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Liquid Crystals Anchored on Mixed Monolayers of Chiral versus Achiral Molecules: Continuous Change in Orientation as a Function of Enantiomeric Excess**

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Dedicated to Professor George M. Whitesides on the occasion of his 75th birthday

Abstract: *The orientations of liquid crystals (LCs) anchored on monolayers formed from mixtures of chiral versus achiral molecules were compared. Changes in the enantiomeric excess of mixed monolayers of chiral dipeptides gave rise to continuous changes in the orientations of nematic LCs, allowing arbitrary tuning of the azimuthal orientations of LCs over a range of ≈100°. In contrast, the same LCs exhibited discontinuous changes in orientation on surfaces presenting mixtures of achiral molecules. These striking differences in the anchoring of LCs on surfaces presenting chiral versus achiral molecules provide insights into the molecular origins of ordering transitions of LCs, and provide new principles based on chiral monolayers for the rational design of surfaces that permit continuous tuning of the orientations of LCs.*

Facile and precise manipulation of the orientational ordering of liquid crystals (LCs) can lead to new technologies, including improved LC displays (e.g. with faster switching speeds, lower power consumption),[1] chemical and biological sensors,[2] and multifunctional materials.[3] In particular, recent studies have highlighted how the orientations assumed by LCs can serve as sensitive probes of the interfacial organization of protein assemblies,[4] the activity of enzymes,[5] and the structure of viruses.[6] These applications are all enabled by the long-range ordering of molecules in LCs (ordering over distances of around 10^5 molecular lengths), which allows molecular-level information to be amplified into bulk LC ordering transitions that can be optically reported using polarized light.[7] Although macroscopic thermodynamic descriptions of surface-induced anchoring transitions of LCs have been reported, the underlying nanoscale interfacial phenomena (i.e. intermolecular interactions, organization of molecular adsorbates) are yet to be fully understood.[7] This is particularly true for the ordering of LCs at interfaces decorated with biomolecules due to their diverse chemical functionality and stereochemistry.

The macroscopic anchoring of LCs on surfaces is often characterized by defining the so-called "easy axis" (η_0) and "anchoring energy" of the LC on a given surface.[7] The easy axis is the orientation of the LC in the absence of external forces (i.e. the equilibrium orientation) and the anchoring energy characterizes the orientation-dependent interaction energy of the LC with the surface. Past studies have reported changes in the orientation of the easy axis of LCs on surfaces as a function of key parameters such as temperature, density and chemical functionality of molecular adsorbates, and topography of surfaces.[8] Arbitrary control of the easy axis of LCs, however, is still difficult to achieve in a predictable manner. For example, a homogeneously mixed surface of two chemical species is predicted to lead to a discontinuous change in the orientation of the easy axis of a LC.[9] Here, we move beyond these past studies to examine the anchoring of LCs on surfaces comprised of a single chemical species present in two stereochemically distinct forms. Specifically, we investigate the influence of mixtures of enantiomers of a dipeptide, when chemisorbed to the surface of gold films, on the orientation of the easy axis of achiral nematic LCs. A key finding we report is that mixtures of chiral enantiomers give rise to continuous anchoring transitions of nematic LCs, allowing arbitrary tuning of the azimuthal orientations of LCs over a range of ≈100°. In contrast, we observe the same LCs to undergo discontinuous anchoring transitions on gold films presenting mixtures of achiral molecules. These striking differences observed in the anchoring of LCs on surfaces presenting chiral and achiral adsorbates provide insights into the molecular origins of continuous and discontinuous ordering transitions of LCs, and provide new principles based on chiral monolayers for the rational design of surfaces that permit continuous tuning of the orientations of LCs.

Our studies used monolayers formed from mixtures of enantiomers of the dipeptide comprised of cysteine (C) and tyrosine (Y) (i.e., mixtures of L-C-L-Y and D-C-D-Y; Figure 1A). Previously, we and others have reported on the orientations of LCs at surfaces with enantiomerically pure species or patterns.[10] Of particular relevance to this paper, we reported that hydrogen bonds formed between the nematic phase of 4-cyano-4′-pentylbiphenyl (5CB) and the OH group of tyrosine play a key role in determining the anchoring of the 5CB on surfaces presenting enantiomerically

