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Effects of Divalent Ligand Interactions on Surface-Induced Ordering of Liquid Crystals

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We report the synthesis of a mesogen that contains two nitrile groups (4-pentyl-3′,4′-dicyanobiphenyl, DCB), and the use of the mesogen in an investigation of the effects of multivalent ligand interactions on the ordering of liquid-crystalline phases at surfaces decorated with copper (Cu^{2+}) ions. Differential scanning calorimetry (DSC) confirmed that DCB was miscible with nematic phases of 4-pentyl-4′-cyanobiphenyl (5CB). Quantitative measurement of the optical retardance of mixtures of DCB and 5CB in contact with surfaces decorated with Cu^{2+} (characterized by X-ray photoelectron spectroscopy, XPS) revealed a continuous ordering transition in the nematic LC as a function of increasing concentration of DCB (0.9−2 wt %). In contrast, Fourier transform infrared (FTIR) spectroscopy of 5 mM Cu^{2+} dissolved in bulk benzonitrile revealed no evidence of a change in nitrile coordination around the Cu^{2+} upon addition of 5CB or DCB, thus leading to the proposition that the effect of DCB on the ordering of the LC phases at Cu^{2+} decorated surfaces is due to divalent coordination interactions of DCB with the immobilized Cu^{2+} ions. This hypothesis was further tested by measurements of FTIR spectra and surface-induced ordering transitions of LC phases of DCB/5CB upon introduction of dimethylmethylphosphonate (DMMP), an organophosphonate that binds competitively with nitrile groups for Cu^{2+}. These results, when combined, lead us to conclude that it is possible to substantially tune surface-induced ordering of LCs by manipulating the valency of the mesogens and thus coordination interactions of the LCs with metal ions immobilized on surfaces. Overall, the results of this study guide the design of multifunctional liquid crystals for use as chemoresponsive materials.

Introduction

Organic and inorganic materials designed to undergo substantial changes in optical, mechanical, volumetric, magnetic and electrical properties upon interaction with specific chemical species offer the basis of general and facile approaches for the realization of new classes of "smart" materials.[1−3] Liquid crystals (LCs) define particularly promising classes of stimuli-responsive materials that have been demonstrated to undergo adsorbate-induced ordering transitions that can be tuned to be sensitive and specific to chemical species.[4,5] Past studies reveal the ordering of LC materials to be sensitive to changes in the structure and chemical functionality of confining surfaces,[4−10] thus offering the basis of passive sensor materials.[10−28]

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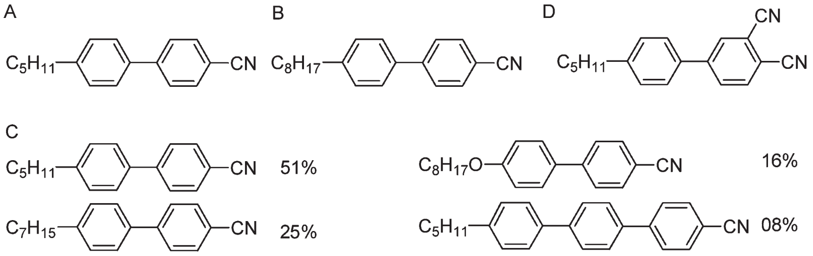

Figure 1. Molecular structures of mesogens (A) 5CB, (B) 8CB, and (C) E7, each of which contains one nitrile group. The mesogen (D) DCB, which was synthesized in this study, contains two nitrile groups.

One approach that has shown particular promise for the design of chemically responsive LC materials combines the use of surfaces that present metal ions with mesogens possessing ligands that are capable of coordinating to the metal ions: competitive binding of the mesogens and targeted chemical compounds for surface-immobilized metal ions leads to the coupling of the order of the LC to the presence/absence of the targeted compounds. Although this approach has been demonstrated to permit detection of parts-per-billion concentrations of some chemical compounds[4] (e.g., organophosphonates), attempts to optimize the design of the ligand-containing mesogens have not been reported. In this paper, we report an investigation in which we evaluate the influence of the valency of ligands (one versus two) designed into mesogens on the ordering of LCs at metal ion-decorated surfaces. We also report on the influence of the valency of the mesogens on surface-induced LC ordering transitions triggered by the presence of an organophosphonate compound.

The study reported in this paper builds on the results of prior investigations in which the orientations of LCs formed from nitrile-containing mesogens have been investigated on surfaces presenting thin films of metal perchlorate salts.[11,17] The mesogens used in these prior studies include 5CB, 8CB, and mixtures such as E7 (see Figure 1A−C). When micrometer-thick films of LCs (nematic and smectic) prepared from these mesogens were contacted with surfaces presenting perchlorate salts of metals with high electron affinity (e.g., Cu^{2+} or Al^{3+}), it was determined that the LCs adopt a perpendicular ordering as a consequence of metal ion-nitrile coordination interactions.[4,17] The role of the coordination interactions was established by using infrared (IR) spectroscopic measurements that characterized changes in the frequency of the nitrile stretching modes.[11] Additional IR studies performed in the presence of a model organophosphonate (dimethylmethylphosphonate, DMMP) demonstrated that the phosphoryl group of DMMP binds Cu^{2+} with sufficient affinity that it will competitively displace the nitrile groups of the mesogens from coordination with the metal ions. This ligand exchange on the surface is accompanied by an ordering transition in the LC that can propagate across a micrometer-thick LC film, thus giving rise to easily detected optical signals that indicate the presence of the DMMP. This principle has been shown to permit selective detection of organophosphorous-based warfare agents.[11,25]

Whereas these past studies have used LCs comprised of mesogens containing a single nitrile group, in this paper, we report the design and synthesis of a mesogen containing two nitrile groups. We report an investigation of the influence of the valency of the mesogen (monovalent versus divalent) on the orientational ordering of LCs on metal-ion-decorated surfaces. This study was motivated by two broad goals. First, by changing the valency of the mesogens, we sought to provide additional insight into the physicochemical phenomena underlying surface-induced ordering of LCs on surfaces presenting coordinating metal ions. In particular, we aimed to determine if an increase in the valency of the mesogens would permit the micrometer-thick films of LCs to be oriented on surfaces that present low surface densities of immobilized metal ions. We note that in past studies using LCs comprising mesogens containing single nitrile groups, high surface loadings of metal salts were used to orient the LCs (see below for additional details).[10,17,25] Second, we sought to determine the influence of divalency of the mesogens on the competitive metal ion-ligand exchange reactions that underlie the ordering transitions induced by organophosphonates. The mesogen designed and synthesized in our study is shown in Figure 1D. We conclude this introduction by also noting that the influence of multivalency on binding interactions (including divalency) has been broadly addressed in a number of biomolecular contexts, a point that we return to in the discussion presented later in this manuscript.

