

experiment might vary, depending on the link optics and on the performance of satellite pointing and tracking (25, 26). Even then, our results represent an encouraging basis for future space experiments with entangled photons.

References and Notes

- E. Schrödinger, *Naturwissenschaften* **23**, 807 (1935).
- D. Bouwmeester, A. Ekert, A. Zeilinger, Eds., *The Physics of Quantum Information* (Springer-Verlag, Berlin, 2000).
- P. R. Tapster, J. G. Rarity, P. C. M. Owens, *Phys. Rev. Lett.* **73**, 1923 (1994).
- W. Tittel, J. Brendel, H. Zbinden, N. Gisin, *Phys. Rev. Lett.* **81**, 3563 (1998).
- G. Weihs, T. Jennewein, C. Simon, H. Weinfurter, A. Zeilinger, *Phys. Rev. Lett.* **81**, 5039 (1998).
- E. Waks, A. Zeevi, Y. Yamamoto, *Phys. Rev. A* **65**, 52310 (2002).
- N. Gisin, G. Ribordy, W. Tittel, H. Zbinden, *Rev. Mod. Phys.* **74**, 145 (2002).
- H.-J. Briegel, W. Dür, J. I. Cirac, P. Zoller, *Phys. Rev. Lett.* **81**, 5932 (1998).
- H. Horvath et al., *J. Geophys. Res.* **107**, 4386 (2002).
- W. T. Buttler et al., *Phys. Rev. Lett.* **81**, 3283 (1998).
- R. J. Hughes, J. E. Nordholt, D. Derkacs, C. G. Peterson, *New J. Phys.* **4**, 43 (2002).
- C. Kurtsiefer et al., *Nature* **419**, 450 (2002).
- C. Kurtsiefer, M. Oberparleiter, H. Weinfurter, *Phys. Rev. A* **64**, 23802 (2001).
- P. G. Kwiat et al., *Phys. Rev. Lett.* **75**, 4337 (1995).
- The low coupling efficiency is mainly due to large beam diameters and high beam divergence because of small telescope lenses. A more sophisticated design of coupling telescopes can certainly achieve the diffraction-limited optimum.
- Materials and Methods are available as supporting material on *Science* Online.
- Correlation measurements were performed independently from the sine-curve measurements (Fig. 2).
- J. F. Clauser, M. A. Horne, A. Shimony, R. A. Holt, *Phys. Rev. Lett.* **23**, 880 (1969).
- J. Bell, *Physics* **1**, 195 (1964).
- A. K. Ekert, *Phys. Rev. Lett.* **67**, 661 (1991).
- C. Fuchs, N. Gisin, R. B. Griffiths, C. S. Niu, A. Peres, *Phys. Rev. A* **56**, 1163 (1997).
- C. H. Bennett, G. Brassard, N. D. Mermin, *Phys. Rev. Lett.* **68**, 557 (1992).
- T. Jennewein, C. Simon, G. Weihs, H. Weinfurter, A. Zeilinger, *Phys. Rev. Lett.* **84**, 4729 (2000).
- M. Aspelmeyer et al., "Quantum communications in space," *Tech. Rep. under contract 16358/02*, European Space Agency, in press.
- J. E. Nordholt, R. Hughes, G. L. Morgan, C. G. Peterson, C. C. Wipf, *Proc. SPIE*, **4635**, 116 (2002).
- J. G. Rarity, P. R. Tapster, P. M. Gorman, P. Knight, *New J. Phys.* **4**, 82 (2002).
- This work was supported by the Austrian Science Foundation (FWF), Sonderforschungsbereich (SFB) 015 "Control and Measurement of Coherent Quantum Systems," the European Commission, Project IST-1999-10033 "Long Distance Photonic Quantum Communication" and by the companies Wien Kanal Abwassertechnologien Ges.m.b.H., Energie AG Oberösterreich, T-systems Austria GmbH (Network Services) and by the City of Vienna. Further funding for team members was provided by the FWF (G.M.-T.), the Austrian Exchange Service ÖAD (T.G.), ARC Seibersdorf research GmbH (H.R.B., A.P.), the Natural Sciences and Engineering Research Council of Canada (K.R.), and the Alexander von Humboldt Foundation (M.A.).

