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o-Phenylene Octamers as Surface Modifiers for Homeotropic Columnar Ordering of Discotic Liquid Crystals

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Supporting Information

ABSTRACT: Large-area homeotropic columnar ordering of π-conjugated discotic liquid crystals (LCs) is crucial for certain device applications but generally hard to achieve. Here we report polymeric *o*-phenylene octamer poly-**1** and its monomer **1** as the first surface modifiers for homeotropic columnar order of a variety of discotic LCs up to a macroscopic length scale. Their octameric *o*-phenylene parts are known to fold helically into a cylinder that is reminiscent of a π-stacked column of discotic LCs. Through-view X-ray diffraction patterns of **1** suggested that this molecule adheres to the glass substrate and directs its cylindrical axis perpendicular to the glass surface. This "face-on" orientation likely nucleates the homeotropic columnar order of discotic LC materials.

With the increasing importance of soft electronic devices, particular attention has been paid to π-conjugated discotic liquid-crystalline materials with a large-area unidirectional structural order.[1] However, in contrast with the case of rod-like liquid crystal (LC) molecules that can uniformly align horizontally on a rubbed polyimide film,[2] an essential issue to consider is the lack of general strategies to realize orientational control of discotic LC molecules.[3] Especially, homeotropic columnar ordering of discotic LCs, which have many potential applications, remains a difficult task.[4] Here we report that polymeric *o*-phenylene octamer poly-**1** (Figure 1b) and its monomer **1** (Figure 1a) serve as the first surface modifiers that can nucleate large-area columnar ordering of discotic LC materials without deteriorating their original phase features. How to manipulate interfacial phenomena remains a big challenge in chemistry and materials science. The present finding sheds light on this fundamental issue.

Recently, we reported that terminally functionalized oligomeric *o*-phenylenes are a new class of stimuli-responsive foldamers[5] that adopt a cylindrical architecture with a 3_1-helical conformation.[6] Because of this molecular structure, these cylindrical motifs, when projected along their longer skeletal axis (Figure 1d), look like triphenylene (TP, Figure 1f). Hence, we envisioned that this cylindrical motif, if properly designed, might be miscible with TP-based LC materials. Thus, *o*-phenylene octamer **1** carrying hexadecyl chains via an ester linker at both ends (Figure 1a) was designed and mixed with **TP**$_8$ (Figure 1e). We found that, up to a mixing ratio of 30 wt%, compound **1** neither destabilizes the LC mesophase of **TP**$_8$ nor changes its packing geometry.[7] These observations indicate that **1** is immiscible with **TP**$_8$ at a molecular level and phase-separated macroscopically, contrary to our expectation. However, we noticed that, in the presence of this immiscible additive, the LC columns of **TP**$_8$ entirely align homeotropically. With this serendipitous finding, we supposed that **1** might efficiently nucleate such a particular columnar orientation at a glass/LC interface. In order to ensure this interesting possibility, we synthesized poly-**1** (Figure 1b),[8] which likely possesses a larger adhesivity than monomer **1** toward the glass surface. In fact, as highlighted in the present Communication, poly-**1** modifies the glass surface more efficiently for homeotropic columnar ordering of **TP**$_8$. Furthermore, this function also operates for other discotic LC materials.

In differential scanning calorimetry (DSC; Figure S1a),[9] poly-**1** upon heating showed two glass transition events at 72 and 151 °C. As expected, the two glassy states displayed a featureless X-ray diffraction (XRD) profile (Figure S1b,c).[9] Thus, poly-**1** itself is substantially an amorphous material. Next, poly-**1** was mixed with **TP**$_8$. In DSC, **TP**$_8$ containing 10 wt% of poly-**1**, for example, displayed a mesophase at 65−85 °C upon heating and 82−42 °C upon cooling (Figure S4a).[9] These phase behaviors are virtually identical to those of **TP**$_8$ alone (Figure S3a and Table S1).[9,10] When this poly-**1**-containing LC material in a glass capillary was exposed to a synchrotron X-ray beam, the through-view XRD pattern showed characteristic diffractions with *d*-spacings of 2.03, 1.17, and 1.01 nm (Figure 2a), whose ratio is consistent with that required for hexagonal packing $(1{:}\sqrt{3}{:}2)$. The observed *d*-spacings are substantially the same as those of **TP**$_8$ alone (Figure S3b).[9] These observations indicate that poly-**1** is phase-separated from the hexagonal columnar (Col$_\mathrm{h}$) LC mesophase of **TP**$_8$.[11] Although phase-separated poly-**1** is not detectable due to its amorphous nature, phase separation was also supported by the

