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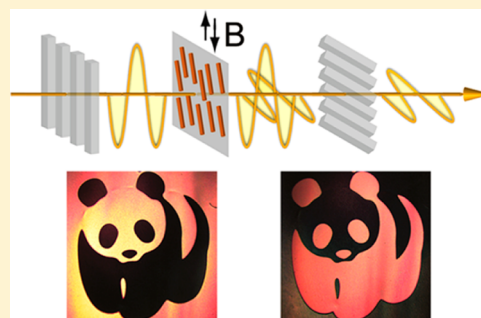
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S Supporting Information

ABSTRACT: Ferrimagnetic inorganic nanorods have been used as building blocks to construct liquid crystals with optical properties that can be instantly and reversibly controlled by manipulating the nanorod orientation using considerably weak external magnetic fields (1 mT). Under an alternating magnetic field, they exhibit an optical switching frequency above 100 Hz, which is comparable to the performance of commercial liquid crystals based on electrical switching. By combining magnetic alignment and lithography processes, it is also possible to create patterns of different polarizations in a thin composite film and control over the transmittance of light in particular areas. Developing such magnetically responsive liquid crystals opens the door toward various applications, which may benefit from the instantaneous and contactless nature of magnetic manipulation.

KEYWORDS: Nanorods, magnetic field, liquid crystals, polarization, reversible tuning, iron oxide



The liquid-like behavior and optical anisotropy of liquid crystals have catalyzed many important applications in modern technology. Their molecular order can be manipulated through external stimuli such as temperature change and electric and magnetic fields, therefore enabling many technological advances, with a particularly successful example being the liquid crystal displays driven by electric fields. Although conventional liquid crystals may be sensitive to magnetic fields, the low magnetic susceptibility of molecular species makes practical applications difficult as extremely strong magnetic fields are required to enable effective switching of the molecular order.^{1–8} While direct incorporation of ferro- or ferrimagnetic materials into liquid crystals has been attempted,^{9–15} a long interaction time is usually required to induce uniform molecular alignment. A more straightforward strategy is to enhance the intrinsic magnetic property of the constituents of liquid crystals, for example, by doping rare earth metal ions into liquid crystal molecules^{16–19} or by developing alternative inorganic building blocks with a higher magnetic susceptibility.^{20–24} However, most such studies have been limited to paramagnetic materials, which can only be aligned in extremely strong external magnetic fields (>1 T). In this regard, the direct use of ferro- or ferrimagnetic inorganic materials represents the best solution to design magnetically responsive liquid crystals because they have higher magnetic susceptibility and can rapidly respond to a relatively weak magnetic field. In such systems, the magnetic interaction energy, instead of the entropic effect in the cases involving diamagnetic/paramagnetic materials, dominates the orientation behavior of liquid crystals, so that the orientational control and the optical switching can be effectively carried out with orders of magnitude reduction in the required field strength but with high magnetic ordering efficiency.²⁵

In his pioneering work, Onsager theoretically predicted the spontaneous nematic ordering of long hard rods in the purely entropic regime,²⁶ leaving the remaining challenges to the development of a controlled synthesis for anisotropically shaped magnetic nanostructures and, more importantly, their effective stabilization as a liquid dispersion because particles with net magnetic dipole moments usually aggregate due to magnetic dipole–dipole interactions. Herein we demonstrate that ferrimagnetic inorganic nanorods can be produced using an indirect synthesis strategy and then be used as building blocks to construct liquid crystals with optical properties that can be instantly and reversibly controlled by manipulating the nanorod orientation using considerably weak external magnetic fields (1 mT). Under an alternating magnetic field, they exhibit an optical switching frequency above 100 Hz, which is comparable to the performance of commercial liquid crystals based on electrical switching. Developing such magnetically actuated liquid crystals opens the door toward various applications, which may benefit from the instantaneous and contactless nature of magnetic manipulation.^{27–31}