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Surface-Driven Switching of Liquid Crystals Using Redox-Active Groups on Electrodes

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Electrochemical control of the oxidation state of ferrocene-decorated electrodes leads to surface-driven changes in the orientations of thermotropic liquid crystals. When the electrodes possess nanometer-scale topography, voltages of 0.0 to 0.3 volts (versus a counter electrode in a two-electrode cell) can drive changes in the orientation of the liquid crystals in the plane and/or out of the plane of the electrodes. Electrodes not supporting ferrocene do not lead to surface-driven orientational transitions. The in-plane transitions are driven by the reorganization of the monolayer of ferrocene upon oxidation of ferrocene to ferrocenium. The out-of-plane transition reflects a dielectric coupling between the liquid crystal and the diffuse part of an electrical double layer that evolves upon oxidation of ferrocene to ferrocenium. These results suggest new ways to couple the orientations of liquid crystals to chemical and electrical stimuli in electro-optical devices and chemical sensors.

Liquid crystalline materials are liquids with anisotropic optical and electrical properties that arise from the preferred orientations of molecules within the liquid (1). These materials, when placed into contact with surfaces, spontaneously assume orientations that depend sensitively on the topography and chemical functionality of the surfaces (2). Past studies have demonstrated that application of an electric field across a liquid crystal oriented by a surface will generally change the orientation of the bulk of the liquid crystal but not regions of the liquid crystal near the

surface (so-called strong anchoring: Fig. 1A, I) (1, 2). This effect forms the basis of most liquid-crystal displays (1). Here we report a method to chemically functionalize electrodes so as to electrically drive the orientations of liquid crystals from surfaces. By using electrodes decorated with redox-active groups that undergo reversible oxidation and reduction, surface-driven orientational transitions in liquid crystals (Fig. 1A, II) are demonstrated at voltages that are small compared with those generally required to complete a change in orientation of liquid crystal in a conventional electro-optical device (3). Surface-induced anchoring transitions of liquid crystals driven by chemical oxidation of patterned redox-active groups are also demonstrated (Fig. 1A, III) (4). These characteristics suggest that surface-driven orienta-

tional transitions using electrodes decorated with redox-active groups might find application in electronic print (5, 6) or chemically responsive soft materials (7, 8).

The design of the experimental system was based on three observations. First, gold electrodes functionalized with ferrocene form the basis of a structurally well-defined metal-electrolyte interface: Ferrocene undergoes a reversible one-electron oxidation to form the ferrocenium cation (Fig. 1B) (9, 10). Second, studies have demonstrated that it is possible to use thermotropic liquid crystals formed from 4,4'-pentylcyanobiphenyl (5CB) and *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA) as solvents for electrochemical studies of electroactive species dissolved in the bulk of liquid crystals (Fig. 1C) (11). Third, the ionization of acids and dissociation of surface-immobilized salts can lead to in-plane and out-of-plane orientational transitions in liquid crystals (12, 13). These observations led us to hypothesize that control of the oxidation state of ferrocene on a ferrocene-decorated electrode may lead to surface-driven orientational transitions in liquid crystals.

We first investigated the influence of the oxidation state of surface-immobilized ferrocene on the orientation of either 5CB or MBBA by using benzoyl peroxide (BP, 20 mM) dissolved in the liquid crystal to oxidize the ferrocene to ferrocenium (14). Polycrystalline gold films were deposited so as to avoid the introduction of anisotropic topography into the structure of the gold films (15) and then patterned with monolayers formed from $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ and $\text{Fc}(\text{CH}_2)_{11}\text{SH}$, where Fc is ferrocene. On both the ferrocene and methyl-terminated monolayers, we measured nematic 5CB to assume an orientation that was parallel (planar) to the surface with-

