

Amphiphilic Design of a Discotic Liquid-Crystalline Molecule for Dipole Manipulation: Hierarchical Columnar Assemblies with a 2D Superlattice Structure**

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Columnar liquid-crystalline (LC) materials composed of disk-shaped aromatic molecules arranged in one-dimensional (1D) columns have attracted increasing attention owing to their potential utility for solution-processable organic electronic^[1] and ionic devices.^[2] Because carrier transport relies on these 1D columns, a long-range intracolumnar molecular order is particularly important. Charge-transfer complexation has been reported to be effective in reinforcing the intracolumnar 1D order of discotic columnar LC assemblies.^[3] Williams and co-workers demonstrated that the incorporation of electron-withdrawing substituents into aromatic mesogens results in the enhancement of π stacking to stabilize the LC state.^[4] This molecular-design strategy based on so-called “ π polarization”^[4,5] probably gives rise to a dipole in the aromatic mesogens. As a result, LC molecules tend to π stack in a head-to-tail manner, and the dipole is canceled out within individual columns (Figure 1b). In this context, one may wonder how LC molecules composed of π -polarized mesogens assemble when they bear a particular functionality that would hamper head-to-tail stacking, and in turn, how the entire LC assembly would cope with the large intracolumnar dipole generated upon head-to-head stacking (Figure 1c). Herein we report the interesting finding that such a molecular

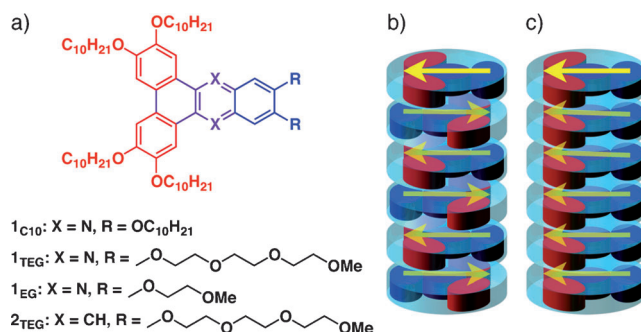


Figure 1. a) Molecular structures of dibenzo[a,c]phenazine derivatives **1**_{C10}, **1**_{TEG}, and **1**_{EG} and the benzo[b]triphenylene derivative **2**_{TEG}. b, c) Schematic illustrations of 1D columnar assemblies with head-to-tail (b) and head-to-head arrangements (c) of the aromatic mesogen. Yellow arrows indicate the dipole moment of the dibenzo[a,c]phenazine core.

design, uncomfortable for the molecule in terms of dipole interactions, leads to the formation of a 2D superlattice structure that is unprecedented in columnar LC assemblies composed of disk-shaped aromatic molecules. We noticed that this hierarchical structure not only has the advantage that the dipoles are canceled out intercolumnarly but also that a homeotropic alignment of the LC columns is adopted.

Dibenzo[a,c]phenazine, which possesses a dipole moment along the longer molecular axis,^[6] is known to serve as a mesogenic core for columnar LC assemblies (see Figure S1a and Table S2 in the Supporting Information).^[4a–d] We previously reported that the derivative with six decyloxy side chains, **1**_{C10} (Figure 1a), exhibits a hexagonal columnar (Col_h) mesophase over a wide temperature range.^[7] In study described herein, we designed an amphiphilic derivative, **1**_{TEG} (Figure 1a), with two triethylene glycol (TEG) chains on the phenazine ring and four decyloxy chains on the fused benzene rings. We anticipated that this amphiphilic derivative could adopt a head-to-head arrangement upon π stacking if micro-phase separation between immiscible TEG and paraffinic side chains occurred in preference to cancellation of the dipole (Figure 1c). Compound **1**_{TEG} was synthesized by a procedure similar to that reported previously (see Scheme S1 in the Supporting Information). As reference molecules, we also prepared **1**_{EG} (Figure 1a), with shorter oxyethylene side chains, and **2**_{TEG}, which was obtained by a ring-closing reaction of the corresponding 2,3-bisphenylnaphthalene derivative (see Scheme S2 in the Supporting Information). All new compounds were characterized unambiguously by ¹H