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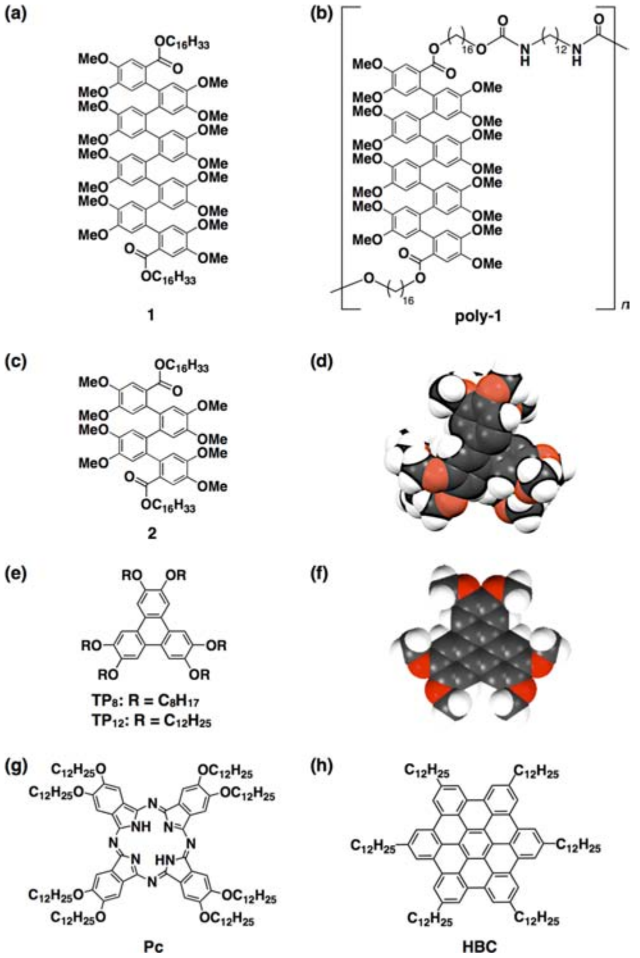

Figure 1. Molecular structures of (a) monomeric (**1**) and (b) polymeric (poly-**1**) *o*-phenylene octamers and (c) *o*-phenylene tetramer (**2**). Molecular structures of discotic LC molecules derived from (e) triphenylene ($\mathbf{TP_8}$ and $\mathbf{TP_{12}}$), (g) phthalocyanine (**Pc**), and (h) hexabenzocoronene (**HBC**). CPK models of (d) a hydrogen-terminated octamer of 1,2-dimethoxybenzene and (f) hexamethoxytriphenylene.

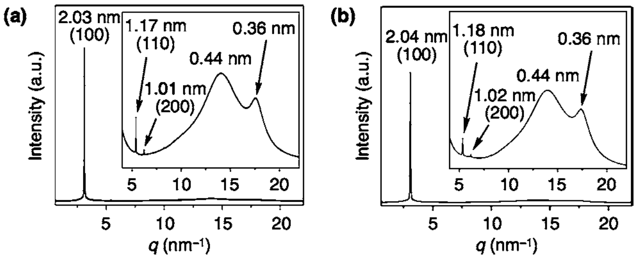

Figure 2. XRD patterns of bulk samples of (a) $\mathbf{TP_8}$ containing 10 wt% of poly-**1** and (b) $\mathbf{TP_8}$ containing 10 wt% of **1** at 70 °C on cooling from their isotropic melts. The samples were placed in a glass capillary (φ = 1.5 mm). Values in parentheses indicate Miller indices. Insets show magnified XRD patterns in a wide-angle region. Based on the *hkl* = 100 diffraction peaks, lattice parameters were determined as 2.34 and 2.35 nm for poly-**1**-containing $\mathbf{TP_8}$ (10 wt%) and **1**-containing $\mathbf{TP_8}$ (10 wt %), respectively.

