Synthesis of Polycatenar-Type Organogelators Based on Chalcone and Study of Their Supramolecular Architectures

Geo San Lim,[†] Byung Mun Jung,[†] Seung Ju Lee,[†] Hyun Hoon Song,[‡] Chulhee Kim,[§] and Ji Young Chang*,[†]

Department of Materials Science and Engineering, and Hyperstructured Organic Materials Research Center, College of Engineering, Seoul National University, Seoul 151-744, Korea, Department of Advanced Materials, Hannam University, Daejeon 300-791, Korea, and Department of Polymer Science and Engineering, Hyperstructured Organic Materials Research Center, Inha University, Incheon 402-751, Korea

Received June 1, 2006. Revised Manuscript Received September 29, 2006

We synthesized a series of compounds belonging to a new class of polycatenar-type organogelators, comprising a cyanochalcone unit and a half disklike phenyl group with two or three long alkoxy chains, and investigated their supramolecular assembly with respect to their molecular structures. They formed very stable organogels in *n*-alkanes, cyclohexane, and alcohols. In the absence of a cyano group, the compound did not show any gelation ability. Dry gels were prepared by freeze-drying the organogels from hexane, and their structures were investigated by SEM and XRD. The SEM images of the dry gels showed the presence of elongated fibers, which formed a gel network. The dry gels exhibited different packing arrangements, depending on the volume fraction of the flexible tails in the gelator. The gelators were assembled into a head-to-tail type dimer by a dipole−dipole interaction between the polar head groups and further organized into columnar or layer structures through a $\pi-\pi$ interaction. The gelators with three alkoxy tails formed hexagonal, square, and rectangular columnar structures, depending on the tail length, while the gelator with two alkoxy tails formed a layer structure. The organogels were photoresponsive. Upon photoirradiation, the [2 + 2] addition reaction of the chalcone units occurred, which induced a gel-to-sol transition.

Introduction

Organogels are thermoreversible and viscoelastic materials consisting of low molecular weight gelators and organic solvents.[1] The gelation of organic solvents is believed to proceed through the self-assembly of the gelator molecules into fibers and their subsequent entanglement. In addition to the noncovalent interactions between the gelator molecules, their affinity for the solvent molecules is an important factor in the gelation process and one that makes the molecular design of new gelators more complicated. Many studies have been conducted on the assembled structures of organogelators in an effort to elucidate the gelation mechanism. Dry gels are frequently used for structural analysis because the concentration of a gelator molecule in the gel state is too low for X-ray measurements.[2] The study of dry gels helps us to better understand not only the structures of organogels but the assembly pathway of the gelator molecules. Dry gels are generally prepared by removing the solvent molecules very slowly from organogels. During the drying process, the gelator molecules can be further organized into thermodynamically favorable structures.

In this work, we synthesized a series of compounds belonging to a new class of polycatenar-type organogelators based on a chalcone unit and investigated their supramolecular assembly with respect to their molecular structures. There have been few systematic studies regarding the effect of the molecular structural changes of an organogelator on its supramolecular structures, even though minor structural modifications of the gelator molecule often dramatically change its gelation ability. Chalcones, which consist of two aromatic rings and an enone group, have interesting biological functionalities. Chalcones are found as intermediates in the biosynthesis of flavonoids, which are a class of water-soluble plant pigments that are well-known for their antioxidant activity.[3] They are prepared synthetically from an aldol condensation between a benzaldehyde and an acetophenone in the presence of a base or acid catalyst. Synthetic chalcones have been investigated for their antibacterial and antifungal properties.[4] Chalcones also show photochemical reactivity. They form a dimer by a [2 + 2] addition reaction

* Corresponding author. Fax: (+82)2-885-1748. E-mail: jichang@snu.ac.kr.
[†] Seoul National University.
[‡] Hannam University.
[§] Inha University.

(1) (a) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133. (b) Abdallah, D. J.; Weiss, R. G. *Adv. Mater.* **2000**, *12*, 1237. (c) de Loos, M.; Feringa, B. L.; van Esch, J. H. *Eur. J. Org. Chem.* **2005**, 3615. (d) Sangeetha, N. M.; Maitra, U. *Chem. Soc. Rev.* **2005**, *34*, 821.

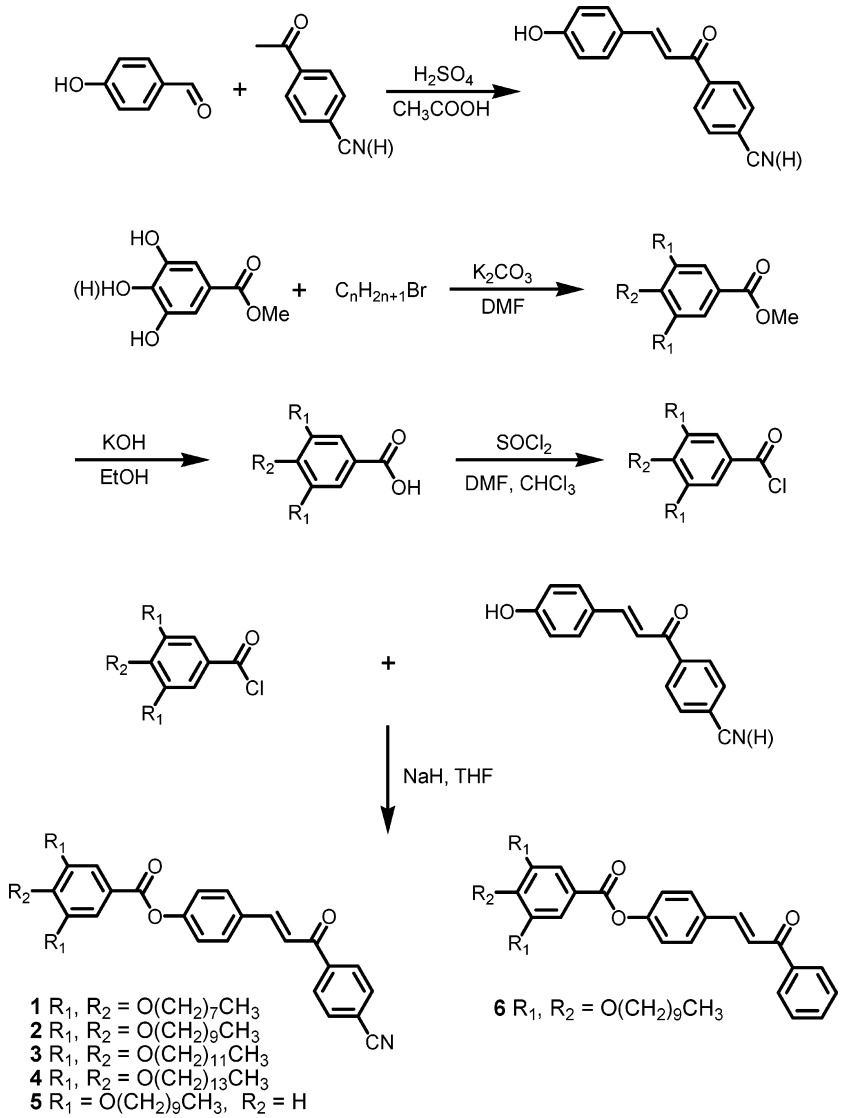
(2) (a) Kishida, T.; Fujita, N.; Sada, K.; Shinkai, S *Langmuir* **2005**, *21*, 9432. (b) Moniruzzaman, M.; Sundararajan, P. R. *Langmuir* **2005**, *21*, 3802. (c) Kishimura, A.; Yamashita, T.; Aida, T. *J. Am. Chem. Soc.* **2005**, *127*, 179. (d) Seo, S. H.; Chang, J. Y. *Chem. Mater.* **2005**, *17*, 3249. (e) Shirakawa, M.; Fujita, N.; Tani, T.; Kaneko, K.; Shinkai, S. *Chem. Commun.* **2005**, 4149. (f) Song, Y.; Park, C.; Kim, C. *Macromol. Res.* **2006**, *14*, 235.