Experimental Section

Materials. 11-Mercaptoundecanoic acid (MUA), sodium nitrite (99.99%), hydrated perchlorate salts of Cu(II), dimethyl methylphosphonate (DMMP), dimethylformamide (DMF), benzonitrile (spectrophotomeric grade 99+%), and tetradecane were purchased from Sigma Aldrich (Milwaukee, WI). The nematic liquid crystal 5CB was purchased from EMD chemicals (Gibbstown, NJ). Titanium (99.999%) and gold (99.999%) were purchased from Advanced Materials (Spring Valley. NY). Petroleum ether, methanol, sodium hydroxide and Fischer's Finest glass slides were purchased from Fischer Scientific (Hamton, NH). 1,2-Dibromobenzene (98%), 4-*n*-pentyl aniline (98%), Cu(I) cyanide, iron(III) chloride, and diethyl ether (99%) were purchased from Alfa Aesar (Ward Hill, MA). Absolute ethanol (anhydrous, 200 proof) was purchased from Pharmco-AAPER

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(Shelbyville, MA). All chemicals and solvents were of analytical reagent grade and used as received without any further purification. All deionized water used in the study possessed a resistivity of 18.2 MΩ cm.

Cleaning of Glass Substrates. Glass microscope slides were cleaned according to published procedures using an acidic 'piranha' solution [70:30 (% v/v) H_2SO_4:H_2O_2 (30%)], as described in detail elsewhere.[29] Briefly, the glass slides were immersed in a piranha bath at 60−80 °C for at least 1 h, and then rinsed in running deionized water for 2−3 min. The slides were then immersed in basic "piranha" solution [70:30 (% v/v) KOH (45%): H_2O_2 (30%)] and heated to between 60 and 80 °C for at least 1 h. Finally, the slides were rinsed sequentially in deionized water, ethanol, and methanol, and then dried under a stream of nitrogen. The clean slides were stored in a vacuum oven at 110 °C overnight. All other glassware was cleaned prior to use.

Deposition of Gold Films. Semitransparent films of gold with thicknesses of 200 Å were deposited onto piranha-cleaned glass slides mounted on a stationary holder within an electron beam evaporator (VEC-3000-C manufactured by Tek-vac Industries, Brentwood, NY). We calculated the angle of incidence of the gold onto the slides to range from 0° to 15° from the surface normal. A layer of titanium (thickness 80 Å) was used to promote adhesion between the glass microscope slides and the film of gold. The rates of deposition of gold and titanium were ~0.2 Å/s. The pressure in the evaporator was maintained at less than 3×10^{-6} Torr before and during each deposition. The gold source was periodically cleaned by sequential immersion in aqua regia (70% HNO_3, 30% HCl) and piranha solutions at 50 °C (30 min in each solution). The cycle was repeated 3−4 times, rinsing between cycles in deionized water.

Formation of Chemically Functionalized Surfaces. Carboxylic-acid-terminated self-assembled monolayers (SAMs) of 11-mercaptoundecanoic acid (MUA) were formed on the gold-coated glass slides by immersing the slides overnight in an ethanolic solution containing 2 mM of MUA. The gold films were then rinsed with copious amounts of ethanol and dried under a stream of nitrogen. Metal ions (Cu^{2+}) were coordinated to the carboxylic-acid-terminated SAMs by spin coating 50 mM $Cu(ClO_4)_2$ (in ethanol) onto the SAMs at 3000 rpm for 60s (WS-400A-6NPP/Lite, Laurell Technologies, North Wales, PA). The SAMs were pretreated with an aqueous solution of 0.01 (N) NaOH prior to spin coating of the metal salt solution. To prepare surfaces with a lower surface density of metal ions, we rinsed the spin-coated surfaces with ethanol to remove excess perchlorate salts (leaving metal ions complexed with the carboxylate groups of the SAMs, see FTIR studies reported below).

Orientations of Liquid Crystals. We measured the orientations of nematic phases of 5CB on SAMs by fabricating optical cells from two films of gold, each of which supported SAMs. The gold films were aligned facing each other, spaced apart using a thin film of Mylar (thickness ~2 μm), and then clipped together using binder clips. A drop of 5CB, heated into its isotropic phase ($T < 45$ °C), was then drawn by capillarity into the cavity between the two surfaces of the optical cell. The cell was subsequently cooled to room temperature and the optical texture was analyzed with an Olympus BX-60 polarizing light microscope (Tokyo, Japan) in transmission mode.

Preparation of the LC from 5CB and 4-Pentyl-3′,4′-Dicyanobiphenyl (DCB). We dissolved a small wt % of DCB into 5CB and then heated the mixture above its nematic-to-isotropic transition temperature ($T_{NI} \approx 35$ °C). The mixture was then vortexed for 30 s to obtain a homogeneous suspension. We prepared mixtures containing a range of different concentrations of DCB (0 , 0.3, 0.5, 0.7, 0.9, 1.5, and 2 wt %).