fact that the enthalpy changes associated with the crystal-to-Col$_h$ and Col$_h$-to-isotropic melt phase transitions, normalized based on the contents of $\mathbf{TP_8}$, remain intact upon the mixing of poly-**1** (Table S2).[9] Figure 3a shows an optical micrograph (OM) of a 2-μm-thick film[12] of this mixture at 70 °C, where a dendritic texture, typical of Col$_h$ LCs, develops entirely. In contrast, its polarized optical micrograph (POM) image was completely dark, without any birefringence (Figure 3a).[4j,13] From these together with its conoscopic interference image (Figure 3b), we conclude that, upon mixing with poly-**1**, the hexagonally packed LC columns of $\mathbf{TP_8}$ align homeotropically with respect to the glass substrate. Even when the doping level of poly-**1** was reduced to 3 wt%, the POM image remained dark (Figure 3c). However, when the content of poly-**1** was below this level, the material, just as $\mathbf{TP_8}$ alone (Figure 3d), was partially birefringent in POM, indicating the occurrence of incomplete homeotropic columnar ordering (Figure S5).[9]

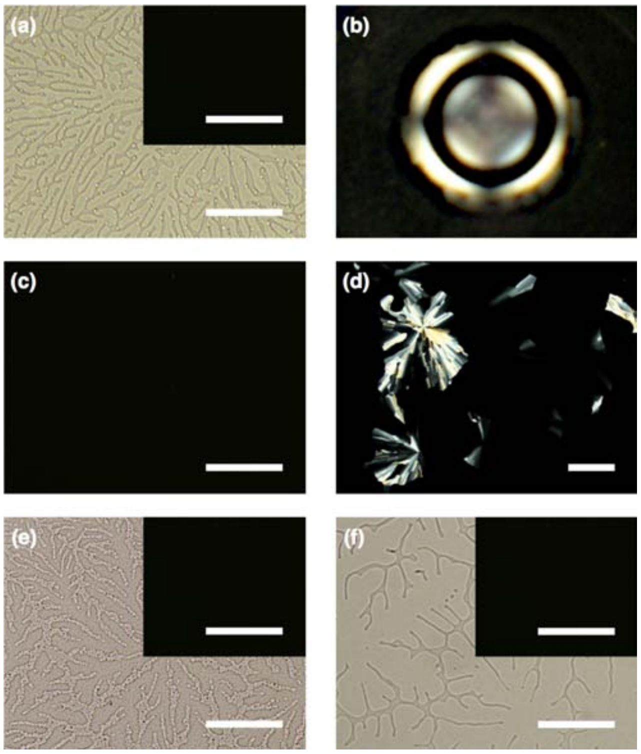

Figure 3. (a) OM and POM (inset) and (b) conoscopic image of a LC film of $\mathbf{TP_8}$ containing 10 wt% of poly-**1**. (c) POM of a LC film of $\mathbf{TP_8}$ containing 3 wt% of poly-**1**. (d) POM of a LC film of $\mathbf{TP_8}$ alone. (e) OM and POM (inset) of a LC film of $\mathbf{TP_8}$ containing 10 wt% of **1**. (f) OM and POM (inset) of $\mathbf{TP_8}$ on a glass substrate spin-coated with poly-**1**. All LC samples were heated once to their isotropic melting point, allowed to cool to 70 °C, and then subjected to microscopy. Scale bars for (a) and (c)−(e) represent 100 μm, and that for (f) denotes 50 μm.

Of interest, not only $\mathbf{TP_8}$ and its longer side-chain version $\mathbf{TP_{12}}$ (Figures 1e and S10)[9] but also other discotic LC molecules having, e.g., phthalocyanine (**Pc**, Figures 1g and S11)[9] and hexabenzocoronene (**HBC**, Figures 1h and S12)[9] cores adopt a homeotropic columnar order in the presence of poly-**1**. The result for **HBC** is noteworthy. As evidenced by a heavily birefringent POM texture in Figure S12e,[9] **HBC** alone in the LC state has a strong preference for horizontal columnar ordering with respect to the glass substrate. However, such a birefringent texture disappeared almost completely when **HBC** was mixed with 10 wt% of poly-**1** (Figure S12f).[9] Just like the case with monomer **1**, none of the DSC and XRD profiles of these discotic LCs were deteriorated by poly-**1** (Figures S10−S12 and Table S1),[9] indicating their immiscibility with poly-**1**.

