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Highly Dichroic Bisazomethine Dye Films on Friction-transferred Poly(tetrafluoroethylene) Layers

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Highly anisotropic thin molecular films have been successfully prepared by depositing a bisazomethine dye under vacuum through evaporation on friction-transferred (FT) poly(tetrafluoroethylene) (PTFE) layers. The layers induce the high orientational degrees showing high dichroic ratios over 20 in their polarized UV–visible absorption spectra. Moreover, by modifying FT layers with the further PTFE evaporated and rubbing, the ratios are improved to remarkable values up to 44.

Highly dichroic materials are favorable for possible applications of π-conjugated molecules to optoelectronics or to photonics. The uniaxial orientation of the molecules provides the efficient interaction between their π electrons and polarized light such as lasers. The degree of polarization dependence, which is usually expressed by the dichroic ratio ($\boldsymbol{D}$) in polarized absorption, indicates such efficiency well. Hence, a large $\boldsymbol{D}$ value should be favorable for many applications such as polarizers,[1] fluorescent polarizers,[2] guest–host liquid crystal displays,[3] polarized light-emitting diodes,[4] optical recording,[5] and organic lasers.[6] Furthermore, slight increase of the interaction from a moderate degree to a high degree often brings about a drastic change particularly in nonlinear optical applications.[7,8] Highly dichroic materials, therefore, are needed in these important fields.

We have demonstrated here remarkable $\boldsymbol{D}$ values of the films of a bisazomethine dye **1** (Chart 1) on friction-transferred (FT) poly(tetrafluoroethylene) (PTFE) layers. The oriented growth on aligned PTFE layers[9] is a promising process for preparation of highly dichroic films. An oligo(*p*-phenylenevinylene) shows a $\boldsymbol{D}$ value of 15 for its deposited film on aligned PTFE.[10] A polydiacetylene derivative also shows a $\boldsymbol{D}$ value up to 50 for film obtained by polymerization with UV light from the deposited film of its monomers on aligned PTFE.[8] Furthermore, some authors reported remarkable $\boldsymbol{D}$ values up to 130 for the films of linear bisazo dye on layers.[11] Such high ratios have been uncommon for other processes for thin molecular films, thus showing high potential for preparing high $\boldsymbol{D}$ films.

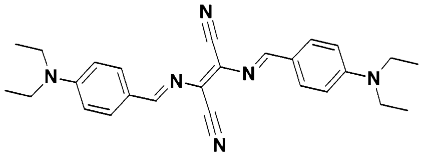

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Chart 1.

Aligned thin PTFE layers were deposited on substrates by FT and/or evaporation. Slide glasses were used as the substrates. FT layers were deposited on them with a DACA Instrument TRIBOTRACK ultrathin PTFE film coater: substrates were rubbed at a pressure of about 5 kg cm^{-2} with the curved surface of a PTFE rod ($\phi = 10$ mm, length $= 20$ mm) sliding in a direction at a constant speed of 1 mm s^{-1} at 300 °C.[12] Layers of another kind were deposited on the substrates by evaporation and rubbing (ER); a PTFE film (50 nm thick) was deposited on substrates under vacuum by evaporating PTFE (molecular weight: 5000–20000, purchased from Wako Pure Chemical Co., Ltd.), and after that the film was rubbed at a pressure of about 5 kg cm^{-2} with a cloth sliding in a direction at a constant speed of 5 mm s^{-1}.[11] Some of the FT layers were modified with evaporated PTFE [evaporation and FT (EFT)]: a PTFE film (20 nm thick) was deposited on FT layers by evaporating the PTFE. Some of the EFT layers were also rubbed in the same manner for ER [evaporation, rubbing, and FT (ERFT)].

Then the oriented thin films of **1** were deposited on these aligned PTFE layers by evaporating it in a vacuum at a pressure of about 10^{-5} Torr with a growth rate of 0.1–0.2 nm s^{-1}. The dye was synthesized by the procedure reported.[13]

The polarized UV–visible absorption spectra of the dye films were recorded on a Cary 5E UV–visible–NIR spectrophotometer equipped with a highly efficient Glan-Thompson polarizer before the sample on the optical path. The spectra were obtained at normal incidence in the transmission mode separately for polarization both parallel and perpendicular to the sliding direction. The reference spectrum taken with an aligned PTFE layer on a substrate for each polarization was subtracted from each sample spectrum during data processing.

