Adsorbate-Induced Ordering Transitions of Nematic Liquid Crystals on Surfaces Decorated with Aluminum Perchlorate Salts

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ABSTRACT We report an investigation of interfacial physicochemical phenomena underlying adsorbate-induced ordering transitions in nitrile-containing liquid crystals (LCs) supported on surfaces coated with metal perchlorate salts. When the mass density of $Al(ClO_4)_3$ deposited onto a surface was low (0.39 ± 0.03 ng/mm^2), we measured 20 μm thick films of nematic 4-cyano-4′-n-pentyl-biphenyl (5CB) to initially exhibit perpendicular (homeotropic) ordering, consistent with the influence of coordination interactions between the nitrile groups of 5CB and Al^{3+} ions on the surface on the ordering of the LC. Furthermore, exposure of freshly prepared LC films to vapors of an adsorbate that coordinates strongly to Al^{3+} ions (dimethylmethylphosphonate, DMMP) triggered an ordering transition in the LC films, supporting our conclusion that the initial perpendicular orientation of the LC was induced by nitrile-Al^{3+} coordination interactions. Subsequent equilibration of the LC on the surface (hours), however, resulted in a slow, time-dependent ordering transition in the absence of DMMP that corresponded to the tilting of the LC away from the surface normal. Measurements of the solubility of $Al(ClO_4)_3$ in nematic 5CB (saturation value of 1.7 μmol/mL) supported our hypothesis that the slow ordering transition observed in the absence of DMMP was due to the loss of metal ions from the surface into the LC film (dissolution). In contrast, the solubilization capacity of a 20 μm thick film of 5CB was determined to be insufficient to dissolve 2.14 ± 0.24 ng/mm^2 of the salt from a surface, and we measured the homeotropic ordering of nematic films of 5CB on these surfaces to persist for days. Equilibration of these samples, however, was accompanied by a loss of response to DMMP (perpendicular orientation of the LC before and after exposure to DMMP). Control experiments performed with a noncoordinating metal perchlorate salt (sodium perchlorate) confirmed our proposition that the loss of response to DMMP was due to formation of an electrical double layer that promoted perpendicular ordering of the LC and thus masked the effects of changes in coordination interactions induced by DMMP on the ordering of the LC (the electric field of the double layer promotes the perpendicular orientation of the 5CB). Finally, by coating surfaces with $Al(ClO_4)_3$ at loadings that were intermediate to those reported above (1.13 ± 0.09 ng/mm^2), we observed (i) perpendicular ordering of the LC in the absence of DMMP, and (ii) reversible ordering transitions induced by DMMP during storage of samples over 4−5 days. These results, when combined, indicate that the ordering of the LC on the metal-salt-decorated surfaces is strongly dependent on the loading of metal salt, with key interfacial physicochemical processes being metal ion−nitrile coordination interactions, dissolution of salt into the LC, and formation of electrical double layers. The results of this study provide guidance for the design of LC films that respond to specific chemical analytes and suggest principles for passive chemical sensors.

KEYWORDS: nematic liquid crystals • surfaces • ordering transitions • aluminum perchlorate

1. INTRODUCTION

Surface-induced orientational ordering of micrometer-thick films of liquid crystals (LCs) has been reported to occur on the surfaces of a wide range of organic and inorganic materials (1−3). Many of the early studies explored relatively simple surfaces (e.g., mechanically rubbed films of polyimides) and were successful in elucidating the underlying intermolecular interactions responsible for the surface-induced order (van der Waals dispersion interactions for the case of polyimides) (2, 4−7). More recent studies, however, have moved to investigate complex surfaces that present a diverse range of chemical functionality with potential application in liquid crystal-based chemical and biological sensors (8−27). For these latter types of surfaces,

the interfacial interactions underlying observations of the ordering of LCs remain poorly understood but potentially include (i) dipolar interactions associated with electrical double layers formed as a result of fixed charges at surfaces (10), (ii) hydrogen bonding between chemical groups presented at the interface and mesogens comprising the LC (9, 17), and (iii) metal ion−ligand coordination interactions between surface-immobilized metal ions and mesogens (8, 12, 18, 27). The study reported in this paper advances our understanding of surface-induced ordering of nitrile-containing LCs at interfaces presenting metal salts that can coordinate with the nitrile groups of the LCs. These surfaces have been reported previously to offer the basis of sensitive and selective sensors for low molecular weight organic molecules, such as organophosphonates (8, 11, 28).

