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A sprayable H-bonding coumarin-containing compound for photoalignment of liquid crystals on a curved surface†

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The success of the photoalignment of liquid crystals provides displays and other optical applications with more possibilities, compared with the surface rubbing technique. Especially, it is highly required for applications requiring liquid crystal alignment on curved surfaces, for which surface rubbing is hard to apply. Photodimerization of photoactive species coated on the substrate under linearly polarized light irradiation is one of the photoalignment methods. In this work, we present a study on the photoalignment behaviors of a novel low-molecular-weight, H-bond donor, acceptor, and coumarin-containing compound that can be spray-coated on curved surfaces. The photoalignment of liquid crystals using this coumarin-containing compound is investigated by monitoring the polarized absorption of a dichroic dye-doped nematic liquid crystal. It is found that the order parameter can reach about 0.5 by adjusting the thickness of the spray-coated layer and the polarized light intensity. In addition to liquid crystal alignment on a curved surface, the reversible photoreaction of coumarin is explored to reprogram the photoalignment layer to achieve control in either the degree or direction of the liquid crystal alignment. The results show that the novel structure of the coumarin-containing compound is promising for photoalignment of liquid crystals.

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1. Introduction

Nematic liquid crystals (LCs), by combining a long-range molecular ordering and the fluid-like movement of molecules, have found a wide range of applications in various fields,^{1–6} such as displays,^{7,8} optical and photonic devices,^{9–13} sensors,^{14,15} energy storage devices¹⁶ and soft actuators.^{17–19} In all applications, the orientation of LC molecules is necessary and often determines their response to an electric field, *i.e.*, the electrooptical property. Obtaining high degree LC orientation and achieving controllable response behaviors are still critical issues in LC research and application.^{20,21} The surface rubbing method for LC alignment is the most used technology in the LC display industry since its birth around the 1960s,^{8,22} despite some drawbacks like generation of static electricity and fine dust particles, which may affect LC devices.²⁰ Unlike flat-surface LC displays, where a thin polymer layer can easily be spin-coated on a substrate surface and then mechanically rubbed, the rubbing method may be difficult to apply for LC photonic devices requiring LC alignment on curved or complex geometric surfaces, as well as patterned or spatially controlled LC orientation. Therefore, the development of

more adaptable and efficient LC alignment technology is challenging and needed.²³

Driven by the above, the use of a surface alignment layer treated by light, instead of mechanical rubbing, to align LC molecules, the so-called photoalignment method, has generated much research interest.^{24–26} In this case, a photosensitive surface layer, generally a polymer, is subjected to linearly polarized light, usually an ultraviolet (UV) light, with adjustable direction and intensity, and the angular selection of absorption of the photoactive species in the surface layer can create optical anisotropy on the surface.^{27–29} When nematic LC molecules are deposited on such a photoalignment layer, the anisotropic interfacial interaction between the surface layer and LC molecules can lead to a long-range orientation of the latter. As one kind of contactless alignment method, it can not only avoid the problem of static electricity and fine dust particles but can also achieve LC alignment in spatially selected regions or in a patterned manner,³⁰ which promises potential applications beyond display.^{31–34}

In order to utilize photoalignment on surfaces that are curved or have complex geometries, it is necessary to coat the substrate with a thin photosensitive material prior to linearly polarized UV light (LPUV) exposure.³⁵ This remains challenging because the usually used spin-coating on flat surfaces cannot be applied. In this regard, other surface layer preparation methods, such as vapor deposition,³⁶ dip-coating³⁷ and spray-coating, are more suitable. Of these methods, spray-coating offers many

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advantages, including high efficiency, cost-effectiveness, versatility and precision.^{13,38} Additionally, spray-coating can make patterns on different kinds of surfaces just with masks. To the best of our knowledge, the use of spray-coating to prepare photoalignment layers on a curved surface has not been reported thus far.

Herein, a novel low-molecular-weight (LMW) compound featuring three photosensitive coumarin units and multiple urethane groups for intermolecular H-bonding was designed and synthesized for preparing photoalignment layers, which can be applied on complex or curved surfaces through spray-coating. As compared to photosensitive polymers, at a given concentration the solution of LMW compounds has lower viscosity and is easier to be sprayed, while upon vaporization of the solvent the multiple intermolecular H-bonding helps in solidifying the film quickly and thus facilitating the obtention of a uniform surface layer. Subsequently, when exposed to LPUV light, the three coumarin moieties in the molecular structure can photodimerize to result in not only an anisotropic surface for LC alignment but also a highly crosslinked coumarin polymer network ensuring the alignment layer's stability. With this H-bonding based LMW compound, the ability to induce LC alignment of the photoalignment layer prepared by spray-coating is found to be basically the same as that of spin-coated surface layer. The demonstrated sprayable coumarin-containing compound is useful for enabling photoalignment of LCs on curved surfaces.

2. Experimental section

2.1. Materials

4-Methylumbelliferone (Aldrich, 98%), 1,6-diisocyanatohexane (Thermo Scientific Chemicals, 98%), dibutyltin dilaurate (TCL America, 99%), 2-bromoethanol (Thermo Scientific Chemicals, 97%), phloroglucinol anhydrous (TCL America, 99%) and 4-cyano-4'-pentylbiphenyl (5CB, Qingdao QY Liquid Crystal Co., Ltd, 95%) were used as received. Unless stated otherwise, all solvents and chemical reagents utilized in this study were purchased from Sigma Aldrich and utilized as received.

2.2. Synthesis of the sprayable coumarin-containing compound

The coumarin derivative 6,8-dihydroxy-4-methyl-2*H*-chromen-2-one and 7-(2-hydroxyethoxy)-4-methyl-2*H*-chromen-2-one was synthesized using a previously reported method.^{39–42} The synthesis of the sprayable coumarin-containing compound is shown in Fig. 1(a). The detailed synthesis procedure is as follows. 1,6-Diisocyanatohexane (8.75 g, 0.05 mol), anhydrous DMF (20 mL) and one or two drops of dibutyltin dilaurate were added to a 100 mL round-bottom flask and placed in a 60 °C oil bath for preheating. Then, 7-(2-hydroxyethoxy)-4-methyl-2*H*-chromen-2-one (2.20 g, 0.01 mol) was dissolved with 20 mL anhydrous DMF and added dropwise into the flask. After 6 h of reaction, excessive 1,6-diisocyanatohexane was removed through extracting with *n*-hexane three times and washed with pentane. After drying, a white powder was obtained. Afterwards, 6,8-dihydroxy-4-methyl-2*H*-chromen-2-one (0.96 g, 0.005 mol) and the reaction product of the previous step (3.98 g, 0.01 mol) were dissolved

with 20 mL anhydrous DMF and reacted for another 6 h. The mixture was then cooled to room temperature and poured into deionized water for precipitation. The crude product, a white powder, was purified by recrystallization in methanol. After drying in a vacuum at 60 °C overnight, the sprayable coumarin-containing compound was obtained (6.78 g, 69.9%).