Prior studies on inorganic liquid crystals have been limited to molecular species or highly polydisperse disk- and rod shaped inorganic colloids such as gibbsite ($\text{Al}(\text{OH})_3$) and boehmite ($\text{AlO}(\text{OH})$) platelets,^{32–34} platelike smectite clays,³⁵ graphene sheets,³⁶ goethite nanorods,^{4,21,25,37} GdPO_4 and LaPO_4 nanorods,^{20,38} or semiconductor nanorods of CdSe .^{39,40} Even with the significant advances in colloidal synthesis achieved in the past two decades, preparation of magnetic anisotropic

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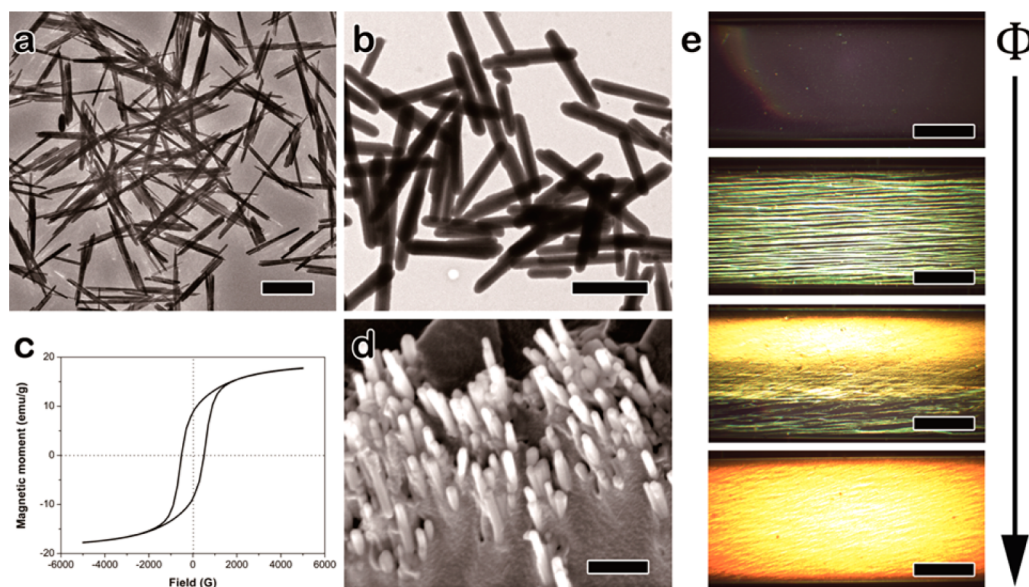


Figure 1. TEM images of (a) FeOOH nanorods and (b) Fe₃O₄@SiO₂ nanorods. Scale bars: 1 μ m; (c) magnetic hysteresis loop of Fe₃O₄@SiO₂ nanorods; (d) SEM image of a fixed magnetic liquid crystal in a polymer matrix showing the ordered arrangement of magnetic nanorods. Scale bars: 1 μ m; (e) POM images of aqueous dispersions of Fe₃O₄@SiO₂ nanorods in a capillary tube at different volume fractions (Φ) of 1%, 3%, 5%, and 10% (from top to bottom). Scale bars: 500 μ m.

nanostuctures with a uniform size, well-defined shape, and good solution dispersity has remained difficult. In this work, we have designed an indirect strategy that involves the preparation of nonmagnetic anisotropic nanostructures as precursors, surface passivation to enhance the colloidal stability, and then conversion of the precursors into magnetic anisotropic nanostructures. More specifically, as direct synthesis of magnetic iron oxide nanorods appeared to be difficult, we chose FeOOH nanorods as the starting material, which can be easily prepared through a hydrolysis reaction. A representative transmission electron microscopy (TEM) image of the nanorods is shown in Figure 1a. The FeOOH nanorods were further coated with a layer of silica through a sol-gel process^{41,42} and then reduced to Fe₃O₄ by diethylene glycol at 220 °C. As shown in Figure 1b, the product maintains a well-defined rod-like morphology, with an average length of 1.5 μ m and diameter of 200 nm. Magnetic measurement confirms the ferrimagnetic nature of the Fe₃O₄ nanorods, showing a saturated magnetization of 18 emu/g and a coercivity of 300 Oe. The surface silica layer plays an important role in the stabilization of the colloidal dispersion of magnetic nanorods: it acts as a physical barrier to separate the magnetic cores from each other, attenuates their magnetic dipole-dipole interactions, and prevents them from aggregating. The abundant hydroxyl groups on the silica surface provide sufficient long-range electrostatic repulsion and short-range solvation forces for stabilizing the magnetic nanorods, granting them excellent dispersibility in various polar solvents such as water and alcohols. Visually, we did not observe obvious sedimentation of the magnetic rods in typical liquid crystal samples sealed in glass capillary tubes within a week. We have also estimated the gravitational stability of the nanorod suspensions experimentally. For a suspension of magnetic rods in water with a volume fraction (Φ) of 1%, we obtained a sedimentation rate of 0.70 μ m·min⁻¹ for measurement from day 2 to day 4 and 0.65 μ m·min⁻¹ for measurement from day 5 to day 6.⁴³ The sedimentation rate is expected to further decrease as the