(3) Strack, D. In *Plant Biochemistry*; Dey, P. M., Harborne, J. B., Eds.; Academic Press: San Diego, CA, 1997; p 387.

(4) (a) Ansari, F. L.; Nazira, S.; Noureenb, H.; Mirzab, B. *Chem. Biodiversity* **2005**, *2*, 1656. (b) Pattanaik, P.; Raman, J.; Balaram, H. *Curr. Top. Med. Chem.* **2002**, *2*, 483. (c) Nielsen, S. F.; Larsen, M.; Boesen, T.; Schønning, K.; Kromann, H. *J. Med. Chem.* **2005**, *48*, 2667.

10.1021/cm061282q CCC: $37.00
Published on Web 01/03/2007

Scheme 1



when exposed to UV light. Photosensitive polymers containing chalcones in their side groups[5] or main chains[6] have been studied as photoalignment materials. A rodlike LC molecule mainly consisting of chalcones as a photoimaging material has been reported by us.[7]

The liquid crystalline properties of polycatenar molecules, which consist of a rodlike rigid core and one or two half-disk moieties, have been studied.[8] They are considered to fill the gap between rodlike and disklike mesogenic compounds. Various mesophases have been reported, depending on the number of aromatic or acyclic rings, as well as the number of aliphatic chains and the polarity of the substituents. In general, when the number of aromatic or acyclic rings is larger than four, stable mesophases are obtained. Despite these interesting structural features of polycatenar compounds, their gelation properties have not been thoroughly studied.

Results and Discussion

Synthesis. Polycatenar compounds **1**−**6**, comprising a rodlike chalcone unit and a half disklike phenyl group with two or three long alkoxy chains, were prepared as potential organogelators according to Scheme 1. In compounds **1**−**5**, a cyano group was introduced into a para-position to a carbonyl group of the first phenyl ring of the chalcone, which would induce the strong polarization. For the purpose of comparison, compound **6** having no cyano group was also prepared. These molecules were expected to self-assemble through dipole−dipole interactions and/or $\pi-\pi$ interactions during the gelation process.

A methyl benzoate derivative with three long alkoxy chains was prepared by the reaction of methyl 3,4,5-trihydroxybenzoate with alkyl bromide in *N*,*N*-dimethylformamide (DMF) in the presence of potassium carbonate. After hydrolysis, the resulting acid was activated by using thionyl chloride. The condensation reaction of 4′-cyanoacetophenone with 4-hydroxybenzaldehyde was carried out under acidic

(5) (a) Makita, Y.; Natsui, T.; Kimura, S.-I.; Nakata, S.; Kimura, M.; Matsuki, Y.; Takeuchi, Y. *J. Photopolym. Sci. Technol.* **1998**, *11*, 187. (b) Akelah, A.; Selim, A.; El-Deen, N. S. *Polym. Int.* **1993**, *32*, 423.
(6) Feng, K.; Tsushima, M.; Matsumoto, T.; Kurosaki, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 685.
(7) Chang, J. Y.; Nam, S. W.; Hong, C. G.; Im, J.-H.; Kim, J.-H.; Han, M. J. *Adv. Mater.* **2001**, *13*, 1298.
(8) Nguyen, H.-T.; Destrade, C.; Malthête, J. *Adv. Mater.* **1997**, *9*, 375.

Table 1. Gelation Test Results of Compounds 1−6 (3 wt %)[a]

solvent	1	2	3	4	5	6
n-hexane	G	G	G	G	G	P
n-octane	G	G	G	G	G	P
n-decane	G	G	G	G	G	P
n-dodecane	G	G	G	G	G	P
cyclohexane	G	G	G	P	G	S
1-butanol	G	G	P	P	P	P
1-hexanol	G	G	P	P	P	P
1-octanol	G	G	G	P	P	P

[a] G, gel; P, precipitation; S, solution.

conditions to give a cyanochalcone, which was reacted with 3,4,5-trialkoxybenzoyl chloride or 3,5-dialkoxybenzoyl chloride to yield compounds **1**−**5**. Compound **6** having no cyano group was prepared in the same manner except that acetophenone was used instead of 4′-cyanoacetophenone. In the ^{1}H NMR spectra of compounds **1**−**6**, vinyl proton peaks showed up around 7.8 and 7.4 ppm. For all six compounds, each of these two peaks appeared as a doublet with $J = \sim 15$ Hz, indicating that the double bond was in the trans configuration.

Gelation Study. A weighed amount (3 wt %) of compounds **1**−**6** in an organic solvent (1 mL) was heated in a septum-capped test tube [5 cm (height) × 1 cm (radius)] until the solid was dissolved. The solution was then left to cool to room temperature in air. The state of the phase was confirmed by visual observation. Gel formation was observed either while cooling or immediately after the cooling process.

Compounds **1**−**5** having a cyano group had the ability to gelate *n*-alkanes, cyclohexane, and alcohols (Table 1). On the other hand, compound **6** without a cyano group did not show any gelation ability. Since no hydrogen-bonding sites were available in compounds **1**−**5**, the intermolecular dipole−dipole and $\pi-\pi$ interactions are likely responsible for the observed gelation. As seen in compound **6**, $\pi-\pi$ interaction alone is not strong enough to induce gelation. Interestingly, none of the molecules showed thermotropic liquid crystal phases despite their structural similarities to the polycatenar mesogenic compounds.[8] Recently Mori and co-workers reported 5-cyanotroponoids to which a 3,4,5-trialkoxyphenyl group was attached through either an amide or ester linkage.[9a] The cyanotroponoid ring is highly deficient of electrons owing to the presence of cyano and oxo groups. These cyanotroponoids exhibited thermotropic smectic phases, but only those having an amide group capable of hydrogen bonding acted as gelators.

The sol−gel transition temperatures (T_{gel}) of compounds **1**−**5** in *n*-hexane as a function of a concentration were determined by the inverse flow method. The critical gelation concentrations of the compounds at 25 °C were 0.3 (**1**), 1.1 (**2**), 2.3 (**3**), 2.8 (**4**), and 0.9 wt % (**5**). T_{gel} increased as the concentration increased, which indicates that the stability of the gel is enhanced by the increase of the concentration. If the sol−gel transition is comparable to melting of crystals, the sol−gel transition enthalpy can be estimated by the van't Hoff relationship (eq 1).[10] ΔH_{gel} of **1** in *n*-hexane determined from the slope of ln[concentration of the gelator molecule] versus T_{gel}^{-1} was 115 kJ mol^{-1}.

$$\frac{\mathrm{d}\ln_{c_g}}{\mathrm{d}\,1/T_g} = -\frac{\Delta H_g}{R} \tag{1}$$

ΔH_{gel} values of compounds **2**−**5** were obtained in the same manner as described for compound **1**, and the values were 111 (**2**), 76 (**3**), 72.9 (**4**), and 75 (**5**) kJ mol^{-1}.