As illustrated in A and B in Figure 1, when micrometer-thick films of nitrile-containing LCs (e.g., 5CB (4-cyano-4′-n-pentyl-biphenyl), 8CB (4-cyano-4′-n-octyl-biphenyl) or E7 (a mixture of 51 wt % 5CB, 25 wt % 4-cyano-4′-n-heptyl-
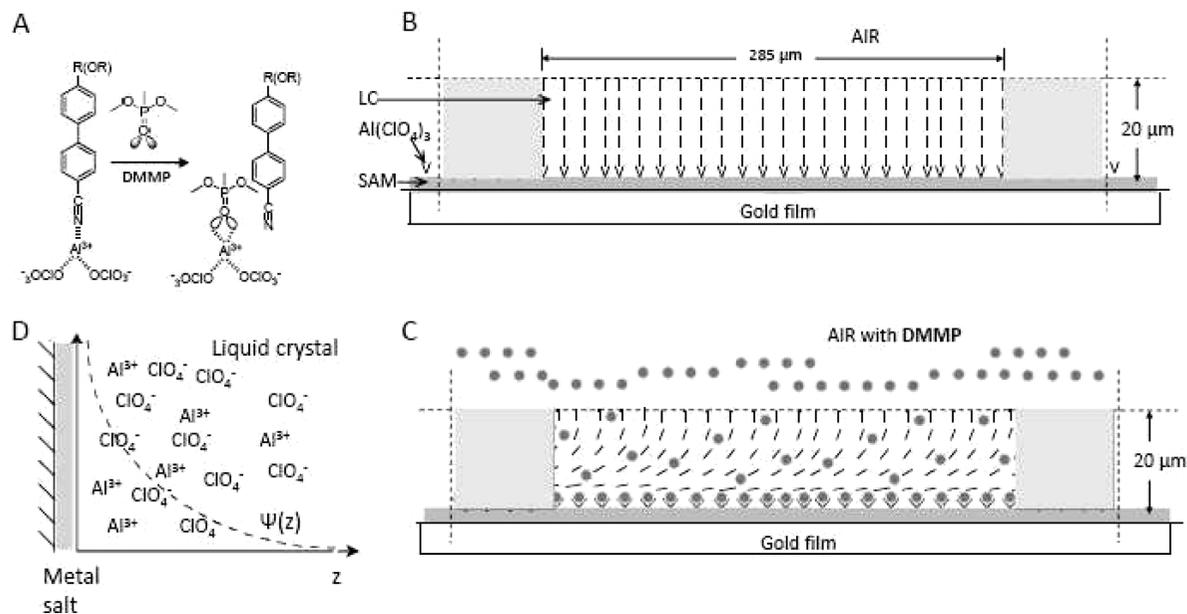
FIGURE 1. Schematic illustration of DMMP-responsive thin films of 5CB hosted within TEM grids supported on metal-salt-decorated surfaces. (A) Illustration of competitive coordination interactions between nitrile groups of LC and phosphoryl groups of DMMP with Al^{3+}, (B) homeotropic anchoring of 5CB at both air and metal-salt-decorated interfaces, (C) exposure of the LC to a vapor of DMMP results in diffusion of DMMP to the Al^{3+}-decorated surface and the triggering of an ordering transition in the LC via displacement of the nitrile groups of the LC from their coordination interactions with the Al^{3+}. (D) Illustration of the formation of an electrical double layer due to the uptake of salt into the LC film from the surface. The electrical potential, $\Psi(z)$ is shown in the vicinity of the surface.

biphenyl (7CB), 16 wt % 4-cyano-4′-n-oxyoctyl-biphenyl (8OCB) and 8 wt % 4-cyano-4′-n-pentyl-p-terphenyl (5CT)) are contacted with surfaces presenting perchlorate salts of metal cations with high electron affinity (e.g., Cu^{2+} or Al^{3+}), infrared spectroscopic studies have revealed that the LCs adopt a perpendicular (homeotropic) ordering as a consequence of coordination interactions between the nitrile groups of the LCs and the cations of the metal salts (11). The perchlorate counterion is used because it is a weakly coordinating ion, and thus it allows the 5CB and DMMP to coordinate with the Al^{3+} ion. Additional studies, also based on IR spectroscopy, determined that the phosphoryl groups of organophosphonate compounds (such as dimethylmethylphosphonate, DMMP) bind these metal cations with sufficient affinity that they can competitively displace the nitrile groups of the LCs from coordinating with the metal ions (Figure 1A). This ligand exchange was shown to be accompanied by an ordering transition in the LC that propagates from the metal-salt-coated surface across the micrometer-thick LC film, thus giving rise to easily detected optical signals (transmission of polarized light) that indicate the presence of DMMP (Figure 1C). These ordering transitions were found to be triggered by parts-per-billion concentrations (ppb) of organophosphonate vapors (8). By patterning different metal ions on a single surface, it was also shown that the (organophosphonate) chemical warfare agents ethyl dimethylphosphoramidocyanidate (GA, tabun), 1,2,2-trimethylpropyl methylphosphonofluoridate (GD, soman), and O-ethyl S-(2-diidopropylaminoethyl) methylphosphonothiolate (VX) can be detected and distinguished using LCs (11, 28).

Whereas the studies reported above establish the potential utility of surface-induced ordering transitions of LCs as the basis of chemical sensors, a complete picture of the underlying interfacial interactions is lacking, and the influence of key parameters of the system on these ordering transitions is not understood. In this paper, we report an investigation of the effects of the surface density of metal perchlorate salt on the interfacial ordering of nematic phases of 5CB, including the response of the LC films to DMMP. We focus our study on aluminum perchlorate as a metal salt that was previously identified (12) to have sufficient electron affinity to orient nematic phases of 5CB but has not been characterized in the context of ordering transitions induced by DMMP.

The study reported in this paper also represents a simple but useful advance in the design of an experimental system that enables fundamental insights into surface-induced ordering transitions in LC films. In particular, in micrometer-scale LC systems, the effects of elastic strain of the LC are often in competition with surface-induced ordering (29, 30). This competition between elastic and surface-induced ordering necessitates careful control of the micrometer-scale geometry of the LC system (e.g., LC film thickness) in order to obtain reproducible and quantitative ordering transitions upon exposure of the systems to adsorbates. To this end, recent studies have used microfabricated wells or arrays of micropillars to control the thicknesses of the films of LCs (8, 11, 26, 28, 31). In preliminary studies performed at the outset of the investigation reported in this paper, we found that the complex topography of microfabricated wells and micropillars prevented precise control over the uniformity and surface density of metal salts deposited by spin or dip coating. To address this issue, we report modification of a procedure described previously by us in which metallic grids are placed onto planar surfaces (as sketched in Figure 1B)

onto which controlled loadings of metal salts have been deposited by spin coating (12). This approach allowed us to systematically manipulate and quantify the amount of metal salt on the surface, and thereby unmask the effects of metal-salt density on the surface-induced ordering of nematic LC phases (including unexpected time-dependent ordering transitions).

A key finding of the study reported in this paper is that the loading of aluminum perchlorate on a surface used to support a nematic film of 5CB has a substantial and previously unappreciated effect on the surface-induced ordering of the LC film as well as the response to DMMP. In particular, we have found that the loading of metal salt on the surface influences dynamic phenomena that occur at the salt−LC interface over time periods that range from hours to days. Our investigation provides fundamental insights into the molecular origins of these dynamic phenomena, identifying dissolution of metal ions into the LC and formation of interfacial electrical double layers as key physicochemical interfacial events (as illustrated in Figure 1D). We also identify conditions and criteria for the design of interfaces that provide stable ordering of LC films for at least 5 days.