volume fraction of magnetic rods and the viscosity of suspension are increased.^{44–46}

Upon the application of an external magnetic field, the magnetic nanorods align themselves along the field direction, producing the orientational order needed for the formation of liquid crystals. Since the average size of the nanorods is much larger than the detection limit of conventional small-angle X-ray scattering measurement, resolving the crystal structure of the sample in the magnetic field is difficult to achieve. An alternative method which allows us to directly observe the alignment of the nanorods is to fix the nanorods in a polymer matrix.⁴⁷ In this case, Fe₃O₄@SiO₂ nanorods were dispersed in a UV curable poly(ethylene glycol) diacrylate (PEGDA) resin at a volume fraction (Φ) of 10%. Under an external magnetic field, the dispersion was exposed to UV light to initiate polymerization. Afterward, the polymerized solid was cut, and its cross section was examined using scanning electron microscopy (SEM). As shown in Figure 1d, a uniform alignment of nanorods could be observed, which confirms the orientational order of the nanorods that leads to liquid crystal properties, although it is still difficult to resolve positional order by using this method. Figure 1e shows the polarized optical microscopy (POM) images of the aqueous dispersions of Fe₃O₄@SiO₂ nanorods at different volume fractions from 1% to 10%, clearly indicating a transition from an isotropic phase to an ordered nematic phase as the volume fraction increased and confirmed the liquid crystal behavior of the dispersions. Further phase transitions from nematic phase to columnar phase or smectic phase are expected at even higher volumetric fractions, as predicted theoretically^{48,49} and proved experimentally,^{4,50} although further confirmation of such transitions requires small-angle X-ray scattering measurements.

We then demonstrated the optical tuning of such liquid crystal by a magnetic field. The orientation of the nanorods was found to vary with the direction of the magnetic field, resulting in visual changes under POM. Note that the strength of the magnetic fields used in this work is fixed at \sim 1 mT, unless

