

Entry of Novel π -Conjugated Molecules into Liquid Crystalline Materials

Liquid crystallization of π -conjugated molecules is an attracting methodology to make ordered molecular assemblies applicable for organic electronic and/or memory devices. Entry of new families of π -conjugated molecules with unique properties for the research community of liquid crystal is important, as it allows to realize not only better performance but also unprecedented functions of such liquid crystalline materials. We have successfully designed the first examples of liquid crystalline fused metalloporphyrin dimer (**1**) [1] and corannulene (**3**) [2] (Fig. 1). The π -conjugated cores did not show any liquid crystallinity, when they were structurally modified, based on the conventional molecular design strategy, with long alkyl side chains (**2** and **4** in Fig. 1). For liquid crystallization of fused metalloporphyrin dimers, we developed an original molecular design strategy, where two incompatible hydrophobic and hydrophilic side chains are site-specifically introduced to the core. By taking advantage of nanoscale phase separation of these side chains, fused metalloporphyrin core can stack one another to form a rectangular columnar lattice with lattice parameters a and b of 65.3 and 37.2 Å, respectively (Fig. 2), which was unambiguously determined by variable-temperature, one- and two-dimensional X-ray diffraction analyses of sheared and unsheared samples at beamlines **BL02B2** and **BL45XU**. On the other hand, for corannulene, we used hydrogen-bonding interaction to induce its columnar assembly, by adding amide functionalities in the side chains. In fact, corannulene **3** forms a hexagonal columnar liquid crystalline phase with a lattice parameter of 35.0 Å, as clearly demonstrated by one-dimensional X-ray diffraction analysis at beamline **BL02B2**. It is

also noteworthy that both **1** and **3** exhibited liquid crystallinity in wide temperature ranges including room temperature (**1**: from -17 to 99 °C; **3**: from -10 to 154 °C on heating), advantageous for device processing and operation.

Because of its extra-large π -conjugated system, fused copper porphyrin dimer **1** has HOMO-LUMO band gap of 1.15 V, which is obviously smaller than those of several representative semiconducting π -conjugated molecules such as perylene diimides (1.4–2.2 V), phthalocyanines (1.4–1.8 V), and C₆₀ (1.7 V). Such a narrow band gap suggests the large potential of fused metalloporphyrin dimers as an organic semiconductor. In fact, **1** was found to serve as an n -type semiconductor. Its intrinsic one-dimensional electron mobility μ_{1D} , as evaluated by non-contacting flash-photolysis time-resolved microwave conductivity (TRMC) measurements of the film samples at the liquid crystalline state, reached up to the order of 10⁻¹ cm²/V·s. μ_{1D} of such value is one-order of magnitude larger than the previous champion data reported for room-temperature columnar liquid crystalline materials, studied by TRMC. Since high-performance n -type organic semiconductors are still rare, this novel liquid crystalline material will give a great impact on the research community of organic electronics.

The columnar assemblies of **1** and **3**, in their as prepared liquid crystalline films, orient randomly on the macroscopic level. We have found, however, that the latter can be aligned electrically. When a liquid crystalline sample of **3** in an applied electric field was continuously monitored by polarized optical microscopy, the birefringent image, initially observed in the entire view of the sample, gradually changed

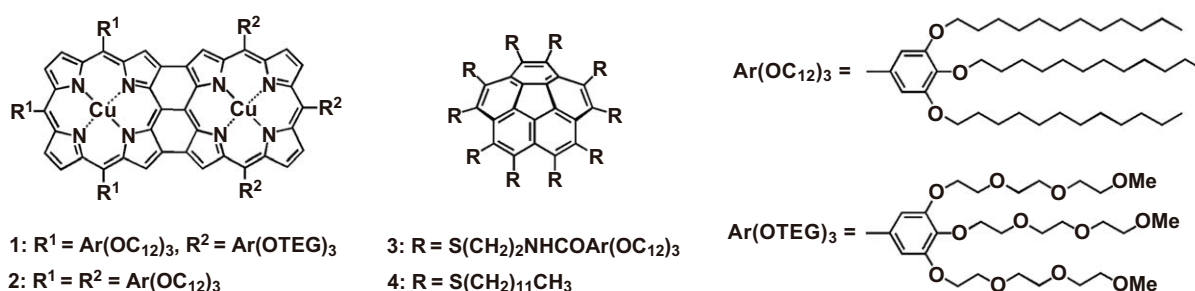


Fig. 1. Molecular structures of fused metalloporphyrin dimers **1**, **2** and corannulenes **3**, **4**.