2. EXPERIMENTAL SECTION

2.1. Materials. 11-Mercaptoundecanoic acid (MUA) and Al(III) perchlorate nonahydrate salts were purchased from Sigma Aldrich (Milwaukee, WI). Nematic 5CB was purchased from EMD Chemicals (Gibbstown, NJ). Titanium (99.999 %) and gold (99.999 %) were purchased from Advanced Materials (Spring Valley, NY). Methanol and Fischer's Finest glass slides were purchased from Fischer Scientific (Hamton, NH). Absolute ethanol (anhydrous, 200 proof) was purchased from Pharmco-AAPER. All chemicals and solvents were of analytical reagent grade and were used as received without any further purification. All deionized water used in the study possessed a resistivity of 18.2 MΩ cm.

2.2. Cleaning of Glass Substrates. Glass microscope slides were cleaned according to published procedures using "piranha" solution [70:30 (% v/v) H_2SO_4:H_2O_2 (30 %)], as described in detail elsewhere (32). 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 [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 an oven at 110 °C. All other glassware was cleaned prior to use.

2.3. Deposition of Gold Films. Semitransparent films of gold with thicknesses of 200 Å were deposited onto piranha-cleaned glass slides mounted on a fixed holder within an electron beam evaporator (VEC-3000-C manufactured by Tekvac Industries, Brentwood, NY). We calculated the angle of incidence of the gold onto the slides to range from 0° to 15° (measured from 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.

2.4. Formation of Chemically Functionalized Surfaces. Carboxylic-acid-terminated self-assembled monolayers (SAMs) of 11-mercaptoundecanoic acid (MUA) were formed on 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 (Al^{3+}) were deposited onto the carboxylic-acid-terminated SAMs by spin coating the desired molar concentration (1, 5, or 10 mM in ethanol) of Al($ClO_4)_3 \cdot 9H_2O$ at 3000 rpm for 60s (WS-400A-6NPP/Lite, Laurell Technologies, North Wales, PA).

2.5. Ellipsometry. The optical thickness of the metal salts deposited onto the SAMs were measured by using a Stokes ellipsometer (model LSE, Gaertner Scientific corporation) at a wavelength of 6328 Å (HeNe Laser light source) and an angle of incidence of 70°. Ellipsometric constants of the gold films were determined to be $n = 0.20$ and $k = 3.58$. Five spots were measured on each of five samples for each sample type. The apparent optical thickness of each SAM formed from MUA and each layer of metal perchlorate salt was calculated assuming a refractive index of $n = 1.5$ (33−35).

2.6. Formation of Thin LC Films. After coating the surface with aluminum perchlorate salt, an 18 μm thick gold-coated TEM grid (electron microscopy sciences, Hatfield, PA) was fastened to the surface by a thin stainless steel plate (0.44 mm thickness). The stainless steel plate contained a 2 mm diameter hole that was aligned with the TEM grid. The TEM grid was composed of squares with lateral dimensions of 285 μm and an overall diameter of 3 mm. Both the TEM grid and stainless steel plate were dip-coated with a perfluorocarbon (Nyebar Fluorocarbon Barrier Film, SmartGrease Company, Fairhaven, MA) layer to prevent wicking of the LC from the TEM grid. The grids were filled with LC using a microcapillary tube, taking care to fill the middle squares of the TEM grid only so as to avoid wicking of the LC away from the grid.

2.7. Ordering Transitions Induced by DMMP. The samples were exposed to 5 ppm DMMP in a home-built-flow system. Air of a controlled humidity generated using an air humidifier (LI-610, LI-COR Biosciences, Lincoln, NE**)** was mixed with 10 ppm DMMP in N_2 (Matheson Tri-Gas Inc., Eagan, MN) in a 1:1 volume ratio so that the humidity of the resulting stream was 30 % (relative humidity, RH) and the concentration of DMMP was 5 ppm. The protocol used for exposure of the LC films to DMMP was as follows: (i) the sample was exposed to air (60 % RH) for 5 min, (ii) 5 ppm DMMP (30 % RH) was introduced into the flow cell for 2 min, (iii) then air (60 % RH) was passed through the cell for 13 min to purge the DMMP from the system. The cycle was repeated to verify the repeatability of the experiment. Optical micrographs through polarizing films were taken every ten seconds and the light intensity of the images was quantified using ImageJ. Control experiments were undertaken to verify that the changes in RH do not affect the ordering of the LC. In these experiments, the air streams (RH 60 %) were mixed in a 1:1 volume ratio with dry N_2 to maintain a 30 % RH through the entire protocol described above. After exposing each sample to DMMP in a flow cell, the sample was stored in a desiccator maintained at 25 °C and 30 % RH.

2.8. Measurements of the Saturation Solubility of Salts in LC. To determine the solubility of metal ions in the LC, excess salts (as solid) were equilibrated with the LC (5CB). The aluminum perchlorate salts were added to 100 μL of 5CB in a small vial. After the desired time of equilibration (days), 50 μL of the LC was withdrawn by pipet and dissolved into 3 mL nitric acid. Care was taken during the withdrawal of the LC from the vial to ensure that no solid particles of the salt were suspended in the LC. The sample was sonicated and vortexed with extensive shaking and tumbling for 10 min to extract all salts into the nitric acid solution. The nitric acid extract was used to measure the ion-concentration by chemical analysis (see below).

2.9. Determination of Concentration of Al³⁺ Dissolved into LC. The concentration of Al^{3+} dissolved into the LC was measured by elemental analysis using an inductively coupled plasma emission spectrometer ((ICP-ES, Perkin-Elmer optima 3000DV) at a wavelength of 396.153 nm ($\lambda_{Al}^{3+} = 396.153$ nm)). The detection limit of the instrument was specified to be 0.1 ppb. The argon used was ICP grade. All Al^{3+} solutions were prepared in 2% nitric acid from stock 70% nitric acid (ACS reagent, trace metal grade). Aluminum standard solutions for ICP-ES calibration were prepared using 1000 ppm aluminum ion stock solution (from High-Purity Standards, cat. No. 10001−1) in 2% nitric acid. At least six serial dilutions of the stock were prepared to obtain standard aluminum solutions between 10 ppm and 1 ppb for the aluminum calibration curve. In addition, the 1 ppm aluminum standard was used for quality control (QC).

