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Self-organization and photoreactivity of anthryl dendron having perfluoroalkyl chains at the terminals

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Abstract—A newly designed anthryl dendron having perfluoroalkyl chains at terminals showed thermotropic liquid crystallinity, which was characterized using polarizing optical microscopy, differential scanning calorimetry, and X-ray diffraction. The anthryl dendron forms S_B phase at room temperature below 53 °C, at which temperature a phase transition to $\mathrm{Col_{rd}}$ takes place. In a fluorous solvent, regioselective photodimerization of the anthryl dendron occurred to give head-to-head photodimers, although photodimerization in the S_B phase and chloroform gave both head-to-head and head-to-tail photodimers.

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1. Introduction

Dendritic macromolecules (dendrimers) have received considerable attention during the past three decades.[1] In particular, dendrimers possessing fluorine atoms in some part of their structure[2] offer the potential for applications such as surfactants,[3] electronics,[4b] and liquid crystalline devices.[4] For example, DeSimone and co-workers reported the use of fluorinated dendrimer as a surfactant in biphasic systems (water/supercritical CO_2).[3a] Percec and co-workers reported that fluorinated dendrons with conducting organic donor or acceptor groups exhibit high charge mobilities in their supramolecular liquid crystalline phases.[4b] Although a few examples of fluorinated dendrimer that are functionalized with chromophore have been reported,[4b] much less is known about the photoreactivity of fluorinated dendrimers. We have studied on the synthesis and photodimerization of anthracenes bearing a poly(amidoamine) dendritic substituent (anthryl dendrons).[5] Furthermore, we have recently reported that thermotropic liquid crystallinity can be induced for an anthryl dendron.[5d] In this liquid crystalline phase (S_E), the photodimerization reaction of the anthracene moiety proceeded quantitatively and regioselectively to afford only *anti*-photodimer. During our studies on the synthesis and photoreactivity of anthryl dendrons, we found that an anthryl dendron having perfluoroalkyl end groups shows mesomorphic properties and a micellar formation of the dendron was a key to control regioselectivity of the photodimerization reaction. This paper describes the synthesis, characterization, and photoreactivity of the fluorinated anthryl dendron, along with its mesomorphic properties. To our knowledge, these are the first examples of photoreactions of fluorinated dendrimer in mesomorphic state and micellar aggregate.

2. Results and discussion

The anthryl dendron **1** having perfluoroalkyl chains at the terminals was prepared from a first-generation poly(amidoamine) dendron **2** as shown in Scheme 1. Perfluoroalkyl chains were introduced by the Michael addition reaction of 2-(perfluorooctyl)ethyl acrylate with the terminal NH_2 groups of the dendron **2** to afford dendron **1**, which was purified by HPLC (LC918; Japan Analytical Industry Co. Ltd) on gel permeation column (Jaigel 1H+2H; Japan Analytical Industry Co. Ltd) with chloroform as eluent, in 70% yield (Scheme 1). The structure of the dendron **1** was confirmed by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopies, elemental analysis, and MALDI-TOF-Mass spectrometry. The ^{19}F NMR spectrum showed eight signals, which are assignable with the terminated perfluoroalkyl groups. The MALDI-TOF-Mass spectrum showed clearly the parent peak at m/z 2566.35, which is consistent with the molecular weight of the dendron **1** ($[\mathrm{MH}]^+$, calcd 2566.28) as shown in Figure 1.

