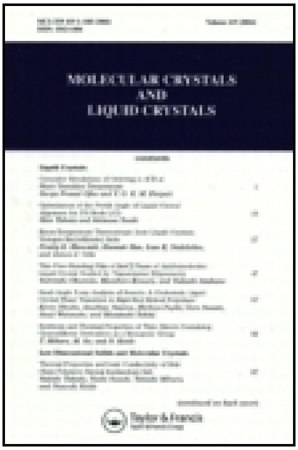

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PREPARATION AND OPTICAL PROPERTIES OF UNIAXIALLY ORIENTED DIHYDRODIPYRAZINOPYRAZINE THIN FILM

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PREPARATION AND OPTICAL PROPERTIES OF UNIAXIALLY ORIENTED DIHYDRODIPYRAZINOPYRAZINE THIN FILM

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Two dicyanopyrazine derivatives (2,3,7,8-tetracyano-5,10-dimethyl-5,10-dihydrodipyrazino[2,3-b:2′,3′-e]pyrazine (DM-dicyanopyrazine) and 2,3,7,8-tetracyano-5,10-di(n-dodecyl)-5,10-dihydrodipyrazino[2,3-b:2′,3′-e]pyrazine (DD- dicyanopyrazine)) were synthesized by intermolecular cyclization of 2-alkylamino-3-chloro-5,6-dicyanopyrazines in the presence of triethyl amine. The crystal structures of DM- and DD-dicyanopyrazine were monoclinic, space group $P2_1/c$ *with dimensions of* $a = 1.10$ *nm,* $b = 0.97$ *nm,* $c = 1.32$ *nm and* $\beta = 100.17°$*, and space group* $P2_1/a$ *with dimensions of* $a = 1.36$ *nm,* $b = 0.84$ *nm, 1.60 nm and* $\beta = 88.9°$*, respectively. DM- and DD-dicyanopyrazine grew epitaxially on a friction-transferred PTFE layer from vapor phase. Dicyanopyrazine molecules adsorbed their side chain almost perpendicular to the substrate surface. The anisotropic features of the DM-dicyanopyrazine/PTFE and DD-dicyanopyrazine/PTFE double layers in optical properties were discussed based on the molecular orientation.*

Keywords: anisotropic feature; polarized absorption; PTFE; pyrazine

INTRODUCTION

2,5-Diamino-3,6-dicyanopyrazine derivatives have strong fluorescence even in the solid state [1,2]. The dicyanopyrazine moiety has a strong electron

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withdrawing ability, and 2,5-diamino-3,6-dicyanopyrazine derivatives can be expected to have strong intra- and inter-molecular charge-transfer interactions in their self-organized aggregates. Three-dimensional molecular stacking was performed by the inter-molecular interactions, which controlled special functionalities such as color changes in crystal morphology [3,4]. Recently the development of new fluorescent chromophores based on 2,5-Diamino-3,6-dicyanopyrazine derivative moiety have many potential interests, e.g. in applications such as electroluminescence devices, solar energy collecting systems and nonlinear optical devices [5]. When the dicyanopyrazine derivative films are applied such devices, it is very important to control the molecular orientation in the film. Generally, a cleaved surface of alkali halide single crystal has been used as the substrate to prepare the orientation-controlled organic film. In this case, organic molecules grow in two or four directions depending on the symmetry of the substrate crystal. In order to solve this problem and fabricate the film of lower dimension, on the other hand, friction-transferred polytetrafluoroethylene (PTFE) was prepared. The PTFE layer has high potential as the substrate for uniaxially grown organic films.

In this study two 2,5-diamino-3,6-dicyanopyrazine derivatives were deposited on a friction-transferred PTFE layer from vapor phase. The structure and optical properties of the films were investigated.

