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Self-Organization of Supramolecular Complex Composed of Rigid Dendritic Porphyrin and Fullerene

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The synthetic availability of dendrimers in a wide range of sizes makes them attractive molecular components for the construction of electronic/photonic nanodevices and smart nanomaterials. Self-organization of dendrimers can provide rapid access to the generation of controlled nanoscopic objects. Various studies have suggested that self-organization of dendrimers and monodendrons can form nanoscopic objects in solution and the bulk through intermolecular noncovalent interaction.[1] Liquid crystalline behaviors of dendritic materials have also received much attention as a methodology to generate macroscopic organized systems exhibiting layered, columnar, and cubic phase structures.[2] To date, liquid crystalline dendrimers have been designed by two different approaches. The introduction of chemically rigid mesogenic branching units or end groups into flexible dendritic architectures can induce liquid crystalline order.[3] On the other hand, Moore et al. discovered the liquid crystallinity of rigid phenylacetylene dendrimers by attachment with flexible oligo(ethylene oxide) chains on the periphery.[4] Their rigid dendritic cores provide mesogenic architectures, and the stacking of numerous rigid dendrimers allows the formation of segregated columnar aggregates.[5]

We earlier reported the convergent syntheses of phenylene-based rigid dendritic porphyrins and their unique functionalities.[6] In this communication, we report the self-organization of rigid dendritic porphyrins, with 8 or 16 long alkyl chains on their periphery. The introduction of long flexible alkyl chains onto the periphery of the rigid dendrimers may lead to the formation of liquid crystalline phases by the occurrence of phase segregation between the rigid dendritic interior and peripheral alkyl chains. Liquid crystalline porphyrins have been synthesized by attaching long alkyl chains with a planar porphyrin molecule.[7] Suslick et al. reported the discotic liquid crystallinity of octa-meta-substituted tetraphenylporphyrins having two protected pockets on both of its faces.[8] Our synthesized dendritic porphyrins also possess regulated nanospaces, which may permit the inclusion of guest molecules without loss of the liquid crystal phase.

Two generations of phenylene-based dendritic porphyrins **1** and **2** were synthesized from 4-dodecylphenylboronic acid, 3,5-dibromo-1-(trimethylsilyl)benzene, and 5,10,15,20-tetrakis(3′,5′-dibromophenyl)porphyrin. All of the intermediate and final dendritic porphyrins were fully characterized by ^1H and ^{13}C NMR spectroscopy, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy, UV−visible spectroscopy, HPLC, and elemental analysis.

Table 1. Transition Temperatures (°C) of Liquid Crystalline Dendrimers **1** and **2**[a]

dendrimers	M^b (g mol^{-1})	thermal transitions[c]
1	2570	g −50 X 43 (3.3) i
2	5134	g −54 X 39 (8.2) Col_r 110 (22.1) i
2+C_{60}[d]	-	K 99 (10.5) Col 250 (30.4) i

[a] Transition enthalpies (KJ mol^{-1}) are given in parentheses. [b] Determined by MALDI-TOF-Ms. [c] Heating rate 10 °C/min; g: glass, X: unidentified phase (X phase could not be assigned by XRD and TPOM), Col_r: rectangular columnar mesophase, Col: columnar mesophase, i: isotropic liquid. [d] [**2**]/[C_{60}] = 1.0.

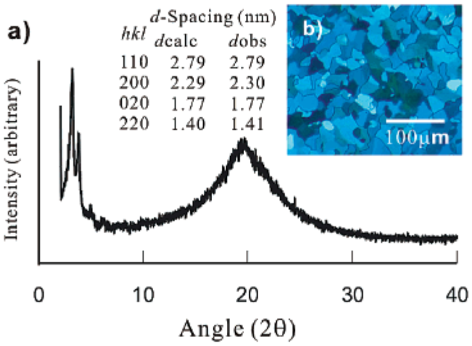
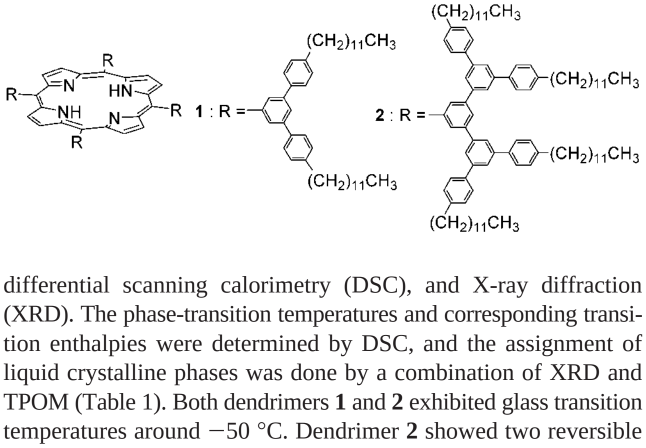


Figure 1. (a) Temperature-controlled XRD patterns of **2** at 100 °C and assigned Miller indices (*hkl*). (b) Polarized optical micrograph of **2** at 75 °C after slowly cooling from the isotropic phase.



