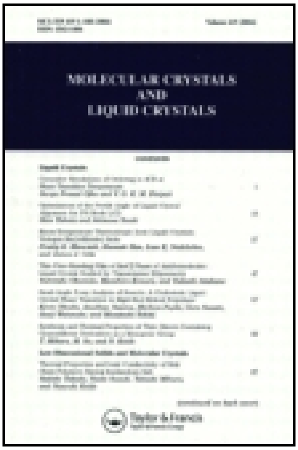

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Photocontrollability of Liquid Crystal Alignment by a Self-Assembled Monolayer Formed from Azobenzene-Containing Tetracation Through Coulombic Interactions

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Photocontrollability of Liquid Crystal Alignment by a Self- Assembled Monolayer Formed from Azobenzene-Containing Tetracation Through Coulombic Interactions

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This paper describes an environmentally benign process to fabricate a photoaligning monolayer for surface-assisted liquid crystal photoalignment by the surface adsorption of an azobenzene-containing tetracationic adsorbate from its dilute aqueous solution through electrostatic interactions. The resulting adsorbed monolayer on a silica plate irradiated with linearly polarized 436 nm light was applicable to azimuthal LC photoalignment.

Keywords: azobenzene; monolayer; command surface; macrocycle; electrostatic assembly; liquid crystal

INTRODUCTION

Surface-assisted regulation of nematic liquid crystal (LC) alignment using photochemical reactions at an outmost organic layer on a substrate surface has been attracting current interest from practical viewpoints because of its versatile practical applicability.[1] The surface-assisted photoaligning layer has been addressed as a command surface since our first observation that the photoinduced reversible alteration of LC alignment is triggered by the photoisomerization of azobenzene molecules covalently bound on a silica surface.[2] We have so far achieved the photocontrol of azimuthal and pretilt angles of LC molecules by irradiation with linearly polarized light and slantwise nonpolarized light.[1]

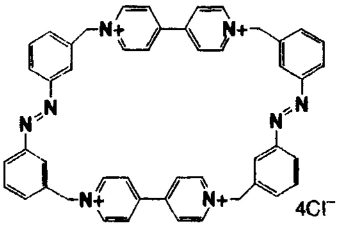

FIGURE 1 Chemical structure of 1.

In a practical viewpoint, convenient preparative ways to perform the photoregulation of LC alignment are highly required so that we have demonstrated the methodology to fabricate the photoaligning layers by means of spin-coating of polymer films[1] and chemical modification of substrate surfaces with photoactive molecules through covalent bonds of silanization[1, 2] and hydrogen bonds.[1, 3, 4] Moreover, the preparative ways had better to be carried out in aqueous systems from an environmental standpoint. We here report on a novel environmentally benign process to fabricate an adsorbed monolayer of photoresponsive tetracation 1 on a silica surface applicable to surface-assisted LC alignment.

EXPERIMENTAL

Materials

The tetracation 1 was obtained as water-soluble chloride salt after an ion-exchange reaction of cyclobis(paraquat-3,3'-azobenzene) hexafluorophosphate[5] with tetraethylammonium chloride in dry acetone. ^{1}H NMR (270 MHz, D_2O): δ 6.03 (8H, s), 7.74 (4H, t, J 7.8 Hz), 7.86-7.90 (8H, m), 7.99 (4H, d, J 7.8), 8.47 (4H, d, J 6.8), 9.20 (4H, d, J 6.8). Anal. Found: C, 66.10; H, 4.60; N, 12.73. Calcd. for $C_{48}H_{40}N_8Cl_4$: C, 66.21; H, 4.60; N. 12.87.

A typical procedure to prepare a monolayer of 1 adsorbed on a silica plate is as following. A fused silica plate cleaned with an alkaline solution of KOH/EtOH was immersed in an aqueous solution of 10^{-4} mol dm^{-3} 1 at 60 °C for 1 h. The silica plate was washed with deionized water thoroughly and dried at 100 °C for 30 min.

A vacant LC cell was fabricated with a lecithin-treated silica plate and a silica plate adsorbing **1** after irradiation with linearly polarized visible light at 436 nm. The plates were separated by two strips of PET spacers of 25 μm in thickness. To the vacant cell, 3 wt% dye-doped nematic LC of NPC-02 (T_{NI} = 35.0 °C; Rodic Co. Ltd.) was injected by a capillary action to give a dye-doped hybrid type LC cell.

Physical measurements and photoirradiation

Absorption spectra were taken on a weak absorption spectrophotometer (MAC-1, JASCO). Linearly polarized 436 nm light (LPL) was obtained by passing light from a 500-W ultra-high pressure mercury arc (Ushio) through suitable glass filters (Toshiba) and a polarizer. Optical textures of the LC cell were observed with a polarized optical microscope (BH-2, Olympus). The direction of LC alignment was determined by measuring the light intensity of a polarized He-Ne laser beam passed through the dye-doped LC cell and a crossed polarizer as a function of the rotational angle of the cell. The detailed experimental optical axis was reported in our previous paper.[1,4]

RESULTS AND DISCUSSION

Molecular design and monolayer fabrication

The tetracationic adsorbate **1** (FIG. 1) was designed as following reasons. First, since **1** possesses four cationic sites, it is anticipated that **1** readily adsorbs on a negatively charged silica surface through electrostatic interactions in a manner similar to the layer-by-layer deposition of polyelectrolytes.[6] Second, a symmetrical chemical structure of **1** probably brings about the formation of an adsorbed monolayer of **1** in a flat-laid manner so that photoresponsive azobenzene units orienting in parallel with the substrate plane are suitable for azimuthal LC alignment. Thirdly, a molecular cavity originated from paraquat spacers probably guarantees a volume for photoisomerization of azobenzene units even in monolayers.

