Liquid Crystals

DOI: 10.1002/ange.201102472

Electric-Field-Responsive Handle for Large-Area Orientation of Discotic Liquid-Crystalline Molecules in Millimeter-Thick Films**

Daigo Miyajima, Fumito Araoka, Hideo Takezoe, Jungeun Kim, Kenichi Kato, Masaki Takata, and Takuzo Aida**

As well-known for liquid-crystalline (LC) displays[1] a variety of rodlike LC molecules that assemble into nematic and smectic phases align unidirectionally under the influence of an electric field (E field). In these cases, the direction of such oriented LC molecules can be controlled as desired. Hence, if semiconducting discotic LC molecules that assemble columnarly[2] can be aligned likewise by an E field, superiorly conducting electronic devices[3] with suitably oriented pathways for carrier transport[4] can be developed. However, discotic LC molecules[5,6] have not been reported to align under an E field. This is mainly because such LC materials with large discotic cores are poorly fluidic because of a 2D structural order of strongly π-stacked 1D columnar components. Therefore, to develop a strategy for designing discotic LC molecules that can be aligned by an E field is a grand challenge. Here, we report that aromatic amides[5a,c] with branched paraffinic tails, when properly spaced from mesogenic discotic cores, serve as an E-field-responsive handle that enables large-area unidirectional orientation of columnarly assembled LC molecules with extended π-conjugated cores. Also important in the view of device fabrication is that the resulting macroscopic orientation can be maintained even after the E field is switched off.

Recently, we reported that a corannulene derivative ($\mathbf{1}_{\mathbf{COR}}$; Figure 1), appended at its bowl-shaped core with 10 aromatic amide groups, forms a columnar LC assembly.[5c] Although the core unit of $\mathbf{1}_{\mathbf{COR}}$ is very large, the LC columns can be oriented in such a way that their columnar axes are parallel to the direction of an applied E field (Figure 2 a).[5c] As corannulene has a dipole because of its nonplanarity,[7] we assumed that the large dipole of its columnar assembly accounts for the observed E-field-induced orientation. To support this hypothesis, we newly synthesized $\mathbf{2}_{\mathbf{TP}}$ (Figure 1), a planar analogue of $\mathbf{1}_{\mathbf{COR}}$ having a triphenylene unit as core part instead of a nonplanar corannulene. Just as other triphenylene derivatives so far reported, this LC molecule columnarly assembled with hexagonal geometry ($\mathrm{Col_h}$) in a rather wide temperature range including room temperature (Figure 1). Furthermore, as in the case of $\mathbf{1}_{\mathbf{COR}}$,[5c] the columnar structure is likely stabilized by a hydrogen-bonding interaction of the amide groups along the column (see Figure S22 in the Supporting Information). To investigate if $\mathbf{2}_{\mathbf{TP}}$ at its LC mesophase can be aligned by an E field, an isotropic melt of $\mathbf{2}_{\mathbf{TP}}$ was introduced into a sandwich-type glass cell composed of patterned ITO electrodes with a gap of 5 μm. A rectangular-shaped 1.0 Hz E field of alternating current (25 $\mathrm{Vpp\,\mu m^{-1}}$) was applied to this sample which was heated at its LC mesophase temperature. Polarizing optical microscopy (POM) of $\mathbf{2}_{\mathbf{TP}}$ under crossed polarizers showed a dark field of a part, operating at an E field, of the sample, which was sandwiched by two ITO electrodes, whereas the other non-operating part, located between an ITO electrode and a glass, remained birefringent (Figure 2 b). When this sample was heated to allow a $\mathrm{Col_h}$-to-Iso phase transition and then cooled without E field to the LC mesophase temperature range, a birefringent texture developed over the entire view of the POM image. However, when the E field was again applied to this sample, the observed birefringence disappeared. Because the dark field, after rotation of the sample, did not display any contrast in the POM images, this observation indicates that the LC columns of $\mathbf{2}_{\mathbf{TP}}$, located under the applied E field, uniformly align homeotropically relative to the substrate. This homeotropic columnar orientation, once developed entirely over the LC sample by an E field, was maintained even after the E field was switched off. The resultant POM image remained dark as long as the oriented sample was kept in the LC mesophase temperature range. These observations exclude the possibility of our initial hypothesis that the nonplanar corannulene core plays a crucial role in the observed E-field responsiveness of the samples. However, these observations beneficially suggest that the amide-appended side-chain motif, commonly incorporated into $\mathbf{1}_{\mathbf{COR}}$ and $\mathbf{2}_{\mathbf{TP}}$, might serve as an E-field-

