Liquid Crystals

DOI: 10.1002/anie.201203077

Wide-Range 2D Lattice Correlation Unveiled for Columnarly Assembled Triphenylene Hexacarboxylic Esters[**]

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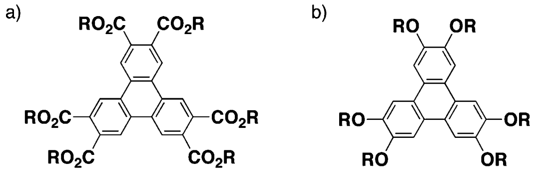
Realization of monodomain liquid crystals (LCs) is a grand challenge in materials science. Herein we propose that even rather small mesogens such as triphenylene, when functionalized with polar ester groups, can develop an exceptionally wide-range 2D lattice correlation in discotic columnar LCs. We recognized a particular role of ester substituents in the course of a study on the LC assembly of triphenylene hexacarboxylic esters (**1**$_n$, $n = 2$, 4, 6, 8, and 10; Scheme 1 a). Our initial motivation of this study was to investigate if π polarization of triphenylene by electron-withdrawing substituents may enhance its π stacking.[1] In relation to this possibility, Bock et al. reported, though without particular notions, that thermally stable columnar LCs are formed with triphenylene tri- and tetracarboxylic esters as mesogens.[2] As soon as we started to explore the LC behaviors of **1**$_n$, we noticed that these molecules are unique in a sense that their LC columns align homeotropically on a wide variety of substrates. Although the homeotropic orientation is well-known for certain discotic LC molecules, it is highly dependent on the type of substrate.[2d,3] Furthermore, we found with a big surprise that columnarly assembled **1**$_n$ commonly display an extremely sharp X-ray diffraction (XRD) peak owing to the (100) plane. Inspired by these observations, we revealed that the columnar LCs of **1**$_n$ feature an exceptionally wide-range 2D lattice correlation. As highlighted herein, the successful crystal structure analysis of **1**$_1$ allowed us to recognize that the ester carbonyl groups of **1**$_n$ can exert an intercolumnar dipole–dipole interaction.[4] This interaction possibly forces the LC columns to be correlated tightly over a wide range.



1$_1$: R = CH_3 **1**$_2$: R = C_2H_5
1$_4$: R = C_4H_9 **1**$_6$: R = C_6H_{13}
1$_8$: R = C_8H_{17} **1**$_{10}$: R = $C_{10}H_{21}$

2$_1$: R = CH_3 **2**$_8$: R = C_8H_{17}

Scheme 1. Molecular structures of a) triphenylene hexacarboxylic esters (**1**$_n$) and b) hexaalkoxytriphenylenes (**2**$_n$).

So far, triphenylene hexacarboxylic esters have scarcely been studied, while only the synthesis of methyl ester **1**$_1$ (Scheme 1 a) was briefly reported in relation to the chemistry of [6]radialene.[5] Compounds **1**$_1$ and **1**$_2$ were prepared by a modified literature procedure[6] and transformed into compounds **1**$_4$–**1**$_{10}$ (Scheme S1 in the Supporting Information).[7] All the ester derivatives thus obtained were unambiguously characterized by ^{1}H and ^{13}C NMR spectroscopy, infrared spectroscopy, and MALDI-TOF mass spectrometry. In an attempt to purify compound **1**$_1$ by recrystallization, single crystals suitable for X-ray crystallography were obtained.[7] As shown in Figure 1 a, **1**$_1$ in the crystalline state stack up on top of each other with an azimuthal rotation angle of 38° to form a 1D columnar assembly, where the lateral displacement with respect to the central benzene ring of **1**$_1$ is negligibly small. A view projected along the columnar axis (Figure 1 b) illustrates a short core-to-core separation (3.32 Å), which is even shorter than the interlayer distance of graphite (3.35 Å). The crystal-packing diagram (Figure 1 a) also showed that the columns of π-stacked **1**$_1$ are nicely arranged into a quasi-hexagonal geometry with an intercolumnar distance of 1.52 nm. This arrangement is in sharp contrast with the case of hexamethoxytriphenylene (**2**$_1$; Scheme 1 b), a representative mesogenic core for columnar LCs, whose reported crystal structure is devoid of any aromatic overlap.[8]

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[**] This work was supported by KAKENHI (21350108 for T.F. and 23750170 for T.K.). The synchrotron X-ray diffraction experiments were performed at the BL45XU in the SPring-8 with the approval of the RIKEN SPring-8 Center (proposal 20100062 and 20110065).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201203077.

