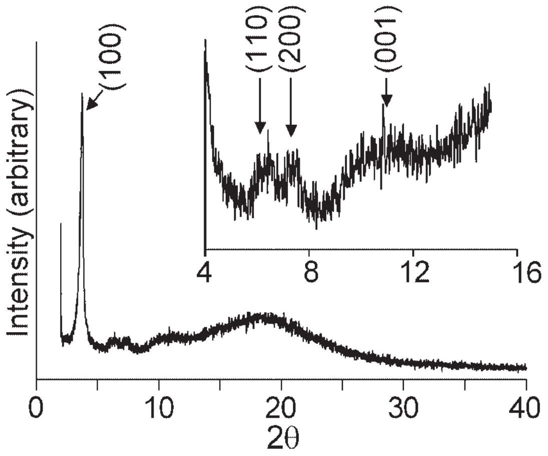


Fig. 2. Polarized optical micrographs (×100) of a): **1**, b): **2**, c): **3**, and d): **4**.

Table 1. XRD Results for the Mesophases of the Anthryl Dendrimers **1**–**4**[a)]

Compound	Mesophase type	Lattice constants/Å
1	Col$_h$	$a = 26.8$, $c =$ ca. 7.5
2	Col$_h$	$a = 31.1$, $c =$ ca. 7.5
3	Col$_h$	$a = 28.6$, $c =$ ca. 7.5
4	Col$_h$	$a = 31.5$, $c =$ ca. 7.5

a) The temperature of the experiments was 150 °C for all the compounds.



Mesophase lattice constants	Spacing/ Å Observed	Calculated	Miller indices (h k l)
Col$_h$ at 150 °C a = 26.8 Å h = $ca.$7.5 Å Z = 2.0 ρ = 1.0	23.2	23.2	(1 0 0)
	13.4	13.4	(1 1 0)
	11.5	11.6	(2 0 0)
	$ca.$7.5		(0 0 1)*
	$ca.$4.5		#

: Halo of molten dendritic substituent
* : Stacking distance

Fig. 3. X-ray diffraction pattern of anthryl dendrimer **1**.

on photoreactivity, structural determination of the liquid-crystalline phases of dendrimers **1**–**4** by X-ray diffraction (XRD) was carried out. From the XRD measurements, dendrimers **1**–**4** exhibited a hexagonal columnar phase (Col$_h$), and the lattice constants are summarized in Table 1. In a typical analysis, the XRD pattern of dendrimer **1** revealed hexagonally packed columnar mesophase ($a = 26.8$ Å) with anthracene planes perpendicular to the columnar axes, based on the two main features (Fig. 3): 1) three reflections ($d = 23.2$, 13.4, and 11.5 Å) at the low-angle region with a ratio of 1, $1/\sqrt{3}$, and $1/\sqrt{4}$, which is typical of a two-dimensional hexagonal lattice as $(hk) = (10)$, (11), and (20), respectively, and 2) a diffuse halo ($d =$ ca. 4.5 Å) arising from liquid-like spacer chains. Additionally, a broad reflection ($d =$ ca. 7.5 Å) in the middle angle region was observed, although typical spacing for π–π stacking is ca. 3.5 Å. The UV–vis spectrum of the mesophase was red-shifted (≈10 nm) compared to the chloroform solution, which suggest significant π–π interaction between anthracene moieties. Thus, an unusual stacking structure involving anthracene moieties must have formed. The dendrimer self-assembles via not only π–π interactions, but also hydrogen bonds, which are formed between the amide groups at 2, 3, 6, and 7 positions of the anthracene moiety. Presumably, the anthracene moieties are alternately arranged (Fig. 4) due to the hydrogen bonds.

To determine the structural differences between the monomer and the photodimer, the mesomorphic behavior of photodimer **14** was investigated. The liquid crystallinity of photodimer **14** was observed using polarized optical microscopy (Fig. 5) and XRD. The XRD pattern of photodimer **14** was similar to that of dendrimer **1**, which was determined to have a hexagonal columnar mesophase (Col$_h$) as shown in Fig. 6. The two-dimensional hexagonal lattice constant was determined to be 28.6 Å, and a broad reflection was observed at ca. 7.5 Å (Fig. 7), which corresponds to the mean interdimer

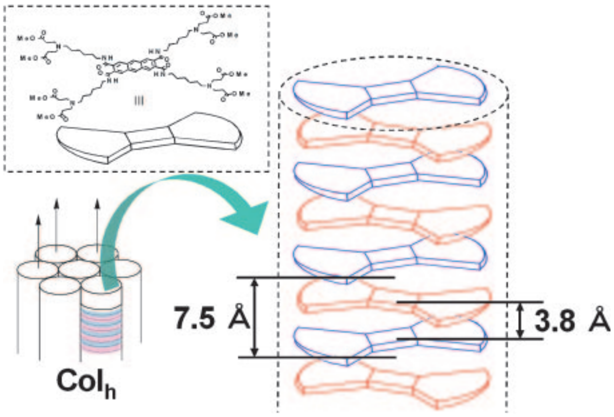


Fig. 4. Schematic illustration of the molecular arrangement of the anthryl dendrimer **1** in liquid-crystalline phases.