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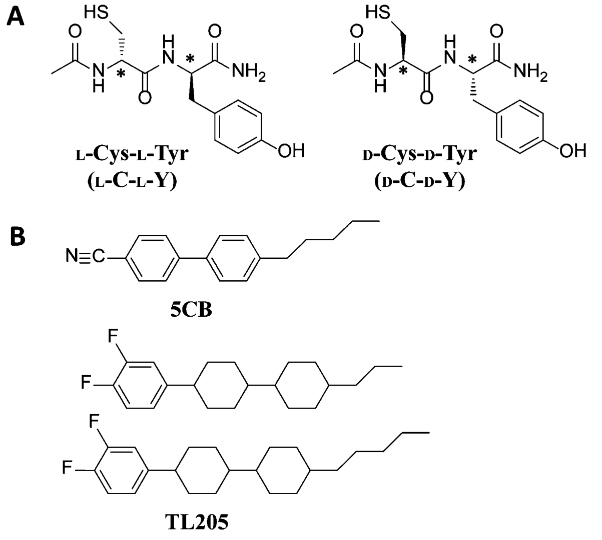

Figure 1. Chemical structures of A) dipeptides (* denotes the position of a chiral center) and B) mesogens used in the experiments reported here.

pure monolayers of the dipeptide C-Y.[10a] In the current study, we spotted mixtures of L-C-L-Y and D-C-D-Y from aqueous solution onto the surfaces of films of gold deposited at an oblique angle of incidence (Figure 2 A). The gold films were prepared by physical vapor deposition using an angle of deposition of 35° (angle measured from surface normal). To determine the orientation of the easy axis of the LC on surfaces decorated with mixtures of enantiomers, we paired gold films decorated with the spots of dipeptide with a second gold film that was functionalized with a monolayer of pentadecanethiol ($C_{15}SH$; Figure 2 A).[10a,11] The two surfaces were spaced apart by 50 μm using a thin polymeric film (see Materials and Methods in the Supporting Information for details), and the cavity between the two surfaces was filled with nematic LC (nematic 5CB or TL205; Figure 1 A). Because the orientation of the nematic LC on the $C_{15}SH$-decorated surface is known (planar anchoring in an azimuthal orientation that is perpendicular to the direction of deposition of the gold),[12] measurement of the angle of rotation of plane polarized light transmitted through the LC film was used to determine the azimuthal orientations of the LC at the dipeptide-decorated surfaces (i.e., the system defines a twisted nematic LC cell with a pitch that is much larger than the wavelength of light). Below we define the azimuthal orientation of the easy axes of the LCs on dipeptide-decorated surfaces as the angle measured relative to the orientation of the LC on a region of the gold film decorated with $C_{16}SH$ (which is parallel to the direction of deposition of the gold films; see Figure 2 A). We define an easy axis that is rotated counterclockwise relative to the direction of gold deposition to be positive (when viewed from above), and a clockwise rotation to be negative (Figure 2 A, right).

Prior to the experiments reported here, we confirmed formation of mixed monolayers of the dipeptides on the gold films by using ellipsometry and X-ray photoelectron spectroscopy (XPS) (see Supporting Information for representative data, and prior studies for more detailed characterization of dipeptide monolayers using polarization-modulation infrared-reflection-absorption spectroscopy and X-ray photoelectron spectroscopy).[10a] Figure 2 B shows a spatial map of the azimuthal orientation of nematic 5CB that we measured on dipeptide-decorated gold films using the experimental procedures described above. The mole fractions of the D-dipeptide in the binary mixture of L- and D-dipeptide in solution were $X_D = 0.00$, 0.10, 0.25, 0.50, 0.75, 0.90 and 1.00. The dipeptide monolayers corresponding to $X_D = 0.00$ were incubated in the left-most column of the peptide array, and the solutions spotted towards the right side of the array contained increasing mole fractions of D-dipeptide (Figure 2 B, with orientations color coded according to the scale on the right side of the image). The spots in the right-most column of Figure 2 B were prepared with pure component L- and D-dipeptides to confirm that the location of the spots of dipeptides on the gold film did not influence the measured orientations of the LCs. Inspection of Figure 2 B reveals that the azimuthal orientation of nematic 5CB assumed on each of