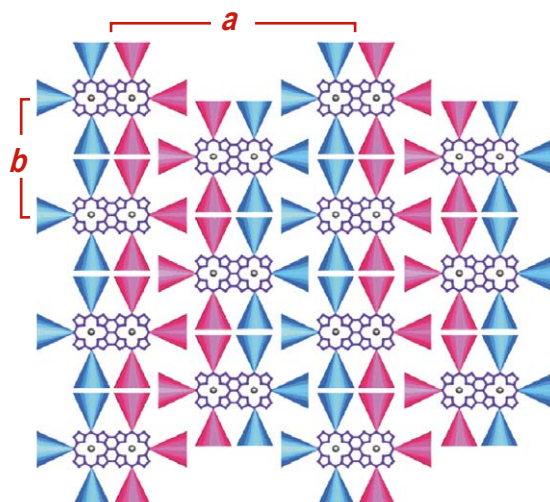


Fig. 2. Schematic representation of rectangular 2D molecular packing diagram of liquid crystalline **1**. The blue and red moieties in the cartoon correspond to the hydrophobic and hydrophilic side chains in **1**, respectively.

and eventually displayed a certain pattern with a dark field only in a section sandwiched by the electrodes (Fig. 3), demonstrating that columns of assembled **3** adopt a homeotropic orientation with respect to the electrodes. Thus corannulene **3** is a rare example of electrically alignable discotic liquid crystals. Due to the bowl-shaped π -conjugated

skeleton, corannulene has concave and convex faces with different electron densities, and hence a dipole moment whose direction is switchable upon inversion of the skeleton. Therefore, liquid crystalline **3** responsive to electric field, possesses unique potentials for e.g., anisotropic charge transporting and ferroelectric applications.

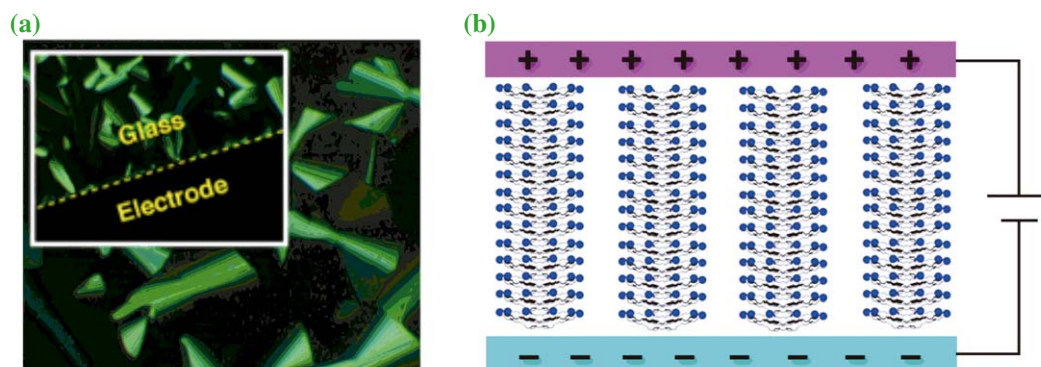


Fig. 3. (a) Polarized optical micrograph (POM) of **3** at 115 °C. Inset shows POM at 125 °C of **3**, sandwiched by glass plates with patterned ITO electrodes (5- μm separation) under an applied electric field of 15 $\text{V}\cdot\mu\text{m}^{-1}$. (b) Schematic representation of the orientation of columnar assemblies of **3** under applied electric fields.

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References

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