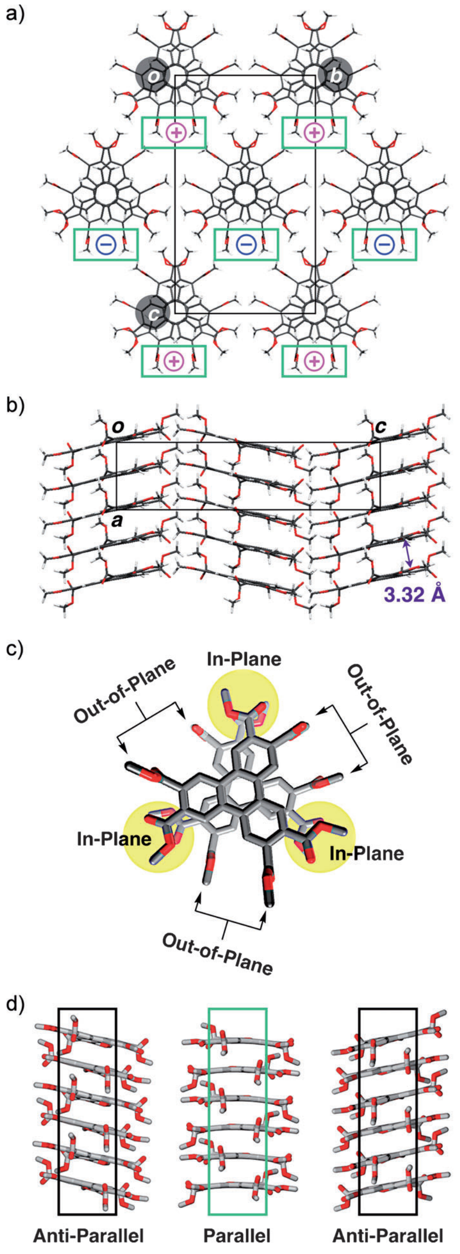

Figure 1. Crystal-packing diagrams of $\mathbf{1}_1$ viewed along the crystallographic a) *a*- and b) *b*-axes (*o* = origin). Schematic illustrations of c) top and d) side views of a single column, where two molecules of π-stacked $\mathbf{1}_1$ are shown in (c) for clarity. Yellow-shaded parts in (c) represent three sets of the ester groups adopting an in-plane conformation relative to the π-stacked cores. Rectangular frames in (d) show relative orientations of the ester carbonyl groups adopting an out-of-plane conformation relative to the π-stacked cores in a single column. Green frames in (a) and (d) highlight adjacent out-of-plane ester carbonyl groups that are oriented parallel to one another along the columnar axis, while black frames in (d) represent those upon antiparallel orientation. Plus and minus symbols in (a) denote directions of the out-of-plane ester carbonyl groups in the frames.