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out a preferred azimuthal orientation (Fig. 2, A and B). In contrast, when BP was dissolved in the 5CB before contact with the functionalized surfaces, we observed 5CB to assume an orientation that was perpendicular (homeotropic) to the surface of the ferrocene-terminated monolayers (Fig. 2, C and D) (16–18). The 5CB near the methyl-terminated monolayers, however, remained planar. The orientation of MBBA with and without BP was measured to be planar on the ferrocene-terminated and methyl-terminated monolayers. The fine grain size observed in the optical texture of MBBA in the presence of BP and ferrocene-terminated monolayers indicates, however, that the interactions between the MBBA and the interface that are responsible for the planar orientation (the anchoring energy) are strengthened by the presence of BP (Fig. 2, E and F) (19, 20). Because the anisotropy of the dielectric constant is positive ($\Delta\epsilon = +13$) for 5CB but weakly negative for MBBA ($\Delta\epsilon = -0.7$) (21), these results are consistent with a dielectric coupling between the liquid crystal and electric field within the diffuse region of the electrical double layer (12) that evolves at the surface upon oxidation of ferrocene to ferrocenium.

Next we used a two-electrode electrochemical cell containing 5CB and 35 mM tetrabutyl ammonium tetrafluoroborate (TBAF) as a nematic solvent to reversibly control the oxidation state of ferrocene immobilized on a gold working electrode (Fig. 3A) (22). The counter

electrode was a gold film (not functionalized with ferrocene). We set the distance between the working electrode and counter electrode at $13.1 \pm 0.5 \mu\text{m}$ by using a spacer made of Saran wrap (supporting online text). Using cyclic voltammetry, we measured the charging characteristics of the functionalized electrode to comprise a single anodic and a single cathodic wave (Fig. 3B). A plot of $\log(\text{scan rate})$ versus $\log(\text{peak current})$ was linear, indicating a surface-confined redox-active species (Fig. 3C) (23). Because this electrode process was absent when we used monolayers formed from $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$, we conclude that the peaks in the cyclic voltammogram are due to oxidation and reduction of ferrocene on the working electrode. Accompanying the measurement of the cyclic voltammogram, we observed a change in the optical appearance of 5CB (Fig. 3, D to F). When the electrode decorated with ferrocene was held at -0.2 V , the 5CB appeared green, consistent with planar alignment of 5CB with no azimuthal preference on the surfaces of both the working and counter electrode (Fig. 3D) (24). In contrast, at 0.12 V (Fig. 3E), regions of the liquid crystal appeared yellow, consistent with planar alignment of the liquid crystal on one surface (counter electrode) but perpendicular alignment on the other surface (working electrode).

Application of 0.28 V completed the transition to perpendicular alignment over the entire working electrode (Fig. 3F). Both the cyclic voltammograms and the changes in color of the liquid crystal were fully reversible. When the working electrode was a gold film supporting a monolayer formed from $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$, we did not observe a change in orientation of 5CB when cycling the voltage between -0.3 and 0.3 V .

Surfaces possessing topography on the nanometer-to-micrometer-scale can cause liquid crystals to assume uniform azimuthal (in-plane) orientations (25, 26). When organized monolayers of molecules are decorated on such surfaces, the azimuthal orientation of the liquid crystal depends strongly on both the chemical functionality and the structural organization of the monolayer (26). To determine if oxidation of ferrocene to ferrocenium on an electrode with nanometer-scale topography could drive azimuthal orientations of liquid crystals, we prepared gold electrodes by the oblique vapor deposition of gold onto stationary silica substrates (15). Prior to oxidation of the ferrocene immobilized on the obliquely deposited gold film, 5CB assumed an azimuthal orientation that was parallel to (along) the least-rough azimuthal direction of the surface, as measured

