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An ABC Stacking Supramolecular Discotic Columnar Structure Constructed via Hydrogen-Bonded Hexamers

Shi Jin,[†] Yuguo Ma,[‡] Steven C. Zimmerman,*[,‡] and Stephen Z. D. Cheng*[,†]

Maurice Morton Institute and Department of Polymer Science, The University of Akron, Akron, Ohio 44325-3909, and Department of Chemistry, University of Illinois, Urbana, Illinois 61801

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Two-dimensionally (2D) ordered discotic columnar liquid crystals (DCLCs) have attracted considerable attention because of their potential application in devices such as field effect transistors,[1] electro-luminescent displays,[2] and coaxially insulated one-dimensional (1D) conducting nanowires in photovoltaic cells.[3] In a DCLC phase, disklike molecules stack together forming columns. These columns pack into lattices, which possess the orientational order of the columns and the 2D positional order in the plane perpendicular to the column long axis. A great deal of attention has been paid to the lateral packing schemes of the columns. Despite the fact that the intracolumn stacking is critically important to charge mobility through the column long axis, much less effort has been devoted to the molecular stacking scheme inside the column. This probably is because, in the majority of DCLC phases, disk-shaped molecules adopt a simple stacking scheme where one disk stacks right on top of another as found in triphenylene and hexabenzocoronene derivatives.[4]

However, if the charge distribution among constitutional skeleton atoms is uneven, resulting in electrostatic interaction between atoms carrying a partial charge, disk-shaped molecules may construct columns with different stacking schemes. Such unevenness can be found in porphyrin and phthalocyanine derivatives,[5] as well as electron-deficient discotics,[6] which exhibit electron transport behaviors promising for light-emitting diodes and photovoltaic devices. Therefore, it is essential not only to understand the column packing structures but also to investigate the molecular stacking schemes within the columns and the corresponding formation mechanisms. In the past, a two-disk suprastructure was proposed for phthalocyanine DCLCs on the basis of 1D wide-angle X-ray diffraction (WAXD) results,[5c] though no further effort was made to explore the detailed stacking schemes within the column. On the other hand, for hydrogen (H) bonded supramolecular DCLCs[7] in which disks formed via intermolecular H-bonding, different stacking schemes within the col-

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* Authors to whom correspondence should be addressed. E-mail: scheng@uakron.edu. E-mail: sczimmer@uiuc.edu.
[†] The University of Akron.
[‡] University of Illinois.

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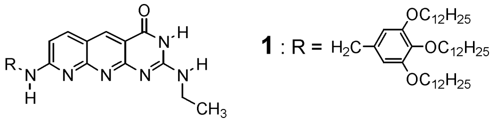
umns could also form, driven mainly by the electrostatic interaction between highly polar H-bond-forming molecules. Herein, we report DCLC phases consisting of H-bonded disklike building blocks $(\mathbf{1})_6$, where intradisk H-bonding interactions are responsible for maintaining the integrity of the disklike building blocks and interdisk interactions stabilize the columns. In particular, an ABC intracolumn stacking scheme has been found via a detailed 2D structural analysis on orientated samples.

The design of compound **1** is based on a previous analogue, which was recently shown to form self-assembled hexadendrons in organic solvents.[8a,8b] Heterocycle **1** contains the complementary donor−donor−acceptor (DDA) and acceptor−acceptor−donor (AAD) H-bonding arrays used by the guanine−cytosine DNA base pair.[8c] Thus, the encoded molecular assembly “programmed” via the cooperative H-bonding leads **1** to spontaneously form stable disk-shaped hexamers where the three flexible dodecyl side chains were incorporated specifically to encourage the hierarchical formation of supramolecular DCLCs.



Comparable to previous reports,[8a,8b] compound **1** was synthesized and the exclusive formation of hexamers $(\mathbf{1})_6$ in aprotic organic solvents was confirmed using ^{1}H NMR, DLLS, and SEC experiments.[9] The self-organization of **1** in the bulk was studied by differential scanning calorimetry (DSC, Perkin-Elmer PYRIS Diamond), polarized light microscopy (PLM, Olympus BH-2), 2D wide-angle X-ray diffraction (WAXD, Rigaku rotating anodes), and Fourier transform infrared spectroscopy (FT-IR, Digilab, FTS 3000).