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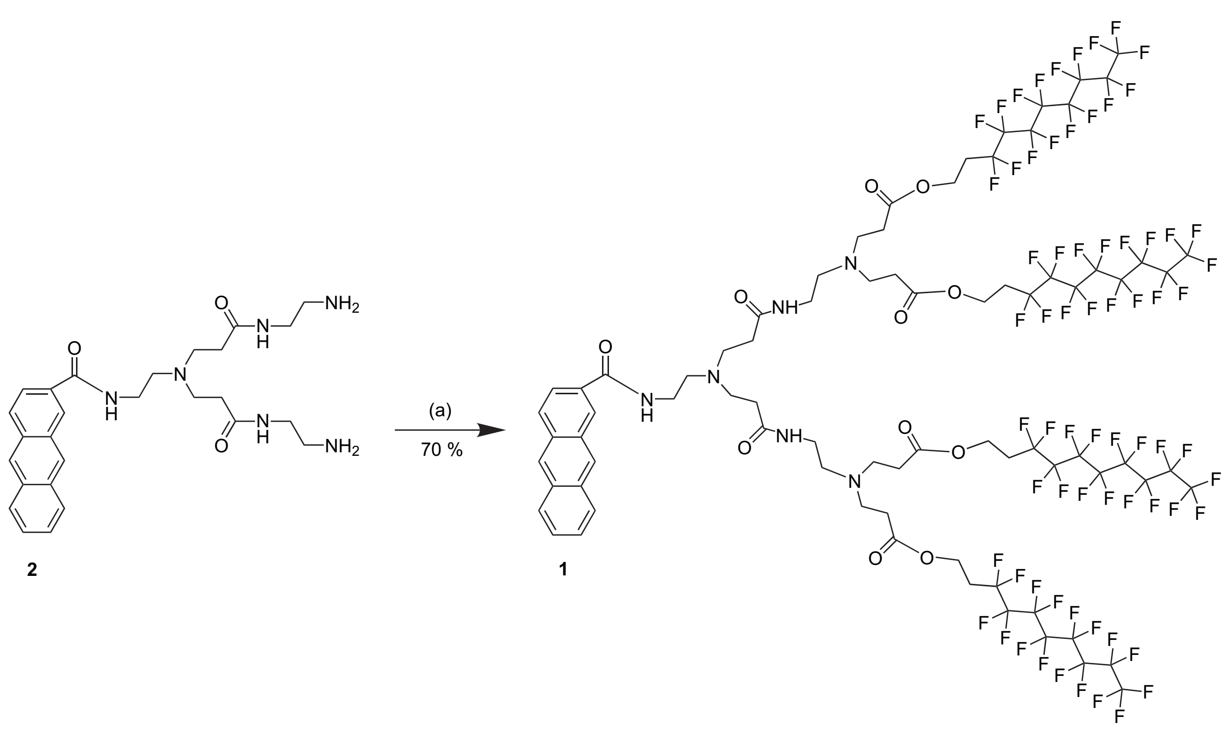


Scheme 1. Reagent and condition: (a) 2-(perfluorooctyl)ethyl acrylate, DMF, 45 °C, 1 week.

In order to evaluate the influence of the fluorophilic end groups for self-organization of dendron **1**, structural analyses of mesophases of dendron **1** were accomplished using a combination of differential scanning calorimetry (DSC), polarized optical microscopy, and X-ray diffraction (XRD). The DSC profile of dendron **1** shows a dominant and endothermic peak at 53 °C (ΔH=43.5 kJ/mol) and smaller one at 87 °C (ΔH=1.82 kJ/mol) as shown in Figure 2. The reversibility of the phase transitions is evidenced by the presence of the corresponding peaks in the cooling curve. A thin sample of dendron **1**, sandwiched between untreated glass plates, was examined between crossed polarizers. Liquid crystallinity of the dendron **1** at room temperature (after annealing at 100 °C) probed by the observation of optical texture showing birefringent as shown in Figure 3a. In agreement with the DSC profile, on heating, a reduction of anisotropy of the polarizability, which should be caused by a change in the molecular arrangement, was observed around 55 °C as shown in Figure 3b. Dendron **1** showed the isotropic phase transition at 87 °C in DSC analysis and POM observation. Identification and unequivocal assignment of mesophases were finally achieved by XRD. Those XRD measurements showed that the mesophases of dendron **1** at room temperature and 60 °C exhibited a smectic phase and a rectangular columnar phase, respectively. The profile for the mesophase of dendron **1** at room temperature shows a sharp reflection at 2Θ=1.98° (44.6 Å), 39.4° (22.4 Å), 5.92° (14.9 Å), 7.88° (11.2 Å), 9.84° (8.98 Å), 11.8° (7.47 Å), and 13.8° (6.40 Å) arising from the smectic layering of molecules (d_{001}, d_{002}, d_{003}, d_{004}, d_{005}, d_{006}, and d_{007}, respectively), and a sharp one at 2Θ=17.6° (5.03 Å) arising