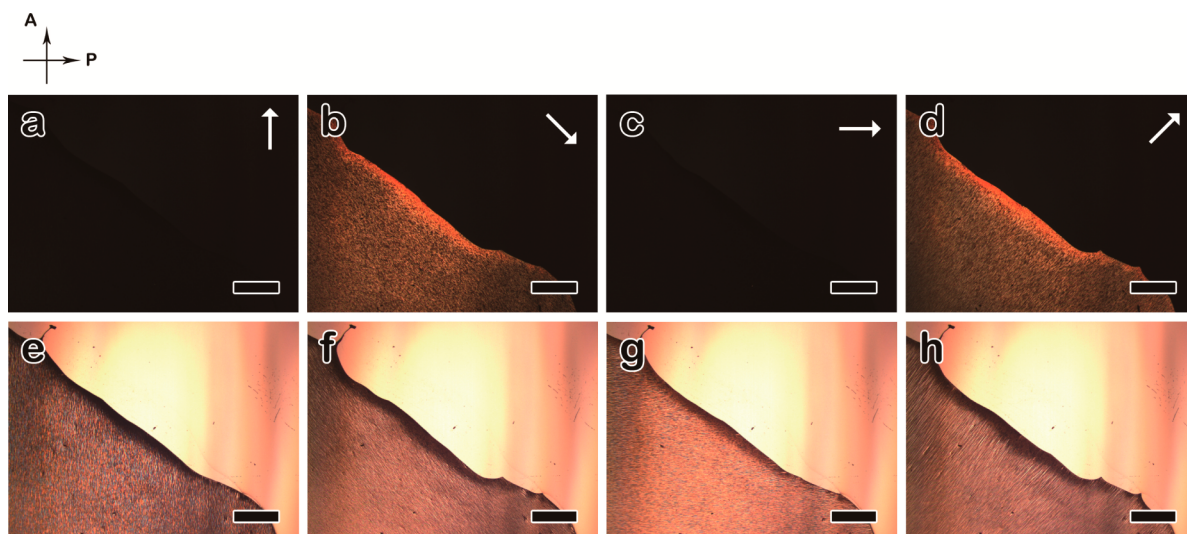


Figure 2. (a–d) POM images and (e–h) bright-field OM images of a magnetic liquid crystal film under magnetic fields oriented in different directions. Black arrows at the top-left indicate the transmission axis of the polarizer (P) and analyzer (A). White arrows indicate the field direction. The top-right corner in each image contains no sample. Scale bars: 500 μm .

otherwise specified. The intensity of light transmitted through a liquid crystal sandwiched between cross polarizers can be typically described as

$$I = I_0 \sin^2(2\alpha) \sin^2(\pi\Delta nL/\lambda) \quad (1)$$

where I_0 is the intensity of light passing through the first polarizer; α is the angle between the transmission axes of the polarizer and the long axis of the liquid crystal; Δn is the difference in the refractive indices along the long axis and short axis for liquid crystals aligned at a specific angle; L is the sample thickness; and λ is the wavelength of incident light.⁵¹ The birefringence of the sample dispersion was measured to be 0.15 and did not show significant change as the field strength increased, indicating good alignment of the nanorods. When the field direction is parallel or perpendicular to the polarizer, α is equal to zero or 90° , leading to dark optical views (Figure 2a and c). As the field direction turns to 45° relative to the polarizer, α changes to 45° , so that the intensity reaches the maximum according to eq 1, resulting in bright views, as shown in Figure 2b and d. In contrast, the corresponding bright field optical microscopy images of the same sample did not show apparent differences in the darkness of the view in response to the changes in the direction of the magnetic field, as indicated in Figure 2e–h.

The magnetic liquid crystals can rapidly respond to changes in the direction of external magnetic fields. The magnetic torque exerted on the nanorods is sufficiently strong to overwhelm the substrate effect of the container walls. As shown in Figure S3, the nanorods initially oriented parallel to the wall of the container in the absence of external magnetic fields but reoriented instantly when a magnetic field was applied. Under an external magnetic field, the rods near the edge and those away from the edge were all oriented parallel to the field direction. In a rotating magnetic field, continuous optical switching of a liquid crystal can also be achieved, as demonstrated in a video included in the Supporting Information. To obtain a quantitative understanding of its switching frequency, we studied the optical properties of the liquid crystal under a high-frequency alternating magnetic field. Upon application of the magnetic field, the nanorods oscillate

as a result of the quick switching of field polarity from one direction to the opposite.^{52–54} As the orientation of the nanorods is temporarily displaced from the equilibrium position, which is parallel to the transmission axis of the polarizer, a laser beam passes through the cross polarizer and gives a detectable signal. The black curve in Figure 3a indicates that this liquid crystal exhibits a rapid response to an alternating 5 mT field. The transmittance changes drastically within 0.01 s, corresponding to a switching frequency of 100 Hz, while in a