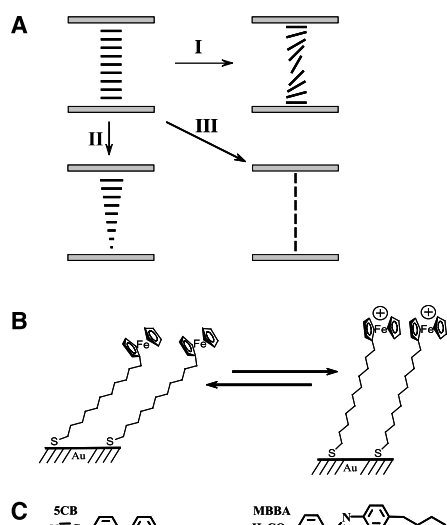
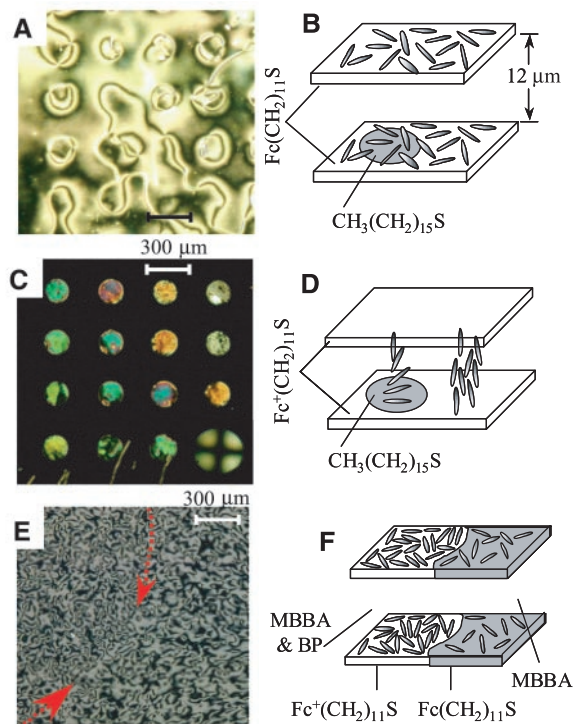


Fig. 1. (A) Schematic illustration of changes in orientations of liquid crystals: (I) Change driven by the action of an electric field on the bulk of the liquid crystal. (II and III) Surface-driven changes in orientation leading to either formation of a helical twist in the liquid crystal (II) or an orientation of the liquid crystal that is perpendicular to the surfaces (III). (B) Schematic illustration of a gold film decorated with ferrocene (left) and ferrocenium (right). (C) The molecular structure of 5CB and MBBA.

Fig. 2. Effect of chemical oxidation of surface-immobilized ferrocene on the orientation of 5CB and MBBA. (A) Optical textures (cross polars) of 5CB in optical cells prepared with one surface supporting an array of microcontact printed circles of a monolayer formed from $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ surrounded by a monolayer formed from $\text{Fc}(\text{CH}_2)_{11}\text{SH}$, and an opposing surface supporting a monolayer formed from $\text{Fc}(\text{CH}_2)_{11}\text{SH}$. (B) Schematic illustration of the alignment of 5CB in (A). 5CB assumes a planar orientation (parallel to surface) with no preferred azimuthal direction on both surfaces. (C) Optical textures (cross polars) of 5CB containing 20 mM BP in the same optical cell as in (A). The inset (black cross in lower right of image) shows a conoscopic image indicating homeotropic alignment of 5CB in the region where both surfaces present ferrocenium. (D) Schematic illustration of the alignment of 5CB in (C). 5CB aligns perpendicular (homeotropic) to regions presenting surface-immobilized ferrocenium, but assumes a planar orientation on the circular regions formed from $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$. (E) Optical image (cross polars) of MBBA with (left side of image) and without (right side of image) BP in an optical cell with surfaces formed from $\text{Fc}(\text{CH}_2)_{11}\text{SH}$. Two MBBA solutions, one pure and the other containing 20 mM BP, were injected into the optical cell from opposite sides of the cell. The curve (highlighted by two dashed red arrows) indicates the transition between two regions distinguished by fine (with BP) and coarse textures (without BP) of MBBA. (F) Schematic illustration of the alignment of MBBA in (E). The distance between the two surfaces of each optical cell was measured to be $13.1 \pm 0.5 \mu\text{m}$ (supporting online text).



by using atomic force microscopy (27). Electrochemical oxidation of the ferrocene, however, was accompanied by the reorientation of 5CB (Fig. 4). At low voltages (<0.3 V),

the 5CB was measured to undergo a 90° change in azimuthal orientation on the surface of the chemically functionalized electrode. Because the azimuthal orientation of