Characterization of LC Mixtures Containing DCB. We characterized DCB and its mixtures with 5CB using a combination of infrared spectroscopy (FTIR) spectroscopy and ^{1}H NMR (Varian Unity, 300 MHz). An IR spectrum of DCB was obtained using a solid sample. ^{1}H NMR spectra were recorded using deuterated chloroform ($CDCl_3$) as the solvent. Tetramethylsilane (TMS) was used as an internal standard. The transition temperatures and associated enthalpies were determined using a differential scanning calorimetry (TA Instruments, Q100) operated at a scanning rate of 2 °C/min during heating. The apparatus was calibrated using indium (156.6 °C) as a standard. The transition temperature was also checked using a polarizing optical microscope (Olympus BX 51) fitted with a heated stage (Mettler FP82HT) and a controller (Mettler FP 90).

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) was used to determine the atomic composition of the surfaces presenting metal salts. The instrument used for the measurements was a Perkin-Elmer PHI 5400 XPS system equipped with Omni-Focus Lens and Al (Kα) X-ray source (1486.6 eV). The XPS spectra were obtained over a surface area of approximately 1 mm × 3 mm. Survey scans with a pass energy of 89.45 eV were first performed to identify the elements present on the surface, followed by acquisition of element-specific spectra with a pass energy of 44.75 eV. The major peaks of interest were Cu ($2p_{3/2}$), Cl (2p), C (1s), O (1s) and Au ($4f_{7/2}$). Data analysis was performed using the RBD Instruments AugerScan (Bend, OR) analysis software. The percentage composition of each element present on the surface was determined, after establishing the baselines, by integrating the area under each peak and correcting for the element specific PHI sensitivity factors.

Transmission IR Spectroscopy. Copper perchlorate was dissolved in benzonitrile and then either 5CB, DCB or mixtures of both mesogens were added. Benzonitrile solutions were then transferred into a liquid IR cell (SL-3, International Crystal Laboratory, Garfield, NJ) equipped with a CaF_2 window having a path length of 0.0529 mm. All solutions transfers were performed using plastic syringes. Between any two experiments, the IR cell was rinsed thoroughly with ethanol, methanol, and then dried with nitrogen. For each IR spectrum, 128 scans were taken at a resolution of 4 cm^{-1} by using a Thermo Scientific Nicolet 380 FTIR spectrometer (Fitchburg, WI).

Measurement of Optical Retardance. To quantify the orientational ordering of the LC within a thin film sandwiched between surfaces decorated with metal salts, we measured the optical retardance (Δr) of the LC film using a CRI Polscope (CRI, Woburn, MA) (a retardance mapping instrument that can measure optical retardance with a precision of ±0.2 nm). The retardance values reported in this paper are the averages of measurements performed at 5 locations in each sample. The effective birefringence (Δn_{eff}) of the LC was calculated as $\Delta n_{\mathrm{eff}} = \Delta r/\Delta d$, where Δd is the film thickness, and then used to calculate the tilt angle (θ, measured from the surface normal) of the LC by numerically solving the equation[30]

$$\Delta n_{\mathrm{eff}} = \frac{n_{\mathrm{o}} n_{\mathrm{e}}}{\sqrt{n_{\mathrm{o}}^2 \sin^2 \theta + n_{\mathrm{e}}^2 \cos^2 \theta}} - n_{\mathrm{o}}$$

where n_{e} and n_{o} are the indices of refraction parallel and perpendicular (so-called extraordinary refractive index and

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Table 1. Atomic Composition of Surfaces Presenting Cu^{2+} Ions, As Measured by XPS[a]

	elemental analysis by XPS [atomic composition shown as percentages]					
	Au	C	O	Cl	Cu	Cu/Cl
without excess salts	11.2 ± 0.2	48.5 ± 1.9	32 ± 1.1	3.2 ± 0.3	5.1 ± 0.3	1.6 ± 0.3
with excess salts	8.0 ± 0.5	38.7 ± 0.5	42 ± 0.6	7.3 ± 0.9	3.6 ± 0.3	0.5 ± 0.1

[a] The surface denoted "with excess salts" was prepared by spin-coating 50 mM $Cu(ClO_4)_2$ (in ethanol) onto a gold-supported monolayer formed from $HOOC(CH_2)_{10}SH$ (pretreated with aqueous 0.01 (N) NaOH prior to spin coating). The surface denoted "without excess salts" was prepared as described above, but rinsed using ethanol to remove the excess salt prior to characterization by XPS.

ordinary refractive index, respectively) to the optical axis of the LC, respectively. The indices of refraction of 5CB were taken to be $n_e = 1.711$ and $n_o = 1.5296$ ($\lambda = 632$ nm at 25 °C).[31]

Ordering Transitions Induced by DMMP. An Olympus IX-71 inverted microscope fitted with a Hamamatsu digital camera (ORCA-ER) controlled by ImagePro software (Minneapolis, MN) was used to capture optical images of the LC films. To monitor the optical response of LC films to DMMP, we prepared films of LC using capillary forces generated by using arrays of micropillars (fabricated by Microfabrication Solutions Inc., Cleveland, OH).[28] The arrays of micropillars were fabricated by photopolymerization of a photoresist made by Promerus Electronic Materials (Brecksville, OH). The mask used during photopolymerization was printed by Photo Sciences, Inc. (Torrance, CA). The diameter and spacing of each pillar within the array was 25 μm and the height of each pillar was 20 μm.[28] Titanium (thickness of 80 Å) and gold (thickness of 200 Å) were deposited sequentially onto the surface of the micropillars using e-beam deposition (see above). Subsequently, SAMs were formed on the conformal gold coating by immersion of the micropillar array into 2 mM ethanolic solutions of MUA for overnight. Upon removal, the samples were rinsed with copius amounts of ethanol to remove residual thiols and dried under a stream of nitrogen. Copper perchlorate was deposited onto the array by spin-coating 5 mM $Cu(ClO_4)_2$ in ethanol (3000 rpm for 60s). The micropillar arrays were filled with LC by spontaneous spreading of LC into the void spaces between the micropillars. The pillar height determines the thickness of the LC film. After the micropillar array was filled using capillary forces, the array was placed into a glass chamber mounted on the microscope. Liquid DMMP (D169102, Sigma-Aldrich), with density 1.145 g/mL at 25 °C, was diluted four times with tetradecane (> 99%, 172456, Sigma Aldrich, bp 252 °C) in an Eppendorf tube, and 0.2 μL of this diluted DMMP was placed on a filter paper located within the glass chamber to generate a DMMP vapor within the chamber.