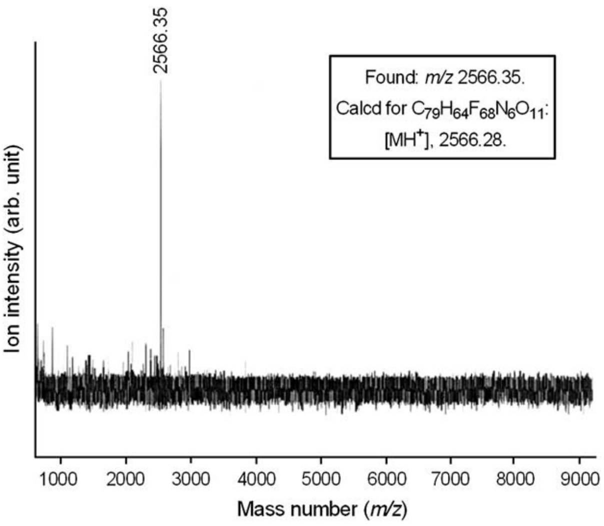


Figure 1. MALDI-TOF spectra of dendron **1**.

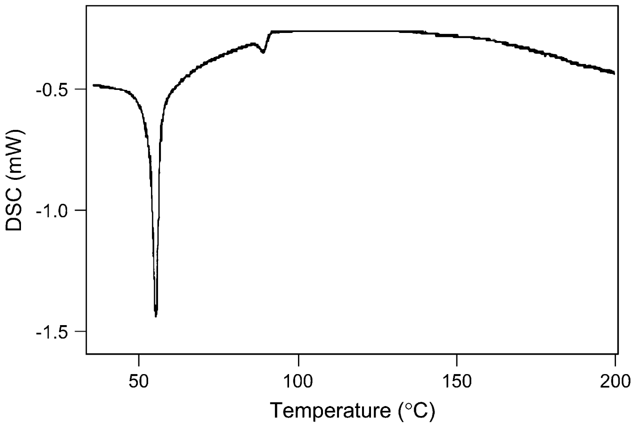


Figure 2. DLC curve for dendron **1**.

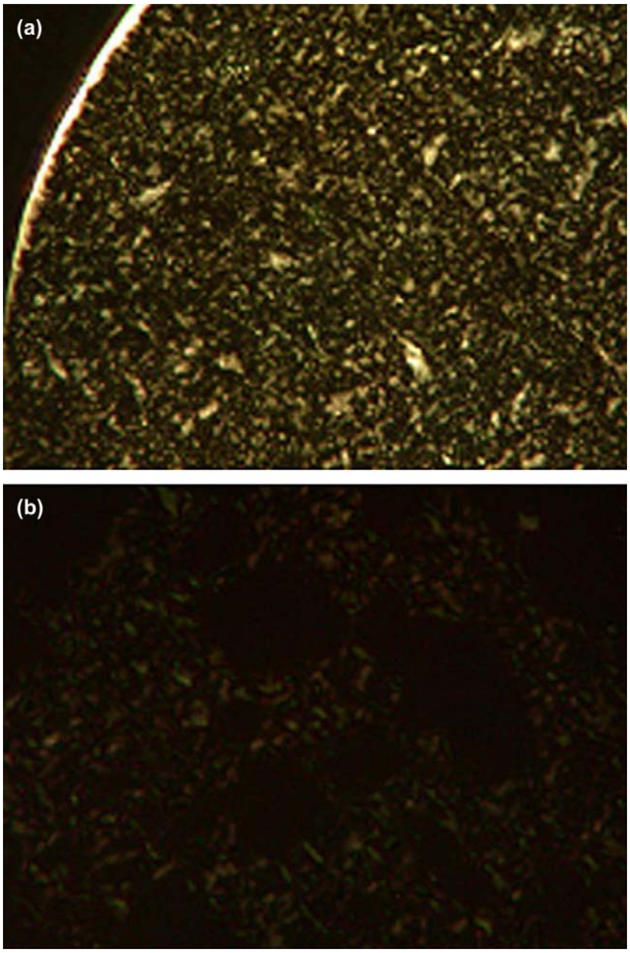


Figure 3. Polarized optical micrographs (×75) of dendron **1** (a) at room temperature and (b) at 60 °C.