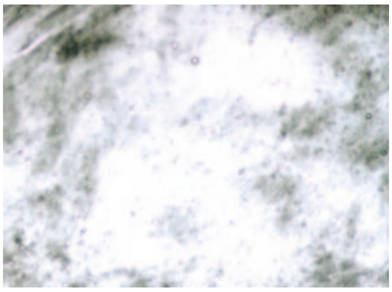
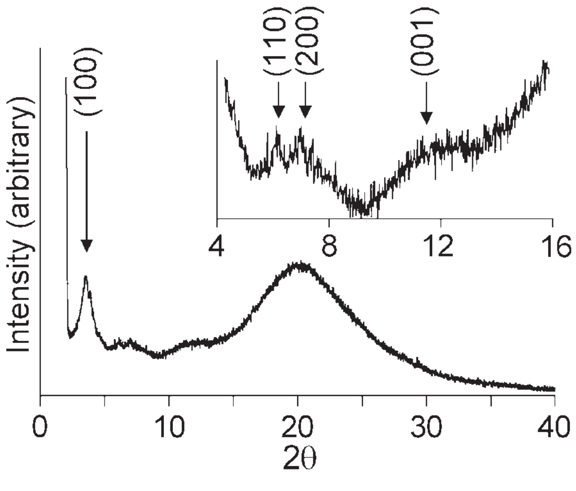


Fig. 5. Polarized optical micrograph (×100) of **14**.



Mesophase lattice constants	Spacing(Å) Observed	Spacing(Å) Calculated	Miller indices (h k l)
Col_h	24.8	24.8	(1 0 0)
at r.t	14.4	14.3	(1 1 0)
a = 28.6 Å	12.6	12.4	(2 0 0)
h = *ca.*7.5 Å	*ca.*7.5		(0 0 1)*
Z = 1.0 ρ = 0.92	*ca.*4.5		#

: Halo of molten dendritic substituent
* : Stacking distance

Fig. 6. X-ray diffraction pattern of the photodimer **14**.

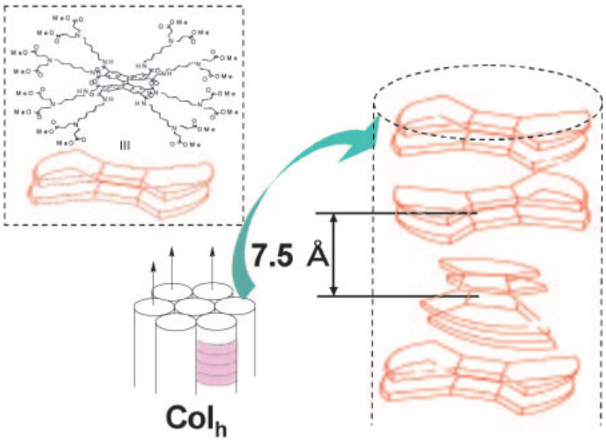


Fig. 7. Schematic illustration of the molecular arrangement of the photodimer **14** in liquid-crystalline phase.

distance of the photodimers. In other words, photoinduced phase transformation from one liquid-crystal state to another might have occurred, if photodimerization in the liquid-crystalline state took place. However, the alternating arrangement of anthracene moieties prevents photodimerization, although little structural change of liquid-crystalline phase is observed between the dendrimer and the photodimer.

In conclusion, we have found novel anthryl dendrimers that show liquid crystallinity. In solution, these anthryl dendrimers show high reactivity upon photoirradiation. However, in the liquid-crystalline phase, photoreaction did not occur in contrast to the liquid-crystalline anthryl dendrimer that we previously reported.[8] Structural analysis of the liquid-crystalline phases revealed that the photoreactivity of anthryl moiety is controlled by the molecular arrangement. We are currently exploring the applications of these liquid-crystalline anthryl dendrimers, such as photoconductive materials.