Following ignition of the plasma in the ICP-ES, the instrument equilibrated for 30 min. The stock aluminum solutions were analyzed, and the calibration curve was accepted only if the correlation coefficient was >0.999. A duplicate sample was run every 10 samples. To accept the ICP-ES data, duplicate samples could not differ by more than 10% or 2.2 times the detection limit of the method (0.0001 ppm, i.e., 0.1 μg/L). The blank could not exceed 2.2 times the method detection limit. The blank and QC standards had to be within three standard deviations of the historical mean. If they were not, the analysis of the samples and QC standard was repeated. For each sample, all measurements were made in triplicate and averaged.

2.10. Measurement of the Surface Density of Salt. To measure the surface density of the Al^{3+} salts, MUA functionalized gold slides (see above) were spin-coated with aluminum perchlorate solutions of known concentration. After deposition, the aluminum perchlorate salt was dissolved into 2% nitric acid and the mixture was vortexed to extract all salt into the nitric acid solution. The concentration of Al^{3+} was measured by using ICP-ES, as described above. Finally, the surface density of the metal salt was calculated from both the ICP-ES data and knowledge of the area of the surface from which the aluminum perchlorate salts were extracted.

3. RESULTS AND DISCUSSION

As described in the Introduction, recent investigations of adsorbate-induced ordering transitions in LC films have reported use of microfabricated wells and micropillar arrays to define the thickness of LC films (11, 26, 31). These approaches, however, do not permit uniform deposition and quantification of the loading of metal salt because of the complex topography of the surfaces. In the study reported in this paper, we have used planar surfaces onto which metal salts were deposited by spin coating. Films of nematic LCs of prescribed thickness were subsequently formed on these surfaces using metal grids and a procedure modified from that reported previously by us (see Materials and Methods for details) (12). The first experiments described below sought to establish uniformity of coverage as well as control over the surface density (mass/area) of metal salt on each surface. To this end, we employed both ellipsometric measurements and elemental analysis (see Methods for details).

Table 1 shows the ellipsometric thickness and surface mass density of aluminum perchlorate deposited onto surfaces by spin coating ethanolic solutions containing either 1.0, 5.0, or 10.0 mM of the salt. Inspection of Table 1 reveals that the ellipsometric thickness of the salt layer varied from ∼1.4 to 18 nm. These thicknesses correspond to the presence of thin films of between ∼3 monolayers and ∼38

Table 1. Ellipsometric Thickness and Surface Mass Density of Aluminum Perchlorate on Surfaces Used in This Study

concentration of Al^{3+} salt (mM)	ellipsometric thicknesses (nm)	surface density of Al^{3+a} (ng/mm²)
1	1.4 ± 0.10	0.39 ± 0.03
5	8.8 ± 0.21	1.13 ± 0.09
10	17.7 ± 0.5	2.14 ± 0.24

[a] Measured using ICP-ES.

monolayers of metal salt. The corresponding surface mass densities of metal salt (measured by ICP-ES) were determined to vary from 0.39 to 2.14 ng/mm². The significance of these values is discussed below, where we establish that the amounts of salt spin-coated from the ethanolic solutions containing 1 and 10 mM aluminum perchlorate lie below and above the solubilization capacity of ∼20 μm thick films of nematic 5CB, respectively. Importantly, our measurements of ellipsometric thicknesses at various locations on a given sample (and on independently prepared samples) confirmed that our procedures led to deposition of uniform layers of metal salts over the surfaces. Below we report on the impact of the different surface loadings of metal salt (as shown in Table 1) on the ordering of nematic phases of 5CB.

First, we characterized the orientational ordering of nematic phases of 5CB on the surfaces presenting the lowest density of aluminum perchlorate (0.39 ± 0.03 ng/mm²) investigated in our study. We sought to determine if 5CB supported on surfaces presenting such a low density of aluminum perchlorate salt would assume a homeotropic ordering (prior studies have not investigated surface loadings of salts as low as those reported here), and if so, whether or not the nematic film would undergo an orientational transition upon exposure to a gas phase containing DMMP. We note that a homeotropic ordering of the LC is desirable because it provides a well-defined initial state of the LC with a distinct optical signature (dark appearance between crossed polarizers) prior to exposure to the DMMP. Finally, we comment that we established through these initial investigations that our experimental procedures provided reproducible responses to DMMP with minimal sample-to-sample variation. In each of our experiments, the intensity of light transmitted through cross polarizing films was measured as the sample was exposed sequentially to (i) air for 5 min, (ii) a gas phase containing 5 ppm DMMP for 2 min, and (iii) air for 13 min (allowing the film to return to its initial state). This sequence was then repeated to examine the reversible behavior of the system. We note that our experimental setup led to changes in humidity and DMMP concentration in most of our experiments (see Materials and Methods for details). To establish that the changes in humidity did not influence the results reported in this paper, we performed several control experiments under conditions of constant humidity (compare Figure S1 of the Supporting Information to Figure 2 discussed below).