2.3. Preparation of the photoalignment layer using the spin- and spray-coating method

The photoalignment layers were prepared through either the spin-coating or spray-coating method, with a chloroform solution of the coumarin-containing compound (0.3 wt%) on quartz plates (flat or curved surface). The preparation procedure is schematically illustrated in Fig. S1 (ESI†). For spin-coating, a spin-coater at 3000 rpm was used. For spray-coating, a pressure of about 20 kPa was applied to the spray gun and the solution was spray coated for 1–8 s. After drying in a vacuum oven at 45 °C for 2–3 h, photoalignment layers were formed and ready for exposure to LPUV light for photodimerization of coumarin groups. An Omni-Cure@Series 1000 UV lamp with a 320–480 nm filter was used, and linear polarization was obtained using a polarizer. For this study, the UV irradiation intensity was adjusted to 5–50 mW cm^{−2}. For the photo-de-dimerization process, a UVS-28 EL Series UV lamp was used (254 nm, 30 mW cm^{−2}).

2.4. Measurement of the photoalignment layer-induced liquid crystal orientation

The orientation of liquid crystals in the sandwiched cells fabricated using the photoalignment layers was measured to assess the efficiency of photoalignment layers. A commercially available, room temperature nematic liquid crystal, namely 4-cyano-4'-pentylbiphenyl (5CB), mixed with 0.4 wt% of a dichroic azo dye (disperse red 1) was filled into a 5 μm gap cell with parallel photoalignment layers in its isotropic phase (heated to 60–70 °C, well above its nematic-to-isotropic transition temperature, *T*_{ni}, at 34.2 °C). After thermal annealing at 55 °C for 8 min to remove the flow history, the cell was cooled slowly to room temperature. Polarized UV-Vis spectra of the cell were recorded to measure the orientation degree (order parameter) of 5CB molecules as revealed by the dichroism of the probing azo dye.

2.5. Characterization

¹H NMR spectra were recorded at room temperature on a Bruker Avance-III 300 NMR spectrometer. The polarized UV-Vis absorption spectra were recorded on a spectrophotometer (Cary series UV-Vis-NIR, Agilent Technologies) equipped with a Glan Thompson polarizer (Harrick Scientific Products, Inc.). The surface topography of spray-coated photoalignment layers was examined using an atomic force microscope (AFM, Dimension Icon ScanAsyst, Bruker) in the tapping mode. Thermal phase transitions were measured using a TA Q200 differential scanning calorimeter (DSC) at a heating rate of 10 °C min^{−1} under a nitrogen atmosphere. The fluorescence emission spectra were recorded with a fluorescence spectrometer (Cary Eclipse, Varian, Inc) using an excitation wavelength of 325 nm. For the