The polarized spectra reveal that the long axes of dye molecules are highly oriented in the direction parallel to the aligned PTFE chains of FT, EFT, ERFT, or ER layers. The absorbance of each dye film at the peak wavelength ($\lambda_{\max}$) is maximized for the polarization direction exactly parallel to the sliding direction at FT and/or at rubbing, as typical spectra are shown in Figure 1. We have confirmed that the moment of their main electronic transition is nearly parallel to their long axes by calculating the molecular orbitals (MOPAC 2002 with PM5 Hamiltonian).[14] Hence, the mean direction of the long axes agree with those of the PTFE chains, which are parallel to the sliding directions at FT or at rubbing.[9,11,12]

The peaks about 620 nm come from J aggregates grown in the films because they are identical with those in its isotropic films vacuum-deposited on glass without PTFE layers.[15] Some authors demonstrated by electroabsorption that the peaks are due

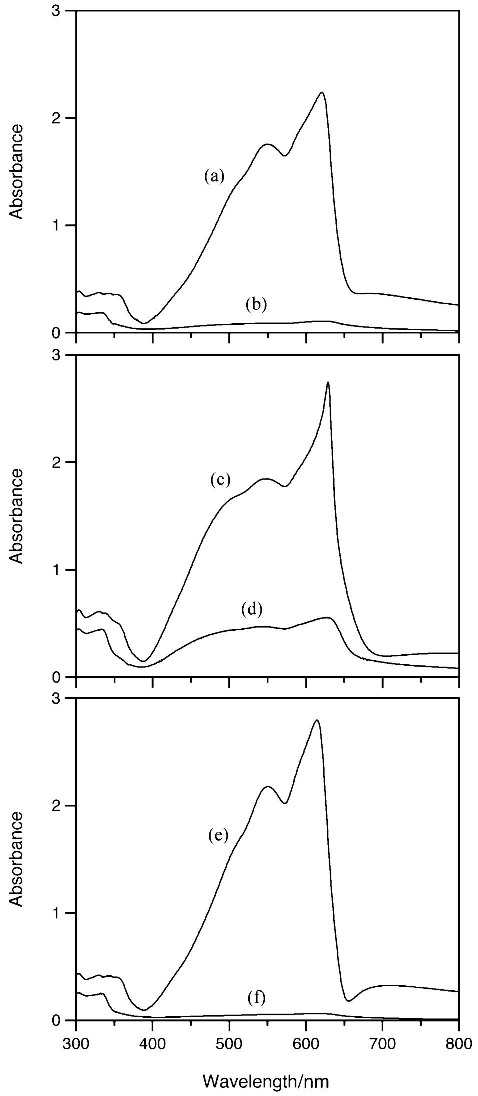

Figure 1. Polarized absorption spectra of the dye **1** oriented film (55 nm of thickness): (a) and (b) on a FT layer; (c) and (d) on an EFT layer; and (e) and (f) on an ERFT layer with the further PTFE rubbed six times. The light polarization is parallel to the aligned PTFE chains in (a), (c), and (e), while it is perpendicular to the chains in (b), (d) and (f).

to Frenkel exitons, thereby showing that they clearly come from the aggregates.[15] In particular, an EFT layer promotes J-aggregate growth well in spite of a lower ***D***. Figure 1c shows a sharp peak having a $\lambda_{\max}$ of 629 nm, which is larger than that from other layers (620 nm: FT, ERFT, and ER) and is close to that from their isotropic film. The growth and structure of these oriented J aggregates have been studied elsewhere.[16]

The degree of the uniaxial orientation can be estimated from the polarized spectra. The ***D*** of the dye films is calculated for a peak in polarized spectra as

$$\boldsymbol{D} = \mathbf{A}_{//}/\mathbf{A}_{+} \qquad (1)$$

where $\mathbf{A}_{//}$ and $\mathbf{A}_{+}$ are the absorbance with the light polarization parallel to the sliding direction and perpendicular to that, respectively.

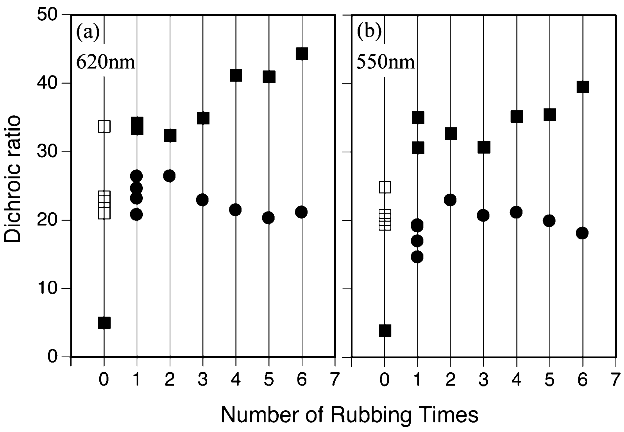

Figure 2. Rubbing times vs. dichroic ratio ***D*** of the dye **1** oriented film (55 nm of thickness): (a) from the peak at ca. 620 nm for J aggregates; (b) from the peak at ca. 550 nm for polycrystals; □: on FT layers; ■: on EFT or ERFT layers; and ●: on ER layers.

The rubbing times for ERFT layers then increase ***D*** values significantly to reaching 44 (Figures 1e, 1f, and 2).

The dye orientation is not driven by graphoepitaxial effects, where grating-shaped mesoscopic topography accounts for it. A few reports argued that the oriented growth of a polysilane[17] or 1,4-bis(5-phenyloxazol-2-yl)benzene[18] on FT PTFE should arise from its mesoscopic linear ridges aligned. However, the ridges of ER layers are bumpy and not as linear as those of FT layers: their AFM images are shown in Figures 3a and 3b. They were recorded on a Seiko Instruments SPA-400 probe system equipped with a SiN cantilever employing its tapping mode in air at room temperature. Although the bumpy ER surfaces should not have a similar graphoepitaxial effect on FT surfaces, both layers induce similar ***D*** values. Therefore, some interaction under mesoscopic scale should account for the orientation.