Compound **1** exhibited two DCLC phases. One DCLC phase appeared after a phase transformation at −20 °C (with a $\Delta H = 17$ kJ mol^{-1}), and at 95 °C, a DCLC ↔ DCLC phase transition took place (with a $\Delta H = 0.7$ kJ mol^{-1}). The isotropization temperature was at 220 °C (with a $\Delta H = 0.8$ kJ mol^{-1}). The IR spectrum of **1** obtained in the bulk at room temperature was essentially identical to that from a toluene solution, suggesting that the $(\mathbf{1})_6$ suprastructure in the bulk also existed as the building blocks. Furthermore, there was no significant change in position of the H-bonding-related vibration modes between room temperature and 240 °C, indicating the preservation of H-bonded disks even in the melt. The studies described below focused on the DCLC inter- and intracolumn structures formed between −20 and 95 °C.

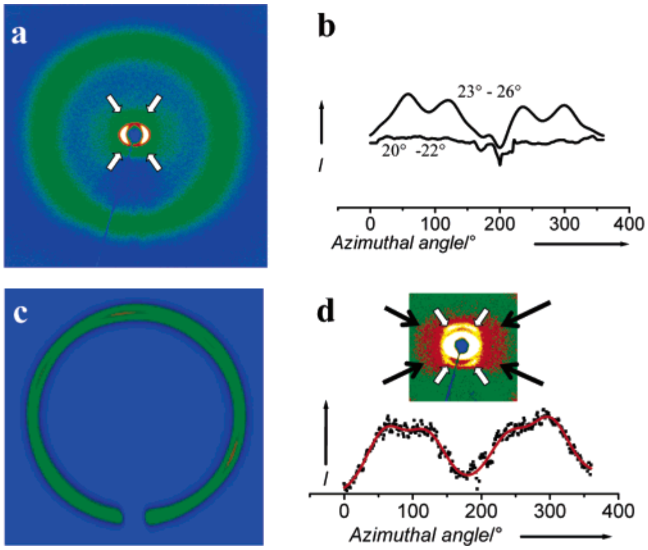


Figure 1. WAXD patterns with the X-ray incident beam perpendicular (a) and parallel (c) to the shear direction (low 2θ angle region); (b) azimuthal scans of different 2θ angle regions 20°−22° and 23°−26° in (a); (d) enlarged low-angle region of (a), four very diffused scatterings were indicated by black arrows and the azimuthal scan of these scatterings (2θ angle 7.5°−9°, the red curve is after smoothing).

Figure 1 shows 2D WAXD patterns of samples oriented through mechanical shearing at 100 °C to obtain structural information. Figure 1a is the pattern obtained by directing the X-ray beam perpendicular to both the shear and shear gradient direction, with the shear direction along the meridian. On the equator, a relatively broad pair of strong diffractions is seen in the low 2θ-angle region at 2.66° (d spacing of 3.32 nm) that can be assigned to the intercolumn spacing. In the wide-angle region, the isotropic scattering halo at $2\theta = 20.4°$ suggests that the alkyl chains are in a disordered, isotropic liquidlike state. This conclusion is supported by the flat azimuthal profile in Figure 1b with a 2θ-angle range between 20 and 22°. In the 2θ range between 23 and 26° (maximum at 23.4°, d spacing 0.38 nm) covering the interdisk spacing, the azimuthal scan in Figure 1b shows four intensity maxima at 29° above and below the equator, suggesting that the disk normal is 61° away from the meridian (long column axis). Therefore, the cross section of a column perpendicular to the column long axis is an ellipse, which favors a rectangular columnar packing instead of a hexagonal packing.

The appearance of an equatorial diffraction pair is not sufficient to establish a 2D lattice. A 2D WAXD pattern with the incident X-ray parallel to the shear direction was thus taken (Figure 1c). Three pairs of low 2θ-angle diffraction arcs were observed not quite 60° apart from one another. They correspond to the pair of strong equatorial diffractions shown in Figure 1a. The d spacings and the widths of the diffractions in the cross directions for these three pairs are also slightly differ-

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(9) Compound **1** gave an acceptable elemental analysis and had ^{1}H and ^{13}C NMR, FT-IR, FDMS, and HRFAB-MS spectra in full accord with its structure. Full details of the synthesis and assembly studies will be published later.