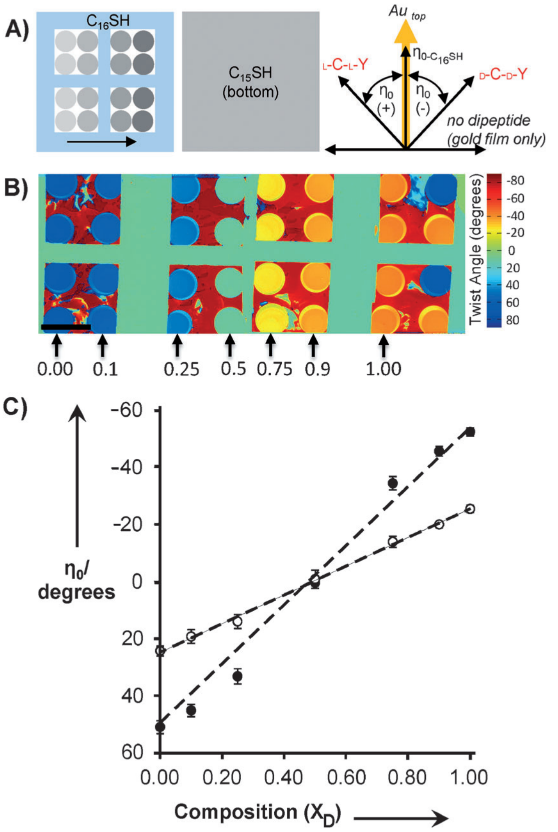

Figure 2. A) Schematic illustration of the top and bottom surfaces of a twisted LC cell with dipeptides on the top surface. The arrow represents direction of increasing mole fraction of D-C-D-Y in mixed monolayers of L-C-L-Y and D-C-D-Y spotted onto the surfaces. B) Two-dimensional map of twist angles (see text) of nematic 5CB on surfaces supporting mixed monolayers of L-C-L-Y and D-C-D-Y (circles). Each column corresponds to one mole fraction of D-C-D-Y (X_D) as shown in (C). Mole fractions are: 0.00, 0.10, 0.25, 0.50, 0.75, 0.90 and 1.00. Scale bar is 2 mm. C) Easy axis (η_0) of 5CB (filled circles) and TL205 (open circles) as a function of the mole fraction of D-C-D-Y (X_D). Error bars represent standard deviations.

the dipeptide monolayers was well-defined and spatially uniform, and that the enantiomeric excess of the dipeptide within the monolayer had a pronounced effect on the orientation of the LC.

We quantified the azimuthal orientation of nematic 5CB on each mixed dipeptide monolayer, and plotted the orientation as a function of the mole fraction of D-dipeptide in the binary dipeptide solution from which the monolayer was formed (Figure 2C). Inspection of Figure 2C reveals that the easy axis of nematic 5CB on monolayers formed from L-dipeptides ($X_D = 0.00$) is rotated 53 ± 1.3° counterclockwise from the azimuthal direction of gold deposition, whereas the easy axis of 5CB on the D-dipeptides ($X_D = 1.00$) is rotated 52 ± 1.6° clockwise relative to the direction of gold deposition (Figure 2A, right). Between the two bounds that correspond to enantiomerically pure surfaces, Figure 2C shows that the azimuthal orientation of the LC changes continuously as a function of the mole fraction of D-dipeptide. We note also that the orientation of the easy axis of 5CB on surfaces decorated with the racemic mixture of D- and L- dipeptides was measured to be mid-way between the orientations measured on the enantiomerically pure monolayers (i.e., parallel to the direction of deposition of the gold film).

We make two additional observations regarding the results shown in Figure 2C. First, we performed experiments to confirm that the orientations of the LC shown in Figure 2C do indeed correspond to the easy axis of the LC. Specifically, we measured the orientation of nematic 5CB in a LC cell comprised of two dipeptide-decorated surfaces. We confirmed that we measured the same azimuthal orientation of the LCs, independent of the magnitude of the twist of the LC (i.e., torque applied to the LC). Second, we confirmed that our observation of a continuous orientational transition as a function of enantiomeric excess of dipeptide was not limited to 5CB. As shown in Figure 2C (open circles), we also measured the orientations of nematic TL205 (a mixture of mesogens comprised of cyclohexanyl-substituted fluorinated biphenyls and fluorinated terphenyls, as shown in Figure 1B) on the surfaces containing the mixed dipeptides. The orientation of the easy axis of TL205 on surfaces decorated with L-C-L-Y differs from the orientation of 5CB on the same surfaces likely, at least in part, because the strength of the hydrogen bond formed between TL205 and the OH group of tyrosine is weaker than that of 5CB. However, more significantly, and similar to 5CB, we measured a continuous change of the easy axis of TL205 as a function of the enantiomeric excess of the dipeptide used to form the mixed monolayer. The similarity of the phenomena (i.e., continuous orientational transition) for two chemically distinct LCs suggests that a common physical mechanism underlies the continuous ordering transition on the dipeptide-decorated surfaces (see below). We end our description of the results in Figure 2 by emphasizing that the measurements of the easy axes of LCs on the mixed dipeptide monolayers were highly reproducible (note the size of the error bars in Figure 2C). The data shown in Figure 2C for 5CB were compiled from three separate batches of gold films, with over 60 regions measured for each composition of the mixed dipeptides (Table S1 in the Supporting Information).