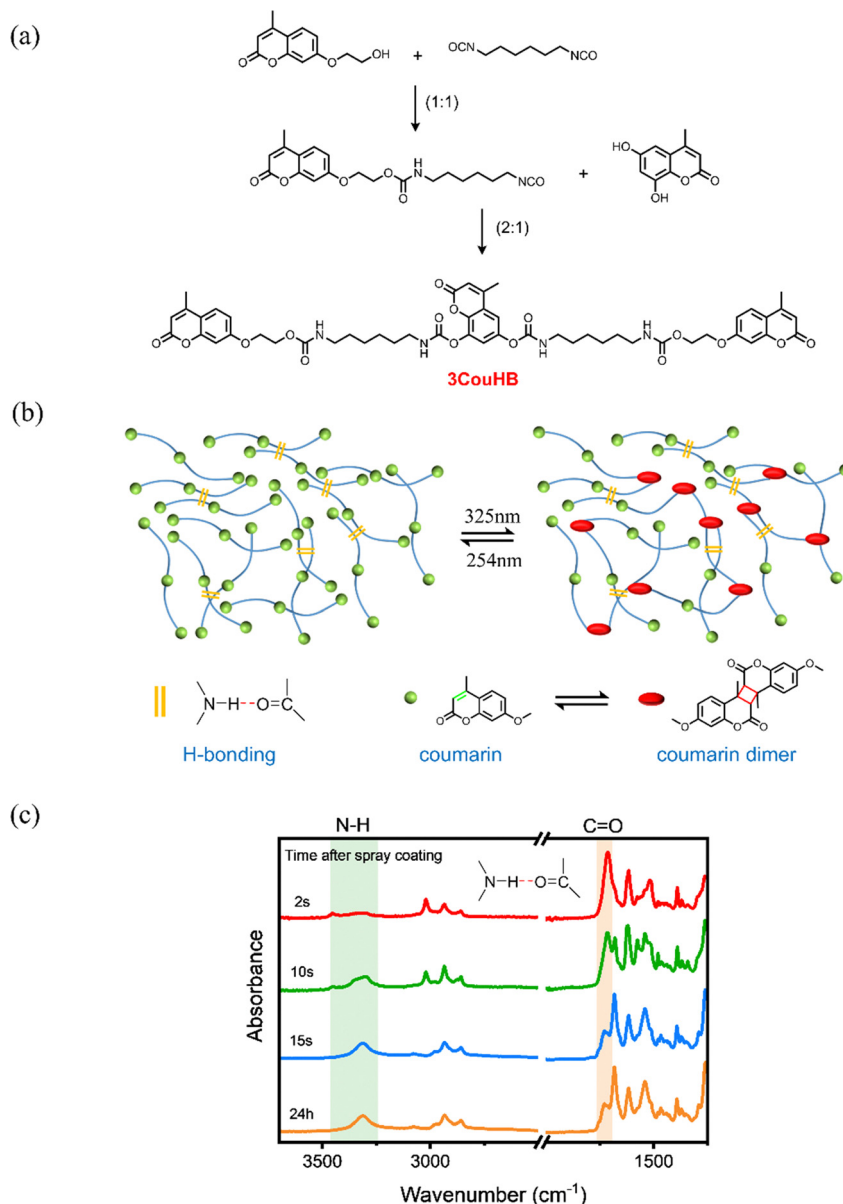


Fig. 1 (a) The synthesis route to the coumarin-containing compound 3CouHB. (b) Schematic illustration of the H-bonded supramolecular assembly of 3CouHB after spin- or spray-coating and its crosslinked polymer structure after LPUV light irradiation leading to intermolecular photodimerization of coumarin groups and, at the same time, surface anisotropy due to angular selective dimerization. The photodimerization of coumarin groups is reversible as photo-de-dimerization occurs upon absorption of UV light of shorter wavelengths. (c) Infrared spectra of 3CouHB at different times after spray-coating its solution (0.3 wt% in chloroform), showing quick formation of H-bonds between urethane groups.

electrooptical measurement, two indium-tin-oxide (ITO)-coated glass plates were spray-coated with the 3CouHB photoalignment layers and then assembled into a 5 μm -gap cell. After filling the cell with 5CB, the transmittance of a 635 nm probe light passing through the cell, to which a voltage could be applied, was measured using a photodetector connected to a digital oscilloscope. The setup detail was previously reported.⁴³

3. Results and discussion

Fig. 1(a) shows the synthetic route to the novel coumarin-containing compounds which can be achieved by spray-coating.

To achieve chain flexibility and establish hydrogen bonding within the system, the structure was infused with 1,6-diisocyanatohexane as a raw material. In the first step, 7-(2-hydroxyethoxy)-4-methyl-2H-chromen-2-one was added dropwise to a solution of 1,6-diisocyanatohexane in a 1:1 molar ratio, resulting in the formation of a coumarin intermediate containing one isocyanate group on one side. In the second step, the coumarin intermediate was further reacted with 6,8-dihydroxy-4-methyl-2H-chromen-2-one in a 2:1 molar ratio to yield the final coumarin-containing compound. Meanwhile, the high reactivity of isocyanate groups with hydroxyl groups makes the overall reaction simple and efficient just through the two-step chemical synthesis process.



In the end, the novel coumarin-containing compound, namely, 4-methyl-2-oxo-2H-chromene-6,8-diyl bis(((6-(((2-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)ethoxy)carbonyl)amino)hexyl)carbamate) was obtained. Hereafter, this LMW coumarin-containing compound is denoted as 3CouHB, which has four urethane groups for H-bonding and three coumarin groups for photodimerization. The three coumarin groups in the structure allow efficient conversion into crosslinked polymer network and the formation of an anisotropic surface through their angular selective photodimerization under LPUV light exposure. The low molecular weight of 3CouHB facilitates its spray-coating on the curved substrate surface, because of its much-reduced solution viscosity as compared to coumarin-containing polymers (Fig. S2, ESI†). Basic characterization of the novel coumarin-containing compound was carried out. Its ^1H NMR spectrum shows the characteristic peaks expected with the molecular structure (Fig. S3, ESI†).

The coumarin-containing compound can be easily dissolved in volatile organic solvents such as chloroform and THF, and the solution can be spray-coated onto a substrate surface. Fig. 1(b) schematically illustrates the expected structures of spray-coated film of 3CouHB before and after exposure to LPUV. Prior to light treatment, the film is solidified by multiple intermolecular H-bonds formed between the urethane groups, *i.e.*, the solid film has an H-bonded supramolecular structure. After LPUV exposure, the angular-selective photodimerization of coumarin groups not only creates an anisotropic surface for the alignment of LC molecules but also forms a covalently crosslinked polymer film. The photodimerization is reversible, as the dimer can be converted to monomeric coumarin upon absorption of short-wavelength UV light. These structural features were confirmed by

spectroscopic measurements. Fig. 1(c) shows the infrared spectra of the film recorded at different times after spray coating (the assignment of the main absorption peaks is given in Table S1, ESI†). As the solvent is evaporated over time, the absorption peaks around 3450 cm^{-1} and 1730 cm^{-1} attributed to free N–H and C=O vibrations, respectively, are shifted to lower wavenumbers due to H-bonding between these groups; and most H-bonds are formed 15 seconds after spray-coating, quickly solidifying the film. On the other hand, as will be shown later (Fig. 2), when a dried spray-coated 3CouHB film is subjected to alternating LPUV (320–480 nm) and unpolarized 254 nm UV light irradiation, the absorption peak of coumarin groups at around 320 nm decreases first (formation of dimers) and then increases (de-photodimerization), respectively. The formation of a covalently crosslinked polymer after the photodimerization of coumarins was also observed by exposing the coumarin-containing compound solution to UV light, as a solid precipitate was formed upon UV light irradiation, which is the insoluble polymer. Differential scanning calorimetry (DSC) was used to characterize the thermal phase transitions of 3CouHB and its photo-crosslinked polymer. While the former displays a melting temperature at around $163\text{ }^\circ\text{C}$, the latter shows a glass transition at about $66\text{ }^\circ\text{C}$ (Fig. S4(a), ESI†).

