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CORRELATION OF MOLECULAR ORIENTATIONS AT THE INTERFACE OF ORGANIC DOUBLE-LAYERED THIN FILMS

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Abstract Correlation of molecular orientations in the respective layers of vapor-deposited double-layered thin films of *N,N'*-dimethylperylene-3,4,9,10-bis(dicarboximide) (DM-PBDCI) and chloroaluminum phthalocyanine (ClAlPc) has been examined by means of X-ray diffraction and (polarized) electronic absorption. After examining molecular orientations in single-layered thin films, correlated orientations in double-layered films were disclosed as ClAlPc(1 $\bar{1}$ 0)/DM-PBDCI (0 1 1)/SS and ClAlPc(1 1 0)/DM-PBDCI(0 0 2)/SS for the films prepared at r.t. and high temperatures, respectively, and DM-PBDCI(1 0 $\bar{2}$)/ClAlPc(0 4 0)/SS, where SS denotes a substrate. Further, it was derived by analyzing the results of electronic absorption spectra that transition dipole moments of two different molecules facing to each other at the interface of double-layered thin films are in most cases perpendicular or parallel to one another, and this could explain the observed correlations in molecular orientations above.

Keywords: Thin film, double layer, molecular orientation, phthalocyanine, perylenebis(dicarboximide), interface

INTRODUCTION

Multi-layered thin films of organic semiconductors have recently been interested in with expectation of their application as molecular electronic devices such as rectifiers, photocells and electroluminants. Their electronic functions should depend on the orientation and/or the electronic state of a molecule in each layer, moreover, correlation of these factors at the interfaces in such a film must be significant. We have therefore started a study of organic double-layered thin films from the former viewpoint together with that of their electronic structure[1], that is, correlation of molecular orientations at the interface of double-layered thin films prepared by the vapor-deposition has been examined to obtain information especially for understanding their electronic behaviors.

In this work we will report on a molecular system of an organic double-layered thin film fabricated by *N,N'*-dimethylperylene-3,4,9,10-bis(dicarboximide) (DM-PBDCI) which is similar to perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and chloroaluminum phthalocyanine (ClAlPc) which is one of phthalocyanine compounds having axial ligands. DM-PBDCI and ClAlPc are known to demonstrate n-

and p-type semiconductivities, respectively, so that the double-layered film could be regarded as an organic electronic device with a p-n junction[2–7]. In practice, this system has already been examined to show a photovoltaic behavior characterized as follows[8]: Open circuit voltage V_{oc} = 0.4 V, short circuit current density J_{sc} = 2.4 mA/cm^2, fill factor ff > 0.4 and energy conversion efficiency η > 0.6%. We have therefore studied structural characteristics, in particular, molecular orientations in respective layers of the film on the basis of refined structures of single crystals of the component materials, by means of X-ray diffraction and polarized electronic absorption spectroscopy, although these methods may be of indirect observation and also of low resolution in comparison with those used for extended work on ultra-thin films of phthalocyanines by Maruyama, *et al.*[9–18]

EXPERIMENTAL

Sample materials of DM-PBDCI and ClAlPc, molecular structures of which are shown in Figure 1, were kindly supplied by M. Yoshikawa at RICOH Co., Ltd., after pre-purification of the materials purchased from B. A. S. F. and Eastman-Kodak Ltd., respectively. Further purification with repeated sublimation under the pressure less than 5×10^{-5} Pa was carried out for the present studies.

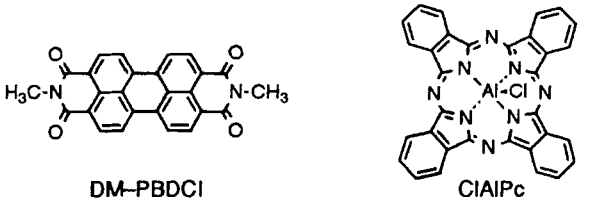

FIGURE 1 Molecular structures of *N,N'*-dimethylperylene-3,4,9,10-bis(dicarboximide) (DM-PBDCI) and chloroaluminum phthalocyanine (ClAlPc).

Single crystals of the two materials were grown by a vacuum sublimation method. Data collection of their X-ray diffraction was made on a Rigaku AFC7R diffractometer with Cu Kα radiation as a source. Structures of DM-PBDCI and ClAlPc were solved by direct methods using the programs MITHRIL90[19] and SIR88[20], respectively. These crystal structural analyses were carried out in particular to refine the atomic coordinates in respective crystals, since the results reported so far for both crystals have some ambiguities so that they appeared to be insufficient for the present studies.

Single- and double-layered thin films were prepared by vapor-deposition under the following conditions: a sample film was deposited onto a quartz glass substrate (to be

abbreviated as SS) at room temperature or 200 °C in a deposition rate of 0.1–3 nm/min under the pressure less than 3×10^{-4} Pa. The thickness of each evaporated layer ranged from 30 nm to 160 nm to fit respective experimental purposes measured on a quartz oscillator monitor. Double-layered thin films were made by a sequential evaporation *in situ*.

Characterization of the obtained films was carried out by X-ray diffraction measured on a Rigaku RADIIB diffractometer, electronic absorption spectra on a Shimadzu UV-2200 spectrophotometer and polarized absorption spectra on a Hitachi U-3400 spectrophotometer.