As described above, compounds $\mathbf{1}_2$–$\mathbf{1}_{10}$ (Scheme 1 a) self-assemble into a LC mesophase adopting a hexagonal columnar ($\mathrm{Col_h}$) geometry (Table S1 in the Supporting Information),[7] where the mesophase temperature ranges, as determined by differential scanning calorimetry (DSC), were much wider than those reported for the corresponding ether versions.[9] For example, $\mathbf{1}_8$ develops a LC mesophase at 34–96 °C on heating (Figure S1e in the Supporting Information),[7] whereas a reference triphenylene derivative with octyloxy side chains ($\mathbf{2}_8$; Scheme 1 b), in contrast, showed a LC mesophase in a much narrower temperature range of 66–85 °C.[9a] Powder XRD analysis of a bulk LC sample of $\mathbf{1}_8$ at 25 °C (on cooling) displayed three peaks (Figure 2 a) indexed as the diffractions from the (100), (110), and (200) planes of the $\mathrm{Col_h}$ structure (Figure S4 in the Supporting Information).[7] The core-to-core separation along the columnar axis was 0.35 nm, as evaluated from the diffraction peak at $q = 17.9\ \mathrm{nm^{-1}}$. Noteworthy is the fact that the diffraction peak from the (100) plane is extremely sharp, featuring a half-maximum full width of only $0.063\ \mathrm{nm^{-1}}$ (Figure 2 a). By applying the Scherrer equation,[10] the correlation length of the 2D hexagonal lattice was evaluated as 180 nm. Based on a literature survey, we confirmed that this correlation length is the second largest in columnar LCs, next to the case of a truxene derivative (ca. 400 nm),[11a] whereas the reported correlation lengths are mostly 20–40 nm[11b] and very rarely 80 nm.[11c] Meanwhile, on the contrary to our expectation, the 1D correlation length along the columnar axis (15 nm) was certainly a little larger than usual but not remarkable, thus indicating that the π polarization effect,[1] if any, is moderate on the columnar stacking of $\mathbf{1}_8$.

What interaction makes such an exceptionally wide-range 2D lattice correlation possible? Having this curiosity in mind, we took a closer look at the crystal structure of $\mathbf{1}_1$ and noticed that each column has a large dipole along the columnar axis. As illustrated in Figure 1 c, three ester carbonyl groups of $\mathbf{1}_1$ adopt an in-plane conformation relative to the triphenylene core, while other carbonyl groups adopt an out-of-plane conformation. In a single column of $\mathbf{1}_1$, the in-plane carbonyl groups of the triphenylene molecules (yellow-shaded areas,

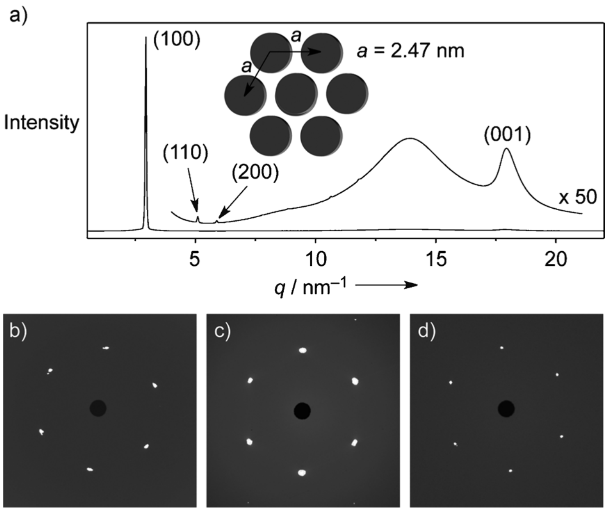

Figure 2. a) 1D XRD pattern and its magnified view (×50, scattering vector $q = 4$–$21\ \mathrm{nm^{-1}}$) of a bulk LC sample of $\mathbf{1}_8$ at 25 °C on cooling from its isotropic melt in a glass capillary (1.5 mm Ø). Values in parentheses indicate Miller indices. Inset shows lattice parameter *a* of the $\mathrm{Col_h}$ structure. b–d) Through-view 2D XRD images of open LC films of $\mathbf{1}_8$ at 25 °C on b) quartz, c) sapphire, and d) Au.

Figure 1c) are directed in such a way that their dipoles are cancelled as much as possible with those of the neighboring π-stacked triphenylene cores.[12] On the other hand, as for the three sets of adjacent out-of-plane ester carbonyl groups in a single column (Figure 1c), two of them are directed antiparallel to those attached to the neighboring π-stacked cores (black frames, Figure 1d), so that their dipoles are cancelled. In contrast, the residual ones are unique in a sense that they are oriented toward the same direction in a single column (green frames, Figure 1a,d), thereby giving rise to a large dipole along the columnar axis. Provided that such a large dipole likewise emerges, even though dynamically, in individual LC columns, the wide-range 2D lattice correlation, as observed for columnarly assembled LC **1**$_{8}$ (correlation length; 180 nm), is rationally explainable. Namely, the LC columns with a large dipole can be bound laterally to one another through an intercolumnar dipole–dipole interaction, so that they are correlated tightly up to a macroscopic length scale. Considering that the intercolumnar distance of columnarly assembled **1**$_{8}$, as evaluated by means of XRD, is 2.47 nm, the 2D correlation length of 180 nm corresponds to 73 columns. Such a wide-range 2D lattice correlation occurs also in other members of **1**$_{n}$ (Figures S2, S3, and S5 in the Supporting Information) upon columnar assembly. As summarized in Table 1, the number of the correlated columns increases from 55 to 73, 83, and then 100, as the observed intercolumnar distance decreases from 2.70 ($n=10$) to 2.47 ($n=8$), 2.23 ($n=6$), and then 1.95 nm ($n=4$). The trend that a shorter intercolumnar distance results in a larger number of the correlated columns suggests that the intercolumnar dipole–dipole interaction operates among the distal as well as proximal columns in the LC mesophase.