The process of preparing photoalignment layers on flat surfaces using spin-coating or spray-coating is shown in Fig. S1 (ESI†). The solution of 3CouHB (0.3 wt% in chloroform) was sprayed on the substrate by controlling the spray time. When the compound solution is spray-coated onto the substrate, it results in the random distribution of coumarin groups across the substrate surface. As mentioned above, to achieve photodimerization using LPUV, the

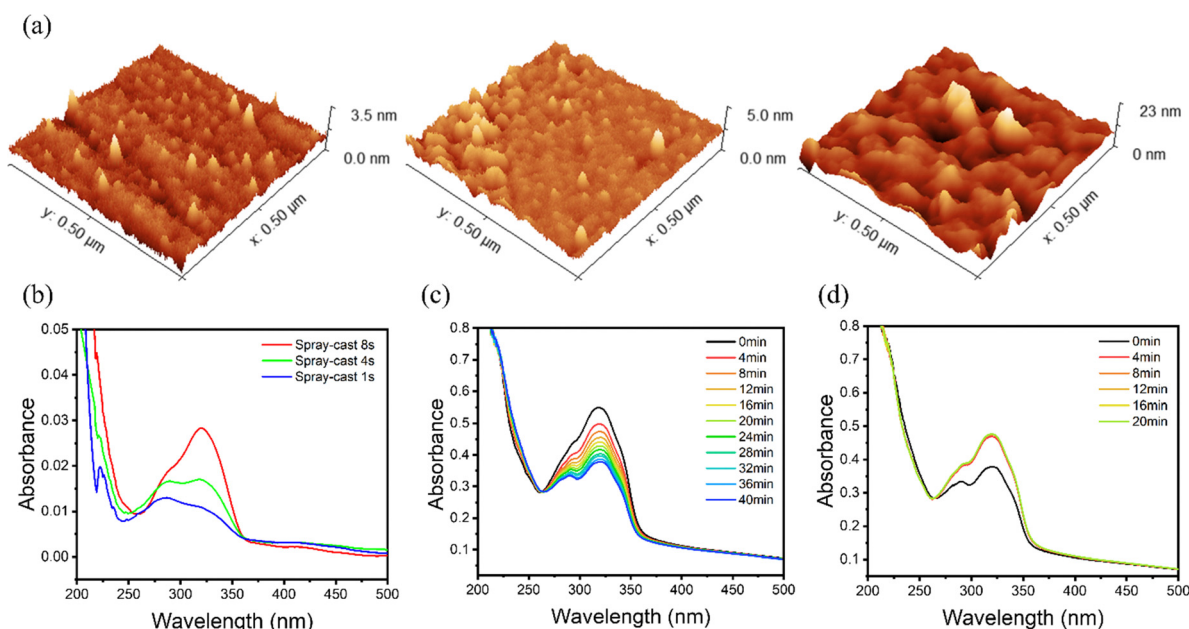


Fig. 2 (a) AFM images of the spray-coated photoalignment surface layer with different spray times: 1, 4 and 8 s. (b) UV-Vis absorption spectra of the photoalignment layers prepared using different spray times. (c) UV-Vis absorption spectra of the surface layer prepared using 20 s solution spray and, after drying, exposed to LPUV light (8 mW cm^{-2}). (d) UV-Vis absorption spectral changes of a prepared spray-coated photoalignment layer upon unpolarized 254 nm UV light irradiation (30 mW cm^{-2}) for different times, the increase in coumarin absorption peak indicates conversion of dimers to monomeric coumarin moieties.



possibility of light absorption depends on the angle between the electronic transition moment of the coumarin group and the polarization direction of UV light. The transition moment is the transition dipole that results from the charge displacement during the transition between the ground and excited state. Consequently, coumarin molecules whose transition moments are parallel to the light electric field vector (P_{\parallel}) are more likely to be excited when irradiated with polarized light. The transition moment of the coumarin group (π - π^* transition) is nearly parallel to the long axis of the coumarin skeleton. As a result, the preferred depletion of coumarin groups occurs along P_{\parallel} , leading to an anisotropic distribution of unreacted coumarin groups in the direction perpendicular to the polarization direction of the light (P_{\perp}) and photochemical products in the P_{\parallel} direction (Fig. 1(b)). When LC molecules are deposited on the surface, the anisotropic intermolecular interaction at the interface determines the direction of the preferential orientation axis of the interacting LC molecules, which results in long-range orientation in the same direction due to the cooperative nature of liquid crystals.

The surface topography of spray-coated photoalignment layers was examined using atomic force microscopy (AFM), with the layers prepared by varying the solution spray time. The AFM images in Fig. 2(a) show that the surface roughness increases with increasing spray time, with the average height of the film being 1.26, 2.35 and 8.81 nm and the film mean roughness being 0.21, 0.26 and 1.83 nm for the layers coated by spraying the 3CouHB solution for 1, 4 and 8 seconds, respectively. At the same time, prolonging the spraying duration correlates with a rise in the coumarin content within the alignment layer, as can be seen from the increased absorption of coumarin groups with increasing spray time (Fig. 2(b)). Since long spraying times are not conducive to forming a uniform and smooth surface, which may affect the LC alignment, the photoalignment layers were prepared using a spraying time of 4 seconds unless otherwise stated.

The investigation of the spray-coated surface layers both before and after exposure to LPUV was conducted, using UV-Vis absorption and infrared spectroscopy to monitor the photodimerization process. To obtain the UV-Vis spectra shown in Fig. 2(c), the 3CouHB solution was sprayed for 30 s on a quartz plate and, after drying, exposed to LPUV (8 mW cm⁻²), while a spectrum was recorded for every 4 min light irradiation. The absorption peak at 320 nm, characteristic of coumarin groups, decreases with irradiation time, while the absorption of coumarin dimers at shorter wavelengths of around 250 nm slightly increases, indicating the occurrence of photodimerization. After 40 min irradiation, almost no further decrease in the absorption peak at 320 nm was observed, indicating that the photodimerization essentially reached the photostationary state under the used conditions. The polarized absorption spectra of the sprayed surface layer showed only slight dichroism for the 320 nm absorption peak, implying the absence of significant orientation of the remaining coumarin moieties within the film. On the other hand, infrared spectra were obtained by spray-coating the 3CouHB solution on an infrared-transparent CaF₂ window. Comparing the spectra of the layer before and after

exposure to LPUV (Fig. S4(b), ESI[†]), the spectral differences, even though small, indicate the [2+2] cycloaddition reaction under LPUV. The broadening of the carbonyl peak in the 1730–1770 cm⁻¹ region results from the formation of nonconjugated carbonyl groups in the coumarin dimer bridged by cyclobutene, and the disappearance of the conjugated enone carbonyl groups is due to the breakage of C=C bonds in the starting coumarin moieties.