The evidence for the intermolecular $\pi-\pi$ interactions in the gel state was provided by ^{1}H NMR analysis. In the ^{1}H NMR spectrum of compound **2** in cyclohexane-d_{12} (3 wt %) taken in the gel state (25 °C) without sample spinning, the vinyl proton peaks appeared at 7.75 and 7.36 ppm. After the gel-to-sol transition (55 °C), the peaks shifted to 7.70 and 7.33 ppm. The peaks for aromatic ring protons also shifted upfield by 0.04 ppm. In the gel state, the peak areas of aromatic and vinyl protons appeared 15% smaller than those calculated on the basis of the peak areas of aliphatic protons.

Molecular Structure versus Self-Assembled Structure. Organogelators **1**−**4** have three alkoxy tails with carbon numbers of 8, 10, 12, and 14, respectively, while **5** has two decyloxy tails. In this study, we were interested to see how the gel structure was influenced by the flexible tail structure. Dry gels were prepared by freeze-drying the organogels from hexane (**1**−**4**) and from cyclohexane (**5**). The visual images of the dry gels of compounds **1**−**4** obtained by scanning electron microscopy (SEM) showed the presence of elongated fibers, while that of compound **5** showed a sheetlike structure. Typical SEM images taken from **3** and **5** are given in Figure 1.

The structures of the dry gels were investigated using the small-angle X-ray diffraction (XRD) technique. A summary of the X-ray data for gelators **1**−**5** is given in Table 2. The dry gels exhibited different packing arrangements, depending on the volume fraction of the flexible tails in the gelator.

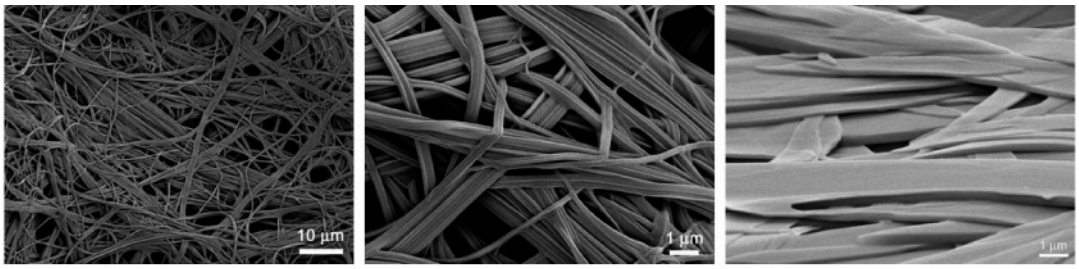


Figure 1. SEM images of the dry gel made from **3** in cyclohexane (3 wt %) at magnifications of (a) 1500 and (b) 10 000, and (c) the dry gel made from **5** in *n*-hexane (3 wt %) at the magnification of 10 000.

Table 2. X-ray Characterization of Dry Gels

compound	lattice[a]	d_{meas}/nm	*hk*	*00l*	n[b]	compound	lattice[a]	d_{meas}/nm	*hk*	*00l*	n[b]
1	Col_h	3.47	10		5.1	**2**	Col_h	3.98	10		6.0
		1.99	11					2.23	11		
		1.73	20					2.08	20		
3	Col_{sq}	3.65	10		4.0	**4**	Col_r	5.44	10		1.7
		2.58	11					2.74	20		
		1.81	20					1.15	01		
		1.61	21					1.10	11		
		1.29	22			**5**	layer	3.64		001	
		1.15	31					1.87		002	
		1.00	32					1.22		003	
		0.88	41					0.86		004	

[a] Col_h, hexagonal columnar lattice; Col_{sq}, columnar square lattice; Col_r, columnar rectangular lattice. [b] *n* is the number of molecules per unit cell.

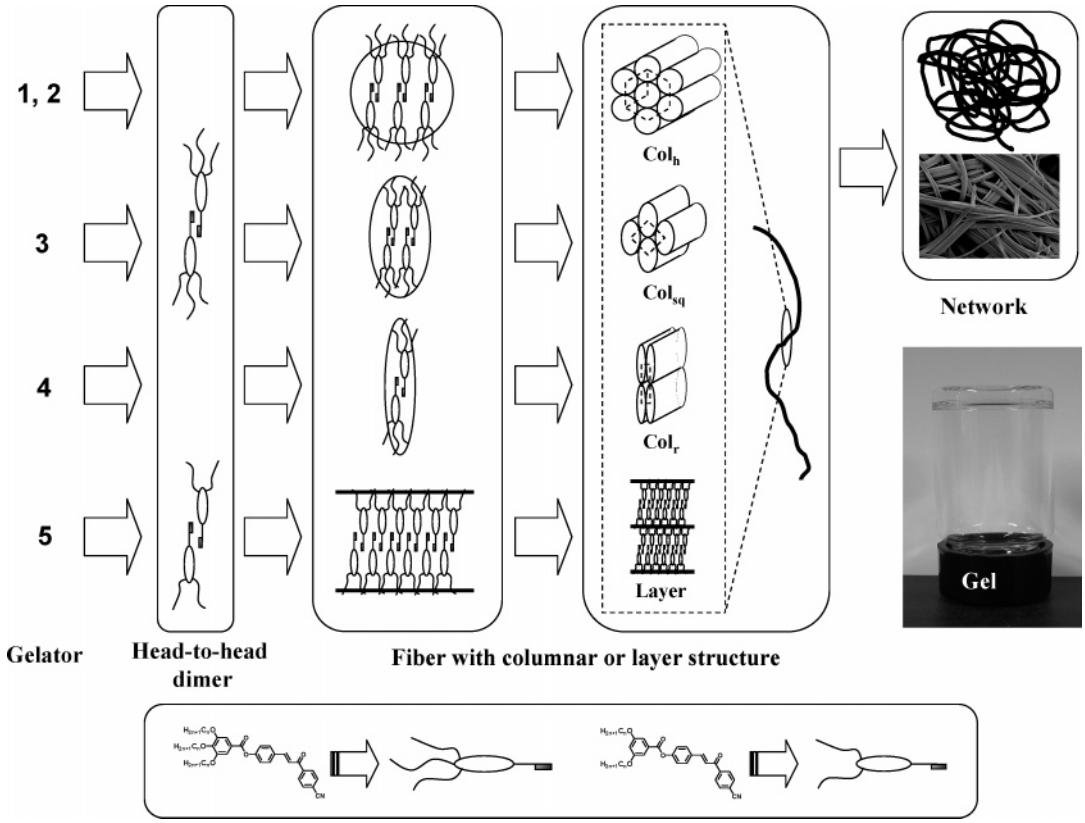


Figure 2. Schematic representation of the gelation process.

The dry gel made from **1** with octyloxy tails showed three reflections corresponding to *d* spacings of 3.47, 1.99, and 1.73 nm. These reflections are indexed in sequence as (100), (110), and (200) of a columnar hexagonal lattice with a lattice parameter of $a = 4.00$ nm. The dry gel made from **2** with decyloxy tails also had a columnar hexagonal structure with a lattice parameter of $a = 4.50$ nm, while the dry gels made from **3** with dodecyloxy tails and **4** with tetradecyloxy tails had a columnar square lattice and columnar rectangular lattice, respectively.

Since the structures of the gelators are not disklike, we assume that a slice of the column comprises more than one molecule. The number (*n*) of molecules constituting a single slice of the column can be estimated according to eq 2.[11]

$$n = V_{cell}(N_A/M)\rho \quad (2)$$

The parameter N_A is Avogadro's number, *M* is the molecular mass of the gelator, and V_{cell} is the volume of the unit cell with a thickness of 0.45 nm, calculated on the basis of the wide-angle X-ray measurements. Assuming a density (ρ) of 1 g cm^{-3}, the estimated values of the number of molecules (*n*) constituting a slice were about five to six for **1** and **2**, four for **3**, and two for **4**. It is noteworthy that the numbers decrease as the length of the alkoxy chain increases. We consider that this tendency has something to do with the affinity of the gelator for solvent molecules, which will

(9) (a) Hashimoto, M.; Ujiie, S.; Mori, A. *Adv. Mater.* **2003**, *15*, 797. (b) Hashimoto, M.; Ujiie, S.; Mori, A. *Chem. Lett.* **2000**, *29*, 758.

