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Self-Assembly of Porphyrin and Fullerene Supramolecular Complex into Highly Ordered Nanostructure by Simple Thermal Annealing

Xiaoli Zhou,[†] Shin-Woong Kang,[‡] Satyendra Kumar,[‡,#] Rahul R. Kulkarni,[§] Stephen Z. D. Cheng,[§] and Quan Li*[,†]

Liquid Crystal Institute and Department of Physics, Kent State University, Kent, Ohio 44240, Department of Polymer Science, University of Akron, Akron, Ohio 44325, Division for Materials Research, National Science Foundation, 4201 Wilson Boulevard, Arlington, Virginia 22230

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Controlling the nature of supramolecular self-assembly by noncovalent interaction is a challenge in science and technology that, when overcome, can lead to a breakthrough in the creation of new molecular devices. Discotic liquid crystals (LCs) capable of being uniformly aligned represent a striking example of self-assembly mainly driven by $\pi-\pi$ interactions. Such discotic LCs, viewed as a new generation of organic semiconductors because they carry charges and excitons more efficiently than conventional conjugated polymers,[1] provide tremendous opportunities as well as challenges in fundamental science that could open the door for the applications such as photovoltaics,[2] light-emitting diodes,[3] and field effect transistors.[4] One of the major challenges for device performance is to develop facile means to produce defect-free large area thin films with directed molecular arrangement.[5]

It is well-established that discotic LCs as active components in high efficient photovoltaic (PV) cells are critically dependent on the supramolecular arrangement of the blend made from an electron donor component and an electron acceptor component. Compared with donor and acceptor bilayer PV cell, a blend can offer a much larger interface between donor and acceptor as a result of an efficient dissociation of excitons in the supramolecular arrangement.[6] Among all the blends, porphyrin−fullerene blend is supposed to be an excellent marriage because porphyrin, which is the basic structure of the best photoreceptor Chlorophyll in nature, is a superior electron donor,[7] whereas fullerene is an excellent electron acceptor.[8] However, to date there appears no report on the alignment of porphyrin−fullerene blend.

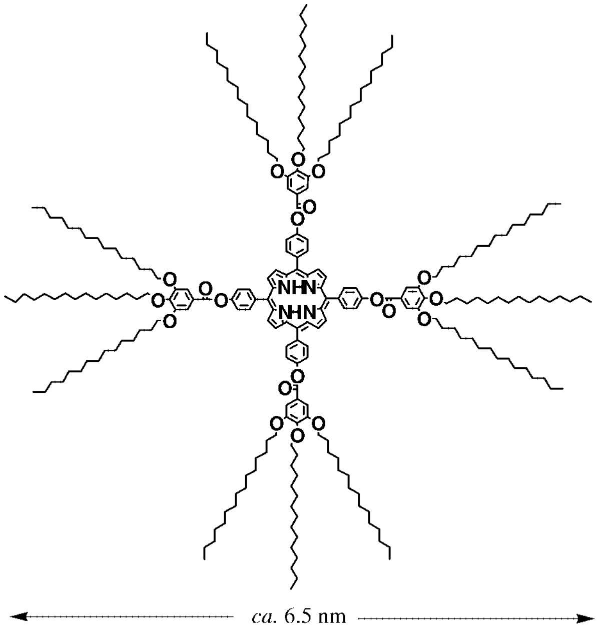

Figure 1. Molecular structure of liquid crystalline porphyrin **1**.

Here, we report the homeotropic alignment of one nanoscale liquid crystalline porphyrin **1** (Figure 1), i.e., the columns formed by intermolecular $\pi-\pi$ stacking are spontaneously perpendicular to the substrate, and the recurrence of homeotropic alignment for porphyrin **1** doped with the widely used fullerene derivative 1-(3-methoxycarbonyl)propyl-1-phenyl-(6,6)C_{61} (PCBM) through maintaining its liquid crystal phase. To the best of our knowledge, this is the first homeotropically aligned crystalline thin film composed of liquid crystalline porphyrin and fullerene supramolecular complex.

The porphyrin **1** was prepared in a facile synthesis. Its chemical structure was well identified by ^{1}H NMR, ^{13}C NMR, MS, IR, UV−vis, and elemental analysis (see the Supporting Information). The porphyrin-fullerene blend **2** (**1**+PCBM) was prepared by mixing porphyrin **1** with PCBM in 30:1 molar ratio in CH_2Cl_2 followed by the removal of solvent under reduced pressure. As expected, its optical measurements show a strong absorption in the solar spectrum

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* To whom correspondence should be addressed. Tel.: (330) 672-1537. Fax: (330) 672-2796. E-mail: quan@lci.kent.edu.

[†] Liquid Crystal Institute, Kent State University.

[‡] Department of Physics, Kent State University.

[§] University of Akron.

[#] National Science Foundation.