Table 1: Lateral correlation lengths (ξ_{100}) of **1**$_{4}$–**1**$_{10}$ in Col$_{h}$ phase.[10]

	T [°C]	d_{100} [nm]	a [nm]	ξ_{100} [nm]	Number of columns
1$_{4}$	25	1.68	1.95	195	100
1$_{6}$	25	1.93	2.23	185	83
1$_{8}$	25	2.14	2.47	180	73
1$_{10}$	40	2.34	2.70	149	55

As briefly described in the introductory part, one of the observations that led us to the above notification is that the LC columns of **1**$_{8}$ spontaneously align homeotropically in large area on a variety of substrates. For example, a film sample (18 mm × 18 mm × 5 μm) of **1**$_{8}$, sandwiched by glass plates at a mesophase temperature (92 °C), showed a dark view entirely in polarized optical microscopy (POM; Figure S7e in the Supporting Information).[7] Its optical microscopy (OM) image, in contrast, displayed a dendritic texture (Figure S7f in the Supporting Information)[7] typical of Col$_{h}$ assemblies.[13] Hence, the dark view in Figure S7e in the Supporting Information indicates that the LC columns of **1**$_{8}$ are oriented homeotropically on a glass substrate. This was also the case with an open LC film cast on a glass plate (Figure 3).[14] Other members of **1**$_{n}$ (Scheme 1a) as well as **1**$_{8}$ underwent such a wide-area homeotropic columnar orientation relative to the glass substrate (Figure S7 in the Supporting Information).[7] Bock and Grelet reported a similar orientation behavior for the Col$_{h}$ LC assemblies of triphenylene tri- and tetracarboxylic esters on glass and SiO$_{2}$ substrates.[2c] However, columnarly assembled **1**$_{n}$ unlikely require particular substrates for the homeotropic orientation. As shown in Figure S8 in the Supporting Information, compound **1**$_{8}$, for example, displayed a dark view in POM on quartz, sapphire, mica, indium tin oxide (ITO), silicon wafer, Au, polyethylene terephthalate (PET), polyvinylidene chloride (PVDC), and polyether ether ketone (PEEK), together with rubbed and unrubbed polyimide films.[7] Again, their OM images clearly showed a dendritic texture. Since quartz, sapphire, Au, and polyimide substrates are transparent for the X-ray beam, film samples of **1**$_{8}$ cast on these substrates were subjected to XRD for obtaining their through-view 2D images. Except for the case on polyimide (Figure S6 in the Supporting Information),[7] these LC films displayed diffraction spots adopting a clear hexagonal geometry (Figure 2b–d) as expected from the LC columns that align homeotropically with a six-fold symmetry. Noteworthy is the case on the Au substrate, where the hexagonal pattern definitely consists of very small and sharp six spots (Figure 2d). These observations indicate that the LC domain of columnarly assembled **1**$_{8}$ is large; at least greater than the X-ray beam size (150 × 100 μm) employed for the diffractometry. For achieving the homeotropic columnar orientation, a key that has mostly been considered is how to enhance nucleation from the substrate/LC interface rather than in the bulk.[2c] However, it is now clear that wide-range 2D lattice correlation can be a dominant factor for the LC columns to align homeotropically in large area.