(10) (a) Eldridge, J. E.; Ferry, J. D. *J. Phys. Chem.* **1954**, *58*, 992. (b) Atkins, P. W. *Physical Chemistry* 6th ed.; Oxford University Press: Oxford, U.K., 1998; pp 179−180.

(11) Chen, B.; Baumeister, U.; Pelzl, G.; Das, M. K.; Zeng, X.; Ungar, G.; Tschierske, C. *J. Am. Chem. Soc.* **2005**, *127*, 16578.

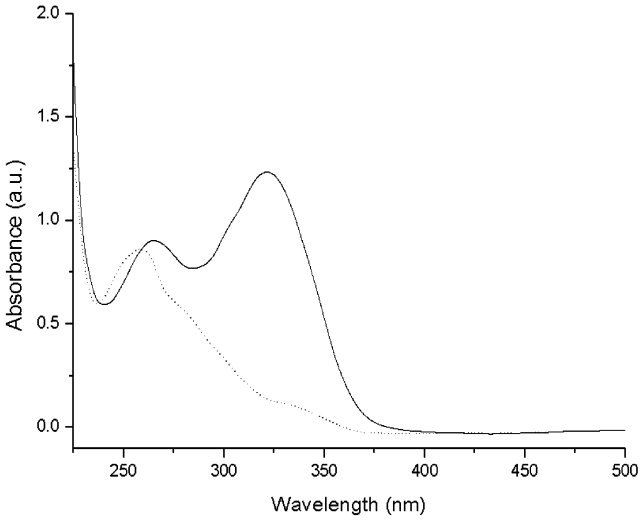


Figure 3. UV spectra of compound **2** in *n*-hexane (3 wt %, gel) before (solid line) and after (dotted line) UV irradiation at room temperature.

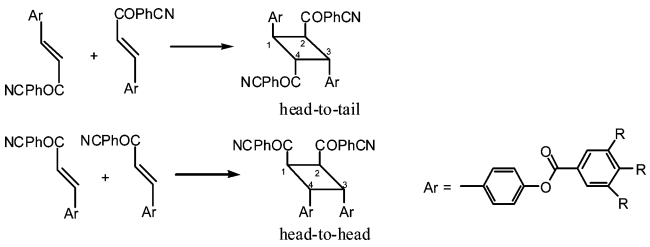
increase as the length of the alkoxy tail increases in the *n*-alkane.

The lengths of **1** and **2** calculated using the MM2 method were close to the radii of the corresponding disks determined by X-ray analysis. The lattice constants $a = 4.00$ nm for **1** and 4.50 nm for **2** are about 1.9 times larger than the extended lengths of the respective compounds (2.13 nm for **1** and 2.33 nm for **2**). Therefore, in combination with the inability of **6** having no cyano group to gelate organic liquids, we presume that the organogelator formed a head-to-tail type dimer, canceling the dipole repulsions between the molecules and diminishing the polarities of the molecules.[9] Figure 2 shows a schematic representation of the gelation process. In the dry gels made from **1** and **2**, three pairs of molecules were likely assembled to form the slice of a column. Further assembly into a column would likely proceed through $\pi-\pi$ interactions. The shape of the slice would be expected to change from a circle to an ellipse as the number of molecules constituting it gets smaller. This is consistent with the observation that, in the dry gel made from **4**, an elliptical slice consisting of one pair of molecules constituted a column, eventually resulting in the formation of a columnar rectangular structure.

In contrast to compounds **1**−**4** having three alkoxy tails, compound **5** with only two alkoxy tails showed a layer structure. This result is attributable to the relatively linear structure of compound **5** compared to those of compounds **1**−**4**. The interlayer distance (3.64 nm) was 1.53 times longer than the extended length of compound **5** (2.33 nm). We presume that interdigitation occurred between the layers.

Gel-to-Sol Transition by Photoirradiation. The organogels of **1**−**5** are photoresponsive. The [2 + 2] addition reaction of the chalcone units by photoirradiation forms a mixture of cyclobutane rings with different configurations, which disrupts the aligned structure of the gelator molecules so as to induce a gel-to-sol transition. Photoresponsive gels have attracted considerable attention due to their potential applications such as chemical switches, separators, and delivery systems.[12] The photoreaction of compound **2** in *n*-hexane (3 wt %) was carried out in the gel state at room

Scheme 2



temperature. When irradiated with UV light (5 mW/cm^2) for 30 min, the gel was transformed to the sol. This gel-to-sol transition was irreversible. The reaction mixture showed two new spots on a TLC plate (20% ethyl acetate in *n*-hexane) in addition to a spot from unreacted compound **2**; one was strong ($R_f = 0.18$) and the other one was very weak ($R_f = 0.26$) under UV light. The products were isolated by column chromatography on silica gel. The major product was identified as a dimer by ^{1}H NMR spectroscopy. The minor product was a cis-isomer of compound **2**. The ^{1}H NMR spectrum of compound **2** showed the peaks for olefinic protons at 7.45 and 7.86 ppm. After isomerization to a cis-form, they shifted to 6.64 and 7.14 ppm, respectively. The conversions to a dimer and a cis-isomer were calculated to be 56 and 9%, respectively, based on the peak area ratios in the ^{1}H NMR spectrum of the reaction mixture. This result was also confirmed by the UV−vis spectroscopy analysis (Figure 3). The characteristic peak of the chalcone unit at 318 nm decreased sharply after the UV irradiation of compound **2** in the gel state. When the photoirradiation of compound **2** was carried out in a tetrahydrofuran (THF) solution (3 wt %), only the isomerization reaction occurred.

The photoreaction of a *trans*-chalcone produces two major cyclobutane structures, the head-to-head and head-tail, depending on substituents and reaction conditions (Scheme 2).[13] The ^{1}H NMR spectrum of each isomer is expected to show two peaks for the ring protons. According to the literature, the peaks corresponding to $H_{1,2}$ and $H_{3,4}$ of a head-to-head structure are well-resolved, while the chemical shifts of the peaks for $H_{1,3}$ and $H_{2,4}$ of a head-to-tail structure are almost the same.[13] The ^{1}H NMR spectrum of the dimer obtained from the gel of compound **2** showed two peaks corresponding to the ring protons at 4.44 and 4.75 ppm, indicating that a head-to-head isomer formed exclusively. This result is also consistent with the proposed gel structure in Figure 2.

Conclusion

We prepared a series of photoresponsive polycatenar-type organogelators based on a chalcone unit and investigated their supramolecular assembled structures in the dry gel state. Compounds **1**−**5** having a cyanophenyl head with a carbonyl group in the para-position formed very stable organogels in *n*-alkanes. They were assembled into a head-to-tail type

(12) (a) Eastoe, J.; Sanchez-Dominguez, M.; Wyatt, P.; Heeman, R. K. *Chem. Commun.* **2004**, 2608. (b) Yagai, S.; Nakajima, T.; Kishikawa, K.; Kohmoto, S.; Karatsu, T.; Kitamura, A. *J. Am. Chem. Soc.* **2005**, *127*, 11134. (c) Yu, H.; Mizufune, H.; Uenaka, K.; Moritoki, T.;

dimer by a dipole−dipole interaction between the polar head groups and further organized into columnar or layer structures through a $\pi-\pi$ interaction. The assembled structures were greatly influenced by the volume fraction of flexible tails in the organogelator. The organogelators (**1**−**4**) with three alkoxy tails formed hexagonal, square, and rectangular columnar structures, depending on the number of molecules constituting a slice of a column, while compound **5** with two alkoxy tails formed a layer structure. Future studies will extend this discovery to the synthesis of advanced functional materials that take advantage of the flexible synthetic methodology developed for the preparation and modification of polycatenar compounds.