A potentially interesting feature of using coumarin for the photoalignment layer is that the photochemical reaction may be reversible, meaning that the coumarin dimer resulting from photodimerization can be converted back to two monomeric coumarin moieties when the dimer absorbs UV light at shorter wavelengths. This was investigated with a spray-coated layer. Indeed, as shown in Fig. 2(d), when a photoalignment layer, prepared by LPUV irradiation, was exposed to unpolarized 254 nm UV irradiation, the absorption of monomeric coumarin groups at around 320 nm increased significantly, reaching the photostationary state after 4 min of irradiation. From the spectral change, it is estimated that about 60% of coumarin dimers are de-dimerized. Infrared spectra of a 3CouHB photoalignment layer exposed to unpolarized 254 nm UV light (Fig. S4(c), ESI[†]) show little change with short irradiation time (up to about 8 min), indicating the absence of any significant photodamage of the surface layer under the used conditions. The fluorescence emission spectra of the photoalignment layer upon LPUV irradiation and subsequent 254 nm UV light irradiation (Fig. S4(d) and (e), ESI[†]) are also consistent with the LPUV-induced dimerization and the 254 nm UV-induced de-dimerization of the chromophores. As demonstrated below, this reversible dimerization can be explored for programming or altering the photoalignment layer.

The ability to induce LC alignment of the surface photoalignment layer made with the sprayable coumarin-containing compound 3CouHB on a flat surface was first investigated using a cell with a 5 μ m gap and two inner surfaces coated with photoalignment layers. The testing cell fabrication is schematically shown in Fig. 3(a). The cell is assembled with two glass (or quartz) plates whose inner surfaces are spray-coated with a photoalignment layer, and it is filled with a room-temperature nematic LC, 4-cyano-4'-pentylbiphenyl (5CB), doped with 0.4 wt% of a dichroic dye (disperse red 1). The LC alignment direction and degree can be determined by measuring the polarized absorption of the dichroic dye. The order parameter of the dye reflects the order parameter of the LC molecules. This push-pull azo dye in the stable *trans* form aligns with LC molecules and displays an absorption band near 500 nm that is not overlapped with the absorption of coumarin groups, allowing the measurement of the order parameter. Polarized absorption spectra were recorded by varying the angle (θ) between the polarization direction of the spectrophotometer's beam and the reference direction taken as the polarization direction of the LPUV used to prepare the surface photoalignment layer. Fig. 3(b) shows the absorbance of the azo dye at 500 nm plotted as a function of the angle θ (complete rotation of 360°) for two LC cells with surface photoalignment layers prepared using spray-coating and spin-coating under the same conditions (8 mW cm⁻², 20 min irradiation time). As the



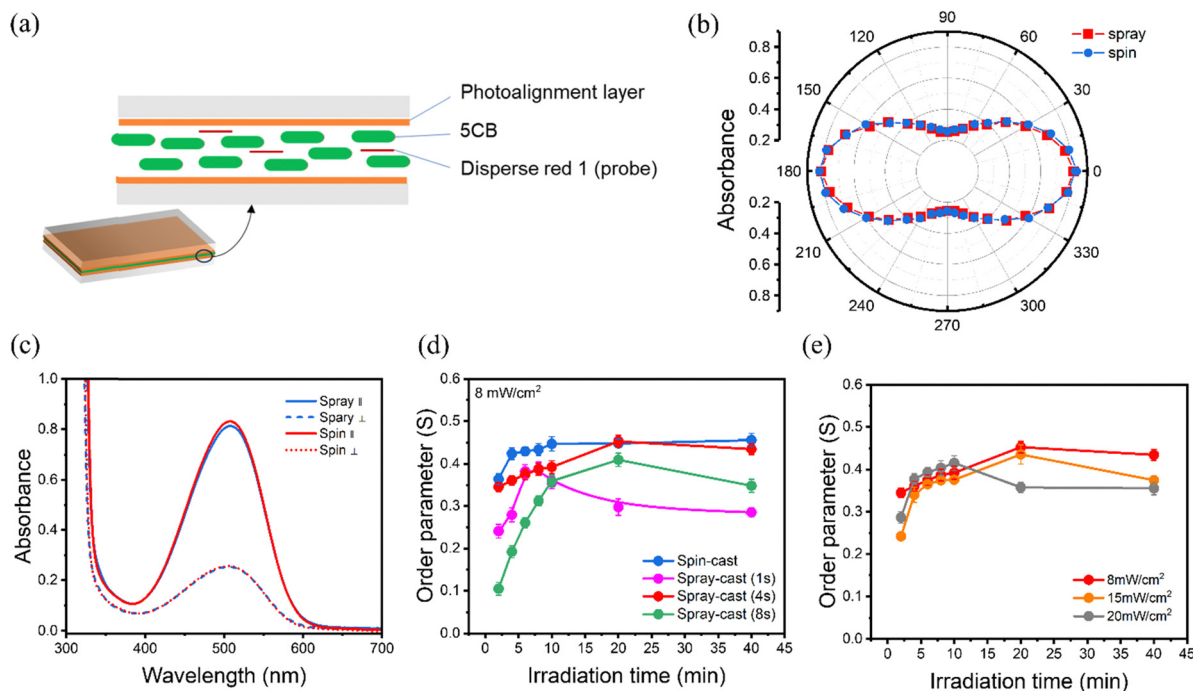


Fig. 3 (a) Schematic illustration of a cell fabricated using spray-coated or spin-coated photoalignment layers and filled with a nematic liquid crystal (5CB) doped with a dichroic azo dye (disperse red 1) for probing liquid crystal orientation. (b) Polar plots of the dye absorption at 500 nm of the cells prepared with spray-coated and spin-coated coumarin photoalignment layers (LPUV irradiation for 20 min), indicating the alignment of liquid crystal molecules along the polarization direction of LPUV. (c) Polarized UV-Vis spectra of cells prepared with spray-coated and spin-coated photoalignment layers, with the spectrophotometer's light beam polarized parallel and perpendicular, respectively, to the reference direction (polarization direction of LPUV used for preparing the photoalignment layer). (d) Plot of order parameter (S) of the dichroic probe dye vs. LPUV irradiation time (light intensity: 8 mW cm^{-2}) for spray-coated surface alignment layers using different 3CouHB solution spray times. (e) Plot of order parameter vs. LPUV irradiation time for the spray-coated surface alignment layer (4 s spray time) exposed to LPUV of different intensities.

electronic transition moment of azo dye is parallel to the long molecular axis, the parallel dichroism indicates the alignment of 5CB molecules along the reference direction. It is seen that the two polar diagrams almost completely coincide, indicating that the spray-coated photoalignment layer has basically the same power to induce LC alignment as the spin-coated layer. The same can be noticed from the example of orthogonally polarized UV-Vis spectra taken at $\theta = 0^\circ$ (A_0) and at $\theta = 90^\circ$ (A_{90}) for the two cells (Fig. 3(c)).