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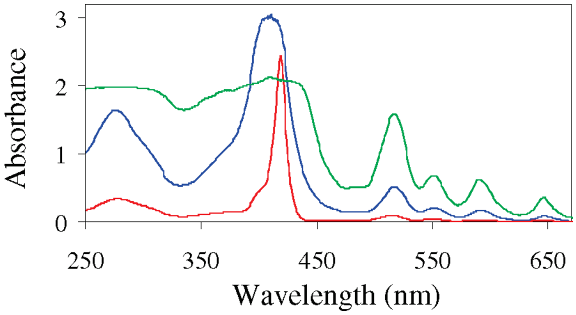

Figure 2. UV−vis absorption spectra of porphyrin−PCBM blend **2** (red, 5.0 μM **2** in CH_2Cl_2; blue, 2 μm; green, 4 μm thick homeotropically aligned thin films sandwiched between two quartz plates).

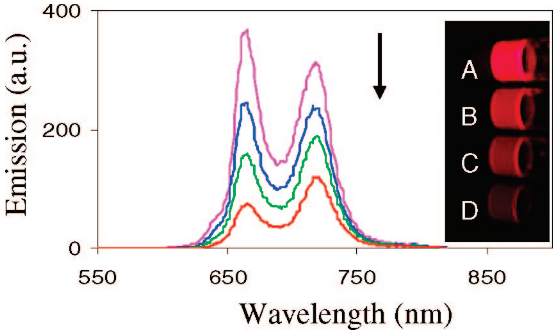

Figure 3. Fluorescence intensity of porphyrin **1** in chlorobenzene with excitation at 520 nm upon addition of PCBM (**1** at all the samples is 4.37 $\times 10^{-4}$ M, PCBM/**1** = 0 (pink line), 0.5 (blue line), 1 (green line), and 2 (red line)). The inset shows the corresponding emission images under 365 nm UV irradiation (A, pink; B, blue; C, green; D, red).

(Figure 2). The blue-shift of the Soret band (407 nm) in a 2 μm thick thin film compared with that (419 nm) in solution indicates the formation of untilted or less tilted stacks (H-aggregates).[9] Interestingly, the thicker thin film (4 μm) has more intense absorption in most regions except around the Soret band than the 2 μm thin film. This might be attributed to the thicker film with less uniform homeotropic alignment. Furthermore, the absorption spectrum of porphyrin **1** in CH_2Cl_2 changed upon the addition of PCBM, and the absorption at the Soret band is decreased whereas the absorptions at about 260 and 327 nm wavelength are increased (see the Supporting Information). The fluorescence emission of **1** in C_6H_5Cl was significantly quenched upon addition of PCBM (Figure 3). These indicate the presence of electron transfer between porphyrin core and C_{60},[10] i.e., the porphyrin−fullerene blend is not only a mixture of two favorable components, but one in which the two components interact.

Both porphyrin **1** and porphyrin−fullerene blend **2** are thermally stable even at 300 °C. Their phase behaviors were investigated by a crossed optical polarizing microscope (POM) equipped with a temperature controller, differential scanning calorimetry (DSC), and synchrotron X-ray diffraction (XRD). The results show both materials **1** and **2** exhibit similar hexagonal liquid crystalline phases (Table 1). For material **2**, on cooling at a rate of 5 °C/min, it first goes into a shearable liquid crystalline phase at 123.4 °C with the growth of distinct dendritic domains. The pattern is characteristic to a formation of a hexagonal columnar phase. This phase then goes into another phase with high viscosity at 97.7 °C, which persists through room temperature. In the phase below 97.7 °C, the texture of the hexagonal columnar phase remains unchanged, but gains positional order along the columns.

Table 1. Phase Transition Temperature (°C) and Enthalpies (J/g)[a]

1	I	130.7 (2.2)	Col_h	104.9 (5.8)	Col_{ho}	2.0 (23.1)	Cr
2	I	123.4 (1.1)	Col_h	97.7 (3.8)	Col_{ho}	1.9 (11.6)	Cr

[a] 2 = 1 + PCBM; I = isotropic liquid; Col_h = hexagonal phase; Col_{ho} = more order hexagonal phase; Cr = crystal.

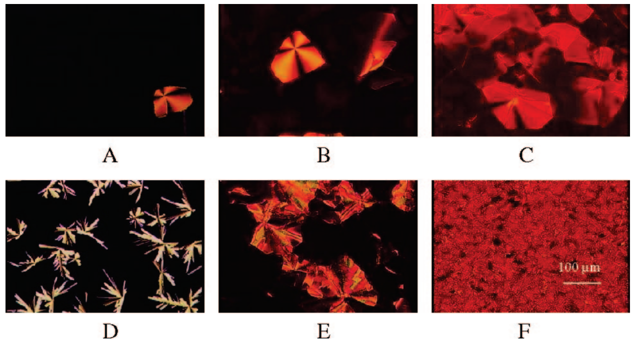

Figure 4. Crossed polarized optical textures of (A−C) **1** and (D−F) **2** at room temperature and different thicknesses: (A, D) 4.5, (B, E) 12, and (C, F) 22 μm. The dark areas in A, B, D, and E represent homeotropic alignment, and the bright domains appear where the porphyrin planes are oblique to the substrates.