---

[*] D. Miyajima, Prof. Dr. T. Aida
Department of Chemistry and Biotechnology
School of Engineering, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
E-mail: aida@macro.t.u-tokyo.ac.jp

Dr. F. Araoka, Prof. Dr. H. Takezoe
Department of Organic and Polymeric Materials
Tokyo Institute of Technology
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552 (Japan)
E-mail: takezoe.h.aa@m.titech.ac.jp

Dr. J. Kim
Japan Synchrotron Radiation Research Institute (JASRI)
1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148 (Japan)

Dr. K. Kato, Prof. Dr. M. Takata
RIKEN SPring-8 Center
1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148 (Japan)

[**] The synchrotron radiation experiments were performed at BL02B2 and BL44B2 in Spring-8 under the Budding Researchers Support Programs and the Priority Nanotechnology Support Program administrated by the JASRI (Proposal Nos. 2008B1777, 2009A1651, and 2009A1699) and with the approval of RIKEN (Proposal No. 20090021). D.M. thanks the JSPS Research Fellowship for young scientists.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201102472.

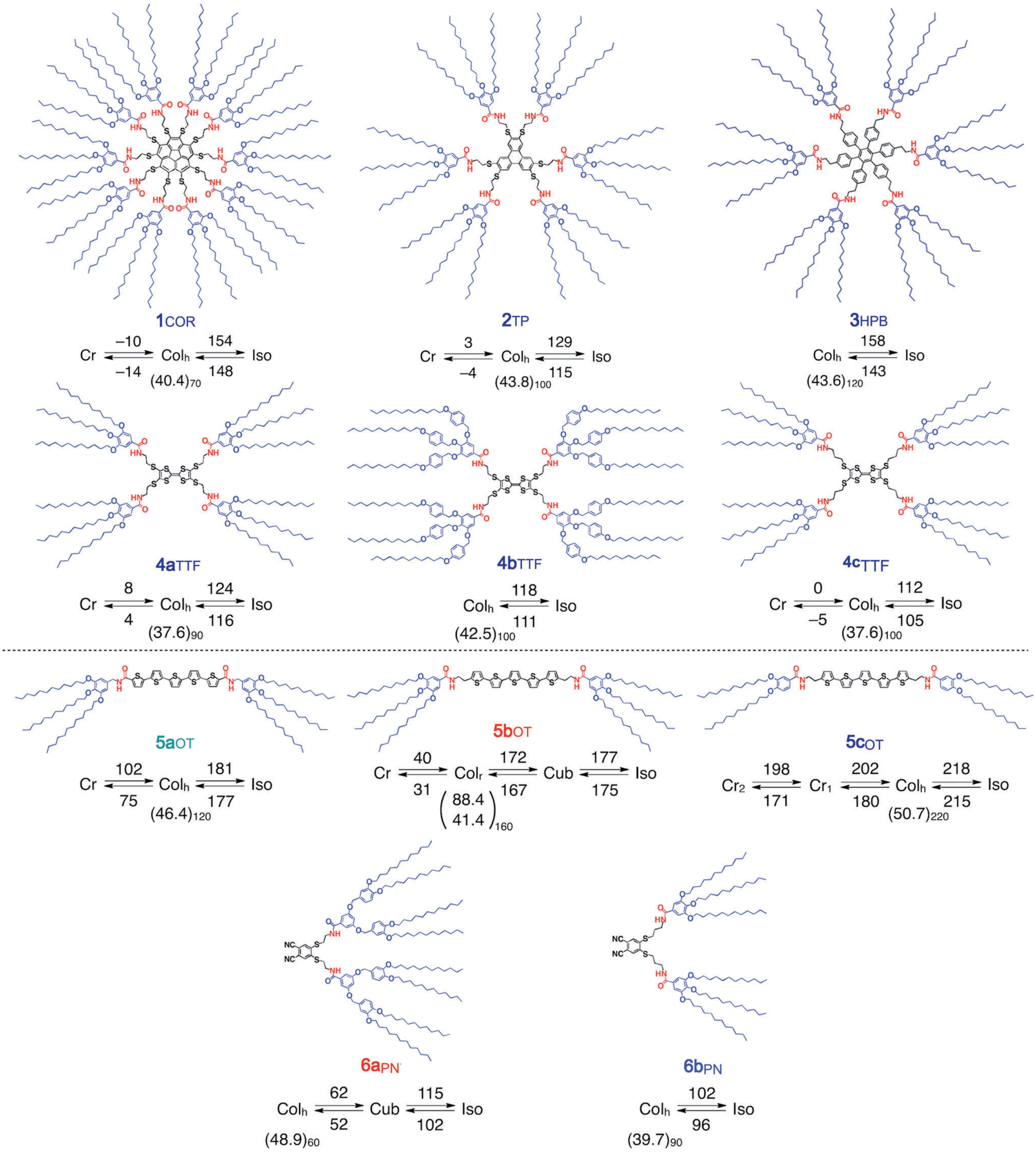

Figure 1. Structures and phase diagrams of LC compounds derived form corannulene ($\mathbf{1}_{\mathrm{COR}}$), triphenylene ($\mathbf{2}_{\mathrm{TP}}$), hexaphenylbenzene ($\mathbf{3}_{\mathrm{HPB}}$), tetrathiafluvalene ($\mathbf{4a}_{\mathrm{TTF}}$, $\mathbf{4b}_{\mathrm{TTF}}$, and $\mathbf{4c}_{\mathrm{TTF}}$), oligothiophene ($\mathbf{5a}_{\mathrm{OT}}$, $\mathbf{5b}_{\mathrm{OT}}$, and $\mathbf{5c}_{\mathrm{OT}}$), and phthalonitrile ($\mathbf{6a}_{\mathrm{PN}}$ and $\mathbf{6b}_{\mathrm{PN}}$). Phase-transition temperatures are in °C. Symbols Cr, $\mathrm{Col_h}$, $\mathrm{Col_r}$, Cub, and Iso denote crystalline, hexagonal columnar, rectangular columnar, cubic, and isotropic phases, respectively. Values in parentheses below the symbol Col are intercolumnar distances in nm, and the subscripted values are the observed temperatures in °C. Compounds with blue or green-colored symbols are responsive to the E field, but only compounds with blue-colored symbols maintain the resultant macroscopic columnar orientation even after the E field is switched off. Compounds with red-colored symbols are not responsive to the E field.

responsive handle for large-area orientation of columnarly assembled discotic LC molecules.

To confirm that the above-mentioned strategy is indeed universal, we synthesized nine LC compounds (Figure 1) in addition to $\mathbf{2}_{\mathrm{TP}}$. Compound $\mathbf{3}_{\mathrm{HPB}}$ bears a hexaphenylbenzene (HPB) core,[8] whereas $\mathbf{4a}_{\mathrm{TTF}}$ and $\mathbf{5b}_{\mathrm{OT}}$ carry tetrathiafluvalene (TTF) and oligothiophene (OT), respectively, which are representative motifs for *p*-type organic semiconductors.[9]