To further assess the spray-coated photoalignment layers, the effect of their preparation conditions was investigated using the order parameter measured from polarized absorption spectra through $S = (A_0/A_{90} - 1)/(A_0/A_{90} + 2)$. First of all, the spray-coating conditions were varied to reveal the effect on the LC alignment ability of the photoalignment layer. Of the parameters that can be varied in preparing spray-coated photoalignment layers, three are obvious: the solution spray time which determines the layer thickness, the surface roughness, and the LPUV light intensity and irradiation time which determine the coumarin photodimerization degree and thus the surface anisotropy as well as the crosslinking density of the resulting surface polymer. Fig. 3(d) plots the change in the order parameter as a function of the LPUV irradiation time (8 mW cm^{-2}) for three spray-coated layers obtained with different solution spray times (1, 4 and 8 seconds) and for a spin-coated layer (in all cases, the coating solution has 0.3 wt% of the coumarin-

containing compound and the LPUV intensity is 8 mW cm^{-2}). The results show that both the UV light irradiation time and the used solution spray time affect the induced LC orientation. Although all the photoalignment layers display a similar ability to induce LC alignment with a maximum order parameter S between 0.35 and 0.45, an LPUV irradiation time of 10–20 min and a solution spray time of about 4 seconds seems to be the most suitable for the photoalignment layer. As for the effect of LPUV light intensity, Fig. 3(e) shows the plots of order parameter vs. light irradiation time for three spray-coated photoalignment layers prepared using different light intensity. Similar results are noticeable, implying the little effect of LPUV intensity within the intensity range used. In all cases (Fig. 3(d) and (e)), the order parameter increases with increasing the LPUV irradiation time (up to about 10 min) before reaching an apparent plateau at longer times. This can be understood through the angular selective photodimerization of coumarin groups. When LPUV is applied, the photodimerization occurs among the coumarin groups with the electronic transition moment parallel to the light electric field vector, while unreacted coumarin groups are dominant in number. As irradiation time increases, the amount of coumarin dimers increases, Both the unreacted coumarin groups and dimers contribute to the surface anisotropy responsible for LC alignment induction. For longer irradiation times over 20 min, a weaker light intensity of 8 mW cm^{-2} gives rise to higher order parameter, probably because the weak light intensity is beneficial



for the angular selective photodimerization of coumarin groups, while high light intensity may increase the possibility of excitation of coumarin groups whose electronic transition moment is not parallel to the light electric field vector and thus contributes less to inducing LC alignment. For all the cells prepared through the spray-coating method, an 8 min irradiation seems to be sufficient to obtain a significant LC alignment with an order parameter of around 0.4. Finally, electro-optical measurements were conducted using a 5CB cell made with spray-coated 3CouHB photoalignment layers (LPUV: 8 mW cm^{-2} , 20 min). The results (Fig. S5, ESI†) are similar to LC cells prepared using photoalignment layers of a coumarin-containing random copolymer in our previous study.²⁸ The cell displayed a planar LC alignment with a pre-tilt angle of about 1° , and the threshold voltage and stability of the electro-optical switching over tens of cycles indicate a sufficient anchoring energy of the LC cell with the 3CouHB photoalignment layers. All of these tests indicate that the spray-coating method provides an effective way to prepare the photoalignment surface layers for LC cells.

The ability to adjust or rewrite a photoalignment surface layer prepared using spray-coating is a useful feature and may be explored in applications. This possibility was investigated using 3CouHB, through the experiment illustrated in Fig. 4. On the left side, the first LC cell (cell i) was assembled with two quartz plates spray-coated with a photoalignment layer (8 mW cm^{-2} LPUV light and 20 min irradiation) and filled with 5CB and the alignment probing dichroic dye. By taking the LPUV polarization direction as the reference direction, the recorded polarized UV-Vis absorption spectra of the cell indicate the alignment of 5CB molecules along the reference direction with an order parameter of about 0.43. In the middle, a second

cell (cell ii) was assembled after the initial photoalignment layer (used for cell i) and was exposed to unpolarized 254 nm UV light (30 mW cm^{-2} , 8 min) for the de-dimerization of coumarin dimers. The corresponding polarized absorption spectra of the cell indicate a much smaller order parameter of about 0.15 for the alignment of 5CB molecules. This observation shows that the 254 nm UV light irradiation can erase, although not completely, the surface anisotropy of the photoalignment layer previously inscribed by LPUV. The last cell on the right side (cell iii) was assembled after the de-dimerized photoalignment layer (used in cell ii) was treated again with LPUV light (8 mW cm^{-2} , 20 min) while rotating the polarization direction by 90° . This cell can induce alignment of 5CB molecules along the new polarization direction of the LPUV light, *i.e.*, perpendicular to the reference direction, with an order parameter of about 0.31. The recovery of the LC alignment ability results from the re-dimerization of coumarin groups. This experiment demonstrates that the revisable dimerization of coumarin groups using UV light at different wavelengths allows the spray-coated photoalignment layer to be reprogrammed. That is, through alternating exposures of the photoalignment layer to LPUV (longer wavelengths for coumarin dimerization and inducing LC alignment) and unpolarized UV (shorter wavelengths for de-dimerization and randomizing LC molecules), it is possible to control or pattern the LC alignment in terms of both degree and direction.