Porphyrin **1** and the blend **2** are fluid in the isotropic phase and can be capillary-filled into thin cells. Very surprisingly, in films thinner than 5 μm, their textures that appear under cooling slower than 2 °C/min are almost completely black between crossed polarizers indicating that the columns formed by strong intermolecular self-assembly are perpendicularly aligned to the substrates, i.e., homeotropic alignment. Moreover, the homeotropic alignment remains stable through room temperature once the transition from the isotropic phase to the hexagonal phase Col_h is complete. Our experimental results also show that modified substrate surface such as ITO-coated glass and polyimide-coated glass with and without mechanical rubbing seems to have no bearing on obtaining uniform homeotropic alignment. The dominant factors to achieve large area uniform homeotropic alignment appear to be film thickness and thermal treatment. The thinner the film, the more uniform homeotropic alignment can be achieved (see Figure 4). By controlling cooling rate from isotropic phase across the hexagonal phase in a thinner cell, a defect-free large area homeotropically aligned crystalline thin film on **1** and **2** was obtained (Figure 5).

Synchrotron XRD obtained from an optically dark homeotropic monodomain in thin film confirms the homeotropically aligned crystal phases of both materials **1** and **2** in which their molecules stack into columns forming a hexagonal lattice. Figure 6 shows the XRD patterns from the homeotropically aligned thin film of the materials **1** and **2**. The *d*-spacings between two columns (center to center) in **1** and **2** are 4.43 nm at 36.7 °C and 4.47 nm at 48.0 °C,

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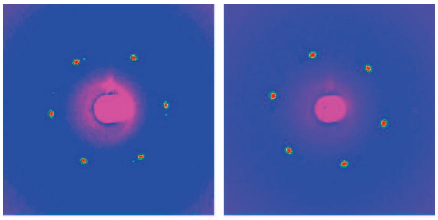
A B

Figure 5. Homeotropically aligned optical textures of **2** at room temperature in a 2 μm thick cell: (A) with crossed polarizers; (B) without crossed polarizers; the textures are thermally stable from about 100 °C through room temperature.



A B

Figure 6. Synchrotron XRD patterns from homeotropic monodomain of the materials (A) **1** and (B) **2** in a 8 μm thick glass cell.

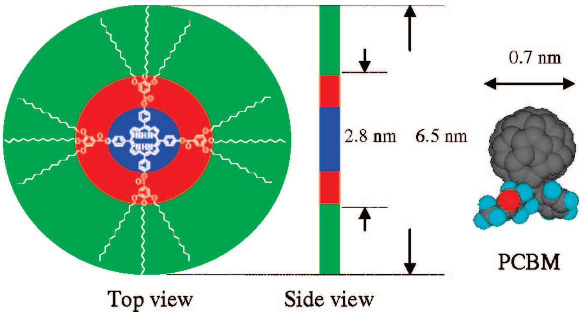


Figure 7. Left: Calculated geometric dimensions of porphyrin **1**. Right: 3D chemDraw spacing-filling model of fullerene derivative PCBM.

respectively. No significant difference is observed between the pure porphyrin **1** and the blend **2**.

It is interesting to see how the fullerene and porphyrin will be arranged in the blend **2**. The diameter of porphyrin is approximately 6.5 nm, whereas the distance between the two neighboring columns from XRD experiment is about 4.4 nm (Figure 7). So we can deduce that the interdigitation of the long flexible chains exists and the lipid chain intercalating length *a* is about 1.6 nm (Figure 8). Considering PCBM size (about 0.7 nm) and its lipophilicity, one possible molecular arrangement is the hexagonal columnar phase of porphyrin with PCBM at interstices of the columns (bottom in Figure 8 left). However, a more possible molecular arrangement is that PCBM is sandwiched between two porphyrin core due to the strong π-donor and π-acceptor interaction (top in Figure 8 left).[11] Regardless of packing arrangement, the porphyrin and PCBM supramolecular complex retains a homeotropically aligned architecture (Figure 8 right) which is very important for PV applications because this favorable molecular arrangement can provide an efficient path for electrons or/and holes along the columnar axis, and the light-harvesting molecules are arranged with the largest area toward the coming light.

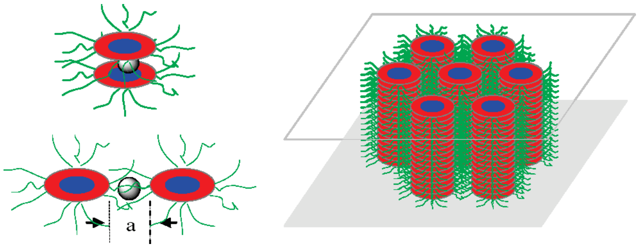


Figure 8. Right: Schematic representations of homeotropically aligned architecture. Left: Possible arrangement of PCBM and **1** in the homeotropically aligned architecture of the supramolecular complex.

In conclusion, highly ordered nanostructured thin films composed of the porphyrin and fullerene supramolecular complex were prepared by simple thermal annealing. The nature of their homeotropic alignment is well-confirmed. The concept demonstration provides new insight on fabricating defect-free large area blend thin films with directed molecular arrangement.

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Supporting Information Available: Synthesis, characterization, optical textures, DSC, and geometric dimensions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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