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In-plane Orientation of Fluorescent Molecules in Friction-transferred Films

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Thin films of fluorescent molecules were prepared by friction-transfer and investigated by UV–vis absorption and PL measurements and TEM observation. Molecules with a long skeleton were aligned nearly horizontally and parallel to the friction direction in the film. Such in-plane orientation is advantageous in fabricating OLEDs with respect to light-outcoupling efficiency.

Considerable progress has been made in the field of organic light-emitting diodes (OLEDs) since the reports of Tang et al.[1–3] Organic thin films are essential for the fabrication of OLEDs. Vacuum deposition techniques are usually used to form thin films of small organic molecules such as phthalocyanine, perylene, pentacene, and *p*-sexiphenyl. Linear molecules tend to align normally in the film. For example, Adachi et al. reported that 1,3-bis[2-(2,2′-bipyridin-6-yl)-1,3,4-oxadiazo-5-yl]benzene (Bpy-OXD) molecules are horizontally oriented in vacuum-deposited films.[4–6] Numerical simulations show that the light-outcoupling efficiency of horizontally oriented molecules can increase by almost 50% compared to that of randomly oriented molecules.[7] Thus, it is very important to control the molecular orientation in order to realize improvements in light-emitting performance. One useful method for preparing orientation-controlled films is friction-transfer. To date, however, friction-transfer has not been applied to small organic molecules.

In this study, we focus on small fluorenes, which have attracted extensive attention as light-emitting materials for OLEDs. To determine the molecular alignment behavior in the friction-transferred films, we discuss the relationship between the molecular structure (sequence of fluorene units and substituents) and the molecular orientation. Furthermore, we demonstrate that nearly horizontal and uniaxial orientations of the fluorescent molecules can be easily achieved using the friction-transfer technique.

Five kinds of fluorenes, the molecular structures which are shown in Figure 1, were purchased from Exiton Inc. (USA): 9,9,9′,9′-tetrapropyl-2,2′-bifluorene (FO-1) is a fluorene dimer, 7,7′-bis(dodecyloxy)-9,9,9′,9′-tetrapropyl-2,2′-bifluorene (FO-2), 7,7′-diphenyl-9,9,9′,9′-tetrapropyl-2,2′-bifluorene (FO-3), and 7,7′-bis(4-methoxyphenyl)-9,9,9′,9′-tetrapropyl-2,2′-bifluorene (FO-4) are fluorene dimers with different end groups, and 7,7″-bis-(4-*tert*-butylphenyl)-9,9,9″,9″-tetraethyl-9′,9′-dipropyl-2,2′;7,2′-terfluorene (FO-5) is a fluorene trimer. Fluorene powders were compressed into pellets and were squeezed on glass and fused silica substrates. The friction-transfer process was carried out by squeezing and drawing the pellets on the substrates kept at 160 °C. The applied load for squeezing was 3 kgf cm^{-2}, and the drawing speed was 0.3 m min^{-1}.

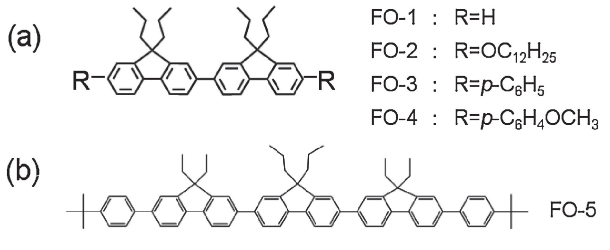

Figure 1. Molecular structures of fluorenes.

Ultraviolet–visible (UV–vis) absorption and photoluminescence (PL) spectra were recorded on Shimadzu UV-2200 and Hitachi F-2500 spectrometers, respectively. Figures 2a and 2b schematically depict the setup for polarized UV–vis and PL measurements, in which Glan–Thompson prisms were used. $A_{\parallel}$ (I_{ZZ}) and $A_{\perp}$ (I_{ZX}) are the absorption (PL) spectra parallel and perpendicular to the friction direction, respectively. The structure and morphology of the films were characterized by transmission electron microscopy (TEM, Hitachi H-7100).

Figures 2c and 2d show the polarized UV–vis absorption and PL spectra of the FO-1 and FO-4 friction-transferred films, respectively. For FO-1, the maximum absorption peak at 340 nm is attributed to the delocalized π–π* transitions of the fluorene backbone skeleton. The absorption profiles of $A_{\parallel}$ and $A_{\perp}$ are almost the same, and the dichroic absorption ratio (D_{abs}) calculated from the peak intensities at 340 nm is approximately 1.3. In the PL spectra, a strong emission intensity with a peak at 390 nm is observed, and the dichroic ratio is approximately 1.2 at the emission peak. Both dichroic ratios are close to one, indicating that FO-1 molecules are aligned randomly. On the other hand, the FO-4 film spectra show significantly different profiles between the polarization directions parallel and perpendicular to the friction direction. In $A_{\parallel}$, a maximum peak associated with the delocalized π–π* transition of fluorene molecules was observed at 360 nm. In $A_{\perp}$, however, the peak intensity was suppressed. D_{abs} is approximately 2.8 at 360 nm. Considering that the π–π* transition moments in fluorenes are almost parallel to the

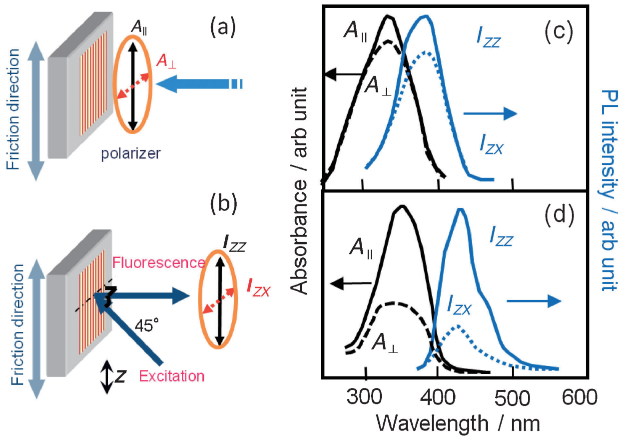

Figure 2. Scheme depicting the setup for polarized UV–vis (a) and PL (b) measurements. Absorption and PL spectra of FO-1 (c) and FO-4 (d) friction-transferred films.