RESULTS AND DISCUSSION

Crystal Structural Refinements

Refined crystal structures[21] of DM-PBDCI and ClAlPc, the final residual values of which became smaller than halves of those in the results reported before (from R = 0.108[22] to R = 0.045 for DM-PBDCI and from R = 0.137[23] to R = 0.065 for ClAlPc), will briefly be described, with determined crystallographic data summarized in Table I.

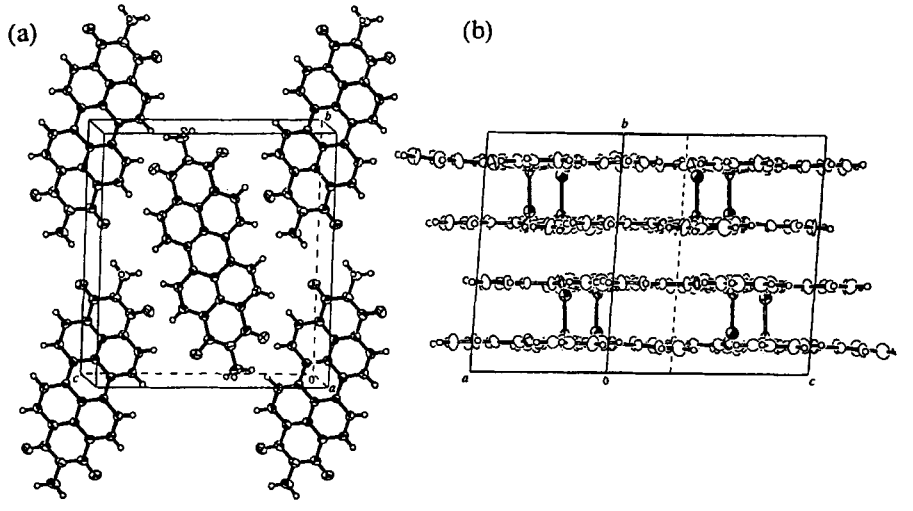

FIGURE 2 Crystal structures of (a) DM-PBDCI and (b) ClAlPc.

Crystal structural analyses show that both molecules are basically planar, while a ClAlPc molecule has an axial ligand projected perpendicularly to the molecular plane, as shown in Figure 2. Accordingly, for further discussion of molecular orientation, it is convenient to represent a configuration of the molecular plane in the crystal using Miller indices ($h\ k\ l$). In practice, a reciprocal lattice vector directed normal to the plane, $\boldsymbol{G}_{\perp}$,

is applied for this purpose. Close examination of the crystal structures has enabled us to determine such vectors as follows: $G_\perp$ = (2 1 3) and (2 $\bar{1}$ 3) for two different molecular sites (to be denoted as A and B sites, respectively) in a unit cell of a DM-PBDCI crystal and $G_\perp$ = (0 1 0) for one practically independent molecular site in a unit cell of a ClAlPc crystal.

TABLE I Comparison of crystallographic data of DM-PBDCI and ClAlPc.

DM-PBDCI	This work[21]	Hadicke and Graser[22]
Crystal dimension / mm^3	0.2 × 0.2 × 0.5	0.2 × 0.05 × 0.01
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / Å	3.867(4)	3.874(1)
b / Å	15.571(2)	15.580(2)
c / Å	14.587(2)	14.597(2)
β / °	97.71(4)	97.65(2)
V / Å^3	870.4(9)	873.19
Z	2	2
No. of observations	1359 ($I > 3.0\,\sigma(I)$)	736 ($I > 3.0\,\sigma(I)$)
Reflection/parameter ratio	7.81	4.23
R, R_w	0.045, 0.059	0.108, 0.098
ClAlPc		
	This work[21]	Wynne[23]
Crystal dimension / mm^3	0.1 × 0.05 × 0.02	0.2 × 0.2 × 0.05
Crystal system	triclinic	triclinic
Space group	$P\,\bar{1}$	$P\,\bar{1}$
a / Å	13.746(2)	13.776(6)
b / Å	14.059(2)	14.059(5)
c / Å	13.746(2)	13.775(4)
α / °	98.37(1)	98.36(3)
β / °	90.01(1)	90.16(3)
γ / °	108.620(9)	108.60(3)
V / Å^3	2483.0(6)	2498.2
Z	4	4
No. of observations	2546 ($I > 2.5\,\sigma(I)$)	2250 ($I > 3.0\,\sigma(I)$)
Reflection/parameter ratio	3.36	4.89
R, R_w	0.065, 0.064	0.137, 0.164

X-ray Diffraction Patterns of Single-Layered Thin Films

To start studies of thin films, X-ray diffraction patterns of single-layered thin films have first been examined. Figure 3 exhibits a comparison of diffraction patterns of DM-

PBDCI between vapor-deposited films prepared with different deposition rates onto substrates at room temperature and the polycrystalline powder; the upper pattern was obtained for a film prepared with a deposition rate faster than that for a film showing the middle pattern. It has turned out that local structures can be the same as each other and that evaporated films demonstrate only three reflections: (0 1 1), (0 0 2) and (0 1 2), while a relative intensity of (0 0 2) reflection depends on deposition rate during preparation of the film.