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[**] This research was supported by KAKENHI (21350108 (T.F.) and 23750170 (T.K.)). The synchrotron X-ray diffraction experiments were performed at BL45XU in the SPring-8 Center with approval (proposal 20110065).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201207708>.

and ^{13}C NMR spectroscopy and MALDI-TOF mass spectrometry.^[6]

In differential scanning calorimetry (DSC) studies, **1**_{TEG} displayed an LC mesophase between 69 and 80 °C (on heating) and between 76 and 57 °C (on cooling; Figure 2;

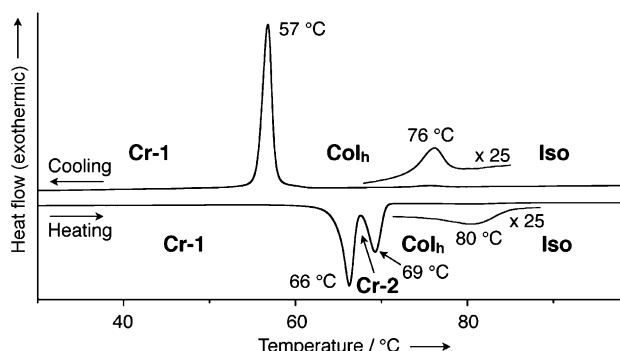


Figure 2. DSC trace for a second heating/cooling cycle (scan rate: 5 °C min⁻¹) of **1**_{TEG}. Cr: crystal, Col_h: hexagonal columnar LC phase, Iso: isotropic melt.

see also Table S1 in the Supporting Information). The powder X-ray diffraction (XRD) pattern of the LC mesophase of **1**_{TEG} in a glass capillary showed four peaks with *d* spacings of 2.21, 1.27, 1.10, and 0.84 nm (Figure 3a; see also Figure S3 in the Supporting Information), which were indexed as diffractions from the (100), (110), (200), and (210) planes, respectively. Thus, LC **1**_{TEG} forms a Col_h structure with a lattice parameter (*a*) of 2.55 nm (Figure 3b, orange hexagon). This value

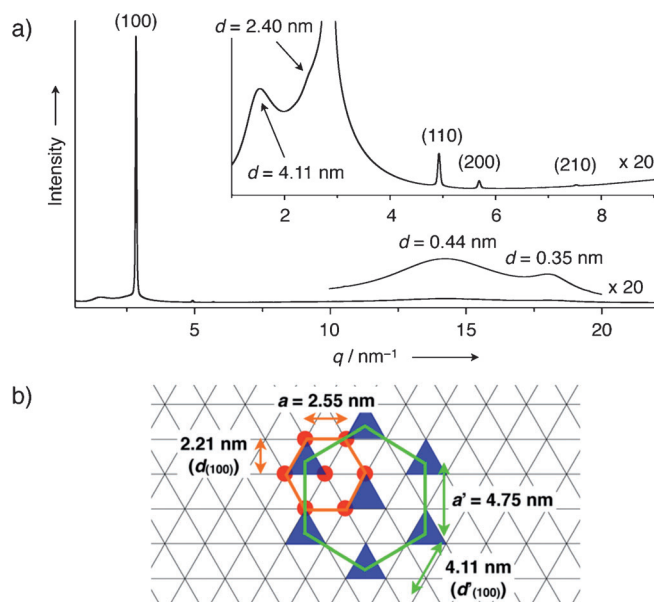


Figure 3. a) Synchrotron radiation XRD pattern of **1**_{TEG} at 75 °C on heating in a glass capillary ($\phi=1.5$ mm) and a magnification of the pattern (inset: $\times 20$, scattering vector $q=1\text{--}9$ nm⁻¹). Values in parentheses are Miller indices. b) Schematic illustration of the small (orange) and large (green) hexagonal lattices observed by XRD for LC **1**_{TEG}.