5CB on the counter electrode (bare gold) did not change, a 90° twist distortion was formed in the liquid crystal (28). The change in orientation of the liquid crystal was a continuous function of the extent of oxidation of the ferrocene to ferrocenium (i.e., voltage applied to the working electrode). At intermediate voltages, corresponding to partial oxidation of ferrocene to ferrocenium, the optical appearance of the 5CB was stable. A step change in voltage from 0 to 0.2 V led to a change in optical appearance over ~130 ms (29), and we demonstrated the transition to be reversible over ~1000 cycles (supporting online text). Application of a voltage greater than 0.4 V was accompanied by a second reversible transition in the orientation of 5CB on the ferrocenium-terminated monolayer that rotated the optical axis of the liquid crystal out of the plane of the surface, thus replacing the twist distortion by a splay/bend distortion (30).

We performed two experiments to determine the origin of the above-described orientational transitions of 5CB. First, we replaced the ferrocenyl monolayer with a monolayer formed from $\text{CH}_3(\text{CH}_2)_{10}\text{SH}$. Over the same range of voltages described above, we did not observe the 5CB to undergo either the azimuthal or out-of-plane orientational transition. This result indicates that the redox reaction on the surface of the electrode is required for both orientational transitions. Second, we dissolved BP in 5CB and MBBA to chemically generate ferrocenium immobilized on the surface of an obliquely deposited gold film. Chemical oxidation of the ferrocene monolayer caused both 5CB and MBBA to undergo the 90° change in the azimuthal orientation. Because 5CB and MBBA have anisotropic dielectric constants that are opposite in sign, this result indicates that the coupling between the liquid crystal and functionalized electrode that gives rise to the azimuthal transition in orientation is not due to dielectric coupling of the liquid crystal to the electric field in the diffuse part of the electrical double layer. Studies have demonstrated that oxidation of ferrocenyl monolayers formed from $\text{Fc}(\text{CH}_2)_{11}\text{SH}$ on gold leads to a reorganization of the monolayer (31–33). Infrared spectroscopy reveals that oxidation leads to a change in the tilt of the alkyl chains of the monolayer toward the normal of the surface, accompanied by rotation of the ferrocenyl group (Fig. 1B). Because studies of monolayers of alkanethiols formed on gold and silver films with nanometer-scale topography have revealed both 5CB and MBBA to assume identical azimuthal orientations that depend on the tilts of the chains and orientations of terminal functional groups (26), we conclude that the azimuthal orientational transitions of 5CB and MBBA induced by the surface-confined redox reaction are consis-

Fig. 3. Electrochemical control of the out-of-plane orientation of 5CB on an electrode decorated with ferrocene. (A) Schematic illustration of a two-electrode electrochemical cell. The working electrode (WE) comprises a ferrocene monolayer supported on a gold film, and the counter electrode (CE) consists of bare gold. The 5CB was doped with 35 mM TBAF. (B) Cyclic voltammograms (50 mV/s) of a ferrocene monolayer formed on a gold film using nematic 5CB (35 mM TBAF) as the solvent. The charge under the anodic wave is $1 \pm 0.1 \times 10^{-10}$ mol/cm², corresponding to oxidation of 25 ± 5% of ferrocene within the monolayer. (C) Plot of log (peak current) versus log (scan rate). (D to F) Optical images and schematic illustration of the orientations of 5CB observed during electrochemical oxidation of the ferrocene monolayer. (D) (−0.2 V), planar; (E) (0.12 V), mixed/tilted; (F) (0.28 V), homeotropic.