Table 1. Absorption maxima and dichroic ratios of friction-transferred fluorene films

	λ_{max} in Abs/nm	D_{abs}	D_{PL}
FO-1	340	1.3	1.2
FO-2	340	1.6	2.0
FO-3	360	2.6	2.5
FO-4	360	2.8	3.3
FO-5	370	4.9	5.0
PFO[8]	400	6.5	10.0

backbone skeletons, the above results indicate that FO-4 molecules are predominantly aligned parallel to the friction direction. In the PL spectra, a strong emission intensity with a peak at 420 nm is observed, with a dichroic ratio (D_{PL}) of approximately 3.3.

Other fluorenes also form films with the thickness of approximately 10–20 nm by the friction-transferred process. However, the degree of molecular orientation in the film is strongly dependent on the molecular structure. Table 1 summarizes the relationships between the molecular structure and the optical anisotropy (D_{abs} and D_{PL}). Here, we estimated D_{abs} and D_{PL} in a batch of friction-transfer in order to avoid the variation from batch to batch. We confirm that alignment behavior indicates similar tendency independent of different batches. We discuss only the dichroic ratios in the absorption properties because the PL dichroic ratios follow the same trend as those in absorption. The FO-2 film has a dichroic ratio of 1.6, which is almost the same as that of the FO-1 film. In both FO-1 and FO-2 films, the maximum absorptions occur at 340 nm. On the other hand, the FO-3 film showed a dichroic ratio of 2.6, which is higher than those of the FO-1 and FO-2 films. The absorption maxima in the FO-3 and FO-4 films were red-shifted compared with those in the FO-1 and FO-2 films, i.e., the peak is at 360 nm. The FO-4 film, end-capped with methoxy groups, has a dichroic ratio of 2.8, which is almost the same as FO-3 film. The FO-5 (fluorene trimer) film has the highest dichroic ratio of 4.9. The maximum absorption of the FO-5 film was observed at 370 nm. According to our previous study, the maximum absorption peak and the dichroic ratio of friction-transferred poly(9,9-dioctylfluorene) (PFO) films were 400 nm and 6.5.[8] These data clearly indicate that the optical anisotropy in the friction-transferred films is proportional to the conjugation length of the molecules.

To clarify the relationship between the optical properties and film structures, we carried out TEM measurements. Figures 3a and 3b show the TEM images and the high-resolution electron diffraction (HRED) patterns of the FO-1 and FO-4 films, respectively. The FO-1 film was composed of thin plates that were approximately 1 µm. The HRED pattern of the film obtained from areas that were approximately 20 µm in diameter showed ring patterns, indicating the random alignment of FO-1 crystallites. On the contrary, the FO-4 film was composed of granular crystallites with sub-micrometer size. The HRED pattern shows the diffraction arcs. The interplaner distances of the intense diffraction arc on the meridian are 0.28, 0.17, 0.14, and 0.11 nm^{-1}, and those on the equator are 0.21 and 0.18 nm^{-1}. These interplanar distances are consistent with the powder diffraction results of FO-4. The alignment of crystallites accompanies the molecular alignment. Unfortunately, we could not clarify the molecular orientation of the film in detail because the crystal structures of the fluorenes have not been measured. However, we surmise that the long axes of the FO-4 molecules are aligned nearly horizontally and parallel to the friction direction in the film, based on their polarized optical properties. This indicates that FO-4 crystallites are aligned along the friction direction.

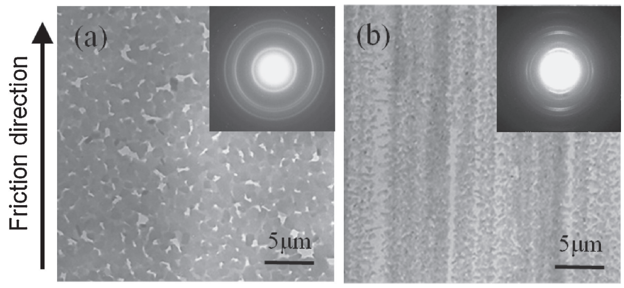

Figure 3. TEM images and electron diffraction patterns of friction-transferred FO-1 (a) and FO-4 (b).

Based on the above results, the friction-transfer mechanism of fluorenes can be explained as follows. When fluorene pellets which consist of aggregates of crystallites are squeezed on the substrate, fluorene aggregates are cleaved into small crystallites by shearing stress. Small crystallites act like as solid lubricant and are transferred to the substrate surface. Fluorene molecules in crystallites also are subjected to a shearing stress, which leads to the longitudinal direction of fluorene molecules aligning along to the friction direction. The alignment of fluorene molecules induces the rearrangement of crystallites. With the increase in the aspect ratio in the linear molecules, greater shearing stress is applied. Therefore, molecules with a long skeleton backbone can be aligned parallel to the friction direction in the film.

In conclusion, we applied friction-transfer to fluorescent molecules. The degree of molecular orientation was related to the length of the rigid parts of the molecules; molecules with long skeleton backbone (FO-3, -4, and -5) were aligned nearly horizontally and parallel to the friction direction in the film. Such in-plane orientation is advantageous in fabricating OLEDs with respect to increasing their light-outcoupling efficiencies.

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