Upon binding to a surface, enantiomers of a chiral molecule within a racemic mixture may either separate to form domains that contain only one enantiomer,[13] associate to form a racemic compound,[14] or mix to form a random solution.[15] We used a combination of AFM and XPS to provide insight into the organization of the chiral dipeptides on the Au(111) surfaces used in our experiments. Before formation of the dipeptide monolayers, the only features resolvable by AFM were consistent with the symmetry and periodicity of gold atoms of Au(111) (Figure 3A and B; 0.2 nm, which compares favorably with the expected value of 0.23 nm[16]). After formation of either pure L-C-L-Y (Figure 3C and 3D) or D-C-D-Y monolayers (Figure 3E and 3F),

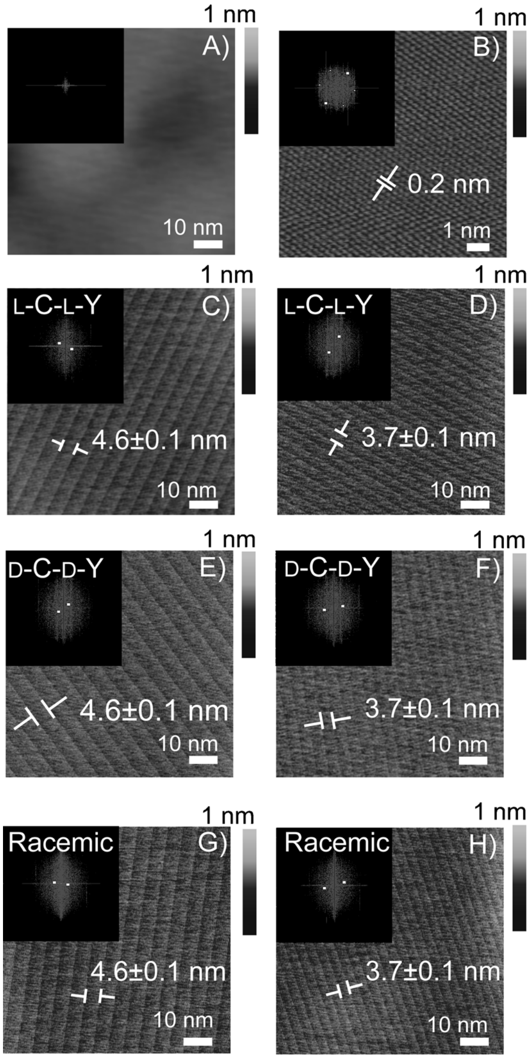

Figure 3. AFM images with corresponding Fourier pattern inserts of A,B) a Au (111) substrate before formation of a dipeptide monolayer. The distance between adjacent gold atoms is 0.2 nm; the insert in (B) shows a Fourier pattern consistent with six-fold symmetry of Au (111). C,D) Regions of striped monolayer formed from L-C-L-Y with periodicity of either 4.6 ± 0.1 nm or 3.7 ± 0.1 nm. E,F) Regions of striped monolayers formed from D-C-D-Y with periodicity of 4.6 ± 0.1 nm or 3.7 ± 0.1 nm. G,H) Racemic monolayer of L-C-L-Y and D-C-D-Y with periodicity of 4.6 ± 0.1 nm or 3.7 ± 0.1 nm (color version of this Figure is available in the Supporting Information, Figure S6).