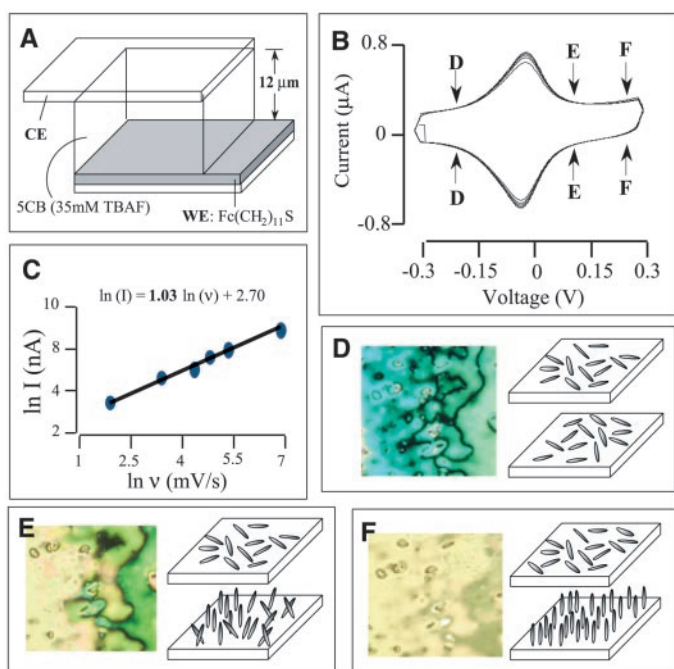
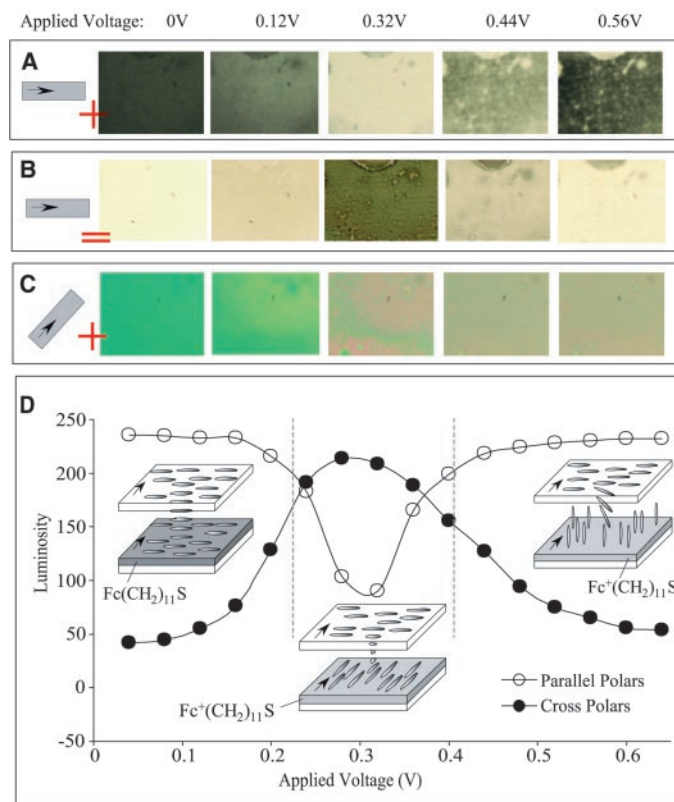


Fig. 4. Electrochemical control of an azimuthal and out-of-plane orientational transition of 5CB supported on a ferrocene monolayer formed on a gold film with nanometer-scale topography. (A to C) Optical images of 5CB (35 mM TBAF) as a function of voltage (indicated above the images) applied between the working and counter electrode; [(A) and (C)] cross polars; (B) parallel polars. The counter electrode was a bare gold film with nanometer-scale topography. The azimuthal directions of maximum roughness (shown by arrows) within the gold films were aligned parallel to each other. The orientation of the polarizers (shown by red bars) is indicated on the left of the images. (D) Plot of the steady-state luminosity of 5CB (cross and parallel polars) at different applied voltages. Schematic illustrations of the orientations of 5CB are shown as insets within the plot.



tent with the effects of a reorganization of the compact part of the electrical double layer (tethered ferrocenium). The out-of-plane re-orientation of 5CB that was observed to accompany the application of substantial over-voltages (~0.5 V) to the surface presenting ferrocenium was not observed when chemical oxidation was used to prepare the ferrocenium monolayers on obliquely deposited films of gold. This orientational transition, which was also not observed when we used working electrodes supporting monolayers formed from CH₃(CH₂)₁₀SH, requires both the presence of the ferrocenium and the overvoltage and is consistent with a dielectric coupling of the liquid crystal with the diffuse part of the electrical double layer (12).