EXPERIMENTAL

2,3,7,8-Tetracyano-5,10-dimethyl-5,10- dihydrodipyrazino[2,3-b:2′,3′-e]pyrazine (DM-dicyanopyrazine) and 2,3,7,8-tetracyano-5,10-di(n-dodecyl)-5,10-dihydrodipyrazino[2,3-b:2′,3′-e]pyrazine (DD-dicyanopyrazine) were synthesized by intermolecular cyclization of 2-dimethylamino-3-chloro-5,6-dicyanopyrazine and 2-dodecylamino-3-chloro-5,6-dicyanopyrazine in the presence of triethylamine. Figure 1 shows the chemical structures of DM- and DD-dicyanopyrazine. Thin layer of PTFE used as a substrate was prepared on glass supports by the method reported by Wittmann and Smith [6]. The thickness of a friction-transferred PTFE layer was about 10–15 nm. Dicyanopyrazine derivatives were vapor-deposited on a friction-transferred PTFE layer kept at various temperature from a fused silica crucible heated by a tungsten coil at a pressure of 10^{-3} Pa. The deposition rate and film thickness were controlled to be about 1 nm/min and 30 nm monitored by a quartz crystal microbalance, respectively. The structure and optical properties of the films were investigated by using atomic force microscope (AFM), transmission electron microscope (TEM), UV-VIS absorption and photoluminescence (PL) spectroscopy.

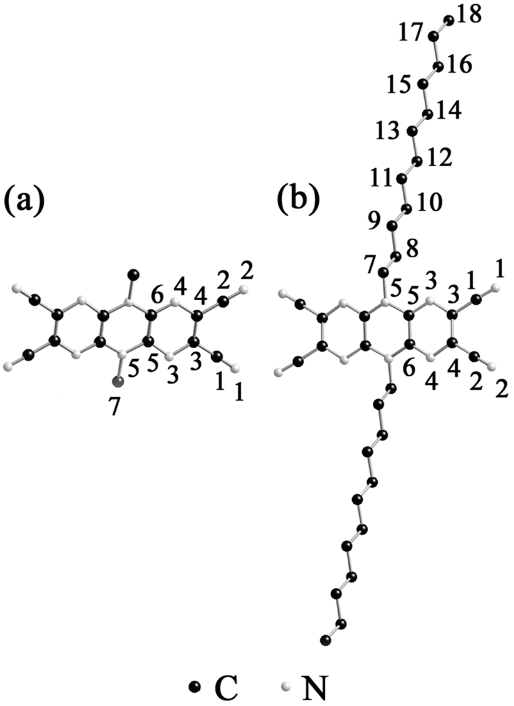

FIGURE 1 Chemical structures and atom labeling of DM-dicyanopyrazine (a) and DD-dicyanopyrazine (b).

RESULTS AND DISCUSSION

The crude products were recrystallized from ethanol to give DM- and DD-dicyanopyrazine as deep red and dark yellow crystals, respectively. The structure analysis of the crystals were performed using Rigaku AFC7R diffractometer. The crystal structure of DM-dicyanopyrazine was monoclinic, belonging to the space group $P2_1/c$ and unit cell dimensions were $a = 1.10\,\text{nm}$, $b = 0.97\,\text{nm}$, $c = 1.32\,\text{nm}$ and $\beta = 100.17°$. On the other hand, the crystal structure of DD-dicyanopyrazine was monoclinic, belonging to the space group $P2_1/a$ and unit cell dimensions were $a = 1.36\,\text{nm}$, $b = 0.84\,\text{nm}$, $c = 1.60\,\text{nm}$ and $\beta = 88.9°$. Figure 1 also shows the DM- and DD-dicyanopyrazine molecules with the atomic numbering scheme employed. Atomic coordinates of molecules are summarized in Table 1.

Figures 2(a) and (b) show the AFM image and the electron diffraction (ED) pattern of the DM-dicyanopyrazine film deposited on a friction-transferred PTFE layer kept at 100°C. The morphology of the

DM-dicyanopyrazine film did not depend on the evaporation conditions such as substrate temperature and deposition rate. The DM-dicyanopyrazine film was composed of small granules. The ED pattern of the DM-dicyanopyrazine/PTFE double layer showed the superposition of the reflection spots from the deposited DM-dicyanopyrazine crystal and the PTFE layer. The ED pattern of the DM-dicyanopyrazine film showed the single net pattern with the diffraction spots corresponding to the interplanar distance of 0.82 nm and 0.67 nm. Ring pattern also appeared. These findings indicated that the DM-dicyanopyrazine molecules oriented partially on the PTFE layer. The diffraction spots of the DM-dicyanopyrazine were not able to index by the unit cell parameters of bulk crystal. Therefore it was concluded that DD-dicyanopyrazine crystallized polymorphic form. Further information concerning to new crystal structure was not obtained from the analysis of ED pattern.