Table 1. X-ray diffraction data for dendron **1**

(a) At room temperature		(b) At 60 °C	
2Θ (°)[a]	d_{obs} (Å)[b]	2Θ (°)[a]	d_{obs} (Å)[b]
1.980	44.62	2.316	38.11
3.940	22.41	2.680	32.94
5.920	14.92	3.984	22.16
7.880	11.21	16.66	5.317[c]
9.840	8.981		
11.84	7.468		
13.82	6.402		
17.62	5.029		

[a] Glancing angle.
[b] *d*-Spacing.
[c] Halo of molten alkyl chains.

from the d_{100} direction (Table 1a). This feature suggests that the molecular arrangement of the smectic phase has a hexagonal order within the layer, where the lateral distance of perfluoroalkyl chains is 5.03 Å. From these results, the mesophase is assigned to the smectic B (S_B). This structural analysis could be supposed from adequate consideration of the molecular model shown in Figure 4a. The smectic layer is formed by an anti-parallel arrangement of two molecules, where the perfluoroalkyl chains are interdigitated, although the arrangement might be partially disordered. The profile for the mesophase of dendron **1** at 60 °C shows a set of reflections corresponding to *d*-spacings of 38.1, 32.9, and 22.2 Å (Table 1b). In combination with the modeling, these reflections could be indexed in sequence as (110), (020), and (210) reflections of a rectangular columnar lattice with the lattice parameters of a=46.7 Å and b=65.8 Å as shown in Figure 4b. The phase transition of the S_B into $\mathrm{Col_{rd}}$ ($P2_1/a$) might be induced by melting of perfluoroalkyl chain, which is in agreement with the transition enthalpy by DSC, and subsequent liquid–liquid phase separation between the