One may wonder why poly-**1** induces homeotropic columnar orientation of these LC materials. We found that the homeotropic orientation becomes more difficult for thicker film samples. For example, when the content of poly-**1** in **TP$_8$** was fixed at 10 wt%, 25- and 50-μm-thick LC films, sandwiched between glass plates, entirely displayed a dark-field POM image (Figure S8a,b).[9] However, a 100-μm-thick LC film was birefringent (Figure S8c).[9] This tendency indicates a possibility that a nucleation event, leading to homeotropic columnar order, is initiated by the adsorption of poly-**1** onto the glass/LC interface. Note that a 50-μm-thick LC film of **TP$_8$** became birefringent when the content of poly-**1** was reduced to 3 wt% (Figure S6).[9] Therefore, an adsorption equilibrium likely exists and determines the amount of adsorbed poly-**1** eligible for the nucleation event. As briefly described in the introductory part, monomer **1** is inferior to poly-**1** in its ability to induce homeotropic columnar order (Figures 2b and 3e). In fact, when the content of **1** in **TP$_8$** was 10 wt%, even a 25-μm-thick LC film was partially birefringent (Figure S9a).[9] This trend seems reasonable, since monomer **1** in such an adsorption equilibrium is less advantageous than poly-**1**, having multiple polar ester and urethane units capable of interacting with silanol groups on the glass surface. Accordingly, when a glass substrate pretreated with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) to protect the silanol groups was employed, even a thin LC film (2 μm) of **TP$_8$**, though containing 10 wt% of poly-**1**, displayed a birefringent POM texture (Figure S7).[9]