Results and Discussion

We prepared two types of Cu^{2+}-decorated surfaces for use in our study. The first type of surface was prepared by spin-coating $Cu(ClO_4)_2$ (in ethanol) onto monolayers formed from MUA ($HOOC(CH_2)_{10}SH$) on thin gold films. The monolayers were pretreated with an aqueous solution of 0.01 (N) NaOH prior to spin coating of the metal salt solution. As described below, these surfaces are decorated with excess metal perchlorate salts.[4,17,25] The second type of surface used in our study was prepared as described above, and subsequently rinsed with ethanol to remove excess perchlorate salt.

Table 1 shows the results of XPS characterization of the two types of surfaces prepared for our study. We make several conclusions from the results presented in Table 1. First, the rinsing of the surfaces leads to an increase in both the gold ((Au ($4f_{7/2}$)) and carbon (C(1s)) signals. This result is consistent with removal of excess salt from the surface upon rinsing (thus decreasing attenuation of the signal from the gold film and SAM beneath the salt film). Second, inspection of Table 1 reveals the presence of Cu^{2+} on both types of surfaces. Substantially more chlorine was present, however, on the surface that was not rinsed after spin coating (7.3 ± 0.9%), as compared to the surface that was rinsed thoroughly with ethanol (3.2 ± 0.3%). For the surface that was not rinsed, the Cu:Cl atomic ratio was determined to be 0.5 ± 0.1, which closely matches the stochiometric ratio of $Cu(ClO_4)_2$. The XPS result is thus consistent with the presence of excess salt on the surface that was not rinsed. In contrast, after rinsing, the Cu:Cl ratio increased to 1.6 ± 0.3. Because the only source of chlorine on the surface is perchlorate (with a Cu:Cl ratio of 0.5), the Cu:Cl ratio measured for the rinsed surface indicates that the majority of the Cu ions present on the rinsed surface (70 ± 10%) form a complex with carboxylate rather than being present as a perchlorate salt.

Next, we measured the orientations assumed by nematic phases of the 5CB (no added DCB) on the above-described surfaces. We characterized the orientations of nematic phases of 5CB by fabricating optical cells from two films of gold treated as described above. The gold films were spaced apart using a thin film of Mylar (thickness of ~2 μm). A drop of 5CB, heated into its isotropic phase, was then drawn by capillarity into the cavity between the two surfaces of the optical cell. The cell was subsequently cooled to room temperature and the optical texture analyzed with an Olympus BX-60 polarizing light microscope in transmission mode. Inspection of Figure 2A reveals that the nematic 5CB confined by the surfaces presenting the excess copper perchlorate salt appears dark when viewed between crossed-polars. This result, when combined with conoscopic observations that revealed a crosslike isogyre, led us to conclude that the 5CB had assumed a homeotropic (perpendicular) orientation at these surfaces. In contrast, a film of 5CB confined by surfaces that were rinsed with ethanol after deposition of the metal perchlorate salts exhibited a bright optical appearance under crossed polars (Figure 2B). This result indicates that the 5CB had assumed a planar or tilted orientation at these surfaces.

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We interpret the results in Figure 2 to indicate that nematic 5CB assumes a homeotropic orientation only in the presence of excess copper perchlorate salt on the surfaces. If the excess salt is largely removed by rinsing with ethanol prior to contact with the LC (see Table 1), the 5CB is observed to adopt a tilted orientation (see below for details; the 5CB is tilted on these surfaces by 45° from the surface normal).

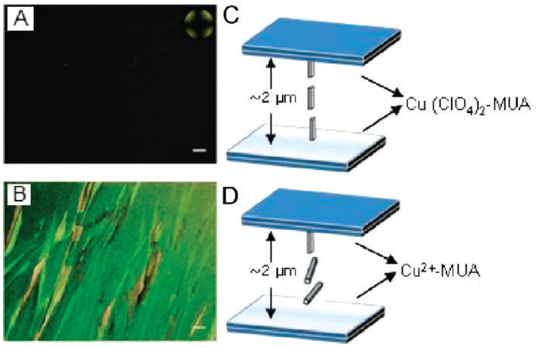
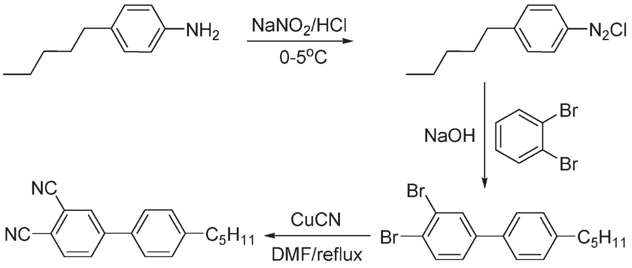


Figure 2. Optical micrographs (crossed polars) of films of 5CB (thickness ~2 μm) confined between two surfaces. (A) Surfaces used to obtain the images in A were prepared by spin coating 50 mM $Cu(ClO_4)_2$ (in ethanol) onto SAMs formed from $HOOC(CH_2)_{10}SH$ that were pretreated with an aqueous solution of 0.01 (N) NaOH prior to spin coating. (B) Surfaces in B were prepared as in A, but after spin-coating with 50 mM $Cu(ClO_4)_2$, the surfaces were rinsed using ethanol to remove the excess salt. The inset in A is a conoscopic image indicating homeotropic alignment of the nematic film of 5CB. (C, D) Schematic illustrations of the orientations of the LCs interpreted from the optical textures shown in A and B, respectively (scale bar = 50 μm).