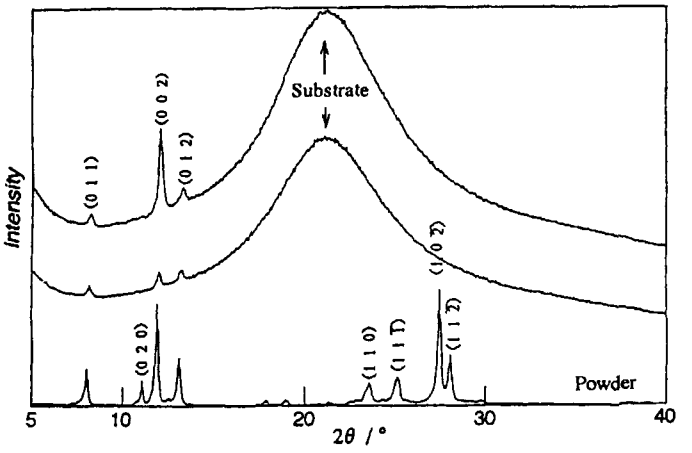

FIGURE 3 Comparison of diffraction patterns of DM-PBDCI between vapor-deposited films prepared with different deposition rates onto substrates at room temperature and the polycrystalline powder.

In the case of ClAlPc films prepared at room temperature, only (0 4 0) reflection corresponding to the molecular orientation parallel to the substrate surface has been observed in most cases, whereas (1 $\bar{1}$ 0) reflection was observed exclusively in only a few cases. Besides, (2 0 3) reflection was noted in addition to (0 4 0) one for films prepared on substrates heated at 200 °C.

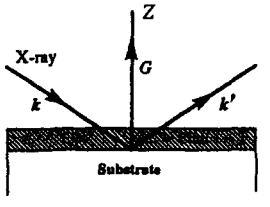

FIGURE 4 Schematic of X-ray diffraction by a thin film.

Taking account of the X-ray diffraction condition for a thin film on a flat substrate, as shown in Figure 4, the following relation should be realized:

$$\boldsymbol{G} = h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^* = \boldsymbol{k}' - \boldsymbol{k}$$

where $\boldsymbol{G}$ is a reciprocal lattice vector corresponding to an observed reflection ($h\ k\ l$), $\boldsymbol{a}^*$, $\boldsymbol{b}^*$ and $\boldsymbol{c}^*$ are fundamental translation vectors for the reciprocal lattice, and $\boldsymbol{k}$ and $\boldsymbol{k}'$ are wave vectors for incident and reflected X-ray, respectively. Since absolute values of $\boldsymbol{k}$ and $\boldsymbol{k}'$ concerning the diffraction are the same, $\boldsymbol{G}$ should always be perpendicular to the surface, so that Z-axis of a Cartesian coordinate set normal to the surface points to the same direction with $\boldsymbol{G}$. When angles θ and ϕ are defined as the angle between $\boldsymbol{G}$ and $\boldsymbol{G}_\perp$ and the angle between $\boldsymbol{G}$ and the molecular long axis, respectively, these angles permit us to examine molecular orientations. However, it is not always straightforward to discuss molecular orientations against the substrate surface on the basis of only those angles.

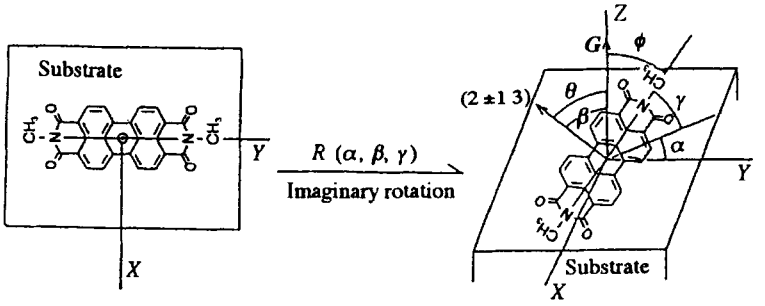

FIGURE 5 Representation of a molecular orientation by an imaginary rotation using the Eulerian angles.

Accordingly, to discuss the orientation of a molecule in a thin film, it is necessary to represent a geometric arrangement of the molecule in relation to the substrate surface. In this work a set of the Eulerian angles, that is, (α, β, γ), is used for this purpose, while α, β and γ here are no longer axial angles of lattice constants of the crystal. The Cartesian coordinate (X, Y, Z) fixed on the substrate surface can therefore be transferred to the coordinate (x, y, z) fixed on the basis of a molecular plane, as shown in Figure 5, when an imaginary rotation $R\ (\alpha, \beta, \gamma) = R_Z\ (\alpha)\ R_y\ (\beta)\ R_z\ (\gamma)$ is applied to the latter coordinate assumed to be overlapped with the former one at the first stage. Here β is the angle between the molecular plane and the substrate surface and γ is the angle between the molecular long axis and the line of intersection between the molecular plane and the substrate surface plane, hence, γ indicates the degree of perpendicularity of a molecule to the substrate surface: the molecule should lie down in the case of $\gamma \approx 0\ °$. On the other

hand, α depends on the reciprocal configuration of the two coordinates before the imaginary rotation applied. Besides, a similar method of the Eulerian rotations is useful also to represent orientations of a crystal unit cell, when polarized absorption spectra of crystalline thin films are analyzed later on.

