A columnar liquid-crystalline shape-persistent macrocycle having a nanosegregated structure[†]

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A shape-persistent macrocyclic molecule having glutamic acid and oligooxyethylene moieties exhibits a hexagonal columnar liquid-crystalline phase at ambient temperature through nanosegregation and the formation of intermolecular hydrogen bonding.

Liquid-crystalline (LC) molecules forming nanosegregated structures can be applied to anisotropic functional materials.¹⁻⁶ A number of LC molecules with new and exotic shapes have been prepared.^{2,7-9} Among the structural motifs of liquid crystals, macrocycles have attracted attention.¹⁰⁻¹⁴ Conjugated, rigid macrocycles are called "shape-persistent macrocycles" (SPMs).¹³⁻¹⁷ Ions and molecules can be incorporated into the nanometer-size pores of SPMs.¹⁸⁻²⁵ If these SPMs can be arranged into mesomorphic tubular assemblies, mobile materials with internal 1D functional nano-space will be obtained. Several LC SPMs have already been reported.^{2,26-30} However, these compounds exhibited LC phases at relatively high temperature ranges. Moreover, the phases were often discotic nematic phases due to weak interactions between the rings.²⁶⁻²⁸

To achieve LC 1D stacks of aromatic molecules, introduction of nanosegregated structures and intermolecular hydrogen bonding into the molecular design is considered to be an important approach.^{2,31-33} Herein we report on an LC SPM having fanshaped L-glutamic acid derivatives bearing bis(alkyloxy)phenyl moieties on its outer part, and oligooxyethylene moieties on its inner part (Fig. 1). The glutamic acid derivatives can be used as a molecular building block to produce stable columnar LC materials via hydrogen bonding.³⁴⁻⁴⁰ Stable 1D assemblies are expected to form through the formation of intermolecular hydrogen bonds. Oligooxyethylene moieties are introduced to fill the internal space of the columns. Moreover, oligooxyethylene moieties are polar and they should be incompatible with the nonpolar alkyl moieties. The segregation between internal and external substituents of SPMs may suppress the formation of nematic discotic phases.

Macrocycle 1 was synthesized from a 3,5-diethynylbenzene derivative of the glutamic acid moiety (2). The dimeric compound was prepared using oxidative Hay coupling⁴¹ of 2. The Eglinton–Glaser coupling⁴² of the dimer under high dilution conditions gave cyclic hexamer 1 as a main product (for detailed synthetic scheme, see ESI†). Cyclic tetramer and octamer were obtained as

by-products, and separated by gel permeation chromatography. Linear oligomers were not formed, which was confirmed by ^1H NMR.

Compound 1 exhibited an LC phase from 0 to 89 °C upon heating. In this temperature region, birefringence was observed by polarizing microscopy. The texture was nonspecific to columnar phases, and the size of the LC domains was smaller than 10 μ m (Fig. 2a). However, the material could easily be sheared. The boundaries of the domains disappeared after shearing, which indicates the uniaxial orientation of the columns (Fig. 2b). Fig. 3 presents the DSC thermogram of 1. The thermogram shows sharp transition peaks, despite the high molecular weight (8165.8 g mol⁻¹) of 1.

The small angle X-ray diffraction profile for 1 at 25 °C is shown in Fig. 4. The diffraction pattern gives three reflections of 5.17 (100), 2.97 (110), and 2.63 nm (200). The ratio of the *d*-spacing is $1:1/\sqrt{3}:1/2$, indicating a hexagonal columnar (Col_h) arrangement. The intercolumnar distance of 1, which corresponds to the lattice parameter, is 6.0 nm. By molecular modeling, the diameter of 1 was estimated to be 6.0 nm, which is in agreement with the experimental result (Fig. 5). The oxyethylene chains are considered to be assembled in the center of the hexagonal columns, because of incompatibility with alkyl chains.

The diameter of the conjugated macrocycle part was estimated to be 1.8 nm by molecular modeling. The diffraction of compound 1 also exhibited a broad halo around 0.5 nm (see ESI[†]). No sharp peaks ascribed to the order of the rings in the direction of the columnar axis were seen in the diffraction pattern.

It is of interest that the precursor **2**, which is not macrocyclic, showed only a crystalline phase. It was reported that imidazolium salts having similar fan-shaped L-glutamic acid derivatives showed columnar LC phases.⁴⁰ The polarity of oligooxyethylene chains is lower than that of imidazolium salts, which would be the reason why the precursors were not mesomorphic. However, with the help of the macrocycle core, compound **1** formed stable columns in which the oligooxyethylene moieties were segregated from the alkyl chains at the periphery.

The infrared spectra for **1** were obtained in the neat state to examine the molecular interactions between the stacked macrocycles. The broad N–H stretching band was observed at 3300 cm⁻¹ at 25 °C in the Col_h state. The C=O stretching band of the glutamic acid moieties was seen at 1639 cm⁻¹ at 25 °C. These results show the formation of intermolecular hydrogen bonds. The hydrogen bonds between macrocycles should contribute to the induction of the one-dimensional columnar assembly (Fig. 5). It is considered that the rotation of hydrogen bonds. However, rotational disorder of the assembled single column in the hexagonal lattice may be possible.

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[†] Electronic supplementary information (ESI) available: Synthetic scheme, wide angle X-ray diffraction pattern, and IR spectrum of compound 1; experimental details for compounds **1–6**; ¹H and ¹³C NMR spectra for compounds **3–6**. See DOI: 10.1039/b908669b







Fig. 1 Molecular structures of liquid-crystalline macrocycle 1 and its precursor 2.

In summary, a macrocyclic columnar liquid crystal was prepared from a shape-persistent macrocycle. For the design of LC assemblies, the combination of the molecular shape, nanosegregation of the building blocks, and the intermolecular interactions is important.^{2-4,43,44} The molecule formed columnar structures guided by the nanosegregation between the oligooxyethylene chains inside the macrocycle and the alkyl chains



Fig. 2 Polarizing optical photomicrographs of 1 in the Col_h phase at $87 \,^{\circ}$ C (a) on simple cooling, (b) after applying mechanical shear. Directions are A: analyzer; P: polarizer; S: shearing.



Fig. 3 DSC thermogram of 1 on the 2nd heating.



Fig. 4 Small angle X-ray diffraction pattern of 1 at 25 °C. "Kapton" is the diffraction peak of the polyimide film used in the measurement.

at the periphery, and the formation of hydrogen bonds between the amide groups. The 1D LC assembly may incorporate ions into it, therefore it has potential as an ion-conductive channel.^{2,3,45-50}



Fig. 5 Molecular model of the self-assembled structure of 1.

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