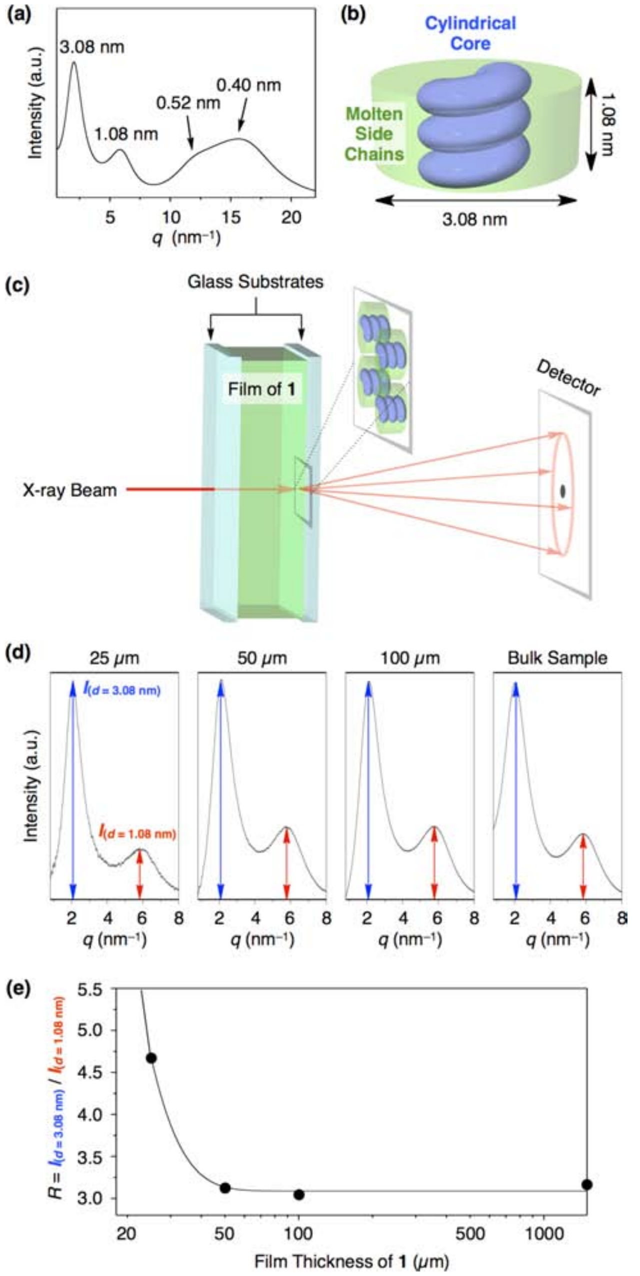

Figure 4. (a) XRD pattern of a bulk sample of **1** at 80 °C on heating in a glass capillary (φ = 1.5 mm). Schematic illustrations of (b) molecular structure of **1** and (c) experimental setup for obtaining through-view XRD images of **1**. (d) XRD patterns of **1** measured at 80 °C on cooling from its isotropic melting poing when sandwiched between two glass plates using 25-, 50-, and 100-μm spacers and in a glass capillary (φ = 1.5 mm). (e) Plots of film thickness versus intensity ratio (R) of diffraction peaks, $I_{d=3.08\text{nm}}$ and $I_{d=1.08\text{nm}}$, observed at 80 °C.

Although monomer **1**, as a surface modifier, is inferior to poly-**1**, this compound gave an important notion as to why these cylindrical motifs drive the homeotropic columnar order of discotic LC materials. As observed by DSC (Figure S2a),[9] monomer **1**, upon heating, showed a phase behavior featuring a glassy state (<57 °C), a mesophase (57−91 °C), a soft-crystalline phase (91−109 °C) displaying multiple XRD peaks (Figure S2b),[9] and an isotropic melt (>109 °C). In POM, the mesophase displayed a birefringent texture (Figure S2c).[9] Powder XRD analysis of the mesophase at, e.g., 80 °C in a glass capillary displayed four broad diffraction peaks with d-spacings of 3.08, 1.08, 0.52, and 0.40 nm (Figure 4a). Judging from the X-ray crystal structure of an o-phenylene octamer analogous to **1**,[6a] the XRD peaks with d-spacings of 1.08 and 0.40 nm are attributable to the molecular length and helical pitch, respectively (Figure 4b). Provided that the hexadecyl chains of **1** are folded along the cylindrical molecular axis, the d-spacing of 3.08 nm agrees well with a calculated molecular diameter (Figure S2d).[9] Furthermore, the diffraction peak with a d-spacing of 0.52 nm most likely arises from the side chains in the molten state. We noticed that the intensity ratio (R) of diffractions, $I_{d=3.08\text{nm}}/I_{d=1.08\text{nm}}$, which was 3.1 for the bulk state of **1**, increased remarkably to 4.7 when the sample was processed into a thin film (25 μm) sandwiched between glass plates and exposed to a synchrotron X-ray beam from its perpendicular direction (Figure 4c,d). However, this change became less explicit when the film was made thicker, where R eventually dropped to 3.1 when the film thickness exceeded 50 μm (Figure 4e). Therefore, **1** adsorbed on the glass surface aligns anisotropically. Considering the dimensional aspect, adsorbed **1** most likely adopts a "face-on" geometry by directing its cylindrical axis perpendicular to the glass surface (Figure 4c). We consider that, in the LC media of **TP$_8$**, **TP$_{12}$**, **Pc**, and **HBC**, this particular orientation possibly occurs at a glass/LC interface, probably by an interaction of the polar ester termini of **1** (and poly-**1**) with the silanol groups, and nucleates the homeotropic columnar order.[4d] In this nucleation event, the cylindrical shape of **1** plays a crucial role, because no homeotropic columnar order of **TP$_8$** was driven by o-phenylene tetramer **2** (Figures 1c and S13),[9] which is incapable of folding into a stable cylinder (Figure S13f).[6a]

Finally, we would like to emphasize that poly-**1** functions properly on a glass surface simply by spin-coating. For example, a glass substrate was spin-coated beforehand with poly-**1** using its $CHCl_3$ solution and then heated at 100 °C for annealing. Next, on this spin-coated glass surface, **TP$_8$** was heated once to its isotropic melting point and then cooled to 70 °C. As shown in Figure 3f, even an open LC film[14] thus processed entirely showed a dark-field image without any birefringence in POM, and displayed a dendritic texture in OM.