Considering that the Eulerian rotation $R(\alpha, \beta, \gamma)$ enables a molecule initially fixed as $G_{\perp}$ and its long axis coincided with Z- and Y-axes of the Cartesian coordinate above, respectively, to orient in the thin film to exhibit a $(h\ k\ l)$ diffraction, the following relations:

$$\cos\theta = \boldsymbol{e}_Z \cdot R(\alpha, \beta, \gamma)\,\boldsymbol{e}_Z = \cos\beta, \quad \cos\phi = \boldsymbol{e}_Z \cdot R(\alpha, \beta, \gamma)\,\boldsymbol{e}_Y = \sin\beta\sin\gamma$$

where $\boldsymbol{e}_Y$ and $\boldsymbol{e}_Z$ are unit vectors in the directions of Y- and Z-axes, respectively. From these relations, equations of angles among θ, ϕ and the Eulerian angles are obtained as follows:

$$\beta = \theta, \quad \gamma = \sin^{-1}(\cos\phi / \sin\theta)$$

Besides, the angle α will be arbitrary so that $\alpha = 0°$ could be acceptable in most cases below, since orientations of crystallites in a plane parallel to the substrate are considered to be almost random, and in such cases correlation functions of angular components concerning α result in 0 on the average with the angle.

TABLE II Molecular orientations in single-layered thin films of DM-PBDCI and ClAlPc against the substrate surface

Compound	h	k	l	Site	β / °	γ / °
DM-PBDCI	0	0	2	A	62.0	14.1
				B	62.0	14.1
	0	1	1	A	74.3	56.5
				B	65.3	32.5
	0	1	2	A	67.6	40.0
				B	61.8	13.4
ClAlPc	0	4	0		0	—
	1	$\bar{1}$	0		125.2	63.5
	2	0	3		72.3	120

On the basis of the discussion above, the experimental data of X-ray diffraction by single-layered thin films of DM-PBDCI and ClAlPc have been analyzed to lead results

summarized in Table II. This table shows that a DM-PBDCI molecule is oriented with its molecular plane placed at about 60° to the substrate surface and that a ClAlPc molecule is placed parallel to the substrate surface in most cases, while oriented with its long axis, a diagonal of a square formed by four nitrogen atoms in a molecule, at about 60° to the substrate in other cases.

X-ray Diffraction Patterns of Double-Layered Thin Films

X-ray diffraction patterns of double-layered thin films were measured for both ClAlPc/DM-PBDCI/SS and DM-PBDCI/ClAlPc/SS systems, where SS indicates the substrate. In the former case, (1 $\bar{1}$ 0) other than (0 4 0) is the only reflection observed for ClAlPc in a film prepared at room temperature, as shown in Figure 6, while (1 1 0) reflection for ClAlPc, which was not observed in the single-layered film, is found in the film prepared onto a DM-PBDCI/SS system (prepared beforehand by evaporating DM-PBDCI onto the substrate heated at 115 °C) heated at 200 °C. On the other hand, only (1 0 $\bar{2}$) reflection, which was also unobserved in the neat film, is detected as for DM-PBDCI in the latter case, while its intensity is weaker for the film deposited on a ClAlPc film prepared at room temperature than the film on a ClAlPc layer prepared at 200 °C. Thus, these results show clearly that the molecular orientation in the underlayer of a double-layered thin film can control that in the upper layer.

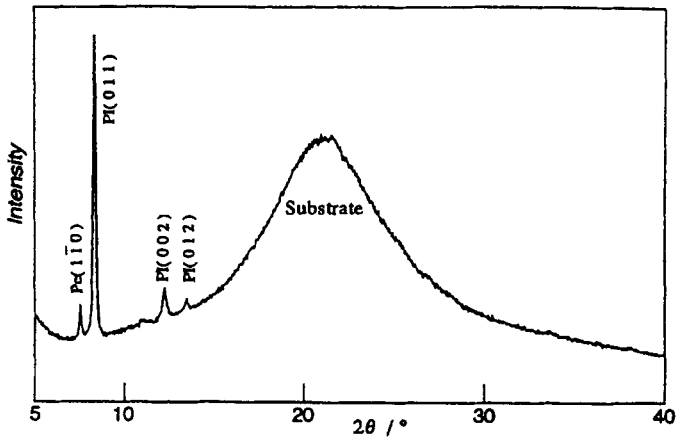

FIGURE 6 X-ray diffraction pattern of a ClAlPc/DM-PBDCI/SS double-layered system. Pc and PI indicate ClAlPc and DM-PBDCI, respectively.

To consider the observed correlation of molecular orientations between the underlayer and the upper layer of double-layered thin films, an Eulerian angle β determined from a reflection observed for every layer is compared with each other as

listed in Table III. Consequently, a fairly distinct correlation such that $\Delta\beta$ is rather low has been noted, where $\Delta\beta$ is the absolute value of the difference in β for the upper layer and the underlayer.

TABLE III Correlation of molecular orientations in double-layered thin films

Under layer	Upper layer	Site	$\beta_{DM\text{-}PBDCI}$/°	β_{ClAlPc}/°	$\Delta\beta$/°
DM-PBDCI(0 0 2)	ClAlPc(1 1 0)		62.0	35.7	26.2
DM-PBDCI(0 1 1)	ClAlPc(1 $\bar{1}$ 0)	A	74.3	54.8	19.5
		B	65.3		10.5
ClAlPc(0 4 0)	DM-PBDCI(1 0 $\bar{2}$)		8.4	0	8.4

Electronic Absorption Spectra

Electronic absorption spectra of the two compounds in various states were measured in detail to obtain further information of molecular orientations in thin films.