Finally, the spray-coating method was applied to the curved surface and the resulting photoalignment layer was characterized. Fig. 5(a) depicts a test cell fabricated with two curved quartz plates. Before assembly, the 3CouHB solution was spray-coated on the concave side of one quartz plate and on the convex side of the other quartz plate to obtain the photoalignment layers

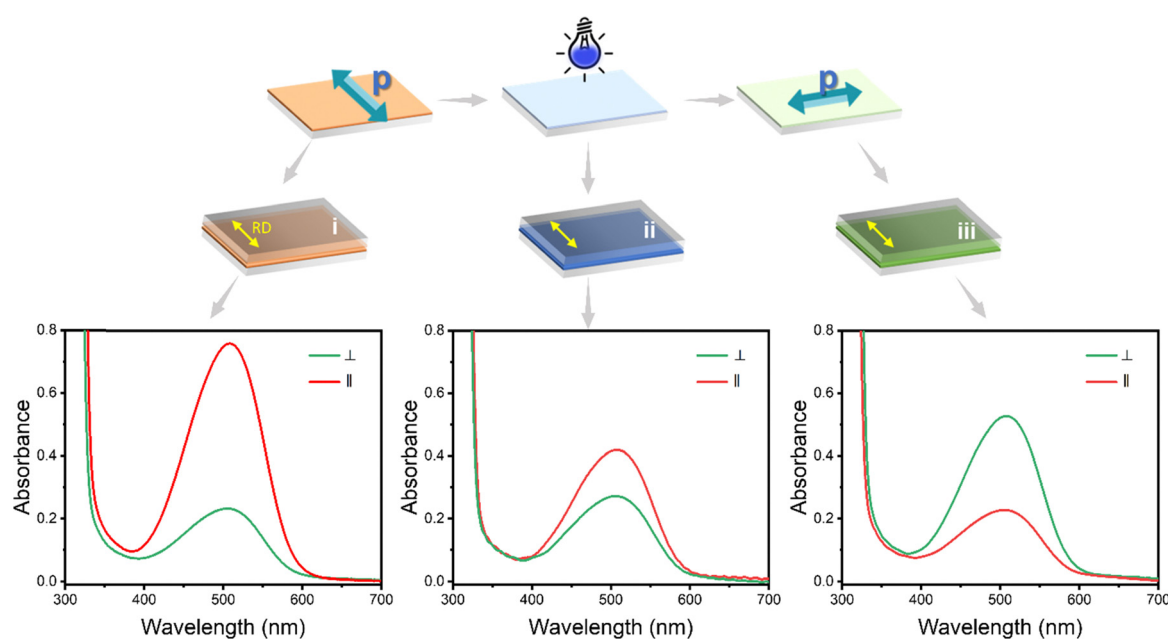


Fig. 4 Schematic illustration of rewriting the photoalignment layers in LC cells through de-dimerization of coumarin dimers and re-dimerization of coumarin groups. The changing degree and direction of LC alignment are shown by the polarized UV-Vis absorption spectra of the respective cells (i, ii, iii), either parallel or perpendicular to the marked reference direction (RD).



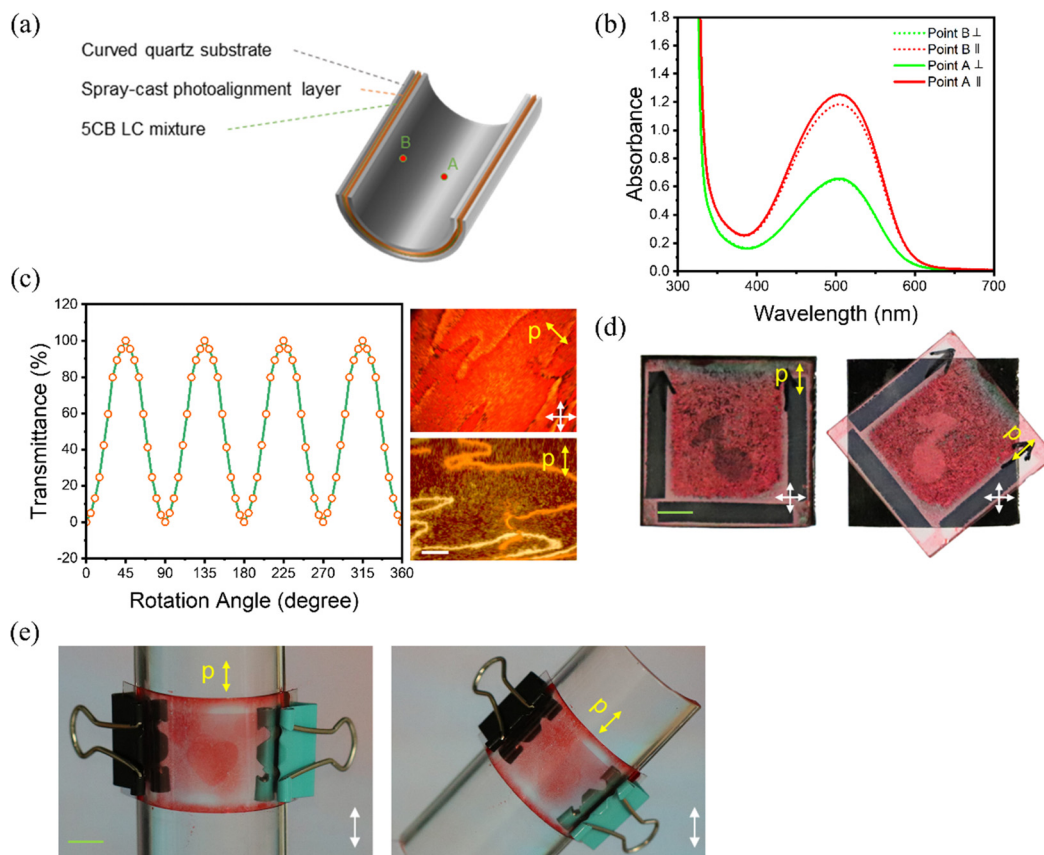


Fig. 5 (a) Schematic illustration of a curved cell fabricated using spray-coated photoalignment layers and filled with nematic liquid crystal 5CB containing a dichroic dye (Disperse red 1). Two small areas at the valley and on the wall, marked A and B respectively, are taken for recording polarized absorption spectra. (b) Polarized UV-Vis spectra of areas A and B on the curved cell indicating the same alignment of 5CB molecules (the reference direction is the polarization direction of the LPUV used to prepare the photoalignment layer). (c) POM images (scale bar: 100 μm) of the point A on the curved cell, with the LPUV polarization direction marked by a yellow arrow and the crossed polarizers marked by white arrows. The corresponding plot of transmitted light intensity vs. angle between crossed polars and LPUV polarization is also shown. (d) Photographs under crossed polarizers of a flat cell (scale bar: 0.5 cm) with patterned photoalignment layers forming a musical note, which is prepared by spraying a 3CouHB solution through a mask. The yellow arrow indicates the LPUV polarization direction, and the white arrows show the crossed polarizers. (e) Photographs under one polarizer of a curved cell (scale bar: 0.25 cm) with patterned photoalignment layers forming an image of heart, which is prepared by spraying a 3CouHB solution through a mask. The yellow and white arrows indicate the polarization directions of LPUV and the polarizer respectively.