The liquid crystalline properties of **1** and **2** were studied by temperature-controlled polarizing optical microscopy (TPOM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). The phase-transition temperatures and corresponding transition enthalpies were determined by DSC, and the assignment of liquid crystalline phases was done by a combination of XRD and TPOM (Table 1). Both dendrimers **1** and **2** exhibited glass transition temperatures around −50 °C. Dendrimer **2** showed two reversible transitions at 39 and 110 °C upon heating in DSC, while **1** exhibited only one transition at 43 °C. When the isotropic liquid of **2** was cooled slowly, a colored mosaic texture appeared in the range of 40−110 °C under the polarized microscope (Figure 1). The XRD studies on **2** at 100 °C gave four Bragg reflections, indicating that

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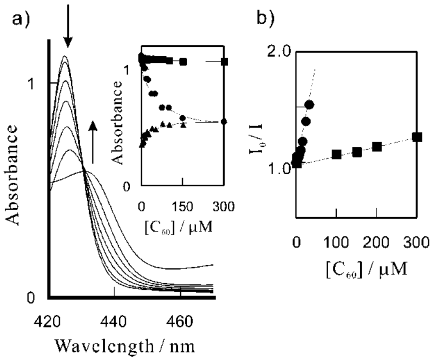

Figure 2. (a) Effect of C_{60} concentration on the absorption spectrum of **2** in toluene solution at room temperature: $[\mathbf{2}] = 3.0\ \mu M$; $[C_{60}]/[\mathbf{2}] = 0$, 1.0, 2.0, 4.0, 8.0, 12.5, 25.0. Arrows indicate the direction of the spectral change. The inset shows the absorbance change of the relationship between C_{60} concentration and absorbance at 425 nm for **1** (■) and **2** (●), and at 433 nm for **2** (▲). (b) Normalized fluorescence intensities of **1** (■) and **2** (●) in degassed toluene depending on the C_{60} concentration: excitation 429 nm, emission 650 nm.

the mesophase consisted of a rectangular columnar structure (Col_r) with lattice constants $a = 4.57$ nm and $b = 3.54$ nm, and the number of molecules in the unit cell $Z = 2$ (Figure 1). The phenylene-based rigid dendritic core in **2** acted as a mesogenic architecture, and the packing of the dendritic cores resulted in the formation of the columnar mesophase structure. On the other hand, the first generation dendrimer **1** did not show liquid crystalline behaviors in any temperature range under TPOM.

Previously, we found that a rigid phenylene-based dendritic porphyrin includes C_{60} within its regulated nanospace through noncovalently interaction.[6b] The inclusion of C_{60} within the nanospace of **2** may affect the mesophase structure.[9] The absorption spectra of **2** in toluene solution changed upon the addition of C_{60}, and the absorption spectral changes showed a clear isosbestic point at 429.0 nm (Figure 2a).[10] In marked contrast to the behavior of the *tert*-butyl-terminated dendritic porphyrin, which formed a precipitate by the addition of C_{60}, **2** with C_{60} was still soluble in toluene solution.[6b] Titration study on **2** with C_{60} on the basis of Job's method indicated the formation of a 1:1 complex.[11] The Soret band of the porphyrin moiety was red-shifted from 424 to 433 nm. The association constant was evaluated to be $2.57 \times 10^4\ M^{-1}$ from the spectral changes. In contrast, the first-generation dendrimer **1** showed no spectral changes in the absorption spectra after the addition of a large excess of C_{60}. The fluorescence of **2** was quenched even at a low C_{60} concentration, suggesting the formation of an associated complex (Figure 2b). Moreover, three reversible electroreduction potentials of C_{60} in the presence of **2** are more negative than that the potentials for the reduction of only C_{60} by 160−370 mV.[12] These results indicate that the second-generation dendrimer **2** can form a stable complex with C_{60}.

Figure 3a shows UV−vis spectra of the spin-coated film of **2** in the presence of an equimolar amount of C_{60} on the quartz plate. The Soret band of the spin-coated film of the mixture also shifted to the longer wavelength, indicating the formation of a complex between **2** and C_{60} in the film. The thin film of the mixture was homogeneous and showed no irregular aggregates of C_{60} by optical microscopy and atomic force microscopy measurements.[13] The 1:1 complex of **2** and C_{60} exhibited two reversible transitions at 99 and 250 °C by DSC (Table 1), and TOPM revealed a needlelike texture in the range of 100−250 °C (Figure 3b). The XRD pattern of the 1:1 mixture of **2** and C_{60} differed from that of **2** alone, indicating that the inclusion of C_{60} within the nanospace of **2** strongly affected the mesophase structure in the thermotropic liquid-crystalline phase. Detailed SAXS and SANS analyses of the self-organized film of **2** with C_{60} are in progress.

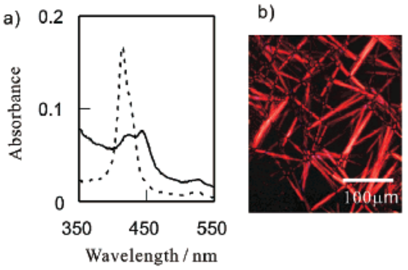

Figure 3. (a) UV−vis spectra of spin-cast film of **2** (dashed line) and the **2**−C_{60} complex (solid line). (b) Polarized optical micrograph of the **2**−C_{60} complex at 200 °C. The domains were grown from the isotropic phase.

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Supporting Information Available: Synthetic procedures, electrochemical results, estimation of *Z*, optical and atomic force micrographs of thin films for **2** and the complex of **2** with C_{60}, and XRD pattern of the complex (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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