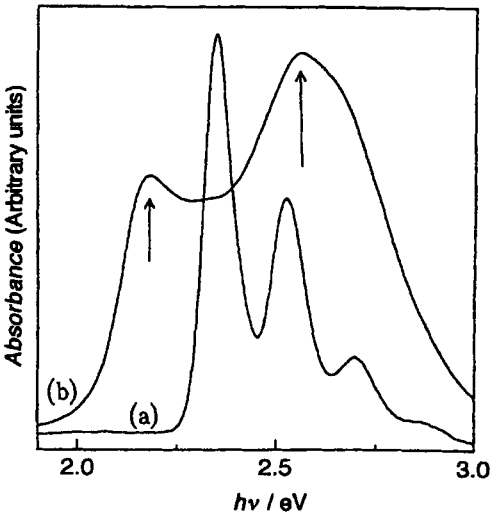

FIGURE 7 Electronic absorption spectra of DM-PBDCI in (a) a 1,1,2,2-tetrachloroethane solution and (b) the polycrystalline state.

Figure 7 compares a spectrum of DM-PBDCI in a 1,1,2,2-tetrachloroethane solution with that of its polycrystal, and demonstrates a spectral splitting in the latter as indicated by arrows. Such a splitting can be understood by considering electronically excited states of a molecule in different states in terms of symmetry as shown in Table

IV. Seen from this table, the absorption peak centered at 2.36 eV in the solution spectrum is to split into two peaks in the polycrystalline one: 2.18 eV peak due to a $B_u \leftarrow A_g$ transition and 2.56 eV peak due to an $A_u \leftarrow A_g$ transition with their polarization characteristics along *ac*-plane and *b*-axis, respectively. This so-called Davydov splitting was also observed in evaporated thin films, as shown in Figure 8, where slightly different spectra were obtained for two films with different relative intensities for (0 0 2) peak in their X-ray diffraction patterns.

TABLE IV Irreducible representations for electronically excited states of a DM-PBDCI molecule in different states.

Molecular state	Symmetry	Irreducible representation for excited states
Free	D_{2h}	B_u
Crystal site	C_i	A_u
Unit cell (in total)	C_{2h}	A_u, $B_u \Rightarrow$ Davydov splitting

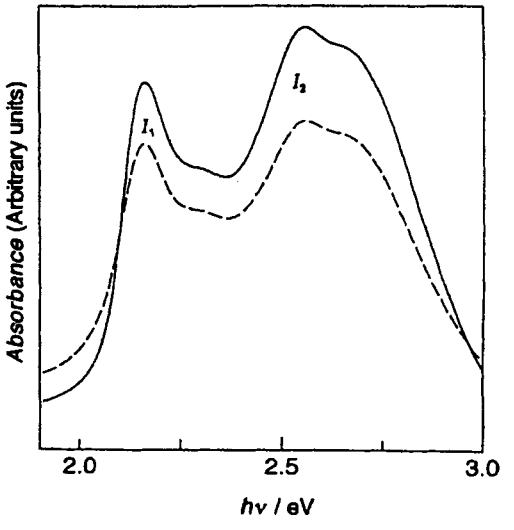

FIGURE 8 Electronic absorption spectra of DM-PBDCI films with different relative intensities for (0 0 2) peak in their X-ray diffraction patterns.

Further, we have proceeded to electronic absorption measurements of such thin films using polarized light, with the experimental arrangements shown in Figure 9. The formalization for polarization experiments will be demonstrated below.

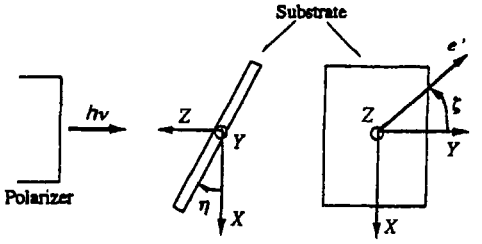

FIGURE 9 Experimental arrangements for polarized electronic absorption measurements. e' indicates the electric vector of incident light.

Each split peak in a spectrum is characterized by absorption intensity I, circular frequency ω, linewidth Γ and transition dipole moment $\boldsymbol{p}$, so that the $B_u \leftarrow A_g$ transition is characterized by I_1, ω_1, Γ_1 and $\boldsymbol{p}_1 = (p_1 \sin\psi,\ 0,\ p_1 \cos\psi)$ which is parallel to ac–plane, and the $A_u \leftarrow A_g$ transition by I_2, ω_2, Γ_2 and $\boldsymbol{p}_2 = (0,\ p_2,\ 0)$ being parallel to b-axis, when the initial arrangement of the unit cell of a DM-PBDCI crystal is given as shown in Figure 10. As polarized absorption spectra were measured with different polarization angles ζ around the light axis defined as Z-axis, it is convenient to again apply the Eulerian rotation of the crystal unit cell, denoted by $R(\alpha, \beta, \gamma)$, to represent its orientations for the analysis of experimental results. Further, considering that transition dipole moments and electric vector of the light (initially, $\boldsymbol{e} = (0, 1, 0)$) were rotated around the Y- and Z-axes, respectively, in the polarization measurement, a transition dipole moment $\boldsymbol{p}'$ and an electric vector of the light $\boldsymbol{e}'$ described on the space-fixed coordinates can be expressed as follows:

$$\boldsymbol{p}' = R_Y(\eta)\, R(\alpha, \beta, \gamma)\, \boldsymbol{p}, \quad \boldsymbol{e}' = R_Z(\zeta)\, \boldsymbol{e}$$