In the case of DD-dicyanopyrazine, the morphology of the film and molecular orientation depended on the evaporation conditions. When the

TABLE 1. Atomic Coordinates of DM-dicyanopyrazine (a) and DD-dicyanopyrazine (b).

	x	y	z		x	y	z
(a)				(b)			
C1	0.565	0.384	0.393	C1	0.207	−0.466	−0.060
C2	0.705	0.184	0.297	C2	0.097	−0.535	0.090
C3	0.303	0.612	0.591	C3	0.136	−0.353	−0.026
C4	0.237	0.706	0.638	C4	0.088	−0.383	0.049
C5	0.128	0.514	0.509	C5	0.058	−0.117	−0.038
C6	0.058	0.603	0.564	C6	0.018	−0.138	0.045
C7	0.135	0.312	0.393	C7	0.937	−0.026	0.173
N1	0.462	0.383	0.378	C8	0.833	−0.085	0.185
N2	0.660	0.097	0.246	C9	0.806	−0.102	0.279
N3	0.565	0.384	0.393	C10	0.698	−0.144	0.293
N4	0.113	0.702	0.623	C11	0.672	−0.169	0.385
N5	0.933	0.592	0.551	C12	0.564	−0.169	0.402
				C13	0.538	−0.169	0.493
				C14	0.429	−0.169	0.507
				C15	0.402	−0.169	0.600
				C16	0.293	−0.169	0.615
				C17	0.264	−0.169	0.706
				C18	0.155	−0.169	0.717
				N1	0.264	−0.169	−0.083
				N2	0.102	−0.169	0.120
				N3	0.119	−0.169	−0.071
				N4	0.029	−0.169	0.086
				N5	0.966	−0.169	0.083

substrate temperature was kept at R.T. and deposition rate was faster than 10 nm/min, the DM-dicyanopyrazine film deposited on PTFE layer was composed of small granules with random orientation. On the other hand, the DD-dicyanopyrazine film deposited at 100°C was composed of plate-like crystals with submicron size aligned along the sliding direction of the PTFE rod, as shown in Figure 2(c). The ED pattern of the DD-dicyanopyrazine/PTFE double layer also showed the same superposition of the reflection spots as the DM-dicyanopyrazine/PTFE double layer, as shown in Figure 2(d). The ED pattern of the DD-dicyanopyrazine film showed the single net pattern with the diffraction spots corresponding to the lattice spacings of 0.84 nm and 0.66 nm. From a comparison of the observed and the calculated lattice spacings, it was concluded that the ED pattern