A silica plate adsorbing **1** was prepared by the immersion of a cleaned silica plate in an aqueous solution of **1**, to be subjected to UV-Vis spectral measurements to monitor adsorption behavior of **1** on a silica plate. The immersion for approximately 30 min gave steady states for each adsorption case even under different temperatures of adsorbate solutions. It was found that the highest adsorption of **1** is achieved by the immersion over 60 °C. UV-Vis spectra of a silica plate adsorbing **1** prepared at 60 °C for 1 h showed an absorption maximum (λ_{max}) at 318 nm arising from the azobenzene units with an absorbance of 0.0080 ± 0.0005. An occupied area of **1** on a silica plate was estimated to be 2.5 nm^2 from the absorbance under the assumption that the absorption coefficient of the chromophore on a silica plate is 1.5 times larger than that in an aqueous solution (ε_{318} = 40000) due to its flat-laid conformation on a silica surface. The flat-laid conformation of the chromophore is unequivocally confirmed by dichroic absorption spectra as shown in FIG. 2. When probing light was incident on the substrate plane at an angle of 45°, *s*-polarized light was more strongly adsorbed than *p*-polarized one. The oblique transmittion ratio ($\Delta Ts/\Delta Tp$)[7] of 1.5 and the estimation of an occupied area of **1** by a CPK model indicate that **1** formed a densely packed self-

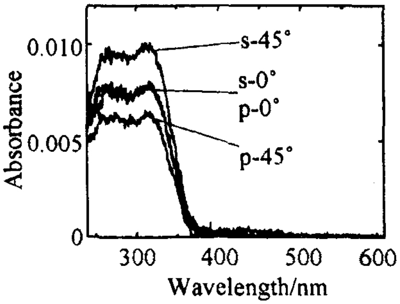

FIGURE 2 Dichroic absorption spectra of a silica plate adsorbing **1** measured by s, p-polarized light.

assembled monolayer through coulombic interactions in which the azobenzene and paraquat units of **1** orient in parallel with the substrate plane.

Polarization photochemistry and LC alignment

A silica plate adsorbing **1** was irradiated with linearly polarized 436 nm light (LPL) and subjected to polarized absorption spectral measurements to reveal the photogeneration of dichroism. Dichroic ratio was defined as $(A_{\perp}-A_{//})/(A_{\perp}+A_{//})$, where $A_{\perp}$ and $A_{//}$ stand for absorbances at 318 nm perpendicular to and in parallel with an electronic vector of the actinic LPL. It was found that the dichroic ratio is leveled off after exposure to the LPL of 400 mJ cm^{-2} to become a constant value of 0.028, indicating that *E*-isomer of the azobenzene of **1** orients perpendicularly to the actinic light.[1]

A dye-doped hybrid type LC cell fabricated with a silica plate adsorbing **1** at 60 °C for 1 h, followed by LPL irradiation at 436 nm of 1.0 J cm^{-2} exhibited homogeneous alignment with high optical quality. The direction of LC alignment determined by monitoring the orientational direction of the guest dye was perpendicular to the electric vector of the LPL as shown in FIG. 3. Thus, LC molecules recognize the orientational direction of azobenzene moieties of **1** on a silica plate induced by the LPL irradiation.[1] To investigate optical resolution of LC alignment

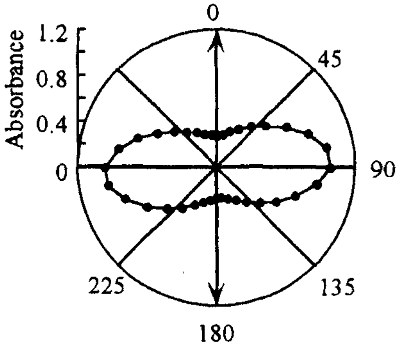

FIGURE 3 Polar diagram of a dye-doped LC cell monitored with a He-Ne laser beam.

by the self-assembled monolayer of **1**, a patterned LC cell was fabricated by photoirradiation of a whole area of a silica plate adsorbing **1** with the LPL at an 1.0 J cm^{-2} exposure energy, followed by the LPL irradiation through a photomask at a rotated optical axis of 45° and cell assembly. A polarized optical microscope image of the LC cell indicates that the self-assembled monolayer possesses the controllability of nematic LC alignment with an optical resolution of 8 μm.

CONCLUSION

We demonstrated a novel strategy to fabricate adsorbed monolayers applicable for the preparation of LC photoaligning films by using photoresponsive tetracationic adsorbate **1**. From its dilute solution, **1** formed a densely packed self-assembled monolayer through coulombic interactions. Linearly polarized visible light irradiation of a silica plate adsorbing **1** generated dichroism of the monolayer to result in azimuthally controlled nematic LC alignment. This environmentally benign process to fabricate photoaligning films is anticipated to play an important role in a practical viewpoint.

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