we observed striped features with periodicities of either 3.7 ± 0.1 nm or 4.6 ± 0.1 nm extending over regions of the Au(111) surface with size ca. 70 nm. A series of control and repeat experiments confirmed the stripes to be formed by assemblies of dipeptides (see Supporting Information). The observation of two periodicities is consistent with prior studies of amino acids on metal surfaces that have reported polymorphism.[13a,17] Significantly, we also measured a racemic monolayer of L-C-L-Y and D-C-D-Y to exhibit stripes of the same periodicity as the enantiomerically pure monolayers. This observation is inconsistent with either 1) formation of a 2D random solution (which would not correspond to a periodic assembly)[15] or 2) a racemic compound (which would not have the same periodicity as the pure enantiomers), but is consistent with the hypothesis that the chiral dipeptides separate to form domains that contain only one enantiomer.[15] Additional support for this hypothesis was obtained from XPS measurements. Past studies[14] of racemic compounds on metal surfaces have reported saturation coverages that differ from pure enantiomers. In contrast, our XPS studies showed similar surface coverages when using pure enantiomers or a racemic mixture (see the Supporting Information for further details).

In contrast to chiral adsorbates, STM studies of mixed monolayers of achiral molecules have revealed segregation of the components of the monolayers to occur only under conditions where the chemical compositions of the adsorbates are substantially different (e.g., hydrogenated versus perfluorinated alkanethiols).[18] Indeed, for mixed monolayers of alkanethiols comprised of similar chain lengths, adsorption isotherms are consistent with molecular-level mixing of the two monolayer.[19] In light of these differences in the mixing of binary chiral and achiral adsorbates in monolayers, and to explore further the role of the chirality of the adsorbates in the continuous ordering transition shown in Figure 2, next we prepared monolayers comprised of two achiral species that were sufficiently similar in structure that they would form homogenously mixed monolayers (i.e., we sought to minimize the likelihood of segregation of the two species on the surface).[20] We also selected the components to give rise to distinct orientations of LCs as pure component monolayers. Specifically, we investigated the orientations of LCs on mixed monolayers formed from hexadecanethiol ($C_{16}SH$) and pentadecanethiol ($C_{15}SH$) (see past publications[21] for a discussion of the anchoring of LCs on alkanethiols containing odd and even numbers of carbons). In these experiments, the gold films were deposited at 49° in order to achieve anchoring energies that were sufficiently large to allow measurements of the easy axis of the LC (at an angle of deposition of 35°, we observed the orientation of the LC to depart from the easy axis). In clear contrast to the continuous ordering transition observed in Figure 2 for the chiral monolayers, as shown in Figure 4A and B, the easy axis of 5CB was measured to undergo a discontinuous change in orientation as a function of the composition of the mixed achiral monolayer. Here we also note that when the orientation of the LC was +90° or −90°, the twist distortion in the LC was 90°, and that both angles were seen with equal probability (Figure 4B) because they correspond to energetically degenerate states of the LC. The key conclusion extracted from the results shown Figure 4 is that, in contrast to Figure 2, the LC did not assume orientations other than those seen on the pure-component monolayers. Previously, we have observed monolayers formed from other mixtures of achiral molecules (e.g., $HOOC(CH_2)_{10}SH$ and $H_3C(CH_2)_{11}SH$) to also cause discontinuous changes in the orientations of LCs.[22]

