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Liquid Crystalline Order from *ortho*-Phenylene Ethynylene Macrocycles

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Triangular *ortho*-phenylene ethynylene (*o*-PE) cyclic trimers, such as **M1**, represent a novel member of shape-persistent macrocycles. In general, shape-persistent cyclic structures remain of great interest as molecular components in the fields of supramolecular materials, host−guest chemistry, and materials science due to their unique properties.[1] Some of these shape-persistent macrocycles have shown discotic liquid crystalline (LC) properties as a result of their pseudo-planar, disk-like topology.[1−3] These disk-like molecules can arrange into one-dimensional columnar structures which are governed by strong $\pi-\pi$ stacking, van der Waals, dipole, and hydrophobic interactions.[2,3] *o*-PE macrocycles have attracted increasing attention in the past few years because of their unique properties, including a small interior pore, which is particularly well suited for transition metal binding; they are structural units of *graphyne* and exhibit unique electronic properties.[1] It is one of the most compact shape-persistent macrocycles known. Despite this interest in *o*-PE macrocycles, liquid crystalline materials have remained elusive.

In this paper, we report novel discotic LC properties from triangular-shaped *o*-PE macrocycles containing branched alkoxy- and/or triethylene glycol (TEG) side chains (see Figure 1). Using polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD), the macrocycles were shown to form thermotropic rectangular columnar ($\mathrm{Col_r}$) (for **M1**), hexagonal columnar ($\mathrm{Col_h}$) (for **M2**), and discotic nematic (for **M3**) mesophases at room temperature.

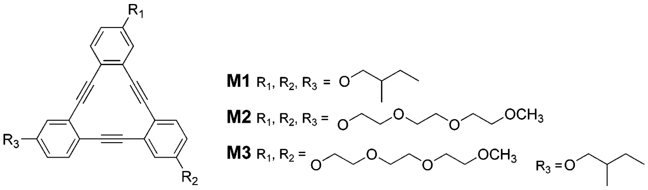

Figure 1. Structure of *ortho*-phenylene ethynylene macrocycles.

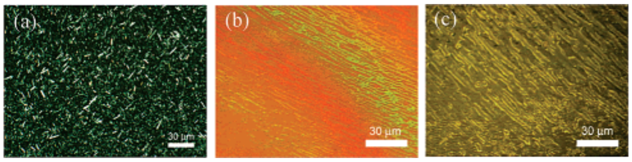

Figure 2. Polarized optical micrograph of (a) the $\mathrm{Col_r}$ mesophase of **M1**, (b) the $\mathrm{Col_h}$ mesophase of **M2**, and (c) discotic nematic mesophase of **M3** obtained with a cooling rate of 10 °C/min at 25 °C on the second cooling.

Synthesis of the macrocycles is outlined in the Supporting Information but uses the traditional ultra-dilute ring closing reaction of an A−B functionalized molecule[4] as the final step. Much recent attention has been given to metathesis cyclization, which can greatly improve the macrocycle yield.[5] However, metathesis does have limitations, including the inability to synthesize **M3**. Metathesis would also create mixtures of **M1** and **M2** by scrambling the monosubstituted side chains, leading to a collection of isomers. Therefore, although metathesis is a powerful new, and sometimes, high yielding approach, traditional macrocyclization is still an important synthetic approach to building designer materials.

Macrocycle **M1** is freely soluble in a variety of organic solvents, including chloroform, tetrahydrofuran, heptane, and methanol. The solubility of macrocycles **M2** and **M3** is similar to that of **M1** except in hydrocarbons due to the hydrophilic TEG side chains. Macrocycles **M1**, **M2**, and **M3** were isolated as a sticky (for **M1**) and oily (for **M2** and **M3**) material at room temperature that exhibited birefringent mesophases when examined with POM. The textures, shown in Figure 2, are nonspecific with short-rod-like (for **M1**), thread-like (for **M2**), and wave-like (for **M3**) structures present. As a result, the macrocycles were assigned to a LC phase at room temperature. The DSC trace of **M1** showed one weak transition at 81 °C with an enthalpy value of 2.52 J/g, consistent with a LC to isotropic transition. Upon cooling **M1** from 100 °C, a weak broad transition at 44 °C was observed with an enthalpy value of 3.86 J/g, corresponding to the isotropic to LC phase transition. A birefringent phase with the same texture appeared at 44 °C on cooling from the isotropic melt and remained until room temperature without any change (Figure 2a). **M2** and **M3** showed thermal behaviors similar to that of **M1** with DSC. Phase transition temperatures and corresponding enthalpy values for compounds **M1**, **M2**, and **M3** are given in Table 1.

Figure 3a,b shows the XRD scan collected for the birefringent phase of **M1** and **M2** at room temperature, respectively. The birefringent phases were confirmed as a $\mathrm{Col_r}$ and $\mathrm{Col_h}$ phase through assignment of the reflections, respectively. The XRD profile of **M1** (Figure 3a) shows seven sharp reflection peaks corresponding to *d* spacings of 17.9, 15.3, 12.3, 8.9, 8.2, 7.4, and 6.8 Å, which were indexed in sequence as (100), (010), (110), (200), (210), (020), and (120) of a $\mathrm{Col_r}$ lattice with the lattice parameter of $a = 17.9$ and $b = 15.3$ Å. In fact, more reflections were visible but began to overlap with scattering from the Mylar sample holder. Regardless, these seven reflections allow definite assignment of the structure. These spacings agree well with those expected from the macrocycle based on a diameter calculated to be 20 Å (Figure 3c,d). It is likely that the branched alkyl side chains interdigitate along the *a*,*b*-axis of the structure and that the rectangular organization is due to the triangular shape, or irregular disk, of this macrocycle with short branched alkyl side chains. Other *o*-PE macrocycles have been reported with unbranched alkyl side chains that did not induce LC order.[5a,d]