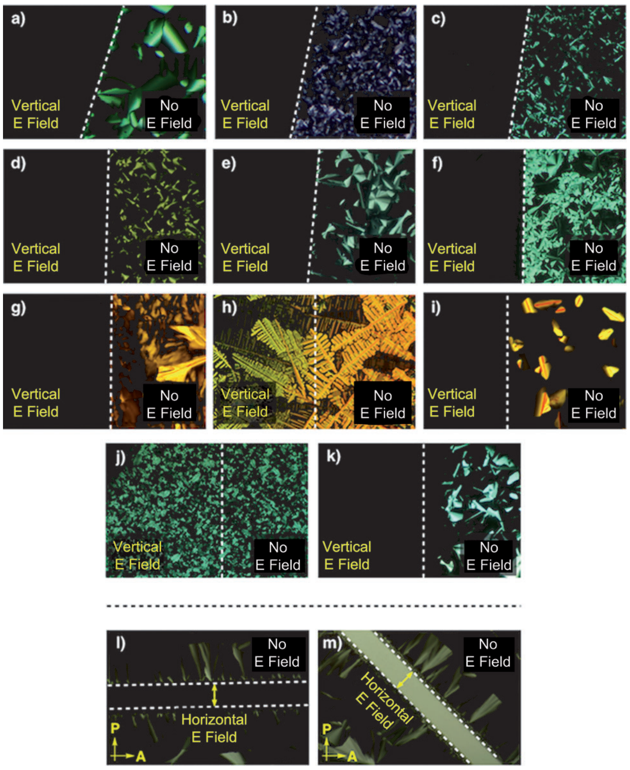

Figure 2. Polarizing optical micrographs (POM) under crossed polarizers. a) $\mathbf{1_{COR}}$ at 140 °C, b) $\mathbf{2_{TP}}$ at 110 °C, c) $\mathbf{3_{HPB}}$ at 140 °C, d) $\mathbf{4a_{TTF}}$ at 105 °C, e) $\mathbf{4b_{TTF}}$ at 105 °C, f) $\mathbf{4c_{TTF}}$ at 100 °C, g) $\mathbf{5a_{OT}}$ at 175 °C, h) $\mathbf{5b_{OT}}$ at 165 °C, i) $\mathbf{5c_{OT}}$ at 210 °C, j) $\mathbf{6a_{PN}}$ at 100 °C, k) $\mathbf{6b_{PN}}$ at 93 °C, l and m) $\mathbf{4b_{TTF}}$ at 105 °C. The dashed lines represent the borders of E-field-operating and non-operating parts. a)–k) A sandwich-type glass cell composed of patterned ITO electrodes with a gap of 5 μm, at which an E field (10–50 Vpp μm^{-1}) was site-selectively applied to a part of each sample, located between the ITO electrodes, from a vertical direction relative to the substrate. l) and m) A glass cell composed of comb-type ITO electrodes with a gap of 50 μm was used, as which an E field (27.5 Vpp μm^{-1}) was site-selectively applied to a part of the sample, located between the ITO electrodes, from a horizontal direction relative to the substrate. m) The micrograph was taken after rotation of the sample by 45° around the optical axis of the configuration in (l).

These three compounds commonly bear side chains that are identical to those of $\mathbf{1_{COR}}$ and $\mathbf{2_{TP}}$. For investigating the flexibility of the design startegy targeting at E-field responsive liquid-crystalline molecules, we also synthesized $\mathbf{4b_{TTF}}$/$\mathbf{4c_{TTF}}$ and $\mathbf{5a_{OT}}$/$\mathbf{5c_{OT}}$, which are structurally diversified versions of their parent molecules in terms of the number of spacing methylene units between the core and amide parts and the pattern of branching in the paraffinic tail attached to the amide handle. In addition to these discotic molecules, nondiscotic references $\mathbf{6a_{PN}}$ and $\mathbf{6b_{PN}}$, bearing a phthalonitrile (PN) core, were synthesized. By means of differential scanning calorimetry (DSC), POM, and X-ray diffraction (XRD) analysis, we confirmed that all these compounds are liquid-crystalline and assemble columnarly (see the Supporting Information). However, there are some variations. Judging from the values of intercolumnar distances summarized in Figure 1, the assembly of the LC compounds, listed above the dashed line, are quite ordinary and the discotic core serves as a mesogen to drive the hexagonal columnar assembly. On the other hand, in the columnar assembly of LC compounds listed below the dashed line in Figure 1, roughly three to four molecules assemble conically to give a supramolecular mesogenic core.[10] We also found that compounds $\mathbf{5b_{OT}}$ and $\mathbf{6a_{PN}}$ display a micellar cubic (Cub) mesophase above the temperature range for the columnar mesophase.