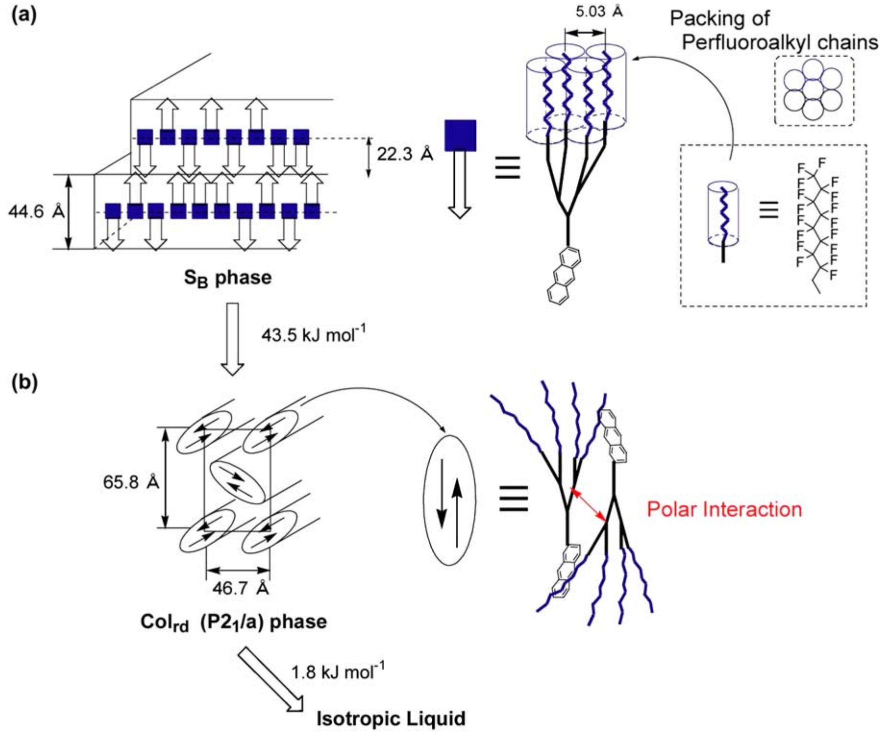
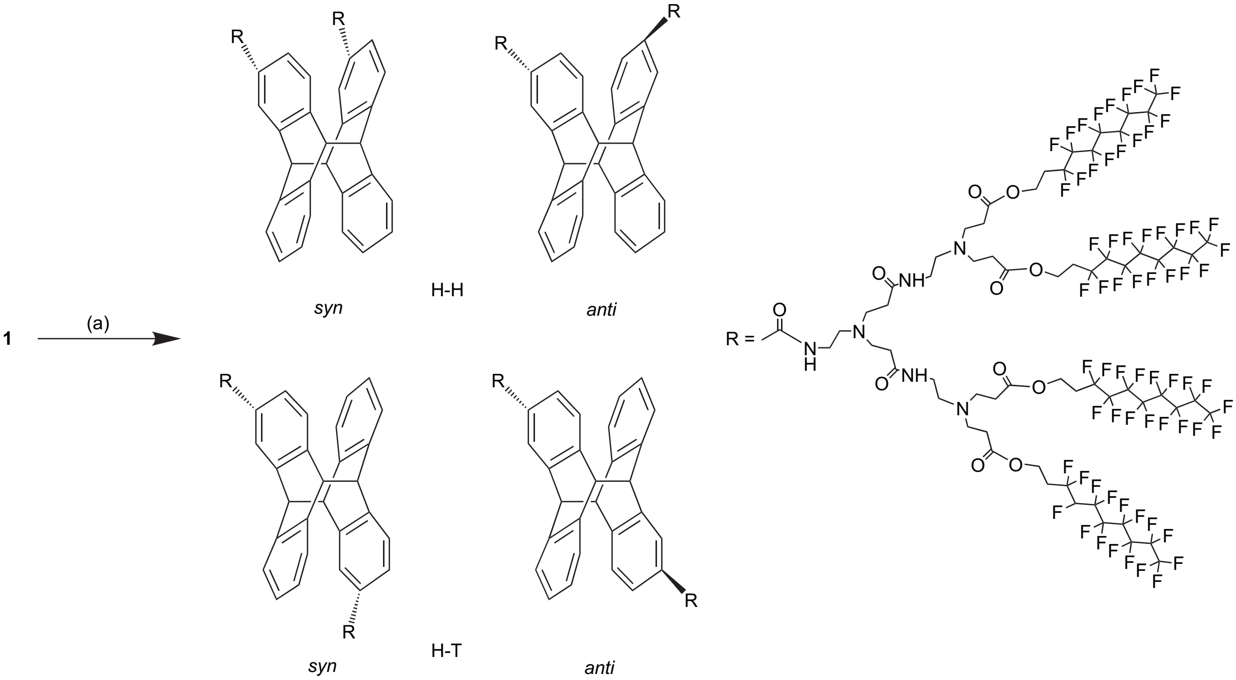


Figure 4. Schematic representation of mesophases of dendron **1** (a) at room temperature and (b) at 60 °C.



Scheme 2. Condition: (a) photoirradiation (>300 nm), rt, 3 h.

molten perfluoroalkyl chains and the polar poly(amidoamine) building blocks.

The photodimerization of 2-substituted anthracene gives four regioisomers (*anti* head-to-tail, *syn* head-to-tail, *anti* head-to-head, and *syn* head-to-head) (Scheme 2).[6] The two head-to-head (H-H) dimers and the two head-to-tail (H-T) dimers arise, respectively, from parallel and anti-parallel pair of the anthracenes. Especially in viscous media, the pairs have insufficient time to reorient themselves during the singlet state of anthryl groups, from which the photodimerization reaction emanates.[7,8] Therefore, the ratio of H-H/H-T should reflect, at least indirectly, the ground state distribution of parallel and anti-parallel pairs of 2-substituted anthracene derivatives.[8] In fact, Weiss and Lin analyzed packing arrangements of cholesteryl 4-(2-anthryloxy)butyrate in its cholesteric liquid crystalline phase, neat isotropic phase, and solution by the distributions of photodimers obtained from each.[8] Therefore, the distributions of photodimers obtained from various phases were analyzed to investigate the packing arrangement of dendron **1**. The mesophase (S_B), chloroform solution, and the perfluorohexane (PFH) solution of dendron **1** were irradiated with a high-pressure mercury lamp at room temperature for 3 h to yield photodimers, which were purified by the use of HPLC. According to the previous report,[8] the ratios of H-H(*syn*:*anti*)/H-T are estimated as shown in Table 2.