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Table 1. Phase Transition Temperatures and Enthalpies [In Parentheses] for Macrocycles **M1**, **M2**, and **M3** as Determined by DSC (scan rate = 10 °C min^{-1})^a

	T (°C) [ΔH_t, J g^{-1}]^a	
compound	heating (°C)	cooling (°C)
M1	$\mathrm{Col_r}$ 81 [2.5] I	I 44 [3.9] $\mathrm{Col_r}$
M2	$\mathrm{Col_h}$ 55 [12.4] I	I 55 [13.0] $\mathrm{Col_h}$
M3	$\mathrm{N_D}$ 54 [2.2] I	I 52 [1.7] $\mathrm{N_D}$

^{a} $\mathrm{Col_r}$, rectangular columnar; $\mathrm{Col_h}$, hexagonal columnar; $\mathrm{N_D}$, discotic nematic; I, isotropic.

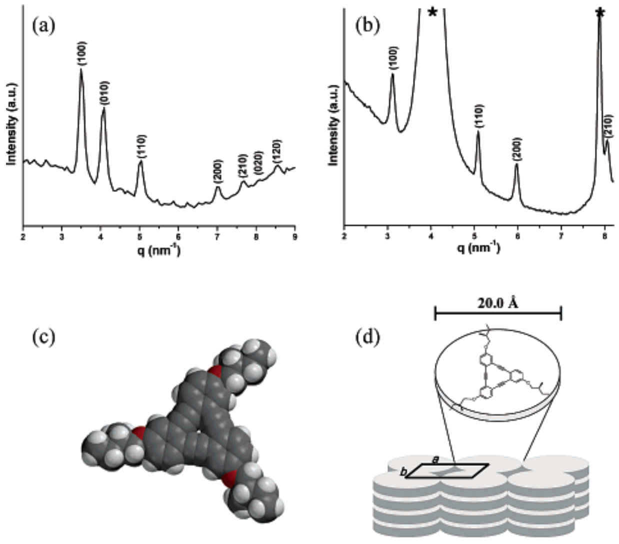

Figure 3. X-ray diffractograms for the (a) rectangular columnar phase of **M1**, (b) hexagonal columnar phase of **M2** obtained at room temperature, (c) CPK model (top view) of macrocycle **M1** created in Spartan, Wavefunction, Inc., and (d) schematic representation of the $\mathrm{Col_r}$ phases. The asterisks (∗) denote diffraction peaks of the imide film used as substrate.

The XRD profile of **M2** (Figure 3b) shows four main sharp reflection peaks corresponding to d spacings of 20.6, 12.1, 10.4, and 7.8 Å, which were indexed in sequence as (100), (110), (200), and (210) of a $\mathrm{Col_h}$ lattice with the lattice parameter of $a = 23.8$ Å. Similar molecular calculations determined the diameter of **M2** to be 36 Å, suggesting that the longer unbranched but polar triethylene glycol tails are interdigitated. The XRD profile of **M3** (see Supporting Information) shows one broad reflection peak corresponding to the d spacing of 44 Å, which is attributed to the average distance between macrocycles of a discotic nematic LC. These XRD results show that the symmetric macrocycles **M1** and **M2** self-assemble into highly ordered columnar structures, in contrast to the asymmetrically substituted macrocycle **M3**, which is less ordered. These are the first LC materials reported from substituted *o*-PE macrocycles, to the best of our knowledge.

A survey of the literature[3b] provides a series of *meta*-based PE (*m*-PE) macrocycles that make an excellent comparison to the *o*-PE macrocycles reported here. Moore showed that a *m*-PE macrocycle containing heptyl chains connected to the carbon-rich backbone through ether functionality formed a discotic nematic phase at elevated temperature as opposed to any other LC phase. Only the electronically mixed system (a macrocycle containing three ethers and three esters) formed a more ordered discotic phase. In contrast, macrocycle **M1** forms a well ordered $\mathrm{Col_r}$ phase with more than seven reflections in the XRD. One of the most striking differences between these two macrocycles is the void space of the central cavity which may inhibit column formation in the *meta* series. The *meta* series has an internal hydrogen to hydrogen distance of about 8 Å, while the spacing-filling molecular model of **M1** in Figure 3c shows the internal cavity is extremely small, approximately 2.4 Å across the macrocycle. In addition to the central cavity size distinction, the connectivity of the *ortho* versus *meta* series leads to differences in the nature of conjugation for the two systems. This work shows clearly that electron-rich PE macrocycles can form LC materials.

In summary, novel LC materials are reported based on *ortho*-PE macrocycles for the first time. The macrocycle **M1** contains short alkyl side chains. Alternatively, if the side chain is hydrophilic, as is the case with **M2**, then the amphiphilicity provides a driving force for organization. These structures demonstrate two side chain chemistries for creating self-assembling materials from *ortho*-PE macrocycles. The ability to create ordered self-assembling materials from these novel electron-rich macrocycles is important in nanotechnology and may enable new materials for applications in membranes and electronics.

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Supporting Information Available: Experimental procedures of macrocycles. including synthesis, UV−vis spectra, and XRD of **M3** at room temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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