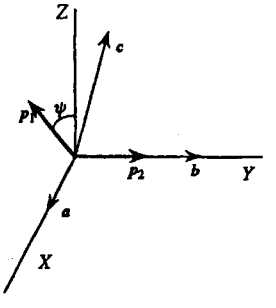

FIGURE 10 Initial arrangement of the unit cell of a DM-PBDCI crystal with transition dipole moments involved in the Davydov splitting.

The scalar product $\boldsymbol{e}' \cdot \boldsymbol{p}'$ is therefore obtained to be

$$\boldsymbol{e}' \cdot \boldsymbol{p}' = \boldsymbol{e} \cdot \boldsymbol{A}\boldsymbol{p} = a_{21}p_X + a_{22}p_Y + a_{23}p_Z,$$

$$\boldsymbol{A} = (a_{ij}) = R^{-1}_Z(\zeta)\, R_Y(\eta)\, R(\alpha, \beta, \gamma)$$

where p is temporarily expressed as (p_X, p_Y, p_Z) and matrix elements a_{ij} are explicit functions of α, β, γ; ζ and/or η.

By making a close study of the cross section of optical transition between two quantum states in the electric dipole approximation,[24] the absorption intensity ratio for the two split peaks above can come out as follows, on the assumption of Gaussian lineshape of a spectral band:

$$I_1 / I_2 = (\omega_1\Gamma_2 / \omega_2\Gamma_1)\, (|\boldsymbol{e} \cdot \boldsymbol{p}_1|^2 / |\boldsymbol{e} \cdot \boldsymbol{p}_2|^2)$$

Further, this relation can be rewritten as follows, by introducing the scalar product $\boldsymbol{e}' \cdot \boldsymbol{p}'$ with $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ to the relation above:

$$I_1 / I_2 = (\omega_1\Gamma_2 / \omega_2\Gamma_1)\, (p_1 / p_2)^2\, (a_{21}^2 \sin^2\psi + a_{23}^2 \cos^2\psi + a_{21}a_{23} \sin 2\psi) / a_{22}^2$$

This equation is used to obtain the intensity ratio from results of polarization absorption measurements, with determining Γ_1 and Γ_2 from spectral deconvolution using two Gaussian functions, when considering that tiny crystallites with a few different kinds of characteristic molecular orientations are mixed in the thin film.

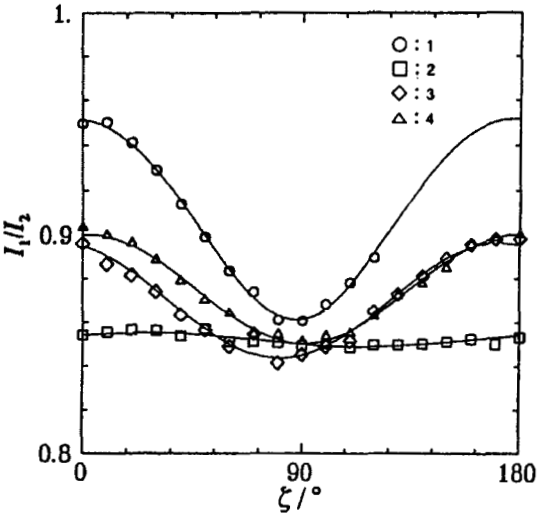

FIGURE 11 Polarization angle dependence of the absorption intensity ratio for four different DM-PBDCI films.

Figure 11 depicts results of polarization angle dependence of the intensity ratio for four different DM-PBDCI thin films; characters corresponding to respective thin films indicate experimental data and solid curves are fitted to their respective series using the equation above. The ratios of the magnitude of transition dipole moments p_1/p_2 and the angle ψ are obtained from these curves as shown in Table V. Besides, N_{hkl} in this table is a normalized ratio of the molecular orientation in a thin film leading (h k l) reflection defined as $(I_{hkl}/I^0_{hkl}) / \Sigma (I_{h'k'l'}/I^0_{h'k'l'})$, where I_{hkl} and I^0_{hkl} are intensities of (h k l) reflection for the film and a randomly oriented polycrystal, respectively, with the latter intensity being calculated from data of X-ray analysis of the single crystal.

TABLE V Ratio of the magnitude and composite direction of transition dipole moments in DM-PBDCI thin films

Film	N_{002}	N_{011}	N_{012}	p_1/p_2	ψ/°	χ/°	υ/°
1	0.25	0.33	0.42	0.66	61.0	74.1	–4.26
2	0.30	0.50	0.20	0.53	53.1	81.3	–2.95
3	0.15	0.69	0.16	0.59	45.1	84.1	–7.24
4	0.22	0.60	0.18	0.57	50.4	81.2	–4.97

Further, the other angles χ and υ represent the direction of a vector sum of transition dipole moments $\boldsymbol{p} = (\boldsymbol{p}_1 + \boldsymbol{p}_2) / \sqrt{2}$, which is proportional to ($\sin\chi\sin\upsilon$, $\sin\chi\cos\upsilon$, $\cos\chi$), on the coordinate fixed at a molecule, as shown in Figure 12. The values of these angles in Table V indicate that transition dipole moments of the molecules in the film slightly deviate from the molecular long axis.