In summary, similar to the case with a rubbed polyimide film for horizontal ordering of rod-shaped LC molecules,[2,15] poly-**1**, a polymeric *o*-phenylene octamer, is the first glass-surface modifier that nucleates large-area homeotropic columnar ordering of discotic LC materials. Homeotropically ordered columnar LCs have the potential for many applications, such as thin-film organic solar cells[1d−g] and ultra-high-density memory devices.[4i] However, reported examples rely on a particular design of the mesogenic cores and/or the side chains of discotic LCs. In contrast, the present surface-modification approach using poly-**1** could be applicable to a wide variety of discotic LC molecules and thus expands the range of their applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of synthesis and characterization of **1**, **2**, and poly-**1**, and DSC, POM, and XRD data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Sage, I. C. In *Handbook of Liquid Crystals: Fundamentals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. *1*, Chap. IX, pp 731−895. (b) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491−1546. (c) Hoogboom, J.; Rasing, T.; Rowan, A. E.; Nolte, R. J. M. *J. Mater. Chem.* **2006**, *16*, 1305−1314. (d) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718−747. (e) Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4832−4887. (f) Pisula, W.; Zorn, M.; Chang, J. Y.; Müllen, K.; Zentel, R. *Macromol. Rapid Commun.* **2009**, *30*, 1179−1202. (g) O'Neill, M.; Kelly, S. M. *Adv. Mater.* **2011**, *23*, 566−584.

(2) (a) Jérôme, B. In *Handbook of Liquid Crystals: Fundamentals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol. *1*, Chap. VII, pp 535−548. (b) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847−1873. (c) Zhu, Z.; Swager, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 9670−9671. (d) Iinuma, Y.; Kishimoto, K.; Sagara, Y.; Yoshio, M.; Mukai, T.; Kobayashi, I.; Ohno, H.; Kato, T. *Macromolecules* **2007**, *40*, 4874−4878.

(3) (a) Zimmermann, S.; Wendorff, J. H.; Weder, C. *Chem. Mater.* **2002**, *14*, 2218−2223. (b) Van de Craats, A. M.; Stutzmann, N.; Bunk, O.; Nielsen, M. M.; Watson, M.; Müllen, K.; Chanzy, H. D.; Sirringhaus, H.; Friend, R. H. *Adv. Mater.* **2003**, *15*, 495−499. (c) Pisula, W.; Menon, A.; Stepputat, M.; Lieberwirth, I.; Kolb, U.; Tracz, A.; Sirringhaus, H.; Pakula, T.; Müllen, K. *Adv. Mater.* **2005**, *17*, 684−689.

(4) (a) Percec, V.; Glodde, M.; Bera, T. K.; Miura, Y.; Shiyanovskaya, I.; Singer, K. D.; Balagurusamy, V. S. K.; Heiney, P. A.; Schnell, I.; Rapp, A.; Spiess, H.-W.; Hudsonk, S. D.; Duan, H. *Nature* **2002**, *419*, 384−387. (b) Steinhart, M.; Zimmermann, S.; Göring, P.; Schaper, A. K.; Gösele, U.; Weder, C.; Wendorff, J. H. *Nano Lett.* **2005**, *5*, 429−434. (c) de Cupere, V.; Tant, J.; Viville, P.; Lazzaroni, R.; Osikowicz, W.; Salaneck, W. R.; Geerts, Y. H. *Langmuir* **2006**, *22*, 7798−7806. (d) Grelet, E.; Bock, H. *Europhys. Lett.* **2006**, *73*, 712−718. (e) Gearba, R. I.; Anokhin, D. V. A.; Bondar, A. I.; Bras, W.; Jahr, M.; Lehmann, M.; Ivanov, D. A. *Adv. Mater.* **2007**, *19*, 815−820. (f) Charlet, E.; Grelet, E.; Brettes, P.; Bock, H.; Saadaoui, H. *Appl. Phys. Lett.* **2008**, *92*, 024107. (g) Pouzet, E.; De Cupere, V.; Heintz, C.; Andreasen, J. W.; Breiby, D. W.; Nielsen, M. M.; Viville, P.; Lazzaroni, R.; Gbabode, G.; Geerts, Y. H. *J. Phys. Chem. C* **2009**, *113*, 14398−14406. (h) Grelet, E.; Dardel, S.; Bock, H.; Goldmann, M.; Lacaze, E.; Nallet, F. *Eur. Phys. J. E* **2010**, *31*, 343−349. (i) Miyajima, D.; Araoka, F.; Takezoe, H.; Kim, J.; Kato, K.; Takata, M.; Aida, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 7865−7869. (j) Osawa, T.; Kajitani, T.; Hashizume, D.; Ohsumi, H.; Sasaki, S.; Takata, M.; Koizumi, Y.; Saeki, A.; Seki, S.; Fukushima, T.; Aida, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 7990−7993. (k) Lee, J. J.; Yamaguchi, A.; Alam, Md. A.; Yamamoto, Y.; Fukushima, T.; Kato, K.; Takata, M.; Fujita, N.; Aida, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 8490−8494.