As a proof of concept, we investigated the assembly of the newly obtained LC compounds under conditions analogous to those for $\mathbf{2_{TP}}$, by applying a rectangular-shaped 1.0 Hz E field (10–50 Vpp μm^{-1}) of alternating current in the sandwich-type glass cell composed of patterned ITO electrodes with a gap of 5 μm. To our surprise, regardless of the structures of core and branched paraffinic tails, assembly and lattice dimensions, seven discotic LC compounds $\mathbf{3_{HPB}}$, $\mathbf{4a_{TTF}}$–$\mathbf{4c_{TTF}}$, $\mathbf{5a_{OT}}$, $\mathbf{5c_{OT}}$, and $\mathbf{6b_{PN}}$, as well as $\mathbf{2_{TP}}$, responded to the applied E field. As shown in Figure 2c–g,i, and k, POM images of these compounds at their LC mesophase displayed site-selectively a dark field in a part, operating at an E field, of the sample, which is sandwiched by the ITO electrodes. The largest attainable film thickness with unidirectional columnar orientation, as confirmed by POM, appeared to reach the millimeter range (Figure 3). For facilitating the POM observation, we chose $\mathbf{6b_{PN}}$ with a small optical interference and prepared its film samples with thickness values of 25, 50, 75, 100, 250, and 500 μm. Then, each LC film was heated, and the resulting isotropic melt was allowed to cool to the LC mesophase temperature in an applied E field. As shown in Figure 3a–f, all LC films displayed a dark field in POM, for which a higher voltage was necessary to make the thicker film entirely non-birefringent. For confirming the homeotropic columnar orientation in the 500 μm-thick film, we measured small-angle X-ray scattering (SAXS) patterns by orientating the film plane of the sample parallel to the incident X-ray beam (Figure 3g). As shown in Figure 3h, the SAXS pattern, observed before E-field treatment, was conical, which indicates that the sample is macroscopically not anisotropic. In contrast, after the LC film was annealed under an applied E field (3.9 Vpp μm^{-1}), only two explicit diffuse spots resulted in the equatorial direction (Figure 3i). The q values (which correspond to d-spacings) for the observed diffuse spots (1.80 nm^{-1}) agreed well with those expected for a (100) reflection of the hexagonal lattice (1.78 nm^{-1}), demonstrating that the (100) plane of the lattice is oriented homeotropically to the film plane. Such a thick LC film composed of unidirectionally oriented columns is unprecedented. Although several methods, for example, substrates with special surface coatings,[11] are known to realize homeotropic columnar orientation of certain discotic LC molecules, the largest attainable film thickness with uniform orientation is in most cases around 20 μm.