Experimental

NMR spectra were measured using a JEOL AL-300 spectrometer. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-Mass) was performed using a Bruker autoflex mass spectrometer using dithranol (1,8,9-anthracenetriol) or α-cyano-4-hydroxycinnamic acid as a matrix. GPC experiments were performed using a Japan Analytical Industry Co., model LC-918V with JAIGEL 1H and 2H (eluent: chloroform). Photoirradiation was carried out in a Pyrex reactor. A 500 W high-pressure mercury lamp was used as the light source. UV–vis spectra were measured using a Shimadzu UV-3150 spectrophotometer. Polarized optical microscopy was performed using Olympus BHA-751-T microscope equipped with a heating stage (Mettler F P80). X-ray diffraction (XRD) patterns were measured with Cu Kα radiation using a Rigaku RAD.

The reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co., Ltd., Kanto Kagaku Co., Ltd., or Aldrich Chemical Co., and were used without further purification. According to the previously reported method,[10] 2,3,6,7-tetrakis(methoxycarbonyl)anthracene (**5**) was synthesized.

Preparation of the Dendrimer 1. A suspension of **5** (200 mg, 0.487 mmol) in methanol (11 mL) was added dropwise to a stirred solution of 1,6-hexanediamine (22.4 g, 192 mmol) in methanol (11 mL) at 45 °C. The mixture was stirred continuously for 2 days.

After removal of the solvent, the residue was washed with excess amount of diethyl ether to obtain compound **9**, which was used in the next reaction without further purification. A mixture of **9** (364 mg, 0.487 mmol), methyl acrylate (86.0 g, 1.00 mol), and methanol (90 mL) was stirred at 45 °C for 5 days. After removal of the solvent, the residue was purified by silica-gel column chromatography (eluent, chloroform/methanol = 20/1) and GPC to afford the dendrimer **1** (250 mg, 0.174 mmol) as a soft waxy material in 36% yield: ^{1}H NMR (300 MHz, CD_3OD) δ 1.23–1.75 (m, 40H), 2.47 (t, $J = 7.2$ Hz, 16H), 2.77 (t, $J = 7.2$ Hz, 16H), 3.42 (t, $J = 6.9$ Hz, 8H), 3.65 (s, 24H), 8.15 (s, 4H), 8.56 (s, 2H); MALDI-TOF-Mass Found: m/z 1436.31. Calcd for $C_{74}H_{114}N_8O_{20}$: [MH$^+$], 1435.81.

Preparation of the Dendrimer 2. A suspension of **5** (50 mg, 0.122 mmol) in methanol (6 mL) was added dropwise to a stirred solution of 1,8-diaminooctane (5.0 g, 34.7 mmol) in methanol (6 mL) at 45 °C. The mixture was stirred continuously for 2 days. After removal of the solvent, the residue was washed with excess amount of diethyl ether to obtain compound **10**, which was used in the next reaction without further purification. A mixture of **10** (97.9 mg, 0.122 mmol), methyl acrylate (5.74 g, 66.7 mmol), and methanol (6 mL) was stirred at 45 °C for 5 days. After removal of the solvent, the residue was purified by silica-gel column chromatography (eluent, chloroform/methanol = 20/1) and GPC to afford the dendrimer **2** (77.7 mg, 0.0502 mmol) as a soft waxy material in 41% yield: MALDI-TOF-Mass Found: m/z 1570.12. Calcd for $C_{82}H_{130}N_8O_{20}$: [MNa$^+$], 1569.93.

Preparation of the Dendrimer 3. A suspension of **5** (50 mg, 0.122 mmol) in methanol (6 mL) was added dropwise to a stirred solution of 1,10-diaminodecane (5.0 g, 29.0 mmol) in methanol (6 mL) at 45 °C. The mixture was stirred for 2 days. After removal of the solvent, the residue was washed with excess amount of diethyl ether to afford compound **11**, which was used without further purification. A mixture of **11** (112 mg, 0.115 mmol), methyl acrylate (5.74 g, 66.7 mmol), and methanol (6 mL) was stirred at 45 °C for 5 days. After removal of the solvent, the residue was purified by silica-gel column chromatography (eluent, chloroform/methanol = 20/1) and GPC to afford the dendrimer **3** (64.5 mg, 0.0389 mmol) as a soft waxy material in 34% yield: MALDI-TOF-Mass Found: m/z 1660.11. Calcd for $C_{90}H_{146}N_8O_{20}$: [MH$^+$], 1660.07.