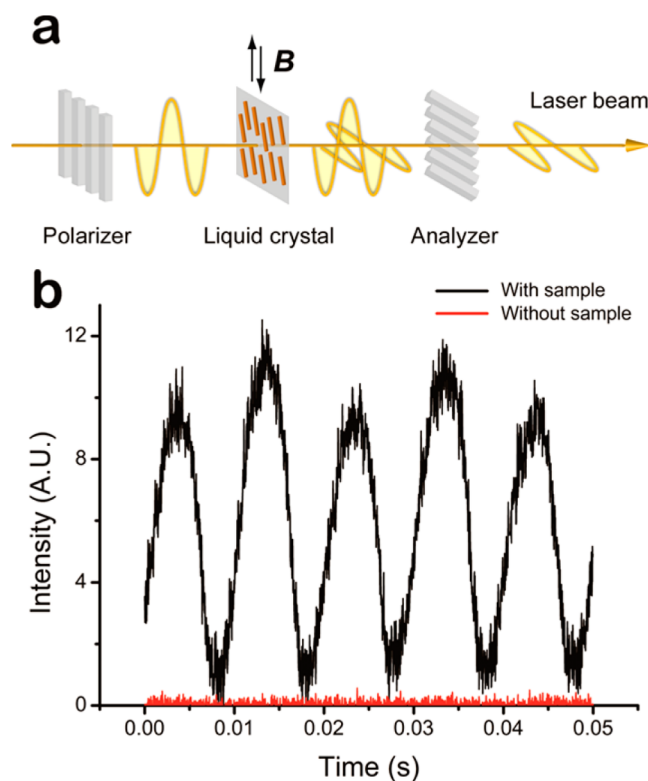


Figure 3. (a) Scheme showing the optical switching process and (b) the transmittance intensity profile of a magnetic liquid crystal under an alternating magnetic field.

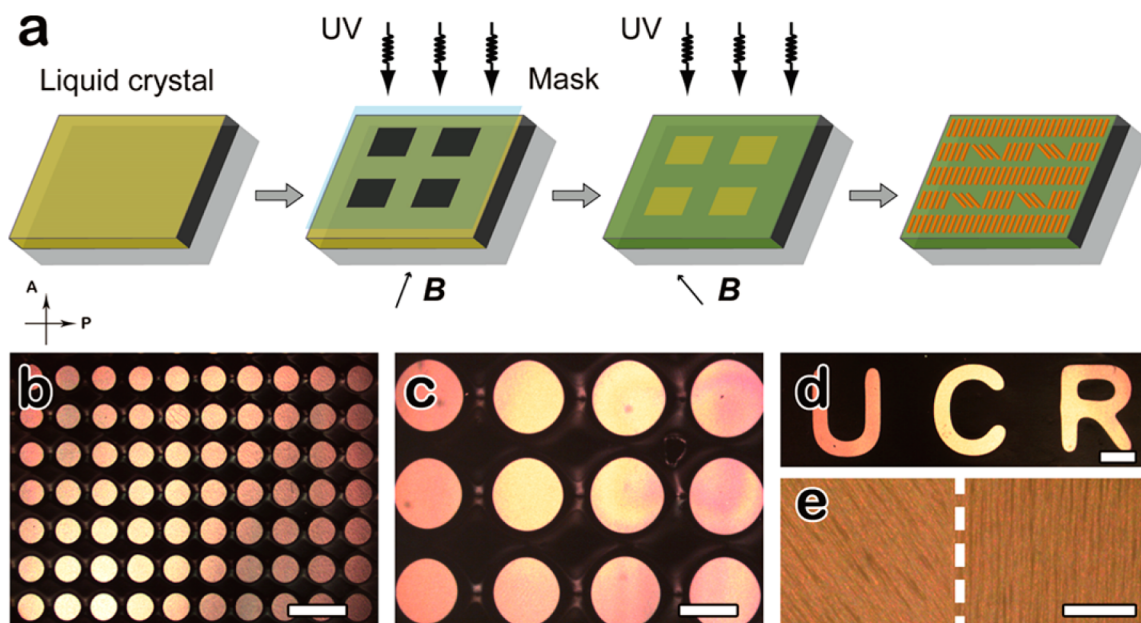


Figure 4. (a) Scheme showing the lithography process for the fabrication of thin films with patterns of different polarizations; (b–d) POM images of various polarization-modulated patterns; (e) enlarged OM image shows the arrangement of nanorods in the pattern (left) and surrounding area (right). Scale bars: (b–d) 500 μm ; (e) 10 μm .