Scheme 1. Synthesis of 4-Pentyl-3′,4′-dicyanobiphenyl (DCB)



Motivated by the hypothesis that the film of 5CB on the rinsed surfaces possesses an insufficient number of coordination interactions with the surface-bound Cu^{2+} to assume a homeotropic orientation, we sought to determine if a LC containing mesogens capable of divalent coordination interactions with Cu^{2+} would differ in its ordering on the rinsed surfaces. We synthesized a mesogen containing two nitrile groups (DCB, Figure 1D) using the scheme shown in Scheme 1. The details of the synthetic procedure are described in Supporting Information. We prepared mixtures of DCB and 5CB by heating the mixture above the T_{NI} and vortexing for 30s. To determine if DCB was well-mixed within the 5CB, we performed DSC of pure DCB (crystal-to-isotropic liquid transition at 52 °C), pure 5CB (nematic-to-isotropic liquid transition at 33 °C) and 1 wt % DCB in 5CB (nematic-to-isotropic transition at 33 °C). Because the thermograms revealed only one phase transition for the mixture (close to the nematic−isotropic transition of pure 5CB, see the Supporting Information, Figure S1), we conclude that the two components are well-mixed in the nematic phase.

Figure 3A shows an optical image of nematic 5CB containing 2 wt % of DCB that is confined between two surfaces that were pretreated with $Cu(ClO_4)_2$ and rinsed with ethanol. As control experiments, we also characterized the orientations of 5CB containing 2 wt % DCB in contact with SAMs formed from $HOOC(CH_2)_{10}SH$ (Figure 3B), and SAMs formed from $HOOC(CH_2)_{10}SH$ that were pretreated with 0.01 (N) NaOH (Figure 3C). Inspection of Figure 3 reveals a key result−in contrast to pure 5CB, nematic 5CB containing 2 wt % DCB assumes a homeotropic orientation on surfaces that are rinsed with ethanol after deposition of the $Cu(ClO_4)_2$ salts.

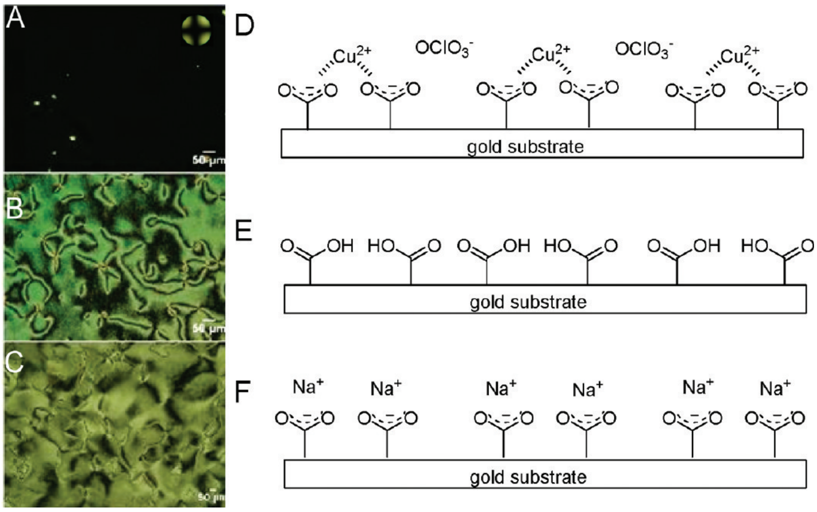


Figure 3. (A) Optical micrographs (crossed polars) of a thin film of nematic LC mixture containing 2 wt % DCB in 5CB that is confined between SAMs formed from $HOOC(CH_2)_{10}SH$ that were pretreated sequentially with aqueous solution of 0.01 (N) NaOH and 50 mM $Cu(ClO_4)_2$, followed by thorough rinse with ethanol. The inset in A is a conoscopic image indicating homeotropic alignment. (B, C) Optical micrographs (crossed polars) of LCs containing 2 wt % DCB in 5CB confined within optical cells with surfaces prepared from either (B) SAMs formed from $HOOC(CH_2)_{10}SH$ or (C) SAMs formed from $HOOC(CH_2)_{10}SH$ and pretreated with 0.01 (N) NaOH. (D−F) Schematic illustrations of the surfaces described in A−C.

Homeotropic alignment of the DCB-containing LC was confirmed by observation of a conoscopic image consisting of two crossed isogyres (see inset in Figure 3A). In contrast, nematic 5CB containing 2 wt % DCB assumed a tilted orientation on the SAM formed from HOOC-$(CH_2)_{10}$SH as well as the SAM formed from HOOC-$(CH_2)_{10}$SH pretreated with 0.01 (N) NaOH. These latter observations suggest that the introduction of the mesogen containing two coordinating ligands (two nitrile groups) into the 5CB gives rise to coordination interactions between the Cu^{2+} ions on the rinsed surfaces and the LC that result in the homeotropic orientation. In the absence of the divalent mesogen, the nematic phase of pure 5CB does not interact with the rinsed surface presenting Cu^{2+} ions to assume a homeotropic orientation.

The results of the control experiments described above also indicate that the homeotropic orientation of the DCB-containing 5CB on the rinsed surfaces is not due to electrical double layer interactions that can form through dissociation of counterions from surfaces into the LC.[8] We note that our past studies have shown that surfaces possessing high densities of sodium carboxylate salts can cause 5CB to adopt an orientation that is perpendicular to the surface (homeotropic).[8] This orientation is caused by interactions of the electric field generated within the diffuse part of an electrical double layer with the mesogens. This effect is, however, observed only in films of LCs that are substantially thicker (>10 μm) than those used in the studies reported here (~2 μm).