Figure 2A shows that nematic films of 5CB (thickness ∼20 μm), when supported on surfaces presenting 0.39 ng/mm² of aluminum perchlorate, exhibited a dark optical appear-
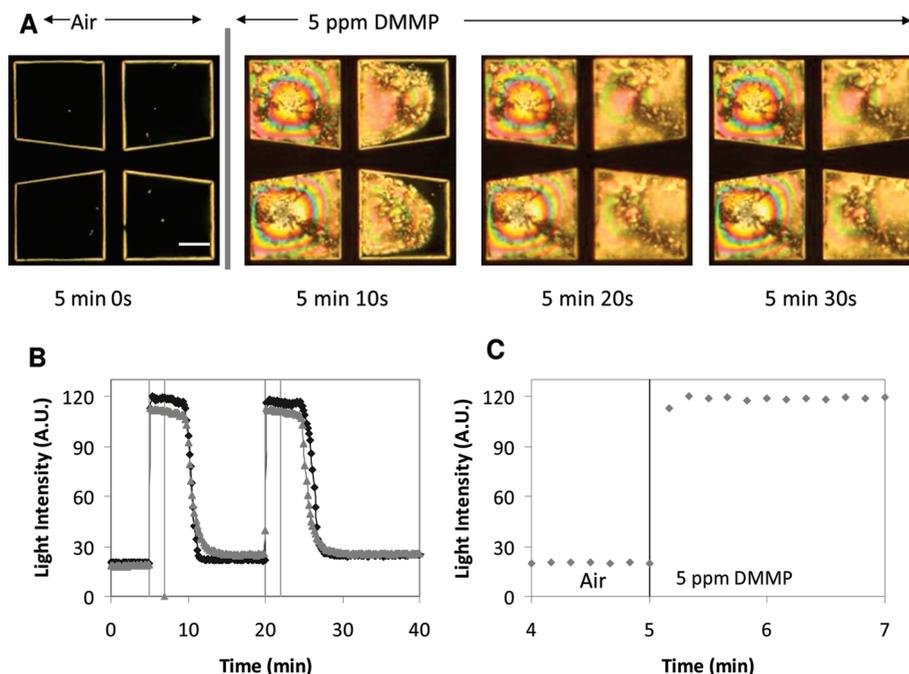
FIGURE 2. Optical response of 5CB supported on surfaces decorated with 0.39 ng/mm² Al perchlorate. (A) Optical micrographs (crossed polarizers) showing the change in optical appearance of the LC film upon exposure to DMMP. The direction of gas flow is from left to right in each optical micrograph. The scale bar corresponds to 100 μm. (B) Intensities of light transmitted through films of 5CB as a function of time: from 0 to 5 min, the sample was exposed to air; from 5 to 7 min, the sample was exposed to 5 ppm DMMP; from 7 to 20 min, the sample was exposed to air; from 20 to 22 min, the sample was exposed to 5 ppm DMMP; and for times over 22 min, the sample was exposed to air. (c) Data from B that shows the response of the LC to 5 ppm DMMP occurs within 10 s and reaches a maximum after 30 s.

ance when viewed between crossed polarizers. Past studies have established that 5CB assumes a homeotropic orientation at its free surface (air-LC interface) (36). The result in Figure 2A, when combined with conoscopic images of the sample, led us to conclude that the nematic film of 5CB did assume a homeotropic ordering immediately after contact with this metal-salt-decorated surface. In addition, when the supported LC film was exposed to 5 ppm DMMP, a change in the optical appearance of the sample was observed (Figure 2A). The initial response was evident within 10 s of exposure to DMMP, and the maximum response was achieved after 30 s. As reported previously (8), the bright optical appearance of the LC is caused by a DMMP-induced ordering transition and associated tilting of the orientation of the LC within the film away from the surface normal. Figure 2B quantifies the intensity of light transmitted through the LC film upon exposure to DMMP. Following exposure to the DMMP for 2 min, we purged the flow cell with a stream of air. After purging with air, we observed the LC film to return to its initial dark state, although it took approximately 10 min for this process to occur. The slow reversal of the response of the LC to DMMP suggests that the dissociation of DMMP and the Al^{3+} ion may be a rate-limiting process in the relaxation of the system. After returning to the homeotropic state, the sample was again exposed to 5 ppm DMMP and a similar cycle was observed. The sample-to sample reproducibility of the experimental system is illustrated in Figure 2B, where the responses of two LC samples to DMMP are presented.

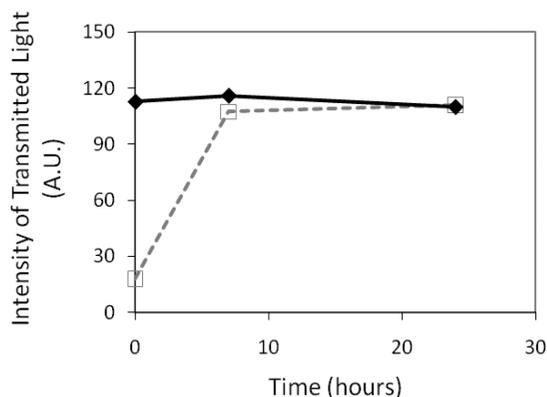The data characterizing the ordering transition induced by DMMP, as shown in Figure 2, was obtained immediately

FIGURE 3. Quantification of the optical response of a film of nematic 5CB supported on a surface decorated with 0.39 ng/mm² Al perchlorate. The solid data points indicate the response of the LC to exposure to 5 ppm DMMP; the open data points show the optical response of the LC prior to exposure to DMMP.

after preparation of the samples (i.e., contact of the LC with the metal-salt-coated surface). Next, we determined if the ordering of the LC supported on the surface, as well as the ordering transition induced by DMMP, was dependent on the length of time for which the LC was equilibrated on the metal-salt-coated surface. After the samples were stored in a controlled humidity environment for a desired length of time, we characterized the state of the LC by measurement of the intensity of light transmitted through the sample (crossed polarizers) before and after exposure to DMMP. As shown in Figure 3, immediately after preparation of the sample, and prior to exposure to DMMP, the LC exhibited homeotropic ordering on the aluminum perchlorate-coated

surface and the corresponding intensity of light transmitted through the sample was low (18 A.U.). The ordering transition induced by exposure of the freshly prepared sample resulted in an increase in the intensity of light transmitted through the sample to 113 A.U. The change in intensity of light transmitted through the sample (~95 A.U.) was reversed upon purging with air. Following equilibration of the LC film on the aluminum perchlorate-coated surface for 7 h, however, we observed the LC to undergo an ordering transition that caused the optical appearance of the LC film to become bright even in the absence of exposure to DMMP (107 A.U., see Figure 3). Furthermore, exposure of the sample to DMMP resulted in no measurable change in the ordering of the LC (and thus no significant change in the intensity of light transmitted through the sample). Equilibration of the LC with the surface for an additional 18 h did not result in any further changes in the ordering of the sample.