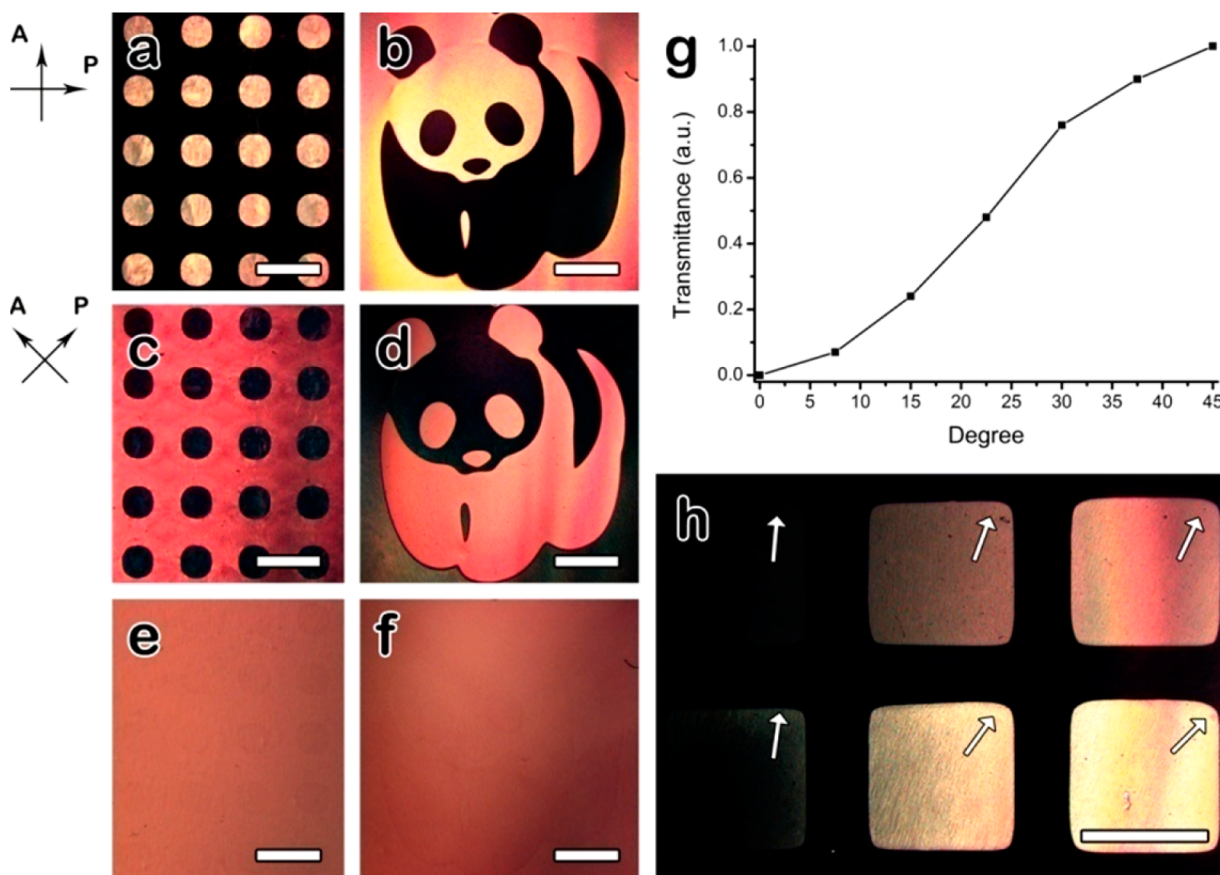


Figure 5. (a–d) POM images of two polarization-modulated patterns under cross polarizers before (a,b) and after (c,d) shifting the direction of the transmission axis of the polarizers for 45°; (e,f) bright-field images of the same patterns; (g) plot showing the dependence of the transmittance of the thin film on the angle between the nanorod orientation and the transmission axis of the polarizer; (h) POM image of a single thin film patterned with different brightness in different areas by controlling the relative orientation of the nanorods, which is indicated by the white arrows. Scale bars: 500 μm . The panda logo is used with permission from the World Wildlife Fund [Copyright 1986 Panda Symbol WWF - World Wide Fund For Nature (formerly World Wildlife Fund)].

control experiment, no transmittance change is observed in the absence of the liquid crystal sample (red curve).