To provide additional insight into the role of metal−ligand coordination interactions underlying the above-described differences between the orientations assumed by pure 5CB and DCB-containing 5CB on surfaces presenting Cu^{2+} ions, we performed FTIR spectroscopy. In these experiments, we used benzonitrile instead of 5CB because benzonitrile forms an isotropic phase at room temperature into which millimolar concentrations of Cu^{2+} ions can be dissolved. Following dissolution of the 5 mM Cu^{2+} ions in the benzonitrile, we investigated the changes in the IR absorption spectra caused by addition of 2 wt % of either 5CB or DCB. In the absence of copper perchlorate, the IR spectrum (measured in transmission mode) of the benzonitrile exhibited a single peak at 2230 cm^{-1} which corresponds to the stretching of the nitrile groups of the benzonitrile (see the Supporting Information, Figure S2). Following the addition of 5 mM copper perchlorate to the benzonitrile, a new secondary peak at 2280 cm^{-1} was evident in the IR spectrum (i in Figure 4). As reported previously,[11] this peak corresponds to the stretching of nitrile groups that are coordinated to copper ions. Next, we added either 2% 5CB or 2% DCB to the benzonitrile solution containing Cu^{2+}. Following the addition of the mesogens, we measured no significant change in the height of the secondary peak associated with the nitrile−Cu^{2+} complex (ii and iii in Figure 4). We also note that the wavenumber of the secondary nitrile peak did not change upon addition of DCB. Because the concentrations of the 5CB and DCB (~80 mM) added to the benzonitrile were much larger than the Cu^{2+} (~5 mM), if either 5CB or DCB had coordinated with the Cu^{2+} in a manner that was significantly different from benzonitrile, a shift in either the intensity or position of the peak corresponding to the nitrile-Cu^{2+} complex would be seen. The absence of any change in the IR spectrum upon addition of DCB is significant in light of the above-described DCB-induced changes in orientational ordering of LCs on surfaces presenting Cu^{2+} ions. Because DCB does change the surface-induced orientational ordering of the nematic LC whereas it does not change the IR spectrum in bulk, we conclude that the influence of the DCB on the surface-induced ordering of the LC phase is due to stronger binding of DCB to the Cu^{2+}-immobilized surface as compared to the Cu^{2+} in solution. This stronger interaction at the surface is consistent with the effects of a multivalent interaction between the mesogens and the Cu^{2+} immobilized on the surface. These results suggest that DCB partitions to the surface and that the two nitrile groups of at least some of the DCB molecules in the LC are coordinating with the Cu^{2+} ions at the surface.

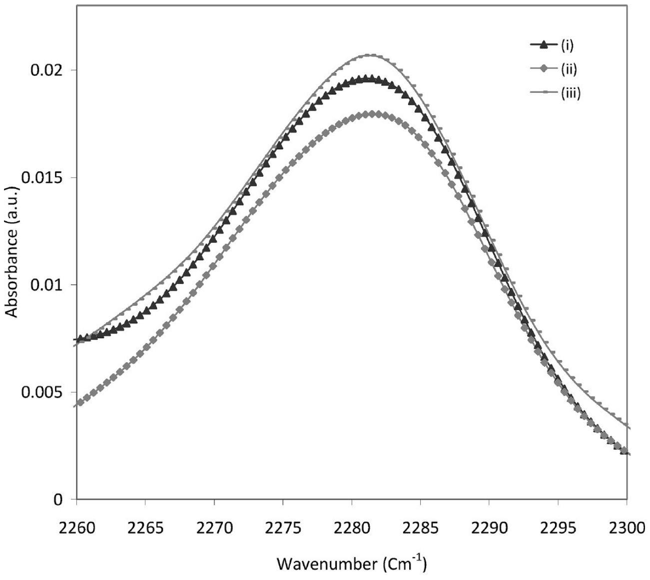


Figure 4. Infrared difference spectra (measured relative to benzonitrile) of (i) 5 mM copper perchlorate in benzonitrile, (ii) 2 wt % 5CB in benzonitrile containing 5 mM copper perchlorate, and (iii) 2 wt % DCB in benzonitrile containing 5 mM copper perchlorate.

The results presented above lead us to propose that the 2 wt % of DCB added to 5CB partitions to the Cu^{2+}-decorated interface of the nematic phase to promote the homeotropic orientation of 5CB. To further test this proposition we examined the influence of the concentration of DCB added to the 5CB on the ordering of the nematic phase on Cu^{2+}-decorated surfaces (rinsed). The tilt angles of the LC mixtures containing varying concentrations of DCB were quantified using a birefringence mapper (see Experimental section for details). Figure 5A shows polarized light micrographs of the LC mixtures containing 5CB and various concentrations of DCB. When the LC contained between 0.9 wt % and 2.0 wt % of the DCB, the orientation of the LC was observed to be