Experimental Section

Materials. Methyl 3,4,5-trihydroxybenzoate (98%), methyl 3,5-dihydroxybenzoate (97%), 1-bromotetradecane, 1-bromododecane, 1-bromodecane, 1-bromooctane, 4-hydroxybenzaldehyde, 4-acetylbenzonitrile (99%), acetophenone (99%), and thionyl chloride were purchased from Aldrich and used without further purification. THF was dried over sodium metal and distilled. DMF was dried over BaO and distilled.

Measurements. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX 300 (^{1}H NMR: 300 MHz, ^{13}C NMR: 75 MHz) spectrometer. Fourier transform infrared (FT−IR) measurements were recorded on a Perkin Elmer Spectrum GX I using KBr pellets. Elemental analysis data were obtained by CE Instrument EA1110. UV−vis spectra were obtained with the use of a SCINCO S-3150. SEM images were taken by JEOL JSM6330F microscope. XRD patterns were recorded by Bruker Xps GADDS (Cu Kα radiation, $\lambda = 1.54$ Å).

Synthesis of 4-Hydroxy-4′-cyanochalcone. To a solution of 4-hydroxybenzaldehyde (0.855 g, 7 mmol) in acetic acid (41 mL) were added 4-acetylbenzonitrile (1.016 g, 7 mmol) and sulfuric acid (98%, 1.25 mL). After being stirred for 24 h at room temperature, the solution was neutralized with an aqueous sodium hydroxide solution (5 N). The product was isolated by filtration and purified by column chromatography on silica gel (33% ethyl acetate in hexane) and recrystallized from methylene chloride (yield: 52%).

Anal. Calcd for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62. Found: C, 77.38; H, 4.45; N, 5.66. ^{1}H NMR (DMSO): δ 10.2 (br, OH, 1H), 8.26 (d, $J = 8.2$ Hz, ArH, 2H), 8.04 (d, $J = 8.2$ Hz, ArH, 2H), 7.77 (d, $J = 8.6$ Hz, ArH, 2H), 7.73 (s, olefinic proton, 2H), 6.85 (d, $J = 8.5$ Hz, ArH, 2H). ^{13}C NMR (DMSO): δ 188.5, 160.9, 146.2, 141.6, 133.1, 131.7, 129.2, 125.9, 118.6, 118.4, 116.2, 115.0. IR (KBr pellet, cm^{-1}): 3346, 2225, 1904, 1650, 1605, 1558, 982, 948, 828, 816, 638, 575, 443.

Synthesis of 4-Hydroxychalcone. To a solution of 4-hydroxybenzaldehyde (0.855 g, 7 mmol) in acetic acid (41 mL) were added acetophenone (0.819 mL, 7 mmol) and sulfuric acid (98%, 1.25 mL). After being stirred for 24 h at room temperature, the solution was neutralized with an aqueous sodium hydroxide solution (5 N). The product was isolated by filtration and purified by column chromatography on silica gel (33% THF in hexane) and recrystallized from methylene chloride (yield: 38%).

Koshima, H. *Tetrahedron* **2005**, *61*, 8932. (d) Ahmed, S. A.; Sallenave, X.; Fages, F.; Mieden-Gundert, G.; Muller, W. M.; Muller, U.; Vogtle, F.; Pozzo, J.-L. *Langmuir* **2002**, *18*, 7096. (e) de Jong, J. J. D.; Tiemersma-Wegman, T. D.; van Esch, J. H.; Feringa, B. L. *J. Am. Chem. Soc.* **2005**, *127*, 13804. (f) van der Laan, S.; Feringa, B. L.; Kellogg, R. M.; van Esch, J. *Langmuir* **2002**, *18*, 7136. (g) Shirakawa, M.; Fujita, N.; Shinkai, S. *J. Am. Chem. Soc.* **2005**, *127*, 4164.

(13) Montaudo, G.; Caccamese, S. *J. Org. Chem.* **1973**, *38*, 710.

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.04; H, 5.36. ^{1}H NMR (DMSO): δ 10.09 (br, OH, 1H), 8.12 (d, $J = 7.2$ Hz, ArH, 2H), 7.75 (d, $J = 8.6$ Hz, ArH, 2H), 7.71 (d, $J = 2.6$ Hz, olefinic proton, 2H), 7.66 (t, $J = 7.3$ Hz, ArH, 1H), 7.56 (t, $J = 7.7$ Hz, ArH, 2H), 6.85 (d, $J = 8.6$ Hz, ArH, 2H). ^{13}C NMR (DMSO): δ 189.3, 160.5, 144.8, 138.3, 133.1, 131.3, 129.0, 128.6, 126.1, 118.8, 116.1. IR (KBr pellet, cm^{-1}): 3206, 1896, 1650, 1599, 1579, 1558, 977, 940, 833, 537.

Synthesis of Methyl 3,4,5-Trioctyloxybenzoate. Potassium carbonate (16.6 g, 120 mmol) was added to a solution of methyl 3,4,5-trihydroxybenzoate (3.6 g, 20 mmol) in DMF (100 mL) at room temperature. After being stirred at 60 °C for 2 h, 1-bromooctane (11.6 g, 60 mmol) was added dropwise. The reaction mixture was stirred at the same temperature for 8 h, cooled to room temperature, and poured into ice/water (1 L). The product was isolated by filtration and recrystallized from acetone (yield: 63%).

^{1}H NMR ($CDCl_3$): δ 7.24 (s, ArH, 2H), 4.0 (tt, overlap, OCH_2, 6H), 3.88 (s, OCH_3, 3H), 1.83−1.73 (m, OCH_2CH_2, 6H), 1.53−1.26 (m, alkyl chain proton, 30H), 0.9 (t, $J = 6.5$ Hz, CH_3, 9H).

Synthesis of Methyl 3,4,5-Tridecyloxybenzoate. This compound was synthesized by the same procedure described for the synthesis of methyl 3,4,5-trioctyloxybenzoate from methyl 3,4,5-trihydroxybenzoate (5.52 g, 30 mmol), potassium carbonate (24.9 g, 180 mmol), and 1-bromodecane (19.9 g, 90 mmol) in DMF (200 mL) at 60 °C (yield: 69%).

^{1}H NMR ($CDCl_3$): δ 7.24 (s, ArH, 2H), 4.0 (tt, overlap, OCH_2, 6H), 3.88 (s, OCH_3, 3H), 1.83−1.73 (m, OCH_2CH_2, 6H), 1.53−1.26 (m, alkyl chain proton, 42H), 0.9 (t, $J = 6.5$ Hz, CH_3, 9H).

Synthesis of Methyl 3,4,5-Tridodecyloxybenzoate. This compound was synthesized by the same procedure described for the synthesis of methyl 3,4,5-trioctyloxybenzoate from methyl 3,4,5-trihydroxybenzoate (5.52 g, 30 mmol), potassium carbonate (24.9 g, 180 mmol), and 1-bromododecane (22.43 g, 90 mmol) in DMF (200 mL) at 60 °C (yield: 67%).