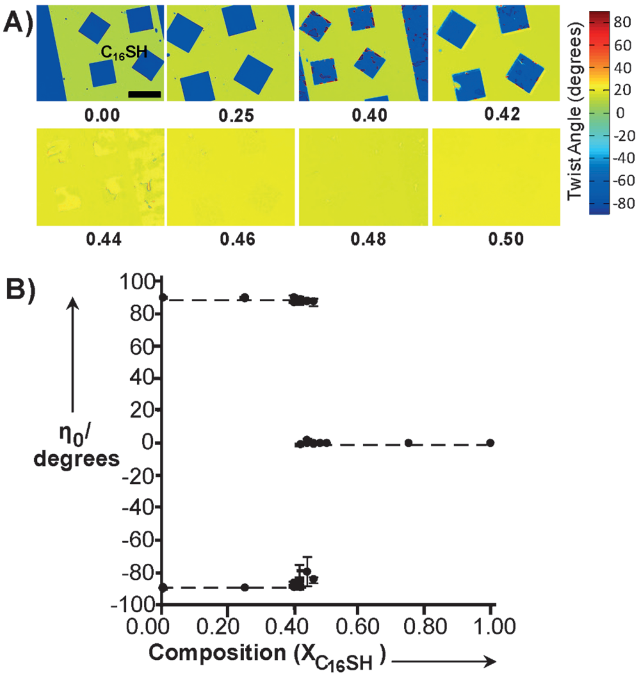

Figure 4. A) Two-dimensional map of twist angles of nematic 5CB on surfaces supporting mixed monolayers of the achiral molecules $C_{16}SH$ and $C_{15}SH$ (squares and diamonds). Mole fractions of $C_{16}SH$ (X_{C16SH}) are indicated. The blue domains in the top line of images correspond to the regions of the surface presenting the mixed monolayers. $C_{16}SH$ was stamped onto the surfaces prior to forming the mixed monolayers and served as a reference region (see text). Scale bar represents 2 mm. B) Easy axis (η_0) of 5CB as a function of the mole fraction of $C_{16}SH$ (X_{C16SH}). Error bars represent standard deviations.

The results described above, when combined, reveal that the qualitative anchoring behavior of LCs on mixed component monolayers is dependent on whether the adsorbates are chiral or not. Our results are consistent with a physical mechanism in which enantiomerically pure nanodomains of dipeptide form on the surface, each locally orienting the LCs through hydrogen bonding (as seen on the enantiomerically pure monolayers shown in Figure 2). In our experiments, the average orientation of the LC, as measured on optical scales, is consistent with the juxtaposition of many enantiomerically pure nanodomains. Our conclusion regarding the origin of the continuous transition in the anchoring of the LCs on the mixed chiral surfaces is also supported by previous studies that observed that LCs supported on microscopically patterned substrates adopt uniform orientations (away from the surface) that lie between the easy axes of the LCs on each of the patterned areas comprising the substrates.[8c,23]

Overall, we report that mixtures of chiral dipeptides, when coadsorbed as monolayers on surfaces, cause the orientation of nematic LCs to change as a continuous function of the enantiomeric excess of dipeptide within the monolayer (over an azimuthal angle of 100°). In contrast, on surfaces decorated with mixtures of achiral alkanethiols that homogeneously mix, we measured the orientations of 5CB to change discontinuously, thus supporting our hypothesis that the nanoscopic segregation of mixed monolayers of enantiomers underlies the continuous ordering transition reported here. These striking differences in the anchoring of LCs on surfaces presenting chiral and achiral adsorbates provide fundamental insights into the molecular origins of continuous and discontinuous ordering transitions of LCs, and define new principles based on chiral monolayers for rational design of surfaces that permit precise and arbitrary tuning of the orientations of LCs. The results also guide the design of LC-based systems with orientations that reflect the diverse chemical functionality and stereochemistry of biomolecules.

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[1] a) T. Kato, Y. Hirai, S. Nakaso, M. Moriyama, *Chem. Soc. Rev.* **2007**, *36*, 1857 – 1867; b) J. Hoogboom, M. Behdani, J. Elemans, M. A. C. Devillers, R. de Gelder, A. E. Rowan, T. Rasing, R. M. Nolte, *Angew. Chem.* **2003**, *115*, 1856 – 1859; *Angew. Chem. Int. Ed.* **2003**, *42*, 1812 – 1815; c) F. Castles, F. V. Day, S. M. Morris, D. H. Ko, D. J. Gardiner, M. M. Qasim, S. Nosheen, P. J. W. Hands, S. S. Choi, R. H. Friend, H. J. Coles, *Nat. Mater.* **2012**, *11*, 599 – 603.

[2] a) I. H. Lin, D. S. Miller, P. J. Bertics, C. J. Murphy, J. J. de Pablo, N. L. Abbott, *Science* **2011**, *332*, 1297 – 1300; b) A. D. Price, D. K. Schwartz, *J. Am. Chem. Soc.* **2008**, *130*, 8188 – 8194; c) J. K. Gupta, S. Sivakumar, F. Caruso, N. L. Abbott, *Angew. Chem.* **2009**, *121*, 1680 – 1683; *Angew. Chem. Int. Ed.* **2009**, *48*, 1652 – 1655.

[3] a) T. Kato, *Angew. Chem.* **2010**, *122*, 8019 – 8021; *Angew. Chem. Int. Ed.* **2010**, *49*, 7847 – 7848; b) N. Hosono, T. Kajitani, T. Fukushima, K. Ito, S. Sasaki, M. Takata, T. Aida, *Science* **2010**, *330*, 808 – 811.

