Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Interfacial Molecular Interactions Between Ferroelectric Liquid Crystal and Polyvinylalcohol Films as Probed by Infrared Reflection Absorption Spectroscopy

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Version of record first published: 23 Sep 2006.

To cite this article: Y. Suzuki , S. Hasegawa & A. Hatta (1995): Interfacial Molecular Interactions Between Ferroelectric Liquid Crystal and Polyvinylalcohol Films as Probed by Infrared Reflection Absorption Spectroscopy, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 264:1, 1-10

To link to this article: http://dx.doi.org/10.1080/10587259508037296

Mol. Cryst. Liq. Cryst., 1995, Vol. 264, pp. 1–10
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Interfacial Molecular Interactions between Ferroelectric Liquid Crystal and Polyvinylalcohol Films as Probed by Infrared Reflection Absorption Spectroscopy

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(Received May 31, 1993; in final form November 8, 1993)

Infrared reflection absorption spectroscopy (IRAS) was used to study the molecular alignment of the ferroelectric liquid crystal material, (*S*)-4-(α-methylheptyloxy)-4′-(4″-*n*-octylphenyl-oxycarbonyl)biphenyl (MHOPOB), on a highly-purity polyvinylalcohol (PVA) film. The molecular alignment was characterized as a function of the temperature and the thickness of the liquid crystal. For the film of 200 nm in thickness, the molecules in the chiral smectic C phase (SmC*) were aligned with their long axes perpendicular rather than parallel with respect to the PVA substrate surface. This alignment was found to disappear at the isotropic phase temperature. A similar molecular alignment was observed for a 20 nm-thick MHOPOB film in the SmC* phase, but the detailed alignment was different from that in the 200 nm-thick film. This alignment in the SmC* phase was sustained even at the isotropic temperature in contrast to the 200 nm-thick film, suggesting a short-range interaction between the PVA film surface and MHOPOB molecules. An experimental support for this short-range interaction is furnished by our polarization modulation IRAS measurements. The effect of PVA rubbing on the alignment is also discussed.

Keywords: Ferroelectric liquid crystal, interface, infrared absorption, molecular alignment, PVA

1. INTRODUCTION

In recent years, much effort has been devoted to the development of information display devices using ferroelectric liquid crystals (FLCs) because of their fast response to an externally applied electric field.[1–4] In order to acquire high performance FLC display devices, one has to control the molecular alignment at the electrode surfaces in the field-off state as well as in the field-on state. In this respect, the knowledge of the anchoring properties of FLC molecules at the substrate surface is of great significance. While many useful techniques have been proposed to align FLCs, the actual mechanisms have not yet been established. This is largely due to the difficulty of characterizing a limited number of the interfacial species.

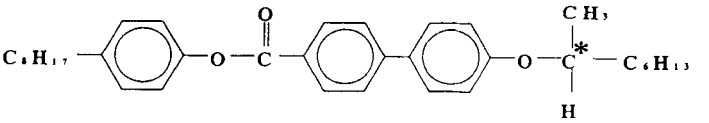
Among various types of surface analytical methods, molecular vibrational spectroscopy has been developed into one of the most powerful tools to obtain direct information on the structure of surface species and their bonding character. High-resolution electron energy loss spectroscopy (HREELS)[5] is a highly sensitive technique to obtain vibrational spectra of adsorbates on metal and semiconductor surfaces in ultra-high vacuum. An alternative method for detecting surface vibrational species is

infrared reflection absorption spectroscopy (IRAS),[6–8] which can be used in relatively high-pressure environments, in contrast to HREELS. In this method, the infrared radiation at the metal surface is polarized normal to the surface and hence the observed spectrum can reveal the alignment of the surface molecules: only those vibration modes that accompany a change in dipole moment normal to the metal surface are observed strongly in the IRAS spectrum.[9,10] In spite of the usefulness of IRAS, studies of the molecular alignment of FLCs by IRAS have not been performed. In the present work, we have used IRAS to investigate the surface-induced molecular alignment in thin films of the FLC material, (s)-4-(α-methylheptyloxy)-4′-(4″-*n*-octyl-phenyl-oxycarbonyl)biphenyl (MHOPOB).

The main mechanisms for the surface alignment of liquid crystals (LCs) can be classified into chemical and topographical effects. In the former the interaction of LC molecules with the substrate surface occurs through their chemical structures, but in the latter the elastic deformation energy of the LC, caused by the surface geometrical structure, is an important factor in determining the alignment.[11] In addition to these substrate effects, interactions between the constituent molecules are clearly important in determining the structures of LC phases. In the ferroelectric chiral smectic C (SmC*) phase for instance, the constituent molecules are in layers and packed in such a way that their long molecular axes are tilted at a definite angle with respect to the layer plane normal but directed differently in going from one layer to another to form a helical orientational structure. This helical structure probably arises from the chirality of the material. Because of the helical distribution of their constituent molecules, the bulk SmC* phase has no net spontaneous polarization. For sufficiently thin FLC films, however, the helical structure can be suppressed by the influence of the substrate surface, resulting in the surface-stabilized ferroelectric states.[12] In the present paper, data in the SmC* phase in particular will be presented which show the interfacial interactions between PVA and MHOPOB films.

2. EXPERIMENTAL

Infrared measurements were performed on a Shimazu FTIR-4200 spectrometer equipped with a liquid nitrogen-cooled HgCdTe detector at 4 cm^{-1} resolution with 1024 interferometric scans. A guaranteed-grade FLC sample of MHOPOB was obtained from Chisso Petrochemicals Co. and used without further purification. The chemical structure of MHOPOB and its phase transition temperatures are shown in Figure 1,



Cryst. $\xrightarrow{54℃}$ SmC* $\xrightarrow{70℃}$ SmA $\xrightarrow{80