The results described above led us to conclude that the ordering of nematic 5CB within films supported on surfaces decorated with 0.39 ng/mm² of aluminum perchlorate does change upon equilibration of the LC film on the salt-coated surface for several hours. In particular, the homeotropic ordering of the LC observed on freshly prepared samples was observed to relax during equilibration to a tilted or planar orientation. Because past studies have established that homeotropic ordering of nematic phases of 5CB on metal-salt-coated surfaces can be induced by coordination interactions between the nitrile groups of 5CB and metal salts with high electron affinity (12, 28), these results suggested to us that coordination interactions between 5CB and Al^{3+} on the surface are lost after a few hours of equilibration of the LC on the surface. This proposition was supported by the absence of the measurable response of the LC to DMMP after 7 h of equilibration of the LC with the surface (as reported in prior studies (12), the response to DMMP is caused by a change in the coordination state of the LC on the surface). It occurred to us that several possible interfacial processes may underlie the apparent loss of the coordination interaction between the LC and surface. It possible, for example, that water from the air may accumulate at the salt-decorated interface of the LC over time, thus leading to a loss of coordination between the nitrile groups of the LC and Al^{3+}. Alternatively metal salts deposited at the surface may dissolve into the LC during equilibration of the LC on the surface, resulting in an insufficient, residual, surface density of metal salt at the surface to coordinate to the LC and thus promote homeotropic ordering of the LC.

To test the proposition that the loss of homeotropic ordering of the LC upon equilibration with the metal-salt-decorated surface was due to dissolution of the metal salt from the surface into the LC, we equilibrated excess solid, aluminum perchlorate salt with nematic 5CB and measured the concentration of salt that dissolved into the LC as a function of time (see Materials and Methods for experimental details). Figure 4 shows the concentration of Al^{3+} dissolved into nematic 5CB as a function of time. Inspection of Figure 4 reveals that nematic 5CB slowly dissolves the
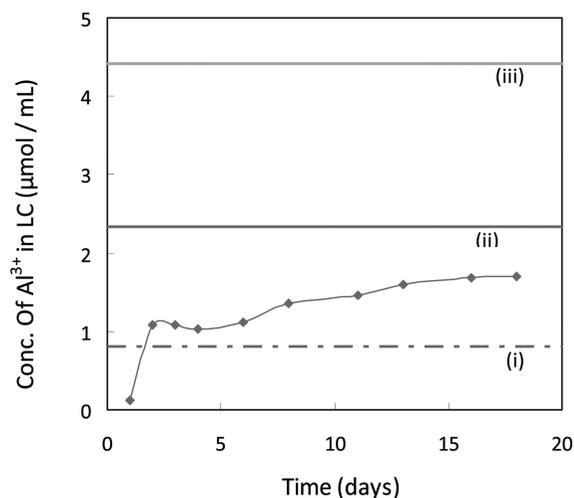

FIGURE 4. Concentration of Al^{3+} dissolved in 5CB as a function of time of contact of the LC with excess Al perchlorate salt. The horizontal lines indicate the concentration of Al^{3+} that would be present in a 20 μm thick film of LC if all metal salt on the surface dissolved into the LC; (i) 0.39 ng/mm² Al perchlorate, (ii) 1.13 ng/mm² Al perchlorate, (iii) 2.14 ng/mm² Al perchlorate.

aluminum perchlorate salt over a period of almost 15 days, finally reaching a saturation concentration of 1.7 μmol/mL. For comparison, the dashed horizontal line (marked as i) indicates the concentration of Al^{3+} that would be present in the LC film if all the metal salt on a surface presenting 0.39 ng/mm² of aluminum perchlorate dissolved into a 20 μm thick film of 5CB. The result in Figure 4 demonstrates that the capacity of the LC film to dissolve the salt does exceed the amount of salt deposited onto the surface (0.39 ng/mm²). This result supports our hypothesis that the loss of homeotropic ordering during equilibration of the LC on the surface decorated with 0.39 ng/mm² of aluminum perchlorate salt was due to dissolution of the salt into the LC film. We note that the area of contact between the salt crystals and LC is substantially different for the systems leading to the results in Figures 3 and 4, and thus the slow dynamics evident in Figure 4 (days) should not be viewed as inconsistent with the proposition that the phenomena seen in Figure 3 (hours) is due to dissolution of salt into the LC. The proposal that dissolution of salt into the LC plays a central role in the time-dependent phenomena observed in these systems is further supported by results shown below based on surfaces that present loadings of aluminum perchlorate that exceed the solubility limit of the 20 μm thick 5CB films.

Motivated by the evidence reported above that the loss of the homeotropic ordering of the LC film reported in Figures 2 and 3 was due to dissolution of the metal salt into the LC, next we sought to determine if a surface density of metal salt that exceeded the solubilization capacity of the LC film would maintain the homeotropic ordering of the LC during equilibration of the LC film on the surface. To this end, we characterized the time-dependent ordering of nematic films of 5CB on surfaces onto which aluminum perchlorate was deposited by spin coating of ethanolic solutions of 10 mM of the salt. As reported in Table 1, these surfaces were determined to present densities of the salt that corresponded to 2.14 ± 0.24 ng/mm². Inspection of Figure 4
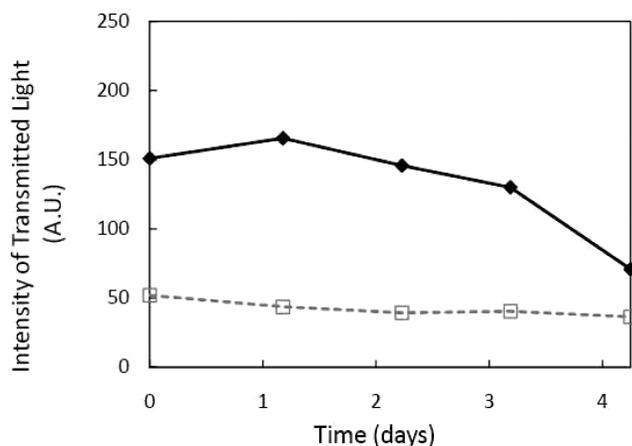
FIGURE 5. Quantification of the optical response of a film of nematic 5CB supported on a surface decorated with 2.14 ng/mm² Al perchlorate. The solid data points indicate the response of the LC to exposure to 5 ppm DMMP; the open data points show the optical response of the LC prior to exposure to DMMP.