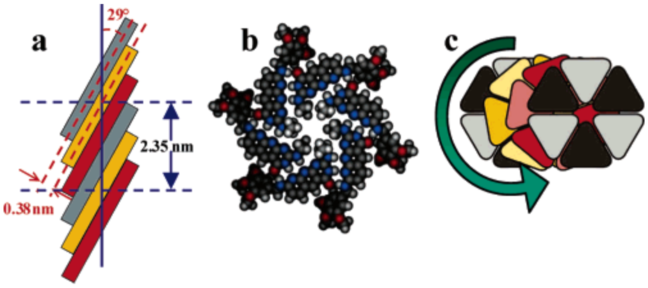

Figure 2. (a) Model of five tilt-stacked hexamers (side view); structurally different disks were in different colors. (b) Model of a $(\mathbf{1})_6$ disk. (c) Model of four stacked $(\mathbf{1})_6$ disks in a column; deep- and light-colored motifs represent molecules with their center ethyl groups pointing up and down out of the disk plane.

ent, revealing a nonhexagonal 2D supramolecular DCLC phase with the columns being aligned along the shear direction. Detailed calculations indicate that these three pairs of diffractions originate from a rectangular lattice where $a = 6.72$ nm and $b = 3.88$ nm.

It is interesting to observe the two pairs of weak scattering maxima in the quadrants at a $2\theta = 4.6°$ (d spacing of 1.92 nm) as shown in Figure 1d (white arrows), which is an enlarged low-angle region of Figure 1a. When a line parallel to the meridian is drawn, the maxima are aligned with the strong low-angle equatorial diffractions. On the other hand, the projection of these maxima on the meridian corresponds to a d spacing of 2.35 nm, which fits well with the 3-fold interdisk distance along the column axis direction. Therefore, generation of these two scattering pairs involves both the three-disk intracolumn and cooperative intercolumn correlations. An ABC stacking model in which three $(\mathbf{1})_6$ disks form one supramolecular structural unit along the column axis can thus be proposed, as shown in Figure 2a. This stacking model is also supported by the existence of broad scattering with a center spacing of ~1.1 nm (3-fold the disk-stacking spacing, 0.38 nm) as designated by black arrows in Figure 1d and their azimuthal scan in this figure. These scatterings are at an angle similar to the disk-stacking scatterings in the wide-angle region ($2\theta = 23.4°$), signifying that they are attributable to the stacking distance between two neighboring ABC stacking units.

To explore the molecular origin of this intracolumn structure, molecular modeling was carried out using a Cerius^2 software package (version 4.6) with the COMPASS force field. Because of the liquidlike nature of the alkyl tails as suggested by the WAXD data, the dodecyl tails were replaced by methyl groups. The conformation having the lowest free energy of the $(\mathbf{1})_6$ is shown in Figure 2b. The diameter of a disklike $(\mathbf{1})_6$ is ~3 nm. The methyl terminuses at the center alternate pointing up and down out of the plane of $(\mathbf{1})_6$ so that the disk possesses a 3-fold axis with respect to the disk normal.[8a] When disks with such a conformation stack together to form a column in which the disk normal is parallel to the column axis, the protruding methyl terminuses sterically hinder interdisk $\pi-\pi$ stacking. To release this steric hindrance without sacrificing interdisk $\pi-\pi$ stacking, the disks stack tilted within the columns. The protruding methyl terminuses can then be accommodated with an interdisk $\pi-\pi$ stacking distance of 0.38 nm to significantly lower the free energy.

Note that the tilt-stacking of disks in a column is equivalent to an offset of each disk along the disk plane with its neighbors, and this promotes quadrupole interactions between π systems.[10] Moreover, modeling suggests that a 40° rotation along the disk normal can further decrease the free energy by decreasing unfavorable Coulombic interactions and by reducing the steric hindrance caused by methyl terminuses on both surfaces of $(\mathbf{1})_6$. Because the ethyl groups, not only methyl terminuses, have to tilt with respect to the disk normal, the clockwise and counterclockwise rotations of a disk no longer have the same energy. As a result, the rotational direction was maintained throughout a column where the $n + 3$rd disk is structurally identical to the nth disk, resulting in an ABC stacking along the column axis as evidenced by WAXD results. Since the rotation axis of disks is 61° away from the column axis, this packing scheme is different from helical structures found in columnar LCs.[11] The calculated diffraction pattern using this modeled structure qualitatively agrees with the experimental data.

In summary, based on the 2D WAXD results, a supramolecular DCLC phase with an intracolumn ABC-stacking regime and highly tilted $(\mathbf{1})_6$ disks formed by strong DDA-AAD H-bonds was proposed. Molecular modeling suggests that this intracolumn suprastructure arises from the subtle balance of $\pi-\pi$ interaction, interdisk electrostatic interactions, and steric hindrance. Our finding may pave the way to understanding intracolumn stacking schemes in other supramolecular and molecular DCLCs with an uneven charge distribution among frame atoms.

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