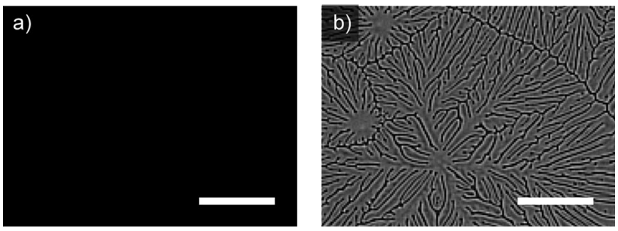

Figure 3. a) POM and b) OM images of an open LC film of **1**$_{8}$ at 92 °C on cooling from its isotropic melt on glass (scale bar = 100 μm).

Flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements demonstrated that the columnar LC assembly of **1**$_{8}$ adopting a homeotropic orientation is highly anisotropic electronically. The FP-TRMC technique allows for evaluating intrinsic carrier transport properties of materials without electrodes.[15] For this experiment, a LC film of **1**$_{8}$, sandwiched by quartz plates, was placed in a microwave cavity in such a way that the electric field (E-field) vector of the microwave can be polarized perpendicular or parallel to the substrate surface. Upon laser flash, the LC film displayed rise and decay profiles of the transient conductivity, given by $\phi\Sigma\mu$ (Figure 4), where ϕ and $\Sigma\mu$ represent photocarrier generation yield and sum of the mobilities of generated charge carriers, respectively. From the FP-TRMC profiles, the maximum transient conductivities ($\phi\Sigma\mu_{\max}$) of the LC film along the perpendicular (Figure 4, red) and parallel (blue) directions to the substrate surface were evaluated as 1.1×10^{-4} and 9.4×10^{-6} cm^{2}V^{-1}s^{-1}, respectively. The degree of aniso-

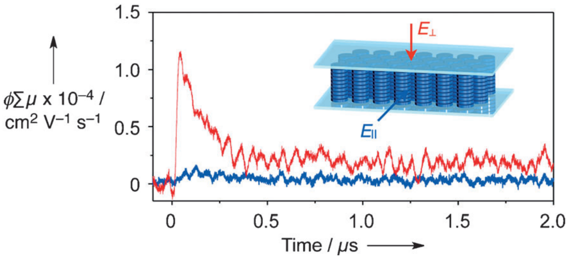

Figure 4. FP-TRMC responses of a LC film of $\mathbf{1}_8$ sandwiched by quartz plates at 25 °C, observed along parallel (blue) and perpendicular (red) directions to the substrate surface.

tropy is therefore 12, which is the largest class among those reported to date.[16] With a time-of-flight (TOF) experiment we also found that $\mathbf{1}_8$ in its columnar LC mesophase serves as a hole transporter. Thus, upon exposure to a 266 nm laser pulse, the LC film of $\mathbf{1}_8$, sandwiched by ITO electrodes, displayed at 25 °C a distinct transient photocurrent in its TOF profile under positive *E*-fields (Figure S9a in the Supporting Information).[7] The hole mobility (μ) at zero *E*-field, as extrapolated from its applied *E*-field dependency (Figure S9b in the Supporting Information),[7] was determined as $0.5\times10^{-2}\,\mathrm{cm^2V^{-1}s^{-1}}$. This mobility is one order of magnitude greater than that reported for a LC sample of $\mathbf{2}_8$, an alkoxy version of $\mathbf{1}_8$ (ca. $1\times10^{-4}\,\mathrm{cm^2V^{-1}s^{-1}}$).[17]

In conclusion, even a small aromatic mesogen such as triphenylene, when functionalized with polar ester groups, enables an exceptionally wide-range 2D lattice correlation in its columnar LC assembly owing to an intercolumnar dipole–dipole interaction. This intercolumnar interaction leads to a large-area homeotropic columnar orientation on a variety of substrates. A rather high hole mobility along with its anisotropic nature, observed for LC $\mathbf{1}_8$, casts aside a potential anxiety that substitution of aromatic mesogens with electron-withdrawing groups may deteriorate the hole-transporting properties of materials. Thus, the present work opens a new avenue for the design of wide-area orientable LC semiconductors.

Received: April 21, 2012

Keywords: liquid crystals · organic semiconductors · self-assembly · X-ray diffraction

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