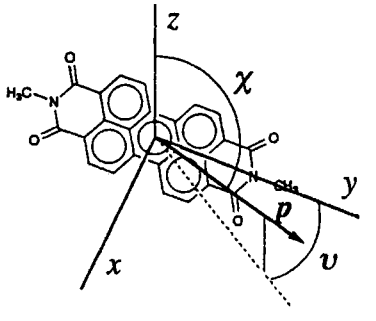

FIGURE 12 Transition dipole moment $\boldsymbol{p} = (\boldsymbol{p}_1 + \boldsymbol{p}_2) / \sqrt{2}$ on the coordinate fixed at a molecule and the related angles.

In the case of ClAlPc films, the spectral Q-band at around $h\nu \approx 1.8$ eV, which corresponds to the lowest energy excitation: e ← a_2 in the case of a molecule, exhibits splitting due to broken degeneracy of the lowest excited state in the crystalline state. Besides, no optical transition in DM-PBDCI is observed in this photon energy range. Accordingly, polarized electronic absorption spectra were again measured for the ClAlPc layer of a ClAlPc(1 $\bar{1}$ 0)/DM-PBDCI(0 1 1)/SS double-layered thin film, to examine the intensity ratio between split spectral features of ClAlPc: Figure 13 depicts the results observed at $\zeta = 0°$ and 90°.

When the degeneracy of the two electronic states in a ClAlPc molecule is lifted by the crystal field as mentioned above, transition dipole moments involving the respective states could be estimated to lie perpendicularly with each other in the molecular plane. This permits the initial arrangement of the transition moments such as one of them to coincide with X-axis and the other with Y-axis, so that absorption intensities directed by these moments can be expressed by I_x and I_y, respectively. Then, the discussion similar

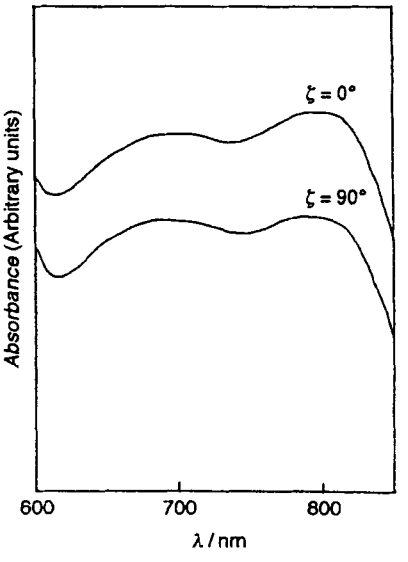

FIGURE 13 Polarized absorption spectra of a double-layered thin film in the spectral region of the Q-band for ClAlPc.

to that described above yields the intensity ratio as follows:

$$I_x / I_y = (\omega_x \Gamma_y / \omega_y \Gamma_x) (p_x / p_y)^2 (a_{21}^2 / a_{22}^2)$$

By this equation, the intensity ratios at particular angles, $\zeta = 0°$ and 90°, will be predicted to be proportional to the following quantities:

$$I_x / I_y \propto (1 - \sin^2\beta \cos^2\gamma) / (1 - \sin^2\beta \sin^2\gamma) \qquad \text{for } \zeta = 0°$$
$$I_x / I_y \propto (1 + \sin^2\beta \cos^2\gamma) / (1 + \sin^2\beta \sin^2\gamma) \qquad \text{for } \zeta = 90°$$

If the directions of transition dipole moments of a molecule in the ClAlPc layer coincided with x- and y-axes of the coordinates fixed on the molecule, relative I_x / I_y values for $\zeta = 0°$ and 90° were 1.9 and 0.74, respectively, since $\beta = 125.2°$ and $\gamma = 63.5°$ are observed for the ClAlPc layer in $(1\ \bar{1}\ 0)$ orientation as shown in Table II. However, the results shown in Figure 13 do not agree with this supposition. The orthogonal transition dipole moments are therefore deviated from the directions of the coordinate axes on a molecule in the layer, and $\gamma \approx 45°$ for the transition moments should be acceptable because of almost the same spectra for $\zeta = 0°$ and 90°. The latter indicates that the angle between the directions of the transition dipole moments and those of the molecular coordinate axes is estimated to be about 18°, with bearing $\gamma = 63.5°$ in mind again. This deviation of the transition moments can be caused by unequal contributions to them from hybridization between split excited states.

Correlation of Molecular Orientations at the Interface of Double-Layered Thin Films

Finally, we will elucidate the correlations of molecular orientations at the interface of the double-layered thin films already demonstrated in Table III, by close examination of the transition dipole moments of the concerned molecules in the respective layer determined above.

