A Hydrogen-bonded Supramolecular Hexagonal Columnar Liquid Crystal Composed of a Tricarboxylic Triphenylene and Monopyridyl Dendrons

Shinsuke Ishihara, Yuusuke Furuki, and Shinji Takeoka*
Department of Applied Chemistry, Graduate School of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555

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Tricarboxylic triphenylene (**TPC5**) and monopyridyl dendron (**DenC12**) were mixed in 1:2, 1:3, and 1:4 molar ratios, and investigation by IR, DSC, and XRD studies proved that **TPC5** and **DenC12** self-assembled to form a hexagonal columnar liquid crystal with 1:3 molar stoichiometry via complementary hydrogen-bonds.

Recently, uniform dispersion of low molecular weight compounds at the center of an array of surrounding heterogeneous molecules[1] has been attracting attention in the fabrication of supramolecular nanomaterials such as nanowires,[2] nanorings,[3] and nanoporous polymers.[4] In particular, several reports have focused on supramolecular columnar liquid crystals composed of an aromatic core and surrounding fan-shaped molecules;[5] however, derivatives of triphenylene,[6] which have great potential in the development of optoelectric nanodevices, have received little attention as core molecules.

In order to fabricate a supramolecular columnar liquid crystal composed of a triphenylene core and surrounding fan-shaped molecules, a symmetric structured triphenylene derivative, 2,6,10-tris(carboxymethoxy)-3,7,11-tris(pentyloxy)triphenylene (**TPC5**), was designed with three carboxymethoxy groups for hydrogen-bonding and three pentyloxy groups to increase compatibility with the surrounding fan-shaped molecules (Figure 1). Incidentally, a symmetric-structured triphenylene is considered promising as a core molecule, because the alternation of the pentyloxy group in **TPC5** with a chiral alkoxy group, a semi-fluoroalkoxy group, or a stimuli-responsive side chain will lead to amplification of the core molecule's properties throughout the entire supramolecular columnar liquid crystal.

As a complementary companion for **TPC5**, the fan-shaped dendron 3,5-bis(3,4-bisdodecyloxybenzyloxy)-*N*-(pyridin-4-yl)-benzamide (**DenC12**) was prepared, having a pyridyl group for hydrogen-bonding between the carboxylic acid groups in **TPC5**[7] (Figure 1). **DenC12** belongs to a class of second generation dendrons and has a wide, flat structure, and the μ value of the dendron, assigned to the number of molecules per disc of the column, is estimated to be 3 or 4, considering the structurally similar dendrons reported by Percec et al.[8] Therefore, **TPC5** and **DenC12** are quite complementary, not only in the hydrogen-bonding system, but also in rotational symmetry.

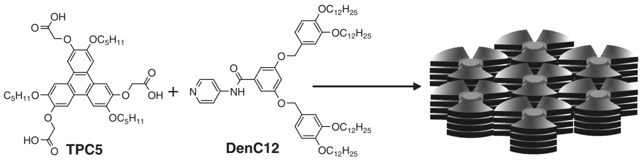

Figure 1. Chemical structures of **TPC5** and **DenC12**, and a self-assembled structure of **TPC5–DenC12 1/3**.

TPC5 was mixed with **DenC12** in 1:2, 1:3, and 1:4 molar ratios, and then the mixtures were dissolved in benzene/methanol, heated at 40 °C, and treated with sonication for 5 min. The resulting homogeneous solutions were dried in vacuo, and the complexes **TPC5–DenC12 1/2**, **TPC5–DenC12 1/3**, and **TPC5–DenC12 1/4** were obtained.

The formation of complementary hydrogen bonds between the carboxylic acid in **TPC5** and the pyridine in **DenC12** was confirmed by infrared (IR) spectrometry. The IR absorption of **TPC5** at 1729 cm^{-1} assigned to the C=O stretching vibration mode of the free carboxylic acid decreased slightly after being mixed with more than three equivalents of **DenC12**, at which time an IR absorption at 1638 cm^{-1} assigned to the hydrogen-bonded C=O stretching vibration mode subsequently appeared.[9] In addition, the solubility of **TPC5** in benzene was drastically improved upon mixing with more than three equivalents of **DenC12**, which supports that **TPC5** forms a hydrogen-bonded complex with three equivalents of **DenC12**, with the hydrophobic dodecyloxy chains directed toward the outside of the resulting disc-like assemblies.

The precise stoichiometry forming the most suitable hydrogen-bonded complex was confirmed by a differential scanning calorimetry (DSC) analysis. The DSC thermogram in Figure 2 indicated that the components of **TPC5–DenC12 1/3** were completely compatibilized, with the subsequent thermally reversible mesophase appearing from 66.9 to 1.1 °C upon cooling and from 7.2 to 76.7 °C upon heating. The DSC thermogram of **TPC5–DenC12 1/2** in Figure 2 is almost similar to that of **TPC5–DenC12 1/3**, because the pure **TPC5** region due to the formation of the most appropriate 1:3 assembly had no thermal phase transition from −20 to 140 °C. On the other hand, **TPC5–DenC12 1/4** revealed an extra endothermal peak at 94.6 °C,