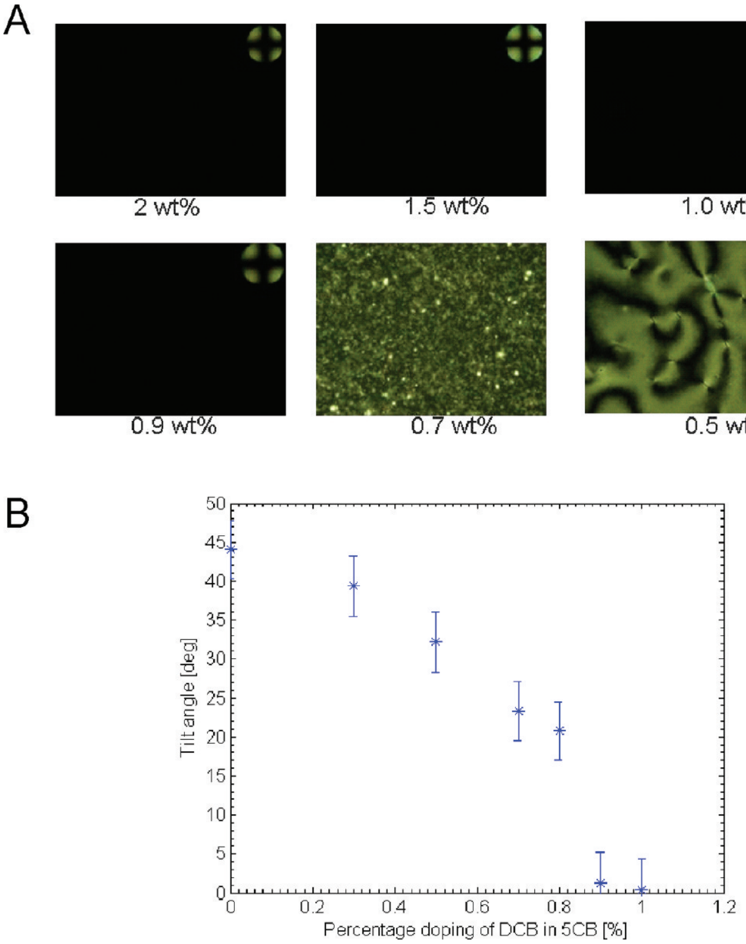


Figure 5. (A) Optical micrographs (crossed polars) of 5CB containing DCB confined between monolayers formed from $HOOC(CH_2)_{10}SH$ that were pretreated sequentially with aqueous solution of 0.01 (N) NaOH and 50 mM $Cu(ClO_4)_2$ followed by a thorough rinse with ethanol. (B) Influence of wt% DCB on tilt (measured from surface normal) of micrometer-thick films of DCB + 5CB anchored on surfaces described in A.

homeotropic. In contrast, samples of LC containing 0.7% or less of DCB assumed either tilted or planar orientations. Inspection of Figure 5B shows that the tilt of the LC from the surface normal decreased continuously from 0° (homeotropic) to 45° as the DCB concentration was decreased from 0.9% to zero. The observation of a continuous change in tilt angle of the LC as a function of the concentration of DCB is consistent with the proposition that the DCB partitions to the Cu^{2+}-decorated surface with increasing concentration, resulting in divalent coordination interactions with the Cu^{2+} that lead to the homeotropic orientation. An additional significant finding is that the tilt of pure 5CB is about 45° on surfaces presenting Cu^{2+} ions (it is not planar). The observation that the tilt angle of pure 5CB is about 45°, and not 90°, indicates that even when using the rinsed surfaces, interactions between the Cu^{2+} ions and the nitrile groups of 5CB influence the orientations of the 5CB (the tilt of 5CB on the carboxylic acid-terminated SAM was measured to be 90°). The influence of those interactions, however, is not sufficient to cause 5CB to assume a homeotropic orientation.

To provide further insight into the consequences of the divalent nature of the DCB interaction with the surfaces decorated with Cu^{2+}, we investigated the effects of dimethylmethylphosphonate (DMMP). To this end, we prepared micrometer-thick films of the LC mixtures (5CB and DCB) that were stabilized mechanically by using arrays of microfabricated pillars (see Materials and Methods for details) decorated with Cu^{2+} ions (rinsed or not rinsed). The LC films were exposed to vapors of DMMP, as described in Materials and Methods. If all DMMP placed into the exposure chamber was to evaporate, the concentration of DMMP in the chamber would be 100 ppm. As a control experiment, we first characterized the ordering transition induced by DMMP when using pure 5CB and a micropillar array with surfaces coated with excess copper perchlorate salt (Figure 6A). Inspection of Figure 6A reveals an initial state of the nematic film of 5CB that is dark when viewed between crossed polars, consistent with homeotropic anchoring of the LC at the surfaces presenting excess copper perchlorate. Approximately 15 s after the drop of tetradecane containing DMMP was placed in the chamber, the optical appearance of the LC in the micropillar array became bright, thus indicating a DMMP-induced ordering transition in the nematic LC. The dark circles that are evident in the images after exposure to the DMMP coincide with the locations of the pillars of the micropillar array.

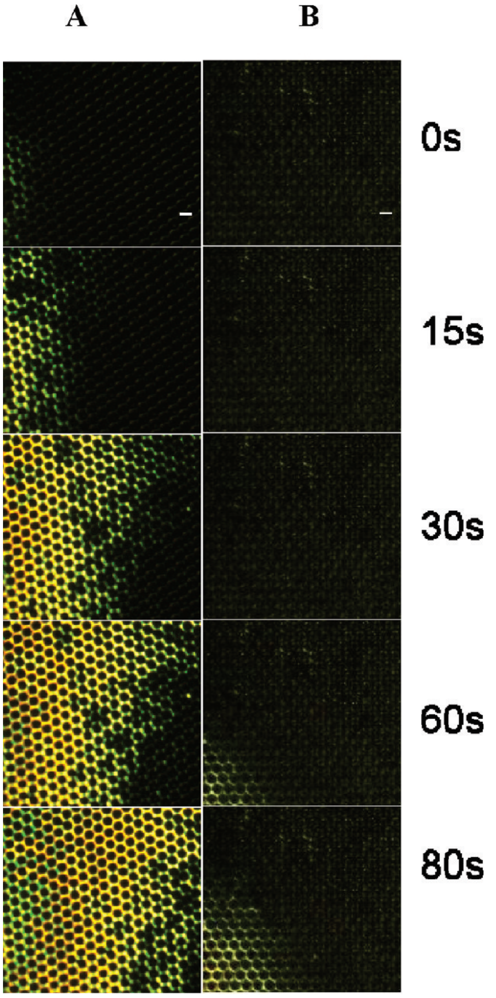


Figure 6. Optical images (crossed polars) of (A) nematic 5CB (no added DCB) and (B) a mixture of 5CB containing 2.0 wt % DCB showing the time-dependent response of the LCs hosted in micropillar arrays to a vapor of DMMP. The micropillars used to obtain the data in A were coated with excess copper perchlorate salts, whereas the micropillars in B were coated with excess copper perchlorate salt and then rinsed with ethanol prior to use. The droplet of liquid used to generate the vapor of DMMP was placed on the left side of the LC samples (scale bar = 50 μm).

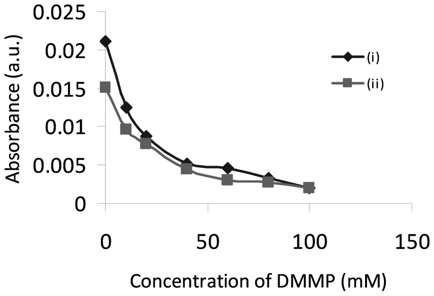


Figure 7. Plot of the intensity of the absorption peak at 2280 cm^{-1} in IR transmission spectra corresponding to nitrile groups that are coordinated with Cu^{2+}, as measured (i) after the addition of DMMP (0, 10, 20, 40, 60, 80, 100 mM) to a solution of 5 mM copper perchlorate in benzonitrile and (ii) after addition of the same concentration of DMMP to 2 wt % DCB in benzonitrile solutions.