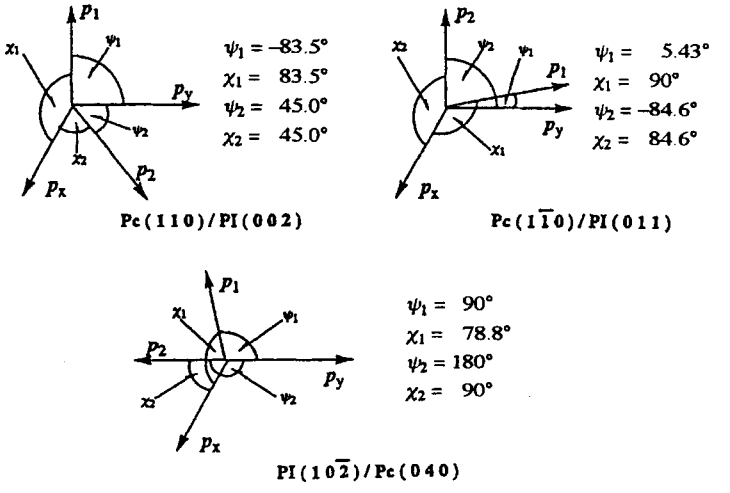

FIGURE 14 Disclosed correlations of transition dipole moments of two different molecules at the interface of double-layered thin films. Pc and PI indicate ClAlPc and DM-PBDCI, respectively.

Figure 14 shows the correlations disclosed so far among the transition dipole moments of DM-PBDCI, $\boldsymbol{p}_1$ (// *ac*-plane) and $\boldsymbol{p}_2$ (// *b*-axis), and those of ClAlPc, $\boldsymbol{p}_x$ and $\boldsymbol{p}_y$ ($\perp \boldsymbol{p}_x$), in the respective layers of the double-layered thin films; Pc and PI in this figure indicate ClAlPc and DM-PBDCI, respectively. The obtained correlations lead to a conclusion that the transition dipole moments of the two different molecules are, in most cases, perpendicular or parallel to one another at the interface of those films: This will explain the observation that a molecular orientation in the underlayer of a double-layered thin film controls that in the upper layer as pointed out above. To understand the conclusion above, the energy of interaction between the transition dipole moments on two molecules facing to each other at the interface of a double-layered thin film should be estimated in detail. A preliminary calculation of such interaction energies and the related consideration suggest that the conclusion above could be rationalized under the restriction that four independent transition dipole moments are by no means perpendicular to one another. Besides, an apparently exceptional angle ($\approx$ 45°) is obtained for only a few cases in Figure 14, and it could be understood by more detailed examination and consideration.

SUMMARY

Correlation of molecular orientations in the respective layers of double-layered thin films prepared by *in situ* vapor deposition of DM-PBDCI and ClAlPc has been examined by means of X-ray diffraction and electronic absorption with polarization measurements in part. Besides, prior to those experiments single crystal structures of the two compounds were refined to obtain their structural data in high accuracy and precision for the analysis and discussion afterwards.

First, molecular orientations in single-layered thin films have been determined by X-ray diffraction as follows: the molecular plane of DM-PBDCI is oriented at about 60° to the substrate surface independent of the orientations of crystallites, on the other hand, the molecular plane is parallel to the substrate surface or both the plane and the molecular long axis are inclined at $\approx$ 60° to it, in the case of ClAlPc. To obtain such results, the Eulerian angles with an imaginary rotational operation have efficiently been used to represent geometric arrangements of a molecule or a crystal in relation to the substrate surface.

Correlations of molecular orientations in double-layered thin films have also been examined. In the case of ClAlPc/DM-PBDCI/SS systems, where SS indicates a substrate, a ClAlPc(1 $\bar{1}$ 0)/DM-PBDCI(0 1 1)/SS orientation is observed for the film prepared at r. t. and a ClAlPc(1 1 0)/DM-PBDCI(0 0 2)/SS orientation for that prepared

at high temperatures up to 200 °C. In turn, a DM-PBDCI/ClAlPc/SS system exhibits a DM-PBDCI(1 0 $\bar{2}$)/ClAlPc(0 4 0)/SS orientation with an intensity of the (1 0 $\bar{2}$) reflection from a DM-PBDCI layer on ClAlPc prepared on the substrate at r. t. being weaker than that from DM-PBDCI on ClAlPc prepared on the substrate at 200 °C. Besides, both (1 1 0) orientation for ClAlPc and (1 0 $\bar{2}$) one for DM-PBDCI are not observed in the respective single-layered films. From these observations, it has been confirmed that molecular orientations in the underlayer can control those in the upper layer for organic double-layered thin films comprising DM-PBDCI and ClAlPc layers.

We have tried to elucidate the correlations of molecular orientations observed above, that is, the relations of Eulerian angles obtained for each pair of characteristic reflections by the two organic layers, with further examination of electronic absorption spectra which have disclosed the relations of transition dipole moments of concerned molecules in the different layers. The derived result that transition dipole moments of two different molecules facing to each other at the interface of double-layered thin films are in most cases perpendicular or parallel to one another could explain the observed correlations in molecular orientations above.

DEDICATION

It is our great pleasure to dedicate this paper to Professor Yusei Maruyama on the occasion of his retirement from the Institute for Molecular Science, in recognition of his outstanding achievements in the research field of fundamental materials chemistry, in particular, physics and chemistry of organic thin films.

ACKNOWLEDGMENTS

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