With only one exception, $\mathbf{3_{HPB}}$, $\mathbf{4a_{TTF}}$–$\mathbf{4c_{TTF}}$, $\mathbf{5c_{OT}}$, and $\mathbf{6b_{PN}}$, which can be oriented in an E field, all showed that their homeotropic columnar orientation, developed by the action of the E field, was maintained even after the applied E field was switched off. In contrast, when $\mathbf{5a_{OT}}$ with aromatic amide handles directly attached to the discotic core was monitored after switching off the E field, roughly 30 % of the dark field

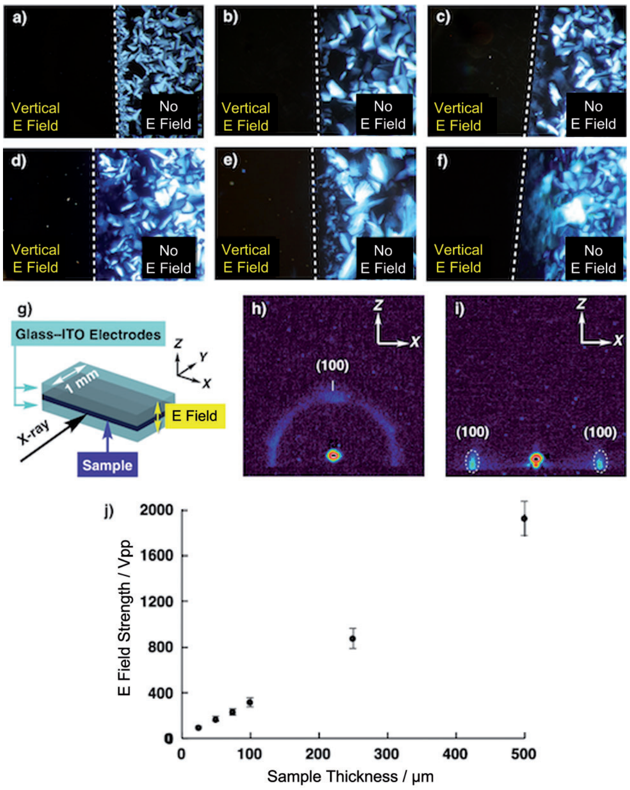

Figure 3. Polarizing optical micrographs (POM) under crossed polarizers at 92 °C. a)–f) Compound $\mathbf{6b}_{\mathrm{PN}}$ was placed in sandwich-type glass cells composed of patterned ITO electrodes with designated electrode gaps ranging from 25 to 500 µm, at which an E field (100–1900 Vpp) was applied site-selectively to a part of each sample, located between the ITO electrodes, from a horizontal direction relative to the substrate. Electrode gaps of a) 25, b) 50, c) 75, d) 100, e) 250, and f) 500 µm. The dashed lines represent the borders of E-field-operating and non-operating parts. Small-angle X-ray scattering (SAXS): g) sample configuration for SAXS measurements using ITO electrodes with a gap of 500 µm. SAXS profiles at 25 °C h) before and i) after applying an E field at 92 °C. j) Plots of the sample thickness (that is, the gap between the electrodes) versus the strength of E field required for homeotropic columnar orientation at 92 °C.

turned to be birefringent after three days at 170 °C. The columnarly assembled compounds $\mathbf{5b}_{\mathrm{OT}}$ (Figure 2 h) and $\mathbf{6a}_{\mathrm{PN}}$ (Figure 2 j) cannot be aligned by the action of the E field, even when its power was increased by changing the applied voltage to 60 Vpp µm^{-1}. In these examples, the phase diagrams in Figure 1 commonly feature a very rigid Cub mesophase, which possibly affects the fluidity of the connecting Col mesophase. Nevertheless, partially modified $\mathbf{5c}_{\mathrm{OT}}$ and $\mathbf{6b}_{\mathrm{PN}}$ can both be aligned unidirectionally by the action of an E field (Figure 2 i, k). Namely, the branched paraffinic tail, when properly designed,[12] supports the implementation of the amide handle for large-area columnar orientation of the discotic LC molecules.