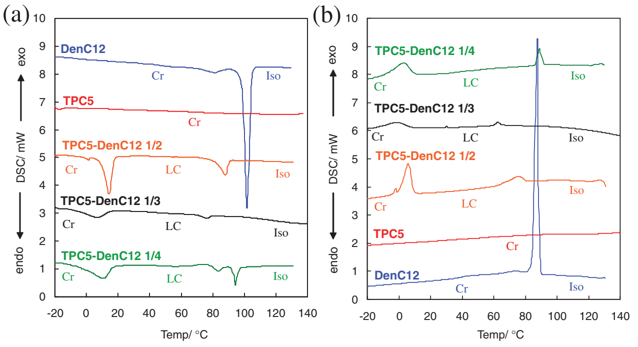

Figure 2. DSC thermograms of **TPC5**, **DenC12**, **TPC5–DenC12 1/2**, **TPC5–DenC12 1/3**, and **TPC5–DenC12 1/4** upon (a) 2nd heating and (b) 2nd cooling at a scan rate of 10 °C/min.

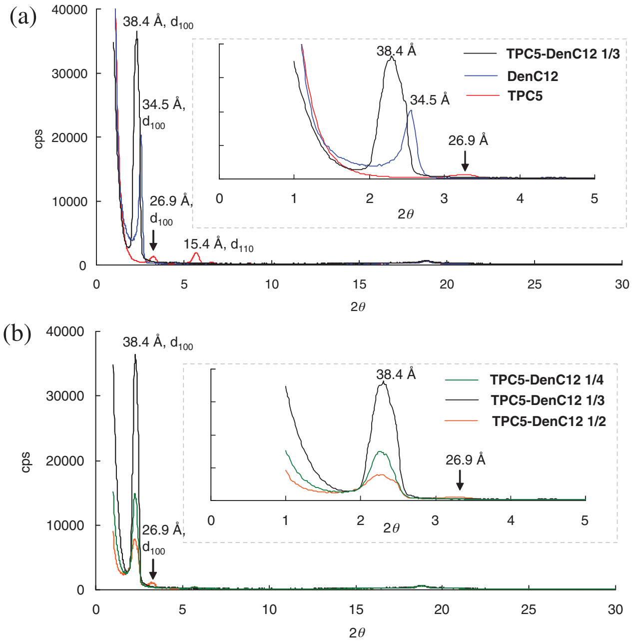

Figure 3. XRD patterns of (a) **TPC5**, **DenC12**, and **TPC5–DenC12 1/3**; (b) **TPC5–DenC12 1/2**, **TPC5–DenC12 1/3**, and **TPC5–DenC12 1/4** at mesophase states upon cooling.

which was assigned to the melting of the pure **DenC12** region. Therefore, the DSC results prove that **TPC5** and **DenC12** self-organized to form a supramolecular complex only in the 1:3 ratio, and this result agreed well with the stoichiometry of the hydrogen-bonding units.

The X-ray diffraction (XRD) patterns of **DenC12** and **TPC5–DenC12 1/3** shown in Figure 3a gave strong diffraction peaks from d_{100} and weak diffraction peaks from d_{110} and d_{200}, which are typical to a disordered hexagonal columnar lattice. The diameters of the columns were calculated to be 31.4, 39.8, and 44.4 Å, respectively. The degree of change in the extended diameter of the column by 4.6 Å from **DenC12** to **TPC5–DenC12 1/3** is somewhat smaller than the molecular size of **TPC5** (approximately 14 Å) owing to the buffering effect of alkyl chain packing. The stronger XRD peak intensity of **TPC5–DenC12 1/3** compared to that of **TPC5–DenC12 1/2** or **TPC5–DenC12 1/4** indicates that **TPC5–DenC12 1/3** is the most structured assembly. The XRD pattern of **TPC5–DenC12 1/2** in Figure 3b is obviously derived from the two segregational domains of **TPC5–DenC12 1/3** and pure **TPC5**. On the other hand, the XRD pattern of **TPC5–DenC12 1/4** in Figure 3b is almost identical to the patterns of **TPC5–DenC12 1/3**, because the segregational domain of pure crystalline **DenC12** is compatible with the adjacent liquid crystalline state of **TPC5–DenC12 1/3** at 60 °C on cooling from a hot melt state, as is shown in the DSC thermogram of **TPC5–DenC12 1/4** in Figure 2.

In conclusion, fabrication of a hydrogen-bonded hexagonal columnar liquid crystal composed of **TPC5** and **DenC12** has been effected, and the precise stoichiometry for constructing the most suitable supramolecular complex was estimated to be a 1:3 ratio. The **TPC5–DenC12 1/3** reported here is the first example of a supramolecular columnar liquid crystal composed of a triphenylene and dendrons organized by noncovalent binding, which can serve as a simple and fundamental model in the fabrication of novel supramolecular nanomaterials. For example, based on this model, triphenylene derivatives having chiral alkoxy, semi-fluoroalkoxy, or stimuli-responsive side chains instead of the pentyloxy group of **TPC5** are being developed to evaluate dynamic transformation throughout the entire supramolecular structure. Furthermore, transcription of structural information of the triphenylene derivatives at the center of the surrounding dendrons, and fabrication of triphenylene nanorods or nanoporous dendron films by molecular imprinting techniques are also now in progress.

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9 Synthesis, IR spectra, polarized optical textures, and XRD were shown in the supporting information. Supporting Information is available electronically on the CSJ-Journal Web site: http://www.csj.jp/journals/chem-lett/index.html.

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