One of the advantages of inorganic-nanostructure-based liquid crystals is the possibility for convenient fixation of the orientational order. Here we further demonstrate that thin films patterned with various optical polarizations can be conveniently produced by combining the magnetic liquid crystals with lithography processes. As schematically shown in Figure 4a, a liquid crystal solution containing magnetic nanorods and PEGDA resin was first sandwiched between a glass coverslip and a glass slide to form a liquid film. A photomask was then placed on top of the sample, followed by the application of a magnetic field. Upon exposure to UV light, the orientation of the nanorods in the uncovered regions was fixed along a specific direction within the plane of the film. The photomask was then removed, and the sample was again exposed to UV light in the presence of a magnetic field rotated 45° (in plane) from the initial field direction. In the end we obtained a thin film with polarization patterns showing different transmittances to a polarized light. Figure 4b–d displays the POM images of as-prepared samples after the application of different patterns. In these cases, the transmission axis of the polarizer was set to be parallel to the initial field direction. The areas cured during the first exposure appear dark under the POM, owing to the parallel arrangement of the nanorods relative to the transmission axis of the polarizer, while the areas cured during the second exposure are bright since all nanorods are oriented 45° relative to the transmission axis of the polarizer. An enlarged bright field optical microscopy image is shown in Figure 4e, which accentuates the alignment of the nanorods at the boundary of the bright (left) and dark (right) areas (separated by the dotted line) and clearly confirms the 45° angle between the two orientations.

Changing the orientation of the nanorods relative to the transmission axis of the polarizer allows convenient modulation of the transmittance intensity. As depicted in the extreme cases in Figure 5a–d, shifting the transmission axis of the polarizer to be parallel to the direction of the second field completely reverses the dark and bright areas, while almost no contrast can be observed under their bright-field optical images (Figure 5e and f). In Figure 5g, we have plotted the dependence of measured transmittance on the angle between the orientation of the nanorods and the transmission axis of the polarizer, which is in accordance with eq 1. The transmittance of the polarized light of the film or consequently its brightness under POM can be fully modulated by controlling the relative orientation of the nanorods in different areas during the lithographic processes. Figure 5h demonstrates a single film with varying brightness in different areas fabricated by a multistep lithography process, in which the magnetic field was gradually shifted from 0° to 45° relative to the transmission axis of the polarizer. The polarization dependent transmittance of the pattern may be immediately applicable in anticounterfeiting devices. Interestingly, if we only perform the first curing process, the uncured areas remain in the liquid phase so that the orientation of the nanorods within can still be tuned by magnetic fields, allowing continuous change in the contrast between the pattern and the background, as illustrated by a video included in the Supporting Information.

In summary, we have successfully produced a magnetically actuated liquid crystal system based on magnetic iron oxide nanorods and demonstrated its instantaneous and reversible orientational tuning using magnetic fields. Depending on the

direction of the applied external field, this liquid crystal alters the polarization of light and is thus able to control the intensity of the light transmitted through it. Optical switching tests indicate that this liquid crystal is extremely sensitive to the directional change of external magnetic fields and exhibits an instant response within 0.01 s. The magnetic nanorods can also be dispersed in a UV curable resin to produce thin film liquid crystals, the orientation of which can be fixed completely or in selected areas by combining magnetic alignment and lithography processes, allowing the creation of patterns of different polarizations and control over the transmittance of light in particular areas. Although the absorption of iron oxide may limit some potential applications, the liquid crystal films involved in most optical applications are typically in the form of thin films which can still allow sufficient transmittance of the light (Figure S4). With the advantageous features such as the electrode-less remote control of the optical properties and the easy fixation of the liquid crystal orientation for creating polarization patterns, the magnetically actuated liquid crystal reported here is expected to provide a new platform for fabricating novel optical devices that can be widely applied in many fields, such as displays, waveguides, actuators, optical modulators, and anticounterfeiting features.

■ ASSOCIATED CONTENT

📄 Supporting Information

Synthetic and analytical methods; transmission spectra; videos for optical tuning. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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