through LPUV irradiation; the two quartz plates were then assembled with their respective photoalignment layer as the inner surface, and the cell was filled with azo dye-doped 5CB. Fig. 5(b) shows the polarized UV-Vis absorption spectra of two areas in the curved cell, at the valley and on the wall, marked as A and B, respectively, in Fig. 5(a). It can be seen that the two areas have a similar alignment of 5CB molecules (order parameter of 0.24 for point A and 0.23 for point B). The curved cell was examined using a polarizing optical microscope (POM). Fig. 5(c) shows the normalized periodic light transmission at point A by varying the angle between the crossed polars and the polarization of LPUV light used to prepare the photoalignment layers, as well as POM images showing the lowest light transmission when the LPUV polarization aligns with one of the polarizers and the highest light transmission when the LPUV polarization makes an angle of 45° to the crossed polarizers. These observations indicate a unidirectional orientation of the 5CB molecules. Similar results were obtained with another curved cell built with a bottom, bent quartz plate spray-coated with

a photoalignment layer and an upper flexible plastic film containing no photoalignment layer. POM images indicate the alignment of 5CB molecules (Fig. S6(c), ESI[†]).

It is worth mentioning that the order parameter calculated from the polarized absorption spectra in Fig. 5(b) is significantly smaller than that achieved with a flat cell using spray-coated photoalignment layers prepared under the same conditions. This decrease would correspond to a reduced surface anisotropy of coumarin groups on the curved surface after LPUV light irradiation. The reason for the apparent decrease in induced LC alignment may be twofold. On the one hand, when LPUV light is applied to a curved surface to prepare the photoalignment layer, the electric field vector of the light may make angles to the electronic transition moments of coumarin groups on the surface due to the curvature, which reduces the angular selective photodimerization of coumarin groups and thus the surface anisotropy. On the other hand, when measuring the LC alignment by recording polarized UV-Vis absorption spectra, the polarization of



the measuring beam can also make angles with the electronic transition moment of the dichroic dye molecule due to curvature, which introduces errors in the spectroscopic measurements. At this point, we do not have the necessary facilities to resolve this issue, which will be addressed in future studies.

An important benefit of using photoalignment layers over mechanically rubbed alignment layers is the ease of creating patterns or organizing the alignment surface layer in spatially selected regions. To demonstrate this feature with spray-coating, as shown in Fig. 5(d) and (e), the spray-coating can be applied through a mask so that only the open areas are coated with the photoalignment layer and can align LC molecules. Both flat and curved cells were used. For the flat cell, as shown in Fig. 5(d), when the polarization direction of the LPUV light used to prepare the spray-patterned surface layer is parallel to one of the crossed polarizers, the spray-coating area (an image of musical note) appears dark, indicating unidirectional LC alignment in this region, in contrast to the birefringent and colorful surrounding where no photoalignment layer was spray-coated to align the LC molecules. The contrast between the sprayed and non-sprayed parts is much reduced after 45° rotation of the cell, as the entire cell becomes birefringent. In the case of the curved cell, the curved, spray-coated area (an image of heart) cannot be clearly viewed under crossed polarizers. Nevertheless, linearly polarized light obtained with one polarizer can reveal the image formed by aligned LC molecules. As shown in Fig. 5(e), when the polarization of LPUV is parallel to the polarization of the white background light, the image of the spray-coated area is visible appearing dark, while the image is blurred after rotation of the cell. The contrast change is likely caused by different absorption of the visible light by azo dye molecules in the spray-coated area (aligned with LC molecules) and non-spray-coated area (no alignment).

4. Conclusions

We have synthesized and investigated a novel kind of H-bonding coumarin-containing compound, 3CouHB, which can be spray-coated on flat and curved surfaces for the preparation of photoalignment layer used to induce LC alignment. A reduced solution viscosity of the low-molar-weight coumarin-containing compound compared to coumarin polymer facilitates spray coating and, once on a substrate surface, the multiple intermolecular H-bonds allow for fast solidification of the surface layer and its retention on the curved surface. When exposed to LPUV light, the angular selective dimerization of coumarin groups occurs, resulting not only in the surface anisotropy required for inducing alignment of LC molecules but also in converting the supramolecular H-bonded layer into stable, covalently crosslinked polymer film. The spray-coated photoalignment layer was found to effectively align nematic liquid crystal molecules along the polarization direction of the LPUV used to prepare the photoalignment layer, achieving an order parameter of about 0.45. Moreover, by exploring the reversibility of the photochemical reaction of coumarin, we showed that de-dimerization of coumarin dimers under 254 nm UV light

irradiation could erase, although not completely, the surface anisotropy and thus the ability to induce LC alignment, whereas a subsequent re-dimerization using longer wavelength UV light could restore the function of the photoalignment layer and align LC molecules in a different direction by changing the polarization of LPUV during the re-dimerization exposure. This feature enables rewriting or reprogramming of the photoalignment layer, which has the potential to pattern the induced LC alignment to varying degrees and directions. Most importantly, the possibility of using the sprayable coumarin-containing compound on a curved surface was demonstrated. Curved cells made with two curved quartz plates with parallel spray-coated photoalignment layers were assembled and found to be able to align LC molecules. The approach of using sprayable low-molecular-weight H-bonding coumarin-containing compounds to prepare photoalignment layer on a curved surface is original and provides a possible means to address the issue of making surface alignment layers in LC cells with curved surfaces or complex geometries.

Author contributions

All authors contributed to the scientific discussion and manuscript preparation. Xinshi Chen: conceptualization, methodology, data curation, formal analysis, investigation, validation, visualization and writing – original draft. Yue Zhao: conceptualization, resources, project administration, supervision, funding acquisition and writing – review & editing.

Data availability

The available data are reported in the main article and in the ESI.†

Conflicts of interest

There are no conflicts to declare.

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