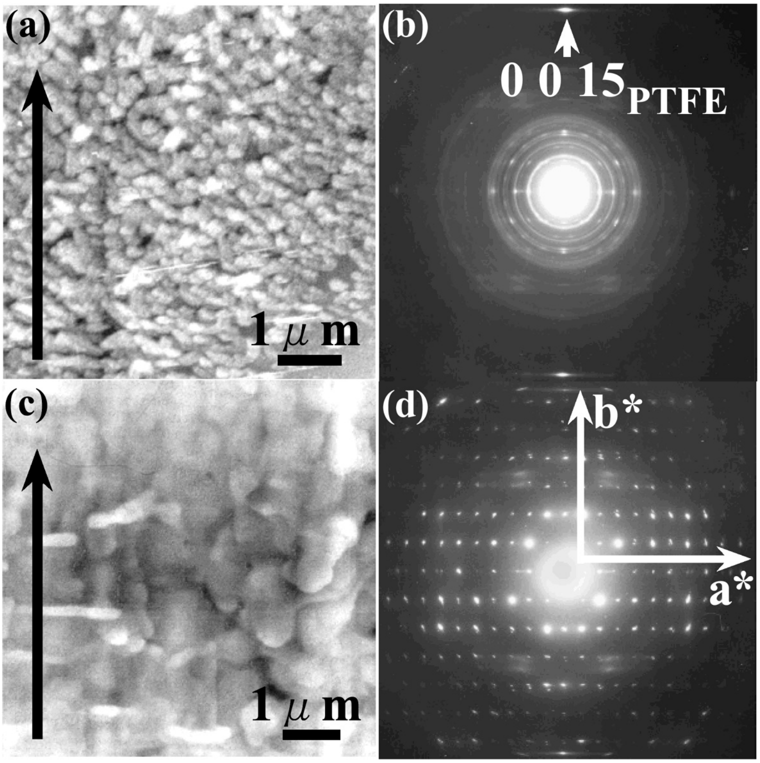

FIGURE 2 AFM images and electron diffraction patterns of DM-dicyanopyrazine film (a), (b) and DD-dicyanopyrazine film (c), (d) deposited on a friction-transferred PTFE layer kept at 100°C. Arrows indicate the sliding direction of a PTFE rod.

corresponds to the single net pattern projected along the c* axis of the DD-dicyanopyrazine crystal. The b axis of the DD-dicyanopyrazine crystal oriented parallel to the c axis of the PTFE crystal. The DD-dicyanopyrazine crystal oriented with respect to the PTFE layer in the relation of $(001)[010]_{\mathrm{pyrazine}}//(100)[0015]_{\mathrm{PTFE}}$. From the mutual relations between the deposit and substrate crystals, it was included that the DD-dicyanopyrazine molecules were arranged on the PTFE layer as represented schematically in Figure 3. The DD-dicyanopyrazine molecules adsorbed their side chain almost perpendicular to the substrate surface and the longitudinal direction of pyrazine ring aligned crossing at 23° to the direction of PTFE chain.

In order to clarify the relation between the molecular orientation and optical properties, the polarized absorption and photoluminescence (PL) measurement was carried out. Figure 4(a) shows the experimental setup for polarized PL measurement. The sample was set up as the sliding direction of PTFE was parallel to the polarized direction of the incident light. The incident excitation light was inclined to the film plane at an angle of 45°, and emission was detected normal to the film plane. The polarization of the excitation light was fixed perpendicular to the optical base. The principal axes of the sample film were labeled as follow; the sliding direction of PTFE (Z), the normal directions with respect to the friction direction (X) and the film surface (Y). Figure 4(b) and (c) show the polarized absorption and emission spectra of the DD-dicyanopyrazine/PTFE and the DM-dycyanopyrazine/PTFE double layers. Each double layer

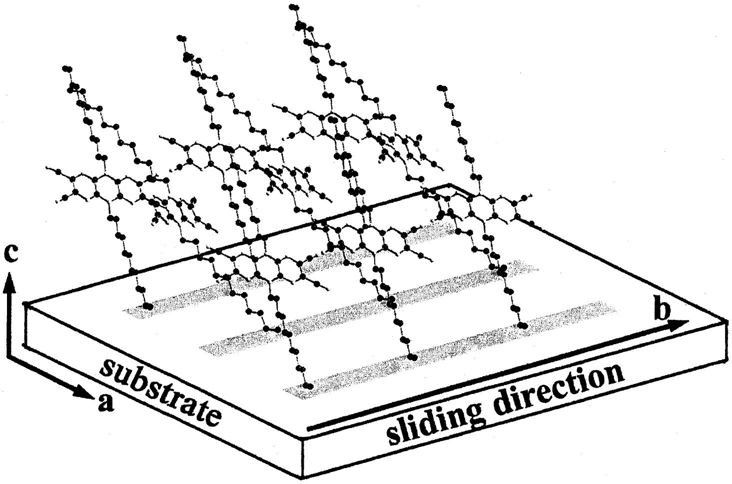

FIGURE 3 Schematic diagram of molecular orientation of DD-dicyanopyrazine on a PTFE layer.