confirms that this surface mass density of aluminum perchlorate is sufficiently high that it can not be dissolved by the ~20 μm thick LC film. Immediately following the preparation of LC films supported on surfaces presenting 2.14 ng/mm² of aluminum perchlorate, we observed the LC films to (i) exhibit homeotropic ordering prior to exposure to DMMP, and (ii) exhibit an ordering transition upon exposure to DMMP that was comparable to that shown in Figure 2. These observations are reflected in the measured intensities of light transmitted through the supported LC film, as shown in Figure 5 (data at $t = 0$). Inspection of Figure 5 also reveals that the initial homeotropic ordering of the LC (observed prior to exposure to DMMP) was preserved during 4 days of equilibration of the LC on the surface. This contrasts to the results obtained with the low surface mass density of metal salt (Figure 2), where the initial homeotropic ordering of the LC was lost within 7 h of equilibration of the LC on the metal-salt-decorated surface. When combined, these two results support our hypothesis that dissolution of metal salt into the LC occurs during equilibration of the LC films on the metal-salt-decorated surfaces. For the surfaces decorated with the low loading of salt, the dissolution of the metal salt results in the loss of coordination interactions and homeotropic ordering of the LC; for the surfaces presenting high loadings of the metal salt, the LC is saturated with salt prior to complete loss of the metal salt from the surface, and thus the homeotropic ordering is preserved during equilibration of the sample.

Although the LC film supported on the high surface loading of aluminum perchlorate exhibited homeotropic ordering over 4 days of equilibration, the results in Figure 5 also reveal that the response of the LC film to exposure to DMMP declined during this period of equilibration. The decrease in the intensity of light transmitted through the LC upon exposure to DMMP indicates that the extent to which the LC tilted away from the homeotropic orientation upon exposure to DMMP decreased with equilibration. After approximately 4 days of equilibration of the LC on the surface presenting 2.14 ± 0.24 ng/mm² of salt, the LC maintained

its homeotropic ordering upon exposure to DMMP (a small change only in the intensity of light transmitted through the sample upon exposure to DMMP is evident in Figure 5). We note here that the absolute intensities of light measured to be transmitted through the samples varied from sample to sample (e.g., homeotropic alignment corresponds to ~20 A.U. in Figure 3 and ~50 A.U. in Figure 5). We note, however, that the change in intensity upon exposure to DMMP was ~100 A.U., independent of the sample. We attribute this variation in absolute intensity to differences in the filling of the TEM grids with LC (see Figure S2 of the Supporting Information).

As noted above, homeotropic ordering of the LC was observed during equilibration of the LC on surfaces decorated with a high loading of metal salts. The absence of a response to DMMP on those surfaces after several days of equilibration, however, suggests that intermolecular interactions between the LCs and surfaces that do not involve coordination of the metal salts and the LC become dominant at the interface over time, thus maintaining the homeotropic orientation of the LC even when ligand exchange (change in coordination) at the interface is induced by the DMMP. Past studies have established that dissociation of sodium cations from surfaces presenting monolayers of carboxylate salts can lead to the formation of electrical double layers in nematic phases of 5CB (10). We note that the static dielectric constants of a nematic phase of 5CB are 6 ($\varepsilon_\perp$) and 18 ($\varepsilon_\parallel$), and thus nematic 5CB can be viewed as a relatively polar but anisotropic oil (37, 38). When an electrical double layer is formed at the interface of the LC, the electric field associated with the diffuse part of the double layer can exert a torque on the LC that promotes homeotropic ordering of the LC (for the case of 5CB with a positive dielectric anisotropy, $\varepsilon_\parallel > \varepsilon_\perp$). We hypothesized that the absence of an ordering transition in the LC film upon exposure to DMMP, as described above, may result from the formation of an electrical double layer at the metal-salt decorated interface as the aluminum perchlorate dissolves into the LC. It is also significant to note that a past study has demonstrated that the influence of electrical double layers on surface-induced orientational ordering of 5CB is most pronounced when high concentrations of salts are present in the LC (because the LC responds to the strength of the electric field associated with the double layer) (10). To test the hypothesis that an electrical double layer can induce homeotropic ordering of nematic 5CB at a surface decorated with a metal perchlorate salt, we formed 20 μm thick films of 5CB on surfaces decorated with varying surface concentrations of sodium perchlorate. Sodium perchlorate was selected because previous studies using IR techniques have demonstrated that sodium perchorate salts do not coordinate with the nitrile group of 5CB (12). We spin-coated sodium perchlorate (10 mM in ethanol) onto a surface and observed the presence of the salt to induce homeotropic ordering of nematic 5CB, consistent with the proposed formation of an electrical double layer. We note that when the concentration of sodium perchlorate was lowered to 1 mM in ethanol, the
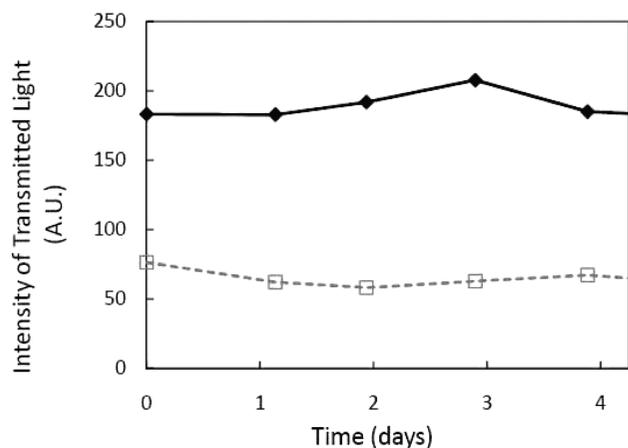
FIGURE 6. Quantification of the optical response of a film of nematic 5CB supported on a surface decorated with 1.13 ng/mm^2 Al perchlorate. The solid data points indicate the response of the LC to exposure to 5 ppm DMMP; the open data points show the optical response of the LC prior to exposure to DMMP.

nematic films of 5CB adopted a planar orientation, suggesting that at low surface loading of metal perchlorate salt any electrical double layer formed at this interface to 5CB is insufficient to influence the ordering of the LC.