^{1}H NMR ($CDCl_3$): δ 7.24 (s, ArH, 2H), 4.0 (tt, overlap, OCH_2, 6H), 3.88 (s, OCH_3, 3H), 1.83−1.73 (m, OCH_2CH_2, 6H), 1.53−1.26 (m, alkyl chain proton, 54H), 0.9 (t, $J = 6.5$ Hz, CH_3, 9H).

Synthesis of Methyl 3,4,5-Tritetradecyloxybenzoate. This compound was synthesized by the same procedure described for the synthesis of methyl 3,4,5-trioctyloxybenzoate from methyl 3,4,5-trihydroxybenzoate (5.52 g, 30 mmol), potassium carbonate (24.9 g, 180 mmol), and 1-bromotetradecane (25 g, 90 mmol) in DMF (200 mL) at 60 °C (yield: 58%).

^{1}H NMR ($CDCl_3$): δ 7.24 (s, ArH, 2H), 4.0 (tt, overlap, OCH_2, 6H), 3.88 (s, OCH_3, 3H), 1.83−1.73 (m, OCH_2CH_2, 6H), 1.53−1.26 (m, alkyl chain proton, 66H), 0.9 (t, $J = 6.5$ Hz, CH_3, 9H).

Synthesis of Methyl 3,5-Didecyloxybenzoate. This compound was synthesized by the same procedure described for the synthesis of methyl 3,4,5-tridecyloxybenzoate from methyl 3,5-dihydroxybenzoate (3.04 g, 20 mmol), potassium carbonate (11.06 g, 80 mmol), and 1-bromodecane (8.84 g, 40 mmol) in DMF (100 mL) at 60 °C (yield: 71%).

^{1}H NMR ($CDCl_3$): δ 7.1 (d, $J = 2.3$ Hz, ArH, 2H), 6.7 (d, $J = 2.3$ Hz, ArH, 1H), 4.05 (t, $J = 6.5$ Hz, OCH_2, 4H), 4.01 (s, OCH_3, 3H), 1.78 (m, OCH_2CH_2, 4H), 1.53−1.27 (m, alkyl chain proton, 28H), 0.88 (t, $J = 6.5$ Hz, CH_3, 6H).

Synthesis of 3,4,5-Trioctyloxybenzoic Acid. To a solution of methyl 3,4,5-trioctyloxybenzoate (7.81 g, 15 mmol) in 95% ethanol (100 mL) was added potassium hydroxide (1.68 g, 30 mmol). After being refluxed for 2 h, the mixture was cooled to room temperature, poured into water (1 L), and acidified with dilute hydrochloric acid to pH 1. The product was isolated by filtration and used for the next reaction without further purification (yield: 86%).

^{1}H NMR ($CDCl_3$): δ 7.3 (s, ArH, 2H), 3.9 (tt, overlap, OCH_2, 6H), 1.68 (m, OCH_2CH_2, 6H), 1.38−1.25 (m, alkyl chain proton, 30H), 0.87 (t, J = 6.5 Hz, CH_3, 9H).

Synthesis of 3,4,5-Tridecyloxybenzoic Acid. This compound was synthesized by the same procedure described for the synthesis of 3,4,5-trioctyloxybenzoic acid from methyl 3,4,5-tridecyloxybenzoate (9.07 g, 15 mmol) and potassium hydroxide (1.68 g, 30 mmol) in 95% ethanol (100 mL) (yield: 76%).

^{1}H NMR ($CDCl_3$): δ 7.3 (s, ArH, 2H), 4.0 (tt, overlap, OCH_2, 6H), 1.84−1.77 (m, OCH_2CH_2, 6H), 1.49−1.27 (m, alkyl chain proton, 42H), 0.88 (t, J = 6.5 Hz, CH_3, 9H).

Synthesis of 3,4,5-Tridodecyloxybenzoic Acid. This compound was synthesized by the same procedure described for the synthesis of 3,4,5-trioctyloxybenzoic acid from methyl 3,4,5-tridodecyloxybenzoate (10.33 g, 15 mmol) and potassium hydroxide (1.68 g, 30 mmol) in 95% ethanol (100 mL) (yield: 85%).

^{1}H NMR ($CDCl_3$): δ 7.3 (s, ArH, 2H), 4.0 (tt, overlap, OCH_2, 6H), 1.82−1.79 (m, OCH_2CH_2, 6H), 1.47−1.26 (m, alkyl chain proton, 54H), 0.88 (t, J = 6.5 Hz, CH_3, 9H).

Synthesis of 3,4,5-Tritetradecyloxybenzoic Acid. This compound was synthesized by the same procedure described for the synthesis of 3,4,5-trioctyloxybenzoic acid from methyl 3,4,5-tritetradecyloxybenzoate (11.6 g, 15 mmol) and potassium hydroxide (1.68 g, 30 mmol) in 95% ethanol (100 mL) (yield: 67%).

^{1}H NMR ($CDCl_3$): δ 7.3 (s, ArH, 2H), 3.9 (tt, overlap, OCH_2, 6H), 1.68 (m, OCH_2CH_2, 6H), 1.38−1.25 (m, alkyl chain proton, 66H), 0.87 (t, J = 6.5 Hz, CH_3, 9H).

Synthesis of 3,5-Didecyloxybenzoic Acid. This compound was synthesized by the same procedure described for the synthesis of 3,4,5-trioctyloxybenzoic acid from methyl 3,5-didecyloxybenzoate (6.48 g, 15 mmol) and potassium hydroxide (1.68 g, 30 mmol) in 95% ethanol (100 mL) (yield: 83%).

^{1}H NMR ($CDCl_3$): δ 7.24 (d, J = 2.3 Hz, ArH, 2H), 6.70 (d, J = 2.3, ArH, 1H), 4.00 (t, J = 6.5 Hz, OCH_2, 4H), 1.78 (m, OCH_2CH_2, 4H), 1.38−1.27 (m, alkyl chain proton, 28H), 0.88 (t, J = 6.5 Hz, CH_3, 6H).

Synthesis of 3,4,5-Trioctyloxybenzoyl Chloride. To a solution of 3,4,5-trioctyloxybenzoic acid (1.01 g, 2 mmol) in methylene chloride (15 mL) was added a catalytic amount of DMF. The reaction flask was cooled in an ice bath, and thionyl chloride (0.16 mL, 2.2 mmol) was added dropwise. Then, the ice bath was removed, and the reaction mixture was stirred for 4 h. After filtration and evaporation, the crude product was used for the next step without further purification.

Synthesis of 3,4,5-Tridecyloxybenzoyl Chloride. This compound was synthesized by the same procedure described for the synthesis of 3,4,5-trioctyloxybenzoyl chloride from 3,4,5-tridecyloxybenzoic acid (1.18 g, 2 mmol) and thionyl chloride (0.16 mL, 2.2 mmol) in methylene chloride (15 mL).

Synthesis of 3,4,5-Tridodecyloxybenzoyl Chloride. This compound was synthesized by the same procedure described for the synthesis of 3,4,5-trioctyloxybenzoyl chloride from 3,4,5-tridodecyloxybenzoic acid (1.35 g, 2 mmol) and thionyl chloride (0.16 mL, 2.2 mmol) in methylene chloride (15 mL).

Synthesis of 3,4,5-Tritetradecyloxybenzoyl Chloride. This compound was synthesized by the same procedure described for the synthesis of 3,4,5-trioctyloxybenzoyl chloride from 3,4,5-tritetradecyloxybenzoic acid (1.52 g, 2 mmol) and thionyl chloride (0.16 mL, 2.2 mmol) in methylene chloride (15 mL).