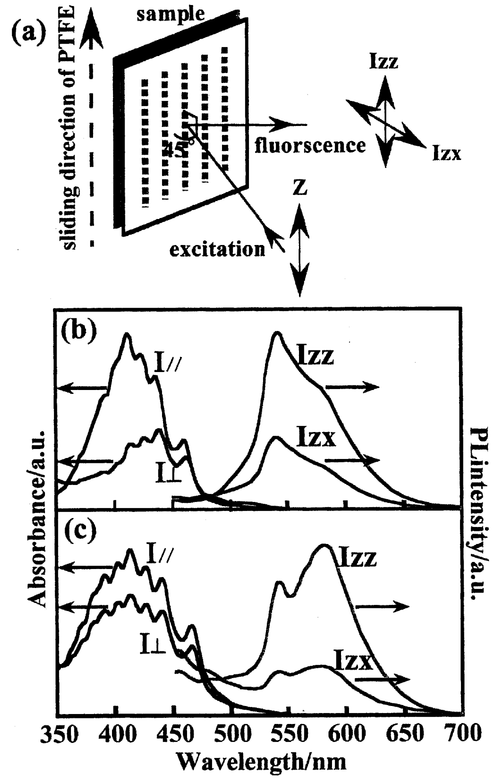

FIGURE 4 Experimental set up for polarized PL measurement (a), polarized absorption and PL spectra of DD-dicyanopyrazine/PTFE double layer (b), and DM-dicyanopyrazine /PTFE double layer (c).

indicates an anisotropic feature in optical properties. The dichroic ratios ($I_{//}/I_{\perp}$ and I_{ZZ}/I_{ZX}) calculated directly from the peak heights of absorption and emission intensity are about 1.8 and 3.5 for the DD-dicyanopyrazine/PTFE double layer and 2.6 and 2.4 for the DM-dicyanopyrazine/PTFE double layer, respectively. The optical anisotropy in the DD-dicyanopyrazine/PTFE double layer attributed to the orientation of the chromophore. As mentioned above, the molecular orientation of the DM-dicyanopyrazine on the PTFE layer was not clear because the DM-dicyanopyrazine crystallized in polymorphic form. However, we are able to propose the orientation model since the optical properties of the DM-dicyanopyrazine/PTFE double layer indicated similar anisotropic feature to the epitaxially grown DD-dicyanopyrazine film. Figure 5 shows the proposed orientation model of the DM-dicyanopyrazine molecules on the PTFE layer. The DM-dicyanopyrazine

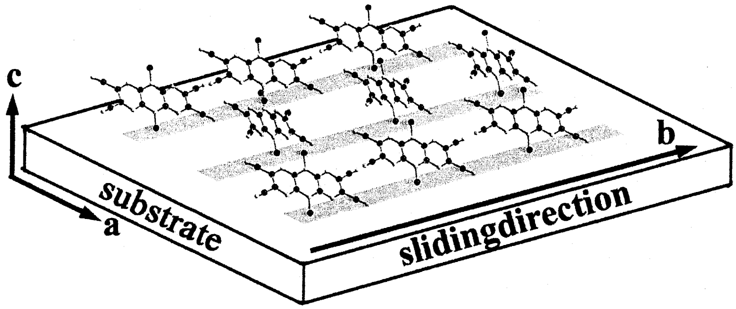

FIGURE 5 Schematic diagram of molecular orientation of DD-dicyanopyrazine on a PTFE layer.

molecules adsorbed the methyl group to the substrate surface and pyrazine ring maybe align crossing at about 30° to the sliding direction of PTFE.

CONCLUSION

Two dicyanopyrazine derivatives (DM-dicyanopyrazine and DD-dicyanopyrazine) were synthesized and were vapor-deposited on the friction-transferred PTFE layer. The DD-dicyanopyrazine crystal oriented with respect to the PTFE layer in the relation of $(001)[010]_{\text{pyrazine}}//(100)[0015]_{\text{PTFE}}$. The DM-dicyanopyrazine also grew epitaxially on the PTFE layer , but crystallized in polymorphic form. The polarized absorption and PL spectra of the DD-dicyanopyrazine/PTFE and DM-dicyanopyrazine/PTFE double layers showed an anisotropic feature. The potential use of epitaxially grown these double layers may be applied to use in polarized PL emitters.

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