corresponds to the lateral core-to-core distance between 1D columns of **1**_{TEG}. The diffraction peak at $q=17.8$ nm⁻¹ can be assigned to the face-to-face distance (0.35 nm) of the π -stacked **1**_{TEG} molecules along the columnar axis. Two diffraction peaks with *d* spacings of 4.11 and 2.40 nm were detected in a smaller-angle region (Figure 3a). By considering the reciprocal spacing ratio (1: $\sqrt{3}$), we attributed these peaks to diffractions from the (100) and (110) planes of an additional hexagonal lattice with a lattice parameter (*a'*) of 4.75 nm (Figure 3b, green hexagon). These observations clearly indicate that LC **1**_{TEG} forms a 2D hexagonal superlattice structure.

As reported previously,^[7] compound **1**_{C10}, which bears decyloxy side chains (Figure 1a), forms a Col_h structure in the LC mesophase with a lattice parameter identical to that of the smaller hexagonal structure observed for LC **1**_{TEG} (2.55 nm). However, even in a detailed XRD study of **1**_{C10} with a synchrotron radiation source, we were unable to detect diffraction peaks indicative of the presence of a 2D superlattice (see Figure S5).^[6] We also investigated the phase behaviors of **1**_{EG} and **2**_{TEG} (Figure 1a) by means of DSC and temperature-dependent XRD and found that neither compound exhibited a LC mesophase but rather that both underwent a crystal-to-melt or glass-to-melt transition (see Figures S2, S4, and S6, and Table S1).^[6] There is a clear difference between the structures of **1**_{TEG} and **1**_{C10}, which only bears paraffinic side chains. Compound **1**_{EG} has oxyethylene side chains, but they are too short to endow the molecule with a distinct amphiphilic character. Although **2**_{TEG} is similar in structure to **1**_{TEG}, its benzo[*b*]triphenylene core is devoid of nitrogen atoms, and the existence of a dipole along the longer molecular axis can hardly be expected (see Figure S1b and Table S3).^[6]

All of the above observations allow us to rationalize the formation of the 2D superlattice structure in LC **1**_{TEG} as shown in Figure 4. We assume that side-chain miscibility prevails over the dipole–dipole interaction and results in a head-to-head π -stacking arrangement of **1**_{TEG} (Figure 4b). To minimize both the net dipole of the LC system and the contact area of the immiscible side chains, π -stacked columns of **1**_{TEG} assemble triangularly into a cylindrical architecture (Figure 4c), with the TEG side chains localized in the center. It is likely that the resultant cylinders, each of which consists of three columns of π -stacked **1**_{TEG}, arrange laterally to form an extended hexagonal lattice (Figure 4d). Indeed, the small ($a=2.55$ nm) and large lattice parameters ($a'=4.75$ nm) determined by XRD are consistent with the geometry of the proposed hierarchical structure.

Interestingly, the LC columns of hierarchically assembled **1**_{TEG} spontaneously align homeotropically on a glass substrate. Under a polarized optical microscope (POM), a film of **1**_{TEG} sandwiched between glass plates at a mesophase temperature (75 °C) showed a dark field over a large area (Figure 5a, inset). On the other hand, optical microscopy (OM) showed dendritic textures (Figure 5a). These observations are typical for homeotropically aligned Col_h assemblies.^[8] In contrast, a POM image of an LC film of paraffinic **1**_{C10} showed both bright birefringent texture and a dark field as a result of LC domains of horizontally and homeotropically aligned col-