Because the reorganization of solvent accompanies almost all electrode-confined redox reactions (34, 35), the coupling that we report between the orientation of liquid crystals and redox groups decorated on electrodes is likely one example of a general phenomenon. When oxidation of the redox group results in a change in the electrical double layer, our results demonstrate that the orientation of the liquid crystal can be directed by its interaction with the diffuse or compact parts of the double layer. Compared with Fredericksz transitions in liquid crystals (36), surface-driven orientational transitions using redox-active groups immobilized on electrodes require small voltages (3), require only the patterning of electrodes on one side of the liquid crystal (because the orientational transition is surface driven), and can be combined with soft lithography (37) to pattern redox-active molecules on surfaces to achieve patterned orientations of liquid crystals.

References and Notes

- P. J. Collings, J. S. Patel, *Handbook of Liquid Crystal Research* (Oxford Univ. Press, New York, 1997).
- B. Jerome, *Rep. Prog. Phys.* **54**, 391 (1991).
- For a conventional 10- μm -thick optical cell with strong anchoring (parallel to surface) that is filled with the liquid crystal PEBAB, the onset of the electric field-induced transition in the orientation of the bulk liquid crystal [Fredericksz transition (36); Fig. 1A, I] occurs at ~ 3 V. The change in optical appearance is 90% complete at ~ 6 V (38). The threshold voltage required for the onset of an electric field-induced change in the orientation of a liquid crystal can be reduced by use of hybrid aligned cells (39) or large pretilts (40) in the orientation of the liquid crystal. Saturation voltages in these systems are typically greater than a few volts. Hybrid aligned cells and pretilts can likely reduce further the switching voltages reported in this paper.
- Photoisomerization of surfaces decorated with azobenzene by using ultraviolet (UV) light can also lead to surface-driven orientational transitions in liquid crystals (41).
- B. Comiskey, J. D. Albert, H. Yoshizawa, J. Jacobson, *Nature* **394**, 253 (1998).
- J. A. Rogers et al., *Proc. Natl. Acad. Sci. U.S.A.* **98**, 4835 (2001).
- T. P. Russell, *Science* **297**, 964 (2002).
- P. Poulin, H. Stark, T. C. Lubensky, D. A. Weitz, *Science* **275**, 1770 (1997).
- C. D. E. Chidsey, *Science* **251**, 919 (1991).
- Water-soluble ferrocene-based surfactants have been used to generate gradients in surface tension and control contact angles of isotropic aqueous solutions (42).
- A. M. Serra, R. D. Mariani, H. D. Abruna, *J. Electrochem. Soc.* **133**, 2226 (1986).
- R. R. Shah, N. L. Abbott, *J. Phys. Chem. B* **105**, 4936 (2001).
- R. R. Shah, N. L. Abbott, *J. Am. Chem. Soc.* **121**, 11300 (1999).
- We used BP because it is soluble in both 5CB and MBBA. The oxidation was initiated by heating the sample to $\sim 37^\circ\text{C}$. We used UV spectrophotometry and cyclic voltammetry to confirm oxidation of ferrocene to ferrocenium in the presence of BP.
- V. K. Gupta, N. L. Abbott, *Langmuir* **12**, 2587 (1996).
- When BP was used to oxidize the ferrocene-terminated monolayer, the liquid crystal was deaerated to remove oxygen (43).
- J. K. Bashkin, P. J. Kinlen, *Inorg. Chem.* **29**, 4507 (1990).
- The addition of 20 mM BP to 5CB and MBBA does not measurably change the birefringence of these liquid crystals and thus their interference colors (fig. S1).
- P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).
- The anchoring of MBBA and MBBA with BP was indistinguishable when measured on a methyl-terminated monolayer.
- L. M. Blinov, V. G. Chigrinov, *Electrooptic Effects in Liquid Crystal Materials* (Springer, Berlin, ed. 2, 1993), p. xiv.
- The addition of 20 to 35 mM TBAF to either 5CB or MBBA does measurably change the birefringence of these liquid crystals and thus their interference colors (figs. S2 and S3).
- A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications* (Wiley, New York, ed. 2, 2001).
- We determined the orientation of 5CB in Fig. 3, D and E, by observing the interference colors of liquid crystals in optical cells prepared using surfaces that cause known orientations of the liquid crystal. The interference colors in Fig. 3, D and E, were also obtained by chemical oxidation (BP) of ferrocenyl monolayers with an optical cell identical to that shown in Fig. 3A (figs. S4 and S5).
- J. Cognard, *Mol. Cryst. Liq. Cryst. Suppl. Ser.* **1**, 1(1982).
- V. K. Gupta, N. L. Abbott, *Science* **276**, 1533 (1997).
- J. J. Skaife, N. L. Abbott, *Chem. Mater.* **11**, 612 (1999).
- At potentials between 0 and 0.3 V, the luminosity increased with potential under crossed polars but decreased under parallel polars (Fig. 4, A and B), indicating the formation of a twisted distortion of liquid crystal within the optical cell.
- We measured the response time by analyzing frames of a video captured at a resolution of 1/30 of a second during a step change in potential from 0 to 0.2 V.
- When the sample was oriented at 45° with respect to one of the crossed polars, application of the overvoltage resulted in a change in color from green to pale yellow (Fig. 4C). This change in the interference color matches the change in color that was observed to accompany the out-of-plane transition of 5CB on the ferrocenium-terminated monolayers.
- S. Ye, Y. Sato, K. Uosaki, *Langmuir* **13**, 3157 (1997).
- L. M. Abrantes, M. Kalaji, A. S. Viana, *J. Electroanal. Chem.* **500**, 290 (2001).
- T. Kondo, S. Horiuchi, I. Yagi, S. Ye, K. Uosaki, *J. Am. Chem. Soc.* **121**, 391 (1999).
- R. A. Marcus, *J. Electroanal. Chem.* **483**, 2 (2000).
- R. A. Marcus, *Biochim. Biophys. Acta* **811**, 265 (1985).
- V. Freedericksz, V. Zolina, *Trans. Faraday Soc.* **29**, 919 (1933).
- Y. N. Xia, G. M. Whitesides, *Angew. Chem. Int. Ed.* **37**, 551 (1998).
- M. Schadt, W. Helfrich, *Appl. Phys. Lett.* **18**, 127 (1971).
- G. Barbero et al., *Liq. Cryst.* **5**, 483 (1986).
- G. P. Bryan-Brown, E. L. Wood, I. C. Sage, *Nature*, **399**, 338 (1999).
- T. Ikeda, O. Tsutsumi, *Science* **268**, 1873 (1995).
- B. S. Gallardo et al., *Science* **283**, 57 (1999).
- I. Noviandri et al., *J. Phys. Chem. B* **103**, 6713 (1999).
- Supported in part by the Biophotonics Partnership Initiative of the National Science Foundation (ECS-0086902), the Center for Nanostructured Interface (NSF 0079983), and the Army Research Office (DAAD19-02-1-0299).

