

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 molecules¹ 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 TPC5⁷ (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 hydro-

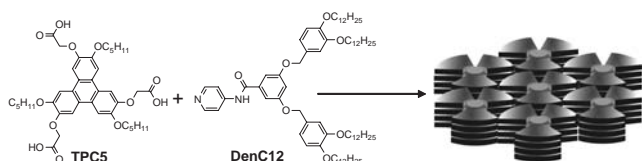


Figure 1. Chemical structures of TPC5 and DenC12, and a self-assembled structure of TPC5-DenC12 1/3.

gen-bonding system, but also in rotational symmetry.

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,

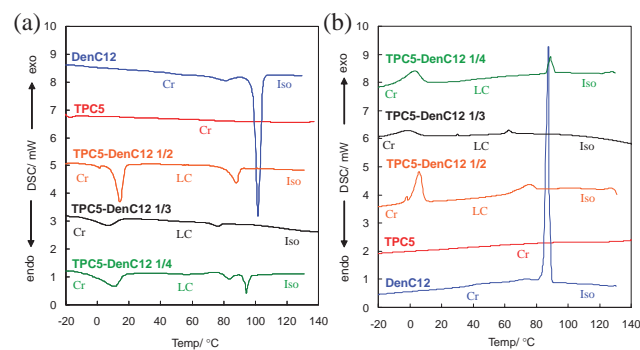


Figure 2. DSC thermograms of TPC5, DenC12, TPC5-DenC12 1/2, TPC5-DenC12 1/3, and TPC5-DenC12 1/4 upon (a) 2nd heating and (b) 2nd cooling at a scan rate of 10 °C/min.

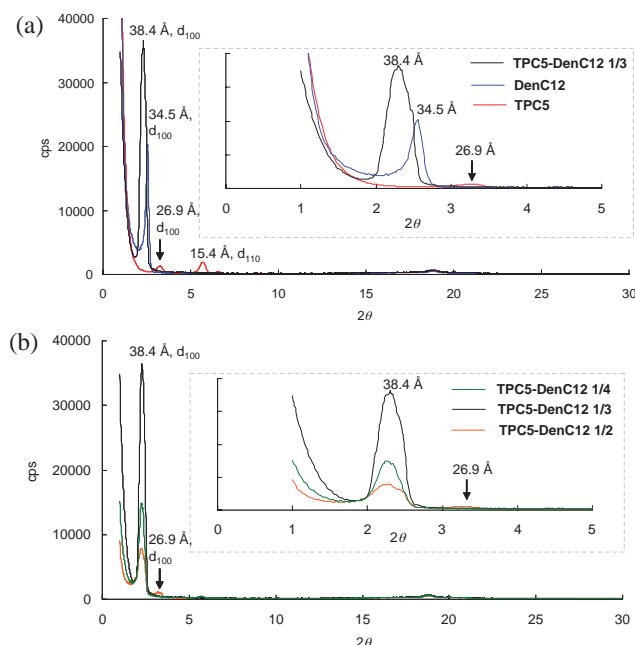


Figure 3. XRD patterns of (a) TPC5, DenC12, and TPC5–DenC12 1/3; (b) TPC5–DenC12 1/2, TPC5–DenC12 1/3, and TPC5–DenC12 1/4 at mesophase states upon cooling.

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>.