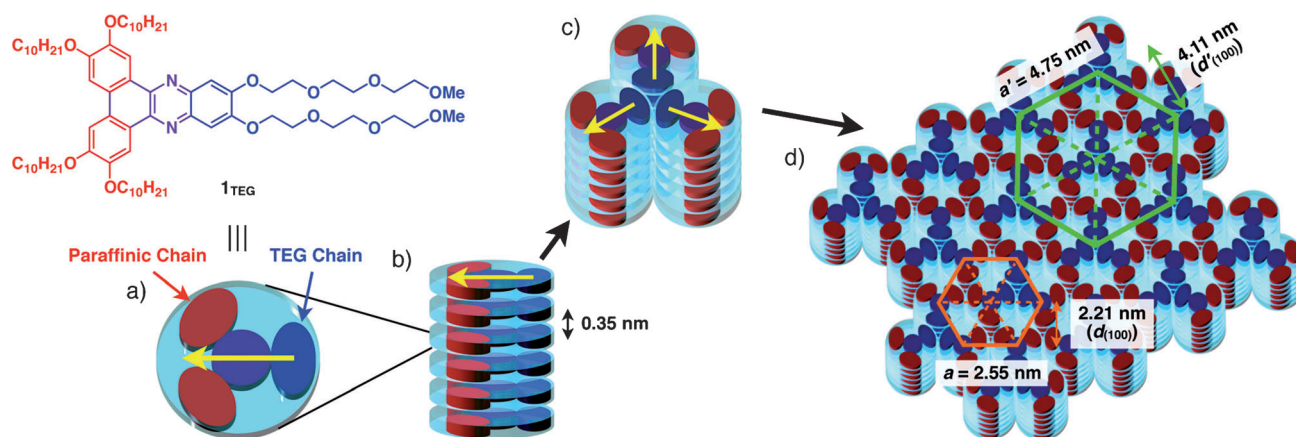


Figure 4. Hierarchical self-assembly of $\mathbf{1}_{\text{TEG}}$: a) $\mathbf{1}_{\text{TEG}}$ molecule; b) π -stacked column of $\mathbf{1}_{\text{TEG}}$ with a head-to-head arrangement; c) triangular assembly of π -stacked columns; d) hexagonal superlattice with structural parameters indicated. The yellow arrows indicate the dipole moment of the dibenzo[*a,c*]phenazine core.

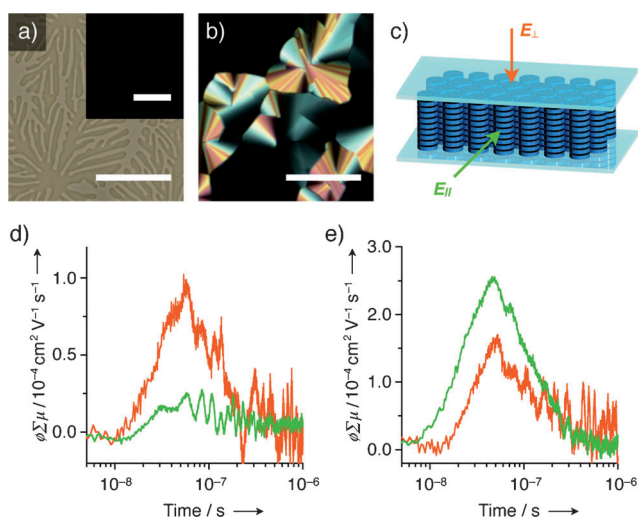


Figure 5. a) OM micrograph (inset: POM micrograph) of $\mathbf{1}_{\text{TEG}}$ at 75 °C and b) POM micrograph of $\mathbf{1}_{\text{C10}}$ at 100 °C, on cooling from the isotropic melt (scale bar: 50 μm). c) Schematic illustration of an LC film of $\mathbf{1}_{\text{TEG}}$ sandwiched between quartz plates for an FP-TRMC experiment. d, e) FP-TRMC profiles at 70 °C of LC films of $\mathbf{1}_{\text{TEG}}$ (d) and $\mathbf{1}_{\text{C10}}$ (e) as measured perpendicular (orange) and parallel (green) to the microwave electric-field vector.

umns, respectively (Figure 5 b). Thus, LC $\mathbf{1}_{\text{C10}}$ does not adopt a homeotropic orientation predominantly.