Depending on the direction of the applied E field, the LC columns can be oriented not only homeotropically but also in other directions. For demonstrating the horizontal columnar orientation relative to the substrate, we used a glass cell composed of comb-type electrodes with a gap of 50 µm, and a rectangular-shaped 1.0 Hz E field (27.5 Vpp µm^{-1}) of in-plane alternating current was applied at 105 °C to $\mathbf{4b}_{\mathrm{TTF}}$ at its LC mesophase. As shown by a polarizing optical micrograph in Figure 2 l taken under crossed polarizers, a part of the sample located between the ITO electrodes displayed a dark field when the applied E field was directed along either of the two polarizer axes (Figure 2 l). Upon rotation of the cell around the optical axis, POM displayed a contrast at every 45° (Figure 2 m). That is, the LC columns are oriented horizontally with respect to the substrate. We also found that the molecular program which can be aligned by the E field, perfectly operates regardless of whether the substrate surface is bare ITO or modified ITO coated with oriented polyimide films such as AL1254 and JALS204 (JSR). As for the E-field-induced large-area alignment of columnarly assembled LC molecules, we propose that the initial event involves unidirectional orientation of the amide handles in such a way that the resulting macroscopic dipole can be directed antiparallel to the applied E field. To confirm the E-field responsiveness of the amide handle, we measured second harmonic generation (SHG) profiles of $\mathbf{2}_{\mathrm{TP}}$ at its Col$_h$ LC mesophase, because SHG is a reliable probe for the detection of macroscopic dipoles in materials.[13] At first, we confirmed that the LC material, as expected, is SHG-silent, regardless of whether the columns are unidirectionally oriented or not. Namely, microscopic local dipoles in the material are cancelled out. Then, we applied an E field (10.0 Hz, 25 V µm^{-1}) of direct current to the LC sample, whereupon an explicit SHG signal emerged (Figure 4). However, when the E field was switched off, the SHG signal vanished instantaneously. Such an on/off SHG profile of the material in response to the E field was repeated many times without any decay. Judging from the molecular structure of $\mathbf{2}_{\mathrm{TP}}$, the E-field-responsive SHG profile can be accounted for by the unidirectional orientation of the hydrogen-bonded amide handles of $\mathbf{2}_{\mathrm{TP}}$.[14] This molecular event, occurring over a macroscopic length scale, could eventually trigger local and then large-area unidirectional orientation of the LC columns. In general, E-field-induced orientation of polar molecules has been considered to occur either dipolarly or dielectrically.[1] In the present system, the former mechanism is more likely, taking into account also the fact that the

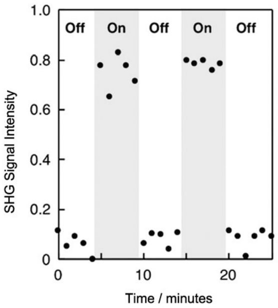

Figure 4. Second harmonic generation (SHG) profiles of a hexagonal columnar liquid-crystalline assembly of compound $\mathbf{2}_{\mathrm{TP}}$ in response to an applied E field. Solely in grey-colored areas, an E field of direct current (10.0 Hz, 25 V µm^{-1}) was applied to the sample at 110 °C.

largest attainable film thickness with unidirectional columnar orientation is proportional to the voltage applied for the action of the E field (Figure 3j).[1]

Overall, we successfully developed the first E-field-responsive handle that enables large-area unidirectional columnar orientation of a variety of extended π-conjugated molecules. By taking advantage of the method using an E field, the columns can be oriented in any directions even in a millimeter-thick film. Furthermore, the columnar orientation, once developed by the action of the E field, is maintained after the E field is switched off. None of the reported methods[15] and molecular design startegies[16] can realize all these features. The concept of E-field-responsive handles is not only promising for the growing field of organic electronics, but also interesting for remote manipulation of designed molecules in bulk state.