The results described above identify two physicochemical phenomena that lead to time-dependent interfacial ordering of films of nematic 5CB supported on aluminum perchlorate-decorated surfaces. Equilibration of nematic 5CB on surfaces presenting low surface densities of the salt results in extraction of the Al^{3+} from the surface into the LC, thus resulting in loss of the initial homeotropic alignment because of loss of coordination interactions between the 5CB and Al^{3+} on the surface. At high surface densities, dissolution of metal salt into the LC leads to an electrical double layer that promotes the homeotropic alignment, and thus masks any ordering transition that would otherwise result from adsorbate-induced disruption of metal ion-nitrile coordination interactions. We next investigated if these two interfacial phenomena could be avoided by using intermediate surface mass densities of aluminum perchlorate. To this end, as described below, we investigated the ordering of nematic 5CB on surfaces presenting 1.13 ± 0.09 ng/mm^2 of aluminum perchlorate (Table 1).

As shown in Figure 6, the initial intensity of light transmitted through a film of nematic 5CB supported on a surface presenting 1.13 ng/mm^2 of the aluminum perchorate was determined to correspond to homeotropic ordering. Following exposure to DMMP, an ordering transition was observed, as indicated in Figure 6 by the increase in intensity of light to ~180 A.U. Significantly, and in contrast to the previously described samples, we observed the homeotropic ordering of the LC in the absence of DMMP to be maintained during equilibration of the LC on the salt-decorated surface for at least 4 days, and we also measured exposure of the sample to DMMP at any point of time during this interval to result in an ordering transition in the LC. This result is significant because it indicates that intermediate surface loadings of the aluminum perchlorate salts (i) orient LCs over prolonged periods through coordination interactions, but (ii) do not lead

to formation of electrical double layers that suppress the response of the LCs to DMMP. We comment that this result is also interesting in light of Figure 4, which suggests that the 20 μm thick LC films do possess the capacity to extract all aluminum salts from surfaces coated with 1.13 ng/mm^2 of the salt. We speculate that interactions between the Al^{3+} ions and the carboxylate-terminated monolayer beneath the aluminum perchlorate may maintain a necessary threshold surface concentration of Al^{3+} to orient the LC through coordination interactions. We also note that in comparison to the surfaces decorated with 0.39 ng/mm^2 of the aluminum perchlorate salt, the driving force for extraction of the salts from the surface into the LC film is lower for the surfaces decorated with 1.13 ng/mm^2 of the salt (because of the higher concentration of salt in the LC). Our results also indicate that the metal salts that dissolve into the LC from surfaces with 0.39 ng/mm^2 Al(ClO$_4$)$_3$ do not lead to electrical double layers with electric fields that are sufficient in intensity to promote the homeotropic ordering of the LC in the absence of coordination interactions.

To provide additional insight into the above physical picture, we presaturated 5CB with aluminum perchlorate prior to formation of a film of the 5CB on a surface decorated with 0.39 ng/mm^2 of the salt (lowest loading of salt used in our study). Whereas surfaces with this density of aluminum perchlorate did not cause homeotropic ordering of pure 5CB for more than a few hours in the absence of DMMP (see Figure 3), when the 5CB pre-equilibrated with metal salt was placed onto the same type of surface, homeotropic ordering was observed to be preserved 20–30 days of equilibration (see Figure S3 of the Supporting Information). In these cases, however, DMMP did not trigger an ordering transition in the LC (see Figure S4 of Supporting Information), a result that is consistent with our proposal that electrical double layers formed by dissolution of high concentrations of aluminum perchlorate salt can prevent ordering transitions induced by surface-based ligand exchange reactions involving the LC.

4. CONCLUSIONS

The study reported in this paper provides two important insights into physicochemical processes that occur at interfaces of films of LCs that are decorated with metal salts. The first insight is that the capacity of the nematic LC films to dissolve metal salts can be sufficiently high so as to deplete the interfaces of the LC of coordinating metal ions. This process of dissolution can lead to ordering transitions in the LC by virtue of the loss of these sites of coordination from surfaces. This phenomenon is encountered with surfaces that are decorated with aluminum perchlorate densities of ~0.39 ng/mm^2, and it is characterized by loss of homeotropic ordering of the nematic 5CB within a few hours of equilibration of the LC with the metal salt-decorated surface. The second insight is that electrical double layers can form at the metal salt-decorated interfaces and that these electrical double layers can lead to interactions with the LC that can compete with the effects of metal ion-nitrile coordination interactions on the LC. In particular, if the concentration of metal salt in the LC is high (>2.14 ± 0.24 ng/mm^2), the

electrical double layers can suppress ordering transitions in the LC induced by adsorbates such as DMMP (i.e., changes in surface coordination of the LC). In addition to identifying the roles of these fundamental physicochemical phenomena, we also established that experimental conditions exist where neither the effects of dissolution of the salts into the LC nor formation of an electrical double layer (i) perturb the homeotropic orientation in the absence of DMMP or (ii) diminish the response of the LC to DMMP during experiments conducted over 4 days. Indeed, for surfaces presenting 1.13 ng/mm^2 of Al(ClO$_4$)$_3$, we observed some samples to respond to DMMP for ~4 weeks following sample preparation. Over these periods of time, however, we observed increased variability in our measurements, likely due to processes other than formation of electrical double layers or dissolution of metal salts taking place in these systems. In future studies, we will seek to identify these processes. In summary, the results presented in this paper provide importance guidance for the design of interfaces of LC for use in chemical sensing.

Supporting Information Available: Response of LC supported on surface presenting 0.39 ng/mm^2 Al perchlorate, optical micrographs of LC supported on surfaces presenting various surface concentrations of Al perchlorate (exposed to air or 5 ppm DMMP), alignment of 5CB presaturated with Al perchlorate salt, response of 5CB presaturated with Al perchlorate to 5 ppm DMMP. This material is available free of charge via the Internet at http://pubs.acs.org.

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