Figure 6B shows the results of an experiment where a nematic phase comprising 2 wt % DCB in 5CB was hosted in a micropillar array with surfaces that were rinsed with ethanol to remove excess copper perchlorate prior to introduction of the LC mixture. The nematic film appeared dark when viewed between crossed polars, thus suggesting that the initial ordering was homeotropic. In comparison to the control experiment shown in Figure 6A, however, the LC containing 2 wt % DCB was observed to respond slowly to the DMMP (Figure 6B) In this case, the response to DMMP occurred over long time periods (~180s, see Figure S3 in the Supporting Information). Similar observations were made with 5CB containing lower concentrations of DCB (0.9, 1.5 wt %, see Figure S4 in the Supporting Information). Also, in the presence of excess salts, the optical response of the LC containing 2 wt % DCB was slow as compared to that observed with pure 5CB. (see Figure S5 in the Supporting Information). We conclude, therefore, that the DMMP-induced ordering transition of LCs containing DCB are hindered on surfaces presenting Cu^{2+} relative to that observed in the absence of DCB. This result supports our proposal that DCB in 5CB orients the LC phase on Cu^{2+}-functionalized surfaces through strong divalent coordination interactions. This stronger coordination interaction makes it more difficult for DMMP to competitively disrupt the nitrile$-$Cu^{2+} coordination interaction and thus trigger an ordering transition in the LC.

As noted above, the observation that DCB changes the LC ordering on the Cu^{2+}-decorated surfaces but does not change Cu^{2+} coordination in bulk solution is consistent with the anticipated effects of multivalent DCB binding at the surfaces. We also performed IR spectroscopy in bulk benzonitrile to determine if the effect of DMMP on the coordination state of the Cu^{2+} in the benzonitrile would be impacted by addition of DCB. Inspection of Figure 7 reveals that the influence of DMMP on the nitrile coordination of Cu^{2+} in bulk benzonitrile solution is independent of the presence/absence of DCB (see also Figure S6 in the Supporting Information). These results support our conclusion that the influence of DCB documented in Figure 6 (influence on the ordering transition of LC induced by DMMP) is a result of the divalent interaction of DCB with the Cu^{2+}-decorated surface.

Prior to concluding this paper, we note that multivalent ligands (including divalent ones − see below) are widely found in natural systems to increase the effective strength of binding interactions.[32−34] Mulitvalent interactions have also been designed into synthetic systems comprised of biological molecules to manipulate binding affinity for a variety of targets. For example, whereas serum-type mannose-binding protein binds monosaccharides with low affinity ($K_d \approx 0.1-1$ mM), by covalently attaching the monosaccharides to a macromolecules carrier, it is possible to generate high affinity ligands ($K_d \approx$ nM).[35]

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Many biological examples also demonstrate that the effects of multivalency are pronounced even at the level of divalency. For example, whereas monovalent interaction of vancomycin with diAc-L-Lys-D-Ala-D-Ala is characterized by a K_d of $\sim 1 \times 10^{-6}$ M, the divalent and trivalent interactions yielded effective K_d values of 1×10^{-9} and 1×10^{-17} M, respectively.[36,37] Similarly, cholesterol recognition using a β-cyclodextrin dimer (CD) yielded a K_d of 1.8×10^{-7} M whereas the monovalent interaction corresponded to a K_d of 5.9×10^{-5} M.[38] Finally, we also comment that IgG antibodies are another common example where divalent interactions are used to increase the avidity of binding of the protein to antigens presented at cell surfaces,[39,40] and that increases in avidity afforded by divalent attachment have also been addressed theoretically by Crothers et al.[41] That we observe pronounced effects of divalent interactions on the orientational ordering of LCs is consistent with these various past studies of biomolecular systems.

Conclusions

In summary, the main findings of the study reported in this paper are 3-fold. First, we have shown that it is possible to tailor the valency of ligand interactions to manipulate the ordering of LCs on surfaces. In particular, we have demonstrated that addition of a small weight percent of a divalent mesogen with two nitrile groups (DCB) to a nematic phase of 5CB leads to changes in the ordering of the LC on Cu^{2+}-decorated surfaces. Second, by changing the weight percent of the divalent mesogen in 5CB, we have determined that the tilt of the nematic LC film on Cu^{2+}-decorated surfaces can be tuned continuously from homeotropic to 45° from the surface normal. In contrast, the addition of DCB to Cu^{2+} dissolved in benzonitrile does not lead to measurable changes in the coordination of the Cu^{2+} in the bulk solution. These two results, when combined, support our conclusion that DCB changes the ordering of the LC through divalent interactions with the surface-immobilized Cu^{2+} ions. Third, measurements of the influence of DMMP on the ordering of the LC are also consistent with the presence of a divalent interaction of the DCB with the immobilized Cu^{2+} ions: the divalent nature of the interaction of the DCB hinders the ordering transition induced by DMMP. Overall, these results suggest that manipulation of the valency of ligand interactions is an effective strategy to tailor surface-induced ordering of LCs, and to tune the response of chemically functionalized LCs as chemoresponsive materials.

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Supporting Information Available: Synthesis of 4-pentyl-3′,4′-dicyanobiphenyl, preparation of LC mixtures from 5CB and DCB, DSC traces of 1 wt % DCB in 5CB, IR spectrum of benzonitrile solutions of 5CB and DCB, optical images of mixtures of 5CB containing different wt% of DCB, and difference IR spectra obtained after the addition of a series of different concentrations of DMMP to a solution of copper perchlorate in benzolnitrile and 2 wt % DCB in benzonitrile (PDF). This material is available free of charge via the Internet at http://pubs.acs.org/.

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