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 Figs. S1 to S6
 Reference

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High-Density Electron Anions in a Nanoporous Single Crystal:



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 Katsuro Hayashi,¹ Toshio Kamiya,^{1,2} Masahiro Hirano,¹
 Isao Tanaka,³ Hideo Hosono^{1,2*}

We removed $\sim 100\%$ of clathrated oxygen ions from the crystallographic cages in a single crystal of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$, leading to the formation of high-density ($\sim 2 \times 10^{21} \text{ cm}^{-3}$) electrons highly localized in the cages. The resulting electron forms a structure that we interpret as an F^+ center and migrates throughout the crystal by hopping to a neighboring cage with conductivity ~ 100 siemens per centimeter, demonstrating that the encaged electron behaves as an anion. The electron anions couple antiferromagnetically with each other, forming a diamagnetic pair or singlet bipolaron. The resulting $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} (4e^-)$ may be regarded as a thermally and chemically stable single crystalline "electride."

Electrides are materials that trap electrons at a stoichiometric concentration in the solid state (1). Chemically, trapped electrons can be viewed as the smallest possible anion, and such materials could serve as strong reducing agents. From a physics standpoint, the stabilization of numer-

ous bound electrons, or F centers, could provide new approaches to preparing conductive materials with unusual optical or magnetic properties. In addition, such materials may find application as low-temperature electron emitters. Most electrides have been either organic species, such as