The contrasting orientational behavior of LC $\mathbf{1}_{\text{TEG}}$ and $\mathbf{1}_{\text{C10}}$ was clearly demonstrated by the measurement of flash-photolysis time-resolved microwave conductivity (FP-TRMC). The FP-TRMC technique enables the evaluation, without electrodes, of the intrinsic carrier-transport properties of materials.^[9] For this experiment, an LC film of $\mathbf{1}_{\text{TEG}}$ sandwiched between two quartz plates was placed in a microwave resonant cavity in such a way that the microwave electric-field (*E*-field) vector could be polarized either perpendicular or parallel to the substrate surface (Figure 5 c). Upon exposure of the LC film to laser light, the transient conductivity of the LC film displayed a rise and decay profile, whereby the transient conductivity is given by $\phi\Sigma\mu$, and ϕ and

$\Sigma\mu$ are the photocarrier-generation yield and the sum of the mobilities of generated charge carriers, respectively (Figure 5 d). From the FP-TRMC profile, the maximum transient conductivities ($\phi\Sigma\mu_{\text{max}}$) along the perpendicular (orange) and parallel (green) directions to the substrate surface were evaluated as 1.0×10^{-4} and $2.7 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Accordingly, the degree of anisotropy ($\phi\Sigma\mu_{\perp}/\phi\Sigma\mu_{\parallel}$) in the LC film of $\mathbf{1}_{\text{TEG}}$ was calculated to be 3.7. Although an LC film of $\mathbf{1}_{\text{C10}}$ also displayed a FP-TRMC signal (Figure 5 e), the value of $\phi\Sigma\mu_{\perp}$ ($1.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) was lower than that of $\phi\Sigma\mu_{\parallel}$ ($2.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), and the degree of anisotropy was as small as 0.7.

It has been suggested that the homeotropic columnar orientation of LC materials is possible when nucleation occurs from a glass/LC interface rather than from the bulk.^[10] A recent report also showed that long-range 2D lattice order can be a dominant factor for such a columnar orientation.^[11] In light of these notions, the strong preference of LC $\mathbf{1}_{\text{TEG}}$ for a homeotropic orientation most likely results from the hierarchical superlattice structure, which could enhance the 2D order of columnar assembly of $\mathbf{1}_{\text{TEG}}$ to a certain upper length scale. Furthermore, the TEG side chains of $\mathbf{1}_{\text{TEG}}$ localize at each lattice point of the superlattice (Figure 4 d), and this arrangement gives rise to hydrophilic domains that can potentially interact with hydroxy groups on a SiO_2 substrate. Presumably, such a surface event also plays a role in the development of homeotropic alignment.

In conclusion, we demonstrated that the LC dibenzo[*a,c*]phenazine $\mathbf{1}_{\text{TEG}}$, which contains decyloxy and TEG side chains, self-assembles to form a 2D hexagonal superlattice. This type of hierarchical structure has not previously been reported for columnar LC assemblies composed of disk-shaped aromatic molecules. In contrast to most reported examples,^[12] we ventured to adopt a molecular design that could hamper a head-to-tail packing arrangement, which is favorable for the canceling out of dipoles between adjacent molecules. As a consequence, $\mathbf{1}_{\text{TEG}}$ chooses an unprecedented way to cancel out the dipoles in the LC material: 1D triangular assemblies consisting of three π -stacked columns of $\mathbf{1}_{\text{TEG}}$ arrange laterally to form a large hexagonal lattice

(Figure 4). Interestingly, the hierarchically assembled LC columns of **1**_{TEG} tend to align homeotropically on a glass substrate over a large area and could thus provide pathways for directional charge transport perpendicular to the substrate.

Received: September 24, 2012

Published online: November 26, 2012

Keywords: amphiphiles · dipole–dipole interactions · liquid crystals · organic semiconductors · self-assembly

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