Synthesis of 3,5-Didecyloxybenzoyl Chloride. This compound was synthesized by the same procedure described for the synthesis of 3,4,5-trioctyloxybenzoyl chloride from 3,5-didecyloxybenzoic acid (1.35 g, 3 mmol) and thionyl chloride (0.24 mL, 3.3 mmol) in methylene chloride (15 mL).

Synthesis of 4-[3-(4-Cyanophenyl)-3-oxo-1-propenyl]phenyl 3,4,5-Trioctyloxybenzoate (1). To a solution of 4-hydroxy-4′-cyanochalcone (0.5 g, 2 mmol) in THF (40 mL) was added sodium hydride (60%, 0.08 g, 2 mmol). After being stirred for 2 h at room temperature, 3,4,5-trioctyloxybenzoyl chloride (1.05 g, 2 mmol) was added, and the mixture was stirred for 24 h at room temperature. After evaporation, the product was isolated by column chromatography on silica gel (14% ethyl acetate in hexane) (yield: 75%).

Anal. Calcd for $C_{47}H_{63}NO_6$: C, 76.49; H, 8.60; N, 1.90. Found: C, 76.65; H, 8.76; N, 1.64. ^{1}H NMR ($CDCl_3$): δ 8.10 (d, J = 6.7 Hz, ArH, 2H), 7.86 (d, J = 14.2 Hz, olefinic proton, 1H), 7.82 (d, J = 6.7 Hz, ArH, 2H), 7.72 (d, J = 8.7 Hz, ArH, 2H), 7.45 (d, J = 15.7 Hz, olefinic proton, 1H), 7.40 (s, ArH, 2H), 7.29 (d, J = 8.6 Hz, ArH, 2H), 4.06 (tt, overlap, OCH_2, 6H), 1.8 (m, OCH_2CH_2, 6H), 1.49−1.29 (m, alkyl chain proton, 30H), 0.88 (t, J = 6.5 Hz, CH_3, 9H). ^{13}C NMR ($CDCl_3$): δ 189.3, 165.0, 153.6, 153.3, 145.8, 143.7, 141.8, 133.0, 132.4, 129.3, 128.8, 123.7, 122.3, 121.5, 116.4, 108.9, 73.9, 69.6, 32.2, 32.1, 30.7, 29.8, 29.7, 29.6, 26.4, 23.0, 14.6. IR (KBr pellet, cm^{-1}): 2925, 2855, 2228, 1731, 1671, 1614, 1586, 973, 948, 860, 830, 796.

Synthesis of 4-[3-(4-Cyanophenyl)-3-oxo-1-propenyl]phenyl 3,4,5-Tridecyloxybenzoate (2). This compound was synthesized by the same procedure described for the synthesis of compound **1** from 4-hydroxy-4′-cyanochalcone (0.5 g, 2 mmol), sodium hydride (60%, 0.08 g, 2 mmol), and 3,4,5-tridecyloxybenzoyl chloride (1.22 g, 2 mmol) in THF (50 mL). After evaporation, the product was isolated by column chromatography on silica gel (20% ethyl acetate in hexane) and recrystallized from acetone (yield: 61%).

Anal. Calcd for $C_{53}H_{75}NO_6$: C, 77.43; H, 9.19; N, 1.70. Found: C, 77.81; H, 9.30; N, 1.70. ^{1}H NMR ($CDCl_3$): δ 8.10 (d, J = 6.7 Hz, ArH, 2H), 7.86 (d, J = 14.2 Hz, olefinic proton, 1H), 7.82 (d, J = 6.7 Hz, ArH, 2H), 7.72 (d, J = 8.7 Hz, ArH, 2H), 7.45 (d, J = 15.7 Hz, olefinic proton, 1H), 7.40 (s, ArH, 2H), 7.29 (d, J = 8.6 Hz, ArH, 2H), 4.06 (tt, overlap, OCH_2, 6H), 1.8 (m, OCH_2CH_2, 6H), 1.49−1.29 (m, alkyl chain proton, 42H), 0.88 (t, J = 6.5 Hz, CH_3, 9H). ^{13}C NMR ($CDCl_3$): δ 189.3, 165.0, 153.6, 153.4, 145.8, 143.7, 141.8, 132.9, 132.4, 130.2, 129.2, 123.7, 123.0, 121.5, 116.4, 109.0, 74.0, 69.7, 32.3, 32.2, 30.7, 30.1, 30.0, 29.9, 29.7, 29.6, 26.4, 23.0, 14.5. IR (KBr pellet, cm^{-1}): 2924, 2852, 2230, 1728, 1663, 1609, 1595, 979, 962, 947, 845, 832, 796.

Synthesis of 4-[3-(4-Cyanophenyl)-3-oxo-1-propenyl]phenyl 3,4,5-Tridodecyloxybenzoate (3). This compound was synthesized by the same procedure described for the synthesis of compound **1** from 4-hydroxy-4′-cyanochalcone (0.8 g, 3.2 mmol), sodium hydride (60%, 0.13 g, 3.2 mmol), and 3,4,5-tridodecyloxybenzoyl chloride (2.2 g, 3.2 mmol) in THF (50 mL). After evaporation, the product was isolated by column chromatography on silica gel (20% ethyl acetate in hexane) and recrystallized from acetone (yield: 82%).

Anal. Calcd for $C_{59}H_{87}NO_6$: C, 78.19; H, 9.68; N, 1.55. Found: C, 78.22; H, 10.04; N, 1.25. ^{1}H NMR ($CDCl_3$): δ 8.10 (d, J = 6.7 Hz, ArH, 2H), 7.86 (d, J = 14.2 Hz, olefinic proton, 1H), 7.82 (d, J = 6.7 Hz, ArH, 2H), 7.72 (d, J = 8.7 Hz, ArH, 2H), 7.45 (d, J = 15.7 Hz, olefinic proton, 1H), 7.40 (s, ArH, 2H), 7.29 (d, J = 8.6 Hz, ArH, 2H), 4.06 (tt, overlap, OCH_2, 6H), 1.8 (m, OCH_2CH_2, 6H), 1.49−1.29 (m, alkyl chain proton, 54H), 0.88 (t, J = 6.5 Hz, CH_3, 9H). ^{13}C NMR ($CDCl_3$): δ 189.3, 165.0, 153.6, 153.4, 145.8, 143.7, 141.8, 132.9, 132.4, 130.2, 129.2, 123.7, 123.0, 121.5, 116.4, 109.0, 74.0, 69.7, 32.3, 32.2, 30.7, 30.1, 30.0, 29.9, 29.7, 29.6, 26.4, 23.0, 14.4. IR (KBr pellet, cm^{-1}): 2953, 2918, 2851, 2228, 1732, 1670, 1614, 1598, 979, 948, 936, 861, 826, 801.

Synthesis of 4-[3-(4-Cyanophenyl)-3-oxo-1-propenyl]phenyl 3,4,5-Tritetradecyloxybenzoate (4). This compound was synthe-

sized by the same procedure described for the synthesis of compound **1** from 4-hydroxy-4′-cyanochalcone (0.75 g, 3 mmol), sodium hydride (60%, 0.12 g, 3 mmol), and 3,4,5-tritetradecyloxybenzoyl chloride (2.33 g, 3 mmol) in THF (40 mL). After evaporation, the product was isolated by column chromatography on silica gel (14% ethyl acetate in hexane) and recrystallized from acetone (yield: 76%).