Received: April 10, 2011

Keywords: hydrogen bonds · liquid crystals · self-assembly · semiconductors · supramolecular chemistry

---

[1] a) P. J. Collings, M. Hird, *Introduction to Liquid Crystals, Chemistry and Physics*, Taylor & Francis, London, **1997**; b) *Liquid Crystals: Applications and Uses*, *Vols. 1–3* (Ed.: B. Bahadur), World Scientific, Singapore, **1990**.

[2] a) S. R. Forrest, M. E. Thompson, *Chem. Rev.* **2007**, *107*, 923; b) A. R. Murphy, J. M. J. Fréchet, *Chem. Rev.* **2007**, *107*, 1066; c) E. Menard, M. A. Meitl, Y. Sun, J.-U. Park, D. J.-L. Shir, Y.-S. Nam, S. Jeon, J. A. Rogers, *Chem. Rev.* **2007**, 107, 1117.

[3] a) H. Sirringhaus, R. J. Wilson, R. H. Friend, M. Inbasekaran, W. Wu, E. P. Woo, M. Grell, D. D. C. Bradley, *Appl. Phys. Lett.* **2000**, *77*, 406; b) M. L. Swiggers, G. Xia, J. D. Slinker, A. A. Gorodetsky, G. G. Malliaras, R. L. Headrick, B. T. Weslowski, R. N. Shashidhar, C. S. Dulcey, *Appl. Phys. Lett.* **2001**, *79*, 1300; c) X. L. Chen, A. J. Lovinger, Z. Bao, J. Sapjeta, *Chem. Mater.* **2001**, *13*, 1341; d) S. Nagamatsu, N. Tanigaki, Y. Yoshida, W. Takashima, K. Yase, K. Kaneto, *Synth. Met.* **2003**, *137*, 923.

[4] a) L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science* **2001**, *293*, 1119; b) C. D. Simpson, J. Wu, M. D. Watson, K. Müllen, *J. Mater. Chem.* **2004**, *14*, 494; c) J. P. Schmidtke, R. H. Friend, M. Kastler, K. Müllen, *J. Chem. Phys.* **2006**, *124*, 174704; d) S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sven, A. Schreivogel, M. Tosoni, *Angew. Chem.* **2007**, *119*, 4916; *Angew. Chem. Int. Ed.* **2007**, *46*, 4832; e) O. Thiebaut, H. Bock, E. Grelet, *J. Am. Chem. Soc.* **2010**, *132*, 6886.

[5] Examples of nondiscotic columnar LCs with H-bonding groups, which can be oriented by an E field: a) M. L. Bushey, T.-Q. Nguyen, C. Nuckolls, *J. Am. Chem. Soc.* **2003**, *125*, 8264; b) K. Kishikawa, S. Nakahara, Y. Nishikawa, S. Kohmoto, M. Yamamoto, *J. Am. Chem. Soc.* **2005**, *127*, 2565; c) D. Miyajima, K. Tashiro, F. Araoka, H. Takezoe, J. Kim, K. Kato, M. Takata, T. Aida, *J. Am. Chem. Soc.* **2009**, *131*, 44.

[6] Examples of nondiscotic columnar LCs, which can be oriented by an E field, with polar groups other than hydrogen-bonding motifs: a) E. Gorecka, D. Pociecha, J. Mieczkowski, J. Matraszek, D. Guillon, B. Donnio, *J. Am. Chem. Soc.* **2004**, *126*, 15946; b) H. Shimura, M. Yoshio, A. Hamasaki, T. Mukai, H. Ohno, T. Kato, *Adv. Mater.* **2009**, *21*, 1591; c) K. Kaneko, A. Mandai, B. Heinrich, B. Donnio, T. Hanasaki, *ChemPhysChem* **2010**, *11*, 3596.

[7] a) F. J. Lovas, R. J. McMahon, J.-U. Grabow, M. Schnell, J. Mack, L. T. Scott, R. L. Kuczkowski, *J. Am. Chem. Soc.* **2005**, *127*, 4345.

[8] a) C. G. Clark, Jr., G. A. Floudas, Y. J. Lee, R. Graf, H. W. Spiess, K. Müllen, *J. Am. Chem. Soc.* **2009**, *131*, 8537; b) Y. Geng, A. Fechtenkötter, K. Müllen, *J. Mater. Chem.* **2011**, *21*, 134.

