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Template-guided organization of chromonic liquid crystals into micropatterned anisotropic organic solids†

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We have developed an approach to generate micropatterns of anisotropic organic materials which exploits the self-organization, driven by π-stacking and hydrophobic interactions, of an ionic perylenebis(dicarboximide) 1 in aqueous solutions.

The construction of devices and materials through molecular self-assembly and self-organization processes is one of the premier frontiers in chemistry.[1] Our research group is interested in the fabrication of micropatterns of anisotropic (direction-dependent) materials because of their potential applications in the microelectronic fields, as holographic films, as viewing angle-dependent optical materials, and in stereoscopic displays.[2] A wide range of methods is available for the micro- and nano-patterning of isotropic (direction-independent) materials including photolithography,[3] soft lithography,[4] and scanning probe techniques.[5] However, micropatterning of anisotropic organic materials is limited to methods that employ either uniaxially stretched polymer films[6] or a photoalignment technique.[2b,7] In this communication, we present a novel approach to generating micropatterns of anisotropic organic materials by exploiting the self-organization of lyotropic (solvent and temperature dependent) chromonic liquid crystals[8] on templates.

In our approach (outlined in Fig. 1), we exploit mesogens (liquid-crystalline prone molecules) that self-organize into ribbon-like domains (because of π-stacking among the plank-shaped aromatic molecules and entropically driven hydrophobic interactions in aqueous solution). The mesogens possess liquid-like mobility while retaining long-range orientational order in the ribbon-like structures. In the absence of a template the chromonic ribbons extend in random directions (Fig. 2). When a template with micro-scaled line features is used, the features serve as containers for the solution and guide the development of the ribbons (Fig. 1). Upon slow evaporation of solvent from under the edge of a glass cover-slip, chromonic ribbons (in which the mesogens are anisotropically oriented) develop in the patterned features of the template. After the entire solution becomes liquid-crystalline and anisotropic, the sample is dried under ambient conditions to yield a micropatterned anisotropic solid. This micropattern can be transferred to the glass cover-slip by peeling off the template.

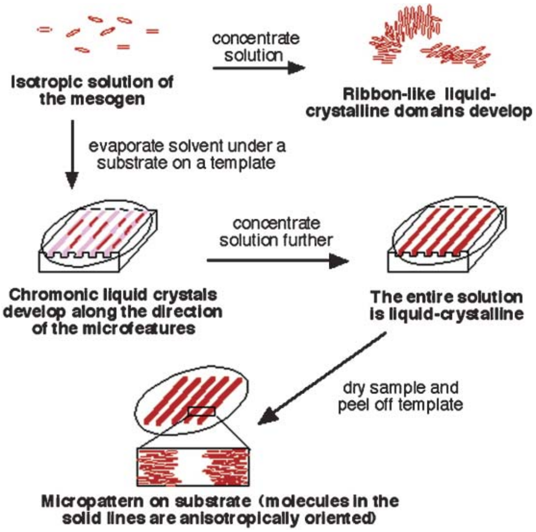

Fig. 1 Schematic representation of the template-guided organization of chromonic liquid crystals leading to a micropattern of anisotropically ordered solid.

The advantages of this approach are the following: (1) The anisotropic features are formed by the self-stacking of organic molecules into long ribbon-like ensembles, a "bottom-up" approach. In principle, the minimum size of the features that can be obtained should only be limited by the size of the molecular aggregates when used with an appropriate template (potentially down to nano-scale). (2) Through the design of the molecular structure of the mesogen, properties of the anisotropic structures can be controlled at the molecular level. (3) By using non-planar templates and interwoven microchannels[9] to guide the

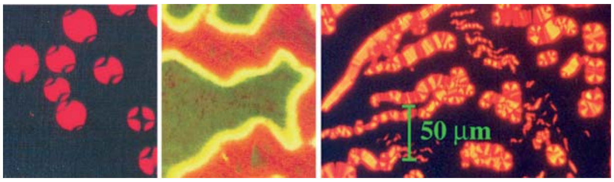

Fig. 2 Photomicrographs of aqueous solutions of **2** (left and middle) and **1** (right) observed between cross polarizers. (Left) Peripheral evaporation experiment showed the liquid-crystalline phase (red droplets) developing out of the 1.7 mM isotropic solution (black regions) of **2**. (Middle) Optical micrograph of 20 wt% (∼ 0.3 M) of **2** in aqueous solution showing a schlieren texture of a chromonic N phase. (Right) Chromonic ribbons developing from an isotropic solution of **1** (∼ 20 wt%) in water.

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organization of the chromonic liquid crystals, 3-D patterns of anisotropic materials may be formed. (4) This method is convenient and inexpensive. The pattern is obtained under ambient conditions with aqueous solvent and a reusable template that does not require mechanical rubbing or stretching of the substrate or photoalignment of the liquid crystal.