Table 2. Distributions of the regioisomer of photodimers

Phase	Dimers	
	H-H (*syn*:*anti*)	H-T
S_B phase	65 (58:42)	35
$CHCl_3$ solution	47 (66:34)	53
PFH solution[a]	100 (50:50)	—

[a] Perfluorohexane solution.

In the cases of the mesophase and chloroform solution, both H-H and H-T regioisomers were obtained, although the photoirradiation of the mesophase gave H-H dimers as slightly rich products. On the other hand, surprisingly, in

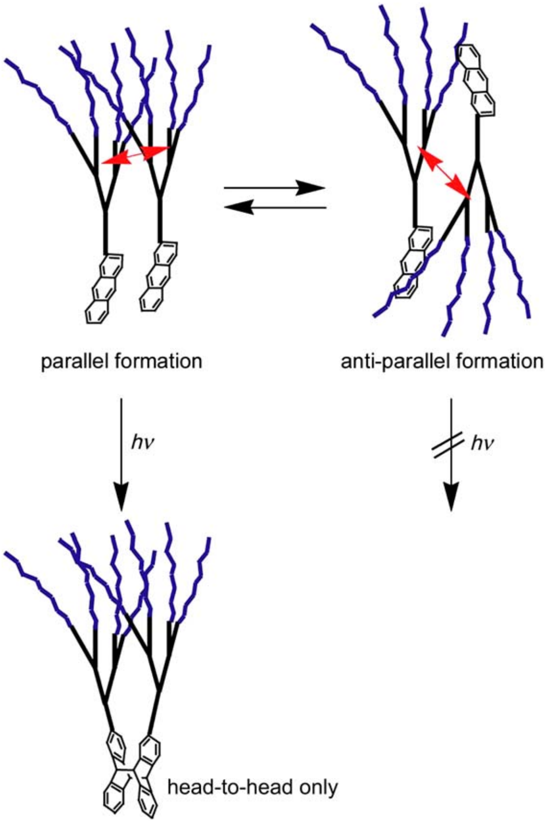


Figure 5. Schematic representation of the photodimerization of dendron **1** in fluorophilic environment.

the case of the PFH solution, only H-H dimers were observed after the photodimerization reaction. Formation of the H-T regioisomers in the S_B phase, but not specific formation of H-H regioisomers, implies that the anthryl group might be interdigitated as in the bilayer, in agreement with the phase structure represented in Figure 4a. The lack of regioselectivity in the case of chloroform solution indicates that dendron **1** can be dissolved molecularly in chloroform. Meanwhile, in the case of the PFH solution, this flourophilic environment induced phase separation of the polar poly(amidoamine) building block of dendron **1** to form micellar aggregates, in which only parallel formation was allowed to form the dimers upon photoirradiation, as shown in Figure 5.

3. Conclusion

In conclusion, we have found the fluorinated anthryl dendron shows the two thermotropic mesophases, of which one is the smectic B phase, which has a lamella structure formed by hexagonal packing of the perfluoroalkyl chains, and another is a rectangular columnar phase, which is induced by the molten perfluoroalkyl chains. Photoirradiation of the mesophase at room temperature gave photodimers with little selectivity. However, photoirradiation of the dendron in perfluorohexane gave only head-to-head regioisomers. This regioselectivity arises from micellar aggregation, which is formed by the phase separation of polar poly(amidoamine) building block in fluorous environment. Further work is in progress to explore the applications and advantages of these mesomorphic properties and micellar formations of fluorinated dendrimers in regioselective syntheses using photoreaction.