[9] a) R. Andreu, J. Garin, J. Orduna, J. Barberá, J. L. Serrano, T. Sierra, M. Sallé, A. Gorgues, *Tetrahedron* **1998**, *54*, 3895; b) T. Yasuda, K. Kishimoto, T. Kato, *Chem. Commun.* **2006**, 3399; c) M. Funahashi, F. Zhang, N. Tamaoki, *Adv. Mater.* **2007**, *19*, 353; d) L. Wang, H. Cho, S.-H. Lee, C. Lee, K.-U. Jeong, M.-H. Lee, *J. Mater. Chem.* **2011**, *21*, 60.

[10] a) B. M. Rosen, C. J. Wilson, D. A. Wilson, M. Peterca, M. R. Imam, V. Percec, *Chem. Rev.* **2009**, *109*, 6275; b) T. Yasuda, H. Ooi, J. Morita, Y. Akama, K. Minoura, M. Funahashi, T. Shimomura, T. Kato, *Adv. Funct. Mater.* **2009**, *19*, 411.

[11] a) S. D. Hudson, H.-T. Jung, V. Percec, W.-D. Cho, G. Johansson, G. Ungar, V. S. K. Balagurusamy, *Science* **1997**, *278*, 449; b) K. Venkatesan, P. H. J. Kouwer, S. Yagi, P. Müller, T. M. Swager, *J. Mater. Chem.* **2008**, *18*, 400.

[12] V. Percec, M. R. Imam, M. Peterca, D. A. Wilson, R. Graf, H. W. Spiess, V. S. K. Balagurusamy, P. A. Heiney, *J. Am. Chem. Soc.* **2009**, *131*, 7662.

[13] T. Watanabe, S. Miyata, T. Furukawa, H. Takezoe, T. Nishi, M. Sone, A. Migita, J. Watanabe, *Jpn. J. Appl. Phys.* **1996**, *35*, L505.

[14] Y. Okada, S. Matsumoto, Y. Takanishi, K. Ishikawa, S. Nakahara, K. Kishikawa, H. Takezoe, *Phys. Rev. E* **2005**, *72*, 020701(R).

[15] a) I. Fischbach, T. Pakula, P. Minkin, A. Fechtenkötter, K. Müllen, H. W. Spiess, *J. Phys. Chem. B* **2002**, *106*, 6408; b) A. Tracz, J. K. Jeszka, M. D. Watson, W. Pisula, K. Müllen, T. Pakula, *J. Am. Chem. Soc.* **2003**, *125*, 1682; c) A. M. Van de Craats, N. Stutzman, O. Bunk, M. M. Nielsen, M. Watson, K. Müllen, H. D. Chanzy, *Adv. Mater.* **2003**, *15*, 495; d) I. O. Shklyarevskiy, P. Jonkheijm, N. Stutzmann, D. Wasserberg, H. J. Wondergem, P. C. M. Christianen, A. P. H. J. Schenning, D. M. De Leeuw, Z. Tomovíc, J. Wu, K. Müllen, J. C. Maan, *J. Am. Chem. Soc.* **2005**, *127*, 16233; e) H. Monobe, K. Awazu, Y. Shimizu, *Adv. Mater.* **2006**, *18*, 607; f) A. Cristadoro, G. Lieser, H. J. Räder, K. Müllen, *ChemPhysChem* **2007**, *8*, 586; g) J.-H. Lee, S.-M. Choi, B. D. Pate, M. H. Chisholm, Y.-S. Han, *J. Mater. Chem.* **2006**, *16*, 2785; h) N. Hosono, T. Kajitani, T. Fukushima, K. Ito, S. Sasaki, M. Takata, T. Aida, *Science* **2010**, *330*, 808.

[16] a) N. Boden, R. J. Bushby, P. S. Martin, *Langmuir* **1999**, *15*, 3790; b) A. N. Cammidge, H. Gopee, *J. Mater. Chem.* **2001**, *11*, 2773; c) K. Hatsusaka, K. Ohta, I. Yamamoto, H. Shirai, *J. Mater. Chem.* **2001**, *11*, 423; d) V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyanovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H.-W. Spiess, S. D. Hudson, H. Duan, *Nature* **2002**, *417*, 384; e) N. Terasawa, H. Monobe, K. Kiyohara, Y. Shimizu, *Chem. Commun.* **2003**, 1678; f) G. Schweicher, G. Gbabode, F. Quist, O. Debever, N. Dumont, S. Sergeyev, Y. H. Geerts, *Chem. Mater.* **2009**, *21*, 5867; g) W. Pisula, Z. Tomovi 'c, B. El Hamaoui, M. D. Watson, T. Pakula, K. Müllen, *Adv. Funct. Mater.* **2005**, *15*, 893.