Preparation of the Dendrimer 4. A suspension of **5** (50 mg, 0.122 mmol) in methanol (4 mL) was added dropwise to a stirred solution of 1,6-hexanediamine (5.6 g, 48.2 mmol) in methanol (4 mL) at 45 °C. The mixture was stirred for 2 days. After removal of the solvent, the residue was washed with excess amount of diethyl ether to obtain compound **9**, which was used without further purification. A mixture of **9** (91.0 mg, 0.122 mmol), *t*-butyl acrylate (3.82 g, 29.8 mmol), and methanol (9 mL) was stirred at 45 °C for 5 days. After removal of the solvent, the residue was purified by silica-gel column chromatography (eluent, chloroform/methanol = 20/1) and GPC to afford the dendrimer **4** (94.1 mg, 0.0530 mmol) as a soft waxy material in 43% yield: MALDI-TOF-Mass Found: m/z 1772.12. Calcd for $C_{98}H_{162}N_8O_{20}$: [MH$^+$], 1772.19.

Formation of the Photodimer 14. A solution (0.012 mM) of dendrimer **1** (13 mg, 9.1 µmol) in chloroform (0.7 mL) was irradiated with a high-pressure mercury lamp ($\lambda > 300$ nm) at room temperature under a nitrogen atmosphere for 1 h to afford photodimer **14**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23–1.50 (m, 64H), 1.61 (t, $J = 6.9$ Hz, 16H), 2.44 (t, $J = 7.2$ Hz, 32H), 2.77 (t, $J = 7.2$ Hz, 32H), 3.33 (q, $J = 6.6$ Hz, 16H), 3.66 (s, 48H), 4.62 (s, 4H), 7.08 (s, 8H), 7.83 (t, $J = 5.4$ Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.88, 27.03, 29.28, 30.39, 32.24, 40.17, 49.12, 51.55, 52.74, 53.71, 128.28, 132.66, 143.08, 169.19, 172.84; MALDI-TOF-Mass Found: m/z 2872.34. Calcd for $C_{148}H_{228}N_{16}O_{40}$: [MH$^+$], 2872.48.

Formation of the Photodimer 15. A solution (0.012 M) of dendrimer **2** (21 mg, 13.6 µmol) in chloroform (1.05 mL) was irradiated with a high-pressure mercury lamp ($\lambda > 300$ nm) at room temperature under a nitrogen atmosphere for 1 h to afford photodimer **15**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20–1.66 (m, 96H), 2.35–2.63 (m, 48H), 2.79 (t, $J = 6.6$ Hz, 32H), 3.29 (q, $J = 6.6$ Hz, 16H), 3.60 (s, 48H), 4.52 (s, 4H), 7.00 (s, 8H), 7.74 (t, $J = 5.4$ Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.96, 27.27, 29.29, 29.38, 29.46, 29.67, 31.85, 40.25, 49.04, 51.67, 53.71, 128.77, 132.71, 143.06, 169.19, 172.58; MALDI-TOF-Mass Found: m/z 3096.85. Calcd for $C_{164}H_{260}N_{16}O_{40}$: [MH$^+$], 3096.90.

Formation of the Photodimer 16. A solution (0.012 mM) of dendrimer **3** (16.7 mg, 10.1 µmol) in chloroform (0.84 mL) was irradiated with a high-pressure mercury lamp ($\lambda > 300$ nm) at room temperature under a nitrogen atmosphere for 1 h to afford photodimer **16**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10–1.60 (m, 128H), 2.23–2.53 (m, 48H), 2.77 (t, $J = 6.6$ Hz, 32H), 3.26 (q, $J = 6.6$ Hz, 16H), 3.60 (s, 48H), 4.50 (s, 4H), 7.00 (s, 8H), 7.75 (t, $J = 5.4$ Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.03, 27.32, 29.34, 29.43, 29.55, 29.60, 29.69, 29.73, 32.00, 39.84, 40.30, 49.08, 51.63, 53.73, 128.13, 132.71, 142.99, 169.17, 172.69; MALDI-TOF-Mass Found: m/z 3321.00. Calcd for $C_{180}H_{292}N_{16}O_{40}$: [MH$^+$], 3321.32.

Formation of the Photodimer 17. A solution (0.012 mM) of dendrimer **4** (15.0 mg, 8.5 µmol) in chloroform (0.70 mL) was irradiated with a high-pressure mercury lamp ($\lambda > 300$ nm) at room temperature under a nitrogen atmosphere for 1 h to afford photodimer **17**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25–1.72 (m, 208H), 2.33–2.57 (m, 48H), 2.79 (m, 32H), 3.33 (q, $J = 6.6$ Hz, 16H), 4.63 (s, 4H), 7.08 (s, 8H), 7.82 (t, $J = 5.1$ Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.93, 27.10, 28.09, 29.31, 29.59, 31.20, 33.39, 40.20, 49.17, 53.70, 79.82, 132.68, 137.54, 143.11, 169.22, 171.73; MALDI-TOF-Mass Found: m/z 3546.72. Calcd for $C_{196}H_{324}N_{16}O_{40}$: [MH$^+$], 3545.76.

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