[4] J. M. Brake, M. K. Daschner, Y. Y. Luk, N. L. Abbott, *Science* **2003**, *302*, 2094 – 2097.

[5] J.-S. Park, N. L. Abbott, *Adv. Mater.* **2008**, *20*, 1185 – 1190.

[6] C. H. Jang, L. L. Cheng, C. W. Olsen, N. L. Abbott, *Nano Lett.* **2006**, *6*, 1053 – 1058.

[7] B. Jerome, *Rep. Prog. Phys.* **1991**, *54*, 391 – 451.

[8] a) J. Bechhoefer, J. L. Duvail, L. Masson, B. Jerome, R. M. Hornreich, P. Pieranski, *Phys. Rev. Lett.* **1990**, *64*, 1911 – 1914; b) J. S. Patel, H. Yokoyama, *Nature* **1993**, *362*, 525 – 527; c) B. Zhang, F. K. Lee, O. K. C. Tsui, P. Sheng, *Phys. Rev. Lett.* **2003**, *91*, 215501.

[9] K. Zhang, N. Liu, R. Twieg, B. Auman, P. Bos, *Liq. Cryst.* **2008**, *35*, 1191 – 1197.

[10] a) Y. Bai, N. L. Abbott, *J. Am. Chem. Soc.* **2012**, *134*, 548 – 558; b) S. Ferjani, Y. Choi, J. Pendery, R. Petschek, C. Rosenblatt, *Phys. Rev. Lett.* **2010**, *104*, 257801; c) M. Nakata, G. Zanchetta, M. Buscaglia, T. Bellini, N. Clark, *Langmuir* **2008**, *24*, 10390 – 10394; d) K. Shiromo, D. Sahade, Y. Oda, T. Nihira, Y. Takanishi, K. Ishikawa, H. Takezoe, *Angew. Chem.* **2005**, *117*, 1984 – 1987; *Angew. Chem. Int. Ed.* **2005**, *44*, 1948 – 1951.

[11] A. M. Lowe, P. J. Bertics, N. L. Abbott, *Anal. Chem.* **2008**, *80*, 2637 – 2645.

[12] J. J. Skaife, N. L. Abbott, *Chem. Mater.* **1999**, *11*, 612 – 623.

[13] a) S. M. Barlow, R. Raval, *Curr. Opin. Colloid Interface Sci.* **2008**, *13*, 65 – 73; b) M. Lingenfelder, G. Tomba, G. Costantini, L. Colombi Ciacchi, A. De Vita, K. Kern, *Angew. Chem.* **2007**, *119*, 4576 – 4579; *Angew. Chem. Int. Ed.* **2007**, *46*, 4492 – 4495; c) R. Raval, *Chem. Soc. Rev.* **2009**, *38*, 707 – 721.

[14] S. Romer, B. Behzadi, R. Fasel, K.-H. Ernst, *Chem. Eur. J.* **2005**, *11*, 4149 – 4154.

[15] M. Forster, M. S. Dyer, M. Persson, R. Raval, *Angew. Chem.* **2010**, *122*, 2394 – 2398.

[16] J. V. Barth, H. Brune, G. Ertl, R. J. Behm, *Phys. Rev. B* **1990**, *42*, 9307 – 9318.

[17] S. M. Barlow, S. Louafi, D. Le Roux, J. Williams, C. Muryn, S. Haq, R. Raval, *Surf. Sci.* **2005**, *590*, 243 – 263.

[18] H. Schönherr, H. Ringsdorf, M. Jaschke, H. Butt, E. Bamberg, H. Allinson, S. Evans, *Langmuir* **1996**, *12*, 3898 – 3904.

[19] J. Folkers, P. Laibinis, G. Whitesides, J. Deutch, *J. Phys. Chem.* **1994**, *98*, 563 – 571.

[20] C. D. Bain, G. M. Whitesides, *J. Am. Chem. Soc.* **1989**, *111*, 7164 – 7175.

[21] S. Follonier, W. J. W. Miller, N. L. Abbott, A. Knoesen, *Langmuir* **2003**, *19*, 10501 – 10509.

[22] R. R. Shah, N. L. Abbott, *J. Am. Chem. Soc.* **1999**, *121*, 11300 – 11310.

[23] F. S. Yeung, J. Y. Ho, Y. W. Li, F. C. Xie, O. K. Tsui, P. Sheng, H. S. Kwok, *Appl. Phys. Lett.* **2006**, *88*, 051910.