4. Experimental

4.1. General

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 (1,8,9-anthracenetriol) as a matrix. HPLC experiments were performed on a Japan Analytical Industry Co. model LC-918V with Jaigel 1H+2H (eluent: chloroform). Photoirradiation was carried out in a Pyrex reactor. A 500 W high-pressure mercury lamp was used as the light source. The polarized optical microscopic studies were performed on Olympus BHA-751-T microscope equipped with a heating stage (Mettler FP80). Differential scanning calorimetry was performed on a SHIMADZU DSC-60. 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. *N*,*N*-Dimethylformamide (DMF) used in reactions, were further purified by general methods. Other solvents and reagents were used as received without further purification. According to a previously reported method,[1] dendron **2** was synthesized.

4.2. Synthesis of dendron 1

A mixture of **2** (30 mg, 0.061 mmol), 2-(perfluorooctyl)-ethyl acrylate (360 mg, 0.695 mmol), and *N*,*N*-dimethylformamide (DMF) (0.3 mL) was stirred at 45 °C for 1 week. Chloroform was added to the reaction mixture and the solution was washed with water to remove DMF. After removal of solvent, the residue was purified by HPLC to afford dendron **1** (109 mg, 0.043 mmol), in 70% yield. ^{1}H NMR ($CDCl_3$) δ 2.27–2.47 (m, 24H), 2.58 (t, J=6.4 Hz, 8H), 2.72 (t, J=5.2 Hz, 2H), 2.82 (t, J=6.0 Hz, 4H), 3.17 (q, J=5.6 Hz, 4H), 3.69 (q, J=5.6 Hz, 2H), 4.31 (t, J=6.4 Hz, 8H), 7.45–7.53 (m, 2H), 7.94–8.04 (m, 4H), 8.42 (s, 1H), 8.55 (s, 1H), 8.72 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 34.7, 36.6, 38.4, 38.5, 49.7, 50.1, 52.0, 52.8, 53.2, 124.9, 126.1, 127.6, 128.9, 129.3, 130.2, 131.7, 132.9, 161.2, 161.4, 174.5, 175.0; ^{19}F NMR ($CDCl_3$) δ −126.7, −124.1, −123.3, −122.5, −122.5, −122.2, −114.2, −81.4; MALDI-TOF-Mass for $C_{79}H_{64}F_{68}N_6O_{11}$ *m/z* calcd, 2566.28 [MH^+]; found, 2566.35. Anal. Calcd for $C_{79}H_{64}F_{68}N_6O_{11}$: C, 36.99; H, 2.51; N, 3.28%. Found: C, 36.82; H, 2.44; N, 3.17%.

4.2.1. Photodimerization of dendron 1. *In chloroform*: A solution of dendron **1** (50 mg, 0.019 mmol) in chloroform (250 μL) was irradiated with a high-pressure mercury lamp through a Pyrex filter for 3 h at room temperature. After removal of the solvent, the residue was purified by HPLC with $CHCl_3$ as eluent to isolate the photodimers (38 mg) in 84% yield (after 92% conversion). *In perfluorohexane*: A solution of dendron **1** (50 mg, 0.019 mmol) in perfluorohexane (250 μL) was irradiated with a high-pressure mercury lamp through a Pyrex filter for 3 h at room temperature. After removal of the solvent, the residue was purified by HPLC with $CHCl_3$ as eluent to isolate the photodimers (16 mg) in 44% yield (after 86% conversion). *Without solvent*: The dendron **1** was placed between Pyrex plates and irradiated with the high-pressure mercury lamp (λ>300 nm) at room temperature. The resulting mixture was purified by HPLC with $CHCl_3$ as eluent to isolate the photodimers (21 mg) in 55% yield (after 86% conversion): ^{1}H NMR ($CDCl_3$) δ 2.00–2.82 (m, 76H), 3.00–3.2 (m, 8H), 3.35–3.60 (m, 4H), 4.32 (t, J=6.4 Hz, 16H), 4.55–4.70 (m, 4H), 6.65–7.00 (m, 14H), 7.30–7.60 (m, 6H).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.06.036.

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