Anal. Calcd for $C_{65}H_{99}NO_6$: C, 78.82; H, 10.07; N, 1.41. Found: C, 78.50; H, 10.33; N, 1.22. ^{1}H NMR ($CDCl_3$): δ 8.10 (d, $J = 6.7$ Hz, ArH, 2H), 7.86 (d, $J = 14.2$ Hz, olefinic proton, 1H), 7.82 (d, $J = 6.7$ Hz, ArH, 2H), 7.72 (d, $J = 8.7$ Hz, ArH, 2H), 7.45 (d, $J = 15.7$ Hz, olefinic proton, 1H), 7.40 (s, ArH, 2H), 7.29 (d, $J = 8.6$ Hz, ArH, 2H), 4.06 (tt, overlap, OCH_2, 6H), 1.8 (m, OCH_2CH_2, 6H), 1.49−1.29 (m, alkyl chain proton, 66H), 0.88 (t, $J = 6.5$ Hz, CH_3, 9H). ^{13}C NMR ($CDCl_3$): δ 189.3, 165.0, 153.6, 153.4, 145.8, 143.7, 141.8, 132.9, 132.4, 130.2, 129.2, 123.7, 123.0, 121.5, 116.4, 109.0, 74.0, 69.7, 32.3, 32.2, 30.7, 30.1, 30.0, 29.9, 29.7, 29.6, 26.4, 23.0, 14.4. IR (KBr pellet, cm^{-1}): 2919, 2850, 2228, 1760, 1731, 1660, 1613, 1596, 981, 959, 857, 829, 802.

Synthesis of 4-[3-(4-Cyanophenyl)-3-oxo-1-propenyl]phenyl 3,5-Didecyloxybenzoate (5). This compound was synthesized by the same procedure described for the synthesis of compound **1** from 4-hydroxy-4′-cyanochalcone (0.3 g, 1.33 mmol), sodium hydride (60%, 0.05 g, 1.3 mmol), and 3,5-didecyloxybenzoyl chloride (0.68 g, 1.5 mmol) in THF (50 mL). After evaporation, the product was isolated by column chromatography on silica gel (25% ethyl acetate in hexane) (yield: 30%).

Anal. Calcd for $C_{43}H_{55}O_5$: C, 77.56; H, 8.33; N, 2.10. Found: C, 77.90; H, 8.41; N, 1.90. ^{1}H NMR ($CDCl_3$): δ 8.10 (d, $J = 6.7$ Hz, ArH, 2H), 7.86 (d, $J = 14.2$ Hz, olefinic proton, 1H), 7.82 (d, $J = 6.7$ Hz, ArH, 2H), 7.72 (d, $J = 8.7$ Hz, ArH, 2H), 7.45 (d, $J = 15.7$ Hz, olefinic proton, 1H), 7.29 (dd, overlap, ArH, 4H), 6.72 (d, $J = 2.3$ Hz, ArH, 1H), 4.00 (t, $J = 6.5$ Hz, OCH_2, 4H), 1.8 (m, OCH_2CH_2, 4H), 1.49−1.29 (m, alkyl chain proton, 28H), 0.88 (t, $J = 6.5$ Hz, CH_3, 6H). ^{13}C NMR ($CDCl_3$): δ 189.3, 160.7, 154.5, 149.1, 145.8, 141.8, 132.9, 132.4, 130.2, 129.2, 122.9, 121.6, 116.4, 115.0, 112.3, 108.6, 68.8, 32.3, 29.9, 29.7, 29.6, 29.5, 26.3, 23.0, 14.4. IR (KBr pellet, cm^{-1}): 2922, 2850, 2227, 1730, 1655, 1594, 985, 955, 887, 808.

Synthesis of 4-(3-Oxo-3-phenyl-1-propenyl)phenyl 3,4,5-Tridecyloxybenzoate (6). This compound was synthesized by the same procedure described for the synthesis of compound **1** from 4-hydroxychalcone (0.3 g, 1.33 mmol), sodium hydride (60%, 0.05 g, 1.3 mmol), and 3,4,5-tridecyloxybenzoyl chloride (0.914 g, 1.5 mmol) in THF (30 mL). After evaporation, the product was isolated by column chromatography on silica gel (20% ethyl acetate in hexane) (yield: 85%).

Anal. Calcd for $C_{52}H_{76}O_6$: C, 78.35; H, 9.61. Found: C, 78.27; H, 9.77. ^{1}H NMR ($CDCl_3$): δ 8.03 (d, $J = 7.1$ Hz, ArH, 2H), 7.83 (d, $J = 15.7$ Hz, olefinic proton, 1H), 7.72 (d, $J = 8.6$ Hz, ArH, 2H), 7.59 (t, $J = 7.3$ Hz, ArH, 1H), 7.52 (dd, overlap, ArH + olefinic proton, 3H), 7.41 (s, ArH, 2H), 7.27 (d, overlap to $CHCl_3$, $J = 8.0$ Hz, ArH, 2H), 4.06 (tt, overlap, OCH_2, 6H), 1.8 (m, OCH_2CH_2, 6H), 1.49−1.29 (m, alkyl chain proton, 42H), 0.88 (t, $J = 6.5$ Hz, CH_3, 9H). ^{13}C NMR ($CDCl_3$): δ 190.7, 165.1, 153.3, 144.1, 133.2, 133.0, 130.0, 129.0, 128.8, 123.8, 122.8, 122.5, 109.0, 74.0, 69.6, 32.3, 30.7, 30.1, 30.0, 29.9, 29.7, 29.6, 26.4, 23.0, 14.5. IR (KBr pellet, cm^{-1}): 2953, 2920, 2851, 1745, 1660, 1594, 989, 958, 942, 850, 815, 792.

Photoreaction of Compound 2. A gel of compound **2** from *n*-hexane (3 wt %) and a solution of compound **2** in THF (3 wt %) were irradiated with UV light (5 mW/cm^2) for 30 min at room temperature. The products were isolated by column chromatography on silica gel (14% ethyl acetate in *n*-hexane). ^{1}H NMR ($CDCl_3$) for a dimer: δ 7.89 (d, $J = 8.3$ Hz, ArH, 4H), 7.72 (d, $J = 8.3$ Hz, ArH, 4H), 7.37 (s, ArH, 4H), 7.09 (br, ArH, 6H), 4.75 (d, $J = 5.6$ Hz, cyclobutane ring proton, 2H), 4.44 (d, $J = 5.8$ Hz, cyclobutane ring proton, 2H), 4.04 (tt, OCH_2, 12H), 1.8 (m, OCH_2CH_2, 6H), 1.49−1.29 (m, alkyl chain proton, 84H), 0.88 (t, $J = 6.5$ Hz, CH_3, 18H). ^{1}H NMR ($CDCl_3$) for a cis-isomer: δ 8.02 (d, $J = 8.6$ Hz, ArH, 2H), 7.72 (d, $J = 8.6$ Hz, ArH, 2H), 7.52 (d, $J = 8.8$, ArH, 2H), 7.36 (s, ArH, 2H), 7.14 (d, $J = 12.0$ Hz, olefinic proton, 1H), 7.10 (d, $J = 8.6$ Hz, ArH, 2H), 6.64 (d, $J = 12.8$ Hz, olefinic proton, 1H), 4.03 (tt, overlap, OCH_2, 6H), 1.8 (m, OCH_2CH_2, 6H), 1.49−1.29 (m, alkyl chain proton, 42H), 0.88 (t, $J = 6.5$ Hz, CH_3, 9H).

Acknowledgment. Financial support from the Korea Science and Engineering Foundation (R11-2005-000-10343-0) is gratefully acknowledged. The work at Seoul National University used HOMRC facilities supported by KOSEF.

CM061282Q