One possibility is atomic groove effect. The ER and FT layers also induce remarkable orientation (***D*** up to 120) of some linear bisazo dyes.[11] Some authors have shown that they are oriented through an atomic groove effect on PTFE: a molecular dynamics simulation demonstrates that a shallow atomic groove is formed between two adjacent PTFE chains owing to their weak helix and that the grooves often trap linear bisazo molecules and orient them along the grooves.[19] However, we have to examine whether the atomic groove exactly can trap a **1** molecule because it has protrusions of two cyano groups at the center, which should repel the grooves by steric hindrance.

The mechanism for the significant ***D*** improvement by rubbing times on ERFT layers is not clear. Linear trenches covered with no PTFE are often observed in the AFM images of FT layers (Figure 3a). Molecules should not orient in the grains on the surface uncovered because the surface without PTFE does not induce the orientation. Corresponding grains in the trenches are clearly observed at an early stage of the deposition as shown in Figure 4. The evaporated PTFE in ERFT should cover somehow the trenches, thereby reducing the number of these grains. Probably such covering takes place and there would be some favorable interaction between FT layers and evaporated PTFE through the rubbing with cloth.

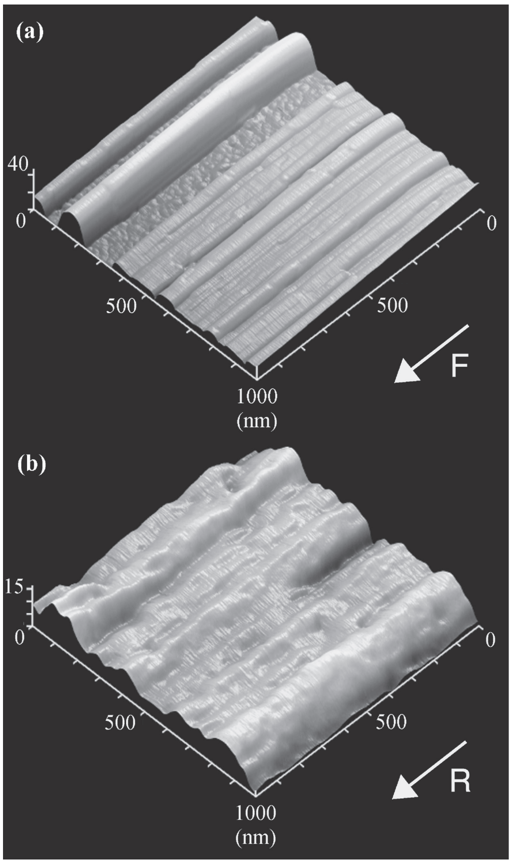

Figure 3. AFM 3D images of aligned PTFE layers: (a) a FT layer and (b) an ER layer. F and R indicate the sliding directions at FT and at rubbing, respectively.

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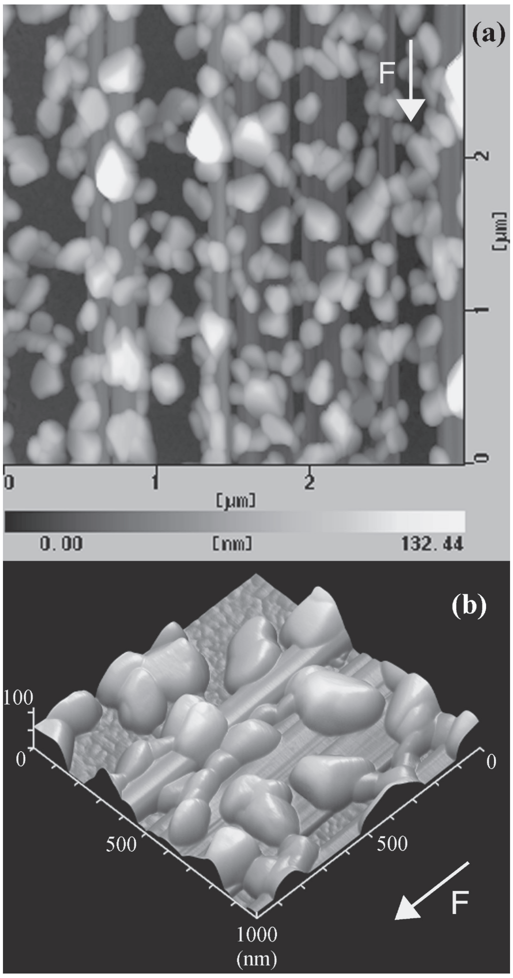

Figure 4. AFM images of the dye **1** oriented film (22 nm of average thickness) on a FT PTFE layer: (a) a 2D topographic image and (b) a 3D image. F indicates the sliding direction at FT.

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