(5) (a) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893−4011. (b) *Foldamers: Structure Properties and Applications*; Hecht, S., Huc, I., Eds.; Wiley-VCH: Weinheim, 2007. (c) Meudtner, R. M.; Hecht, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 4926−4930. (d) He, J.; Crase, J. L.; Wadumethrige, S. H.; Thakur, K.; Dai, L.; Zou, S.; Rathore, R.; Hartley, C. S. *J. Am. Chem. Soc.* **2010**, *132*, 13848−13857. (e) Hartley, C. S.; He, J. *J. Org. Chem.* **2010**, *75*, 8627−8636. (f) Mathew, S. M.; Engle, J. T.; Ziegler, C. J.; Hartley, C. S. *J. Am. Chem. Soc.* **2013**, *135*, 6714−6722.

(6) (a) Ohta, E.; Satoh, H.; Ando, S.; Kosaka, A.; Fukushima, T.; Hashizume, D.; Yamasaki, M.; Hasegawa, K.; Muraoka, A.; Ushiyama, H.; Yamashita, K.; Aida, T. *Nat. Chem.* **2011**, *3*, 68−73. (b) Ando, S.; Ohta, E.; Kosaka, A.; Hashizume, D.; Koshino, H.; Fukushima, T.; Aida, T. *J. Am. Chem. Soc.* **2012**, *134*, 11084−11087.

(7) When **TP**$_8$ was doped with monomer **1** at >30 wt%, DSC showed complicated phase behaviors (Figure S4d).[9] For example, at the doping level of 40 wt%, the phase diagram obtained upon heating displayed an unknown phase below 54 °C, a crystalline phase at 54−65 °C, and a two-phase region at 82−103 °C involving the isotropic phase of **TP**$_8$ and mesophase of **1**.

(8) By means of size exclusion chromatography using polystyrene standards, number-averaged molecular weight (M_n) and polydispersity index (M_w/M_n) of poly-**1** were roughly estimated as 5.3×10^4 g/mol (degree of polymerization, DP = 28) and 1.6, respectively.

(9) See Supporting Information.

(10) When **TP**$_8$ was doped with poly-**1** at >20 wt%, DSC showed complicated phase behaviors (Figure S4b).[9] For example, at the doping level of 30 wt%, the phase diagram obtained upon heating displayed an unknown phase below 54 °C and a crystalline phase at 54−65 °C.

(11) Chandrasekhar, S. In *Handbook of Liquid Crystals: Low Molecular Weight Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol.*1*, Chap. VIII, pp 749−780.

(12) Unless otherwise noted, LC films analyzed were sandwiched between glass substrates.

(13) Dierking, I. *Textures of Liquid Crystals*; Wiley-VCH: Weinheim, 2003; Chap. 11a, pp 145−153.

(14) One side of the LC film was exposed to air.

(15) (a) Shah, R. R.; Abbott, N. L. *Science* **2001**, *293*, 1296−1299. (b) Van Hameren, R.; Schön, P.; Van Buul, A. M.; Hoogboom, J.; Lazarenko, S. V.; Gerritsen, J. W.; Engelkamp, H.; Christianen, P. C. M.; Heus, H. A.; Maan, J. C.; Rasing, T.; Speller, S.; Rowan, A. E.; Elemans, J. A. A. W.; Nolte, R. J. M. *Science* **2006**, *314*, 1433−1436. (c) Tokita, M.; Adachi, M.; Masuyama, S.; Takazawa, F.; Watanabe, J. *Macromolecules* **2007**, *40*, 7276−7282. (d) Cox, J. R.; Simpson, J. H.; Swager, T. M. *J. Am. Chem. Soc.* **2013**, *135*, 640−643.