For a proof of concept, we synthesized novel perylenebis(dicarboximide) **1** as the mesogen and used a slab of polydimethylsiloxane (PDMS)[10] that has a regular pattern of line features as the template. PDMS molds were used in the micromolding of isotropic organic polymers[11*a*] and the microscopic patterning of surfactant tubules that were used for the templated polymerization of mesoscopic silica.[11*b*] We used **1** because perylenebis(dicarboximide)s possess a number of useful properties (dichroic, fluorescent, semiconducting, and photo-conducting) and are stable (thermally and photo-chemically).[12] The control of the molecular orientation of these mesogens in solids of micrometer dimensions may lead to useful optical or electronic properties that are unique to anisotropic materials.

Compound **1** was synthesized in 85% yield by the reaction of **3** with methyl *p*-toluenesulfonate (Scheme 1). As distinct from the previously reported mesogen **2** that forms a chromonic N phase[8,13] in aqueous solutions (Fig. 2, left and middle), **1** displays a chromonic ribbon phase (Fig. 2, right) that consists of anisotropically oriented mesogens in ribbon-like structures.

Evidence for the anisotropic orientation of mesogens in the ribbon-like structures of **1** was provided by studies using polarized optical microscopy. An aqueous solution of **1** ($\sim$ 20 wt%) on a glass slide was concentrated by allowing water to evaporate from the edge of the sample under a glass cover-slip. When viewed between crossed polarizers (Fig. 3, left), birefringent droplets (bright regions) isolated from each other in the isotropic bulk (black background) emerged, indicating the development of a liquid-crystalline phase. Upon further evaporation of solvent, these droplets grew into long ribbon-like structures. Examination of the sample through a single polarizer (Fig. 3, middle and right) revealed that the isotropic solution showed direction-independent absorption of blue and green light, resulting in the observed pink color for the solution. However, the ribbon-like regions exhibited anisotropic absorption of light. Regions in which the direction of growth of the ribbons was perpendicular to the polarization axis of the light absorbed blue and green light. This resulted in more intense red color compared to the isotropic solution. Regions in which the direction of growth of the ribbons was parallel to the polarization axis of the light transmitted visible light and appeared as almost white in color. These results suggest that the principal axis of the electronic transition (that is aligned with the long axis of the molecule)[14] of **1** in the ribbon-like regions is oriented perpendicular to the direction of growth of the ribbons. Since there were no alignment layers or features on the glass substrate to guide the growth of the liquid crystals, the ribbons grew in random directions. Furthermore, the width of the ribbons varied from about 5 μm to 25 μm.

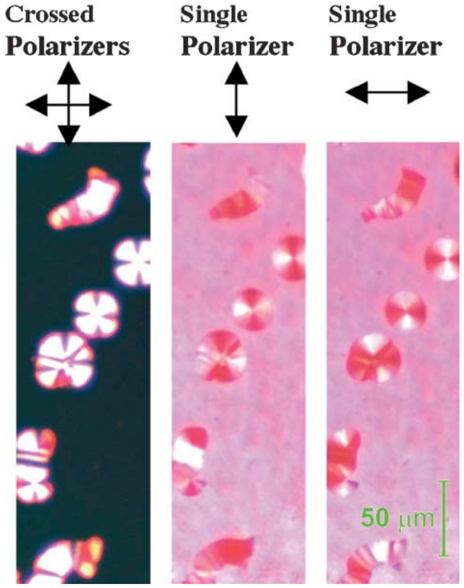
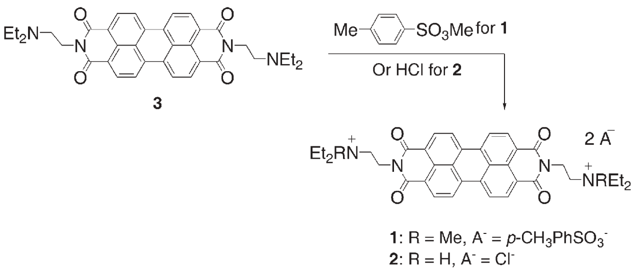


Fig. 3 Optical micrographs showing the chromonic liquid-crystalline phase developing slowly from an isotropic solution of **1** in water. The mesogens in the ribbon-like regions are anisotropically oriented.



Scheme 1

To control the width and the direction of growth of the chromonic ribbons, an isotropic solution of **1** ($\sim$ 20 wt%) in water was added to a PDMS template with regular line features of $\sim$ 9 μm wide, $\sim$ 2 μm deep, and $\sim$ 11 μm apart. The self-organization of **1** on the template upon slow evaporation of solvent (from under the edge of a cover-slip) was monitored by polarized optical microscopy (Fig. 4). When the sample was viewed between crossed polarizers, birefringent optical textures developed, indicating the formation of a liquid-crystalline phase from the isotropic solution on the PDMS template. When viewed with a single polarizer (polarization axis parallel to the line features), the ribbon-like structures were very light pink in color as compared to the isotropic solution (Fig. 4A). In contrast, when the polarization axis of the polarized light was perpendicular to the lines, the ribbons were an intense red in color (Fig. 4B). These results show that the mesogens in liquid-crystalline ribbons are anisotropically oriented and absorb light (blue and green) polarized perpendicular to the line features. Upon further evaporation of solvent, the entire solution became completely liquid-crystalline and anisotropic (Figs. 4C and 4D). After the sample was dried, the PDMS template was peeled off from the cover-slip. The optical micrographs of the patterned solid that was transferred to the cover-slip are shown in Fig. 4E and 4F. These oriented solids exhibit anisotropic optical properties and can serve as micro-sized polarizers. The ratio of the absorbance of light (515–555 nm) polarized perpendicular to the line features to that of light polarized parallel to the line features was determined to be as high as 16 suggesting that **1** was highly anisotropically oriented in the line patterns.

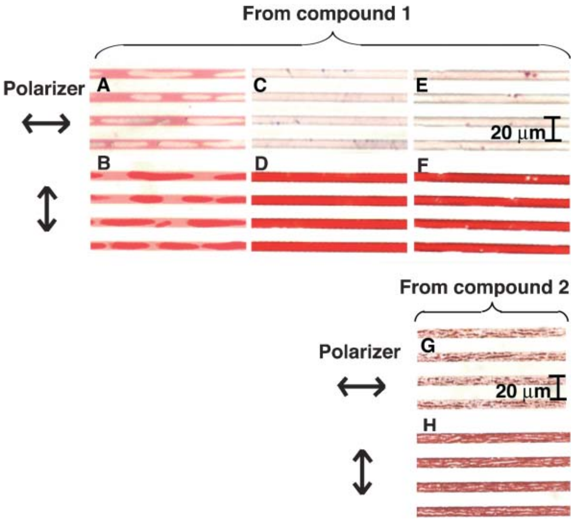


Fig. 4 Optical micrographs: (**A, B**) ribbon-like liquid-crystalline structures developing from an isotropic solution of **1** on a PDMS template, (**C, D**) completely liquid-crystalline and anisotropically oriented solution, (**E, F**) the anisotropic solid of **1** on a glass cover-slip after the template was peeled off, (**G, H**) the micropatterned solid of **2** on a cover-slip.

To verify the importance of the formation of chromonic ribbons in this approach, we repeated the experiment using **2**. We had demonstrated previously that **2** forms anisotropic films when its solution in the chromonic N phase is aligned under a mechanical shearing force.[13] In the absence of a shearing force in the present study, the self-organization of **2** into a chromonic N phase on a PDMS template produced a solid that showed a grainy optical texture when observed under a polarizing microscope (Fig. 4, G and H). The presence of many isotropically oriented domains gave grainy texture even though the molecules of **2** were oriented anisotropically in each domain. These results suggest that the self-organization of **1**, in the absence of a shearing force, into long ribbon-like domains enhances the formation of anisotropic solid lines on templates.

Similar experiments were performed using **1** and a PDMS template that had regular line features that were ∼ 2 µm in depth, ∼ 2 µm in width, and ∼ 2 µm apart. Although the fabrication conditions (*e.g.*, the concentration of the solution, the rate of evaporation, and the cleaning of the template and glass substrates) have not yet been optimized, the results (Fig. 5) demonstrate the feasibility of fabricating anisotropic materials in micropatterns having feature sizes as small as 2 µm.

In summary, this work demonstrates an example of the hierarchical organization of functional organic materials in the microscale utilizing a chromonic mesogen as the building block that self-organizes on a template. The fabrication of nano-sized anisotropic materials and detailed studies of the properties of **1** and the structural factors that govern the formation of a chromonic ribbon phase are underway.

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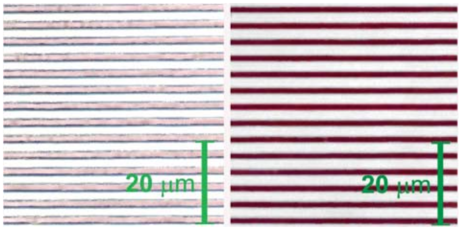

Fig. 5 Optical micrographs showing the anisotropic orientation of **1** in a pattern of 2-µm lines on a glass coverslip. The polarization axis of the incident light was parallel (left) or perpendicular (right) to the lines.

Notes and references

1 (*a*) D. L. Gin, W. Gu, B. A. Pindzola and W.-J. Zhou, *Acc. Chem. Res.*, 2001, **34**, 973–980; (*b*) Y. Xu, W. Gu and D. L. Gin, *J. Am. Chem. Soc.*, 2004, **126**, 1616–1617; (*c*) M. C. Fyfe and J. F. Stoddart, *Acc. Chem. Res.*, 1997, **30**, 393–401; (*d*) K. Campbell, C. J. Kuehl, M. J. Ferguson, P. J. Stang and R. R. Tykwinski, *J. Am. Chem. Soc.*, 2002, **124**, 7266–7267; (*e*) Y. Xia, B. Gates and Z.-Y. Li, *Adv. Mater.*, 2001, **13**, 409; (*f*) R. Shenhar and V. M. Rotello, *Acc. Chem. Res.*, 2003, **36**, 549; (*g*) L. Isaacs, D. Chin, N. Bowden, Y. Xia and G. M. Whitesides, *Perspect. Supramol. Chem.*, 1999, **4**, 1.

2 (*a*) G. Pfaff and P. Reynders, *Chem. Rev.*, 1999, **99**, 1963–1981; (*b*) D. Matsunaga, T. Tamaki, H. Akiyama and K. Ichimura, *Adv. Mater.*, 2002, **14**, 1477–1478.

3 W. M. Moreau, Ed.; *Semiconductor Lithography: Principles and Materials*, Plenum: New York, 1988.

4 (*a*) Y. Xia and G. M. Whitesides, *Angew. Chem., Int. Ed.*, 1998, **37**, 550–575; (*b*) P. Yang, G. Wirnsberger, H. C. Huang, S. R. Cordero, M. D. McGehee, B. Scott, T. Deng, G. M. Whitesides, B. F. Chmelka, S. K. Buratto and G. D. Stucky, *Science*, 2000, 287.

5 (*a*) G. Y. Liu, S. Xu and Y. Qian, *Acc. Chem. Res.*, 2000, **33**, 457–466; (*b*) Y. Xia, J. A. Rogers, K. E. Paul and G. M. Whitesides, *Chem. Rev.*, 1999, **99**, 1823–1848.

6 L. Cardillo, D. Swift and J. Meritt, *J. Imaging Sci. Technol.*, 1998, **42**, 300.

7 (*a*) K. Ichimura, T. Fujiwara, M. Momose and D. Matsunaga, *J. Mater. Chem.*, 2002, **12**, 3380–3386; (*b*) C. Ruslim, D. Matsunaga, M. Hashimoto, T. Tamaki and K. Ichimura, *Langmuir*, 2003, **19**, 3686–3691.

8 (*a*) J. Lydon, Chromonic Liquid Crystals, in *Handbook of Liquid Crystals*, D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, V. Vill, Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2B, pp. 981–1007; (*b*) J. Lydon, *Curr. Opin. Colloid Interface Sci.*, 1998, **3**, 458.

9 P. J. A. Kenis, R. F. Ismagilov, S. Takayama and G. M. Whitesides, *Acc. Chem. Res.*, 2000, **33**, 841–847.

10 (*a*) J. C. McDonald and G. M. Whitesides, *Acc. Chem. Res.*, 2002, **35**, 491–499; (*b*) The PDMS mold was used without any surface treatment.

11 (*a*) E. Kim, Y. Xia and G. M. Whitesides, *J. Am. Chem. Soc.*, 1996, **118**, 5722–5731; (*b*) M. Trau, N. Yao, E. Kim, Y. Xia, G. M. Whitesides and I. A. Aksay, *Nature*, 1997, **390**, 674–676.

12 (*a*) K. Y. Law, *Chem. Rev.*, 1993, **93**, 449–486; (*b*) L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend and J. D. MacKenzie, *Science (Washington, D. C.)*, 2001, **293**, 1119–1122; (*c*) A. B. Gregg and R. A. Cormier, *J. Am. Chem. Soc.*, 2001, **123**, 7959–7960; (*d*) T. D. Carson, W. Seo, S. W. Tam-Chang and S. M. Casey, *Chem. Mater.*, 2003, **15**, 2292–2294; (*e*) M. P. O'Neil, M. P. Niemczyk, W. A. Svec, D. Gosztola, G. L. I. Gaines and M. R. Wasielewski, *Science*, 1992, **257**, 63–65.

13 (*a*) I. K. Iverson and S.-W. Tam-Chang, *J. Am. Chem. Soc.*, 1999, **121**, 5801–5802; (*b*) S. W. Tam-Chang, I. K. Iverson and J. Helbley, *Langmuir*, 2004, **20**, 342–347.

14 M. Hasegawa, T. Matano, Y. Shindo and T. Sugimura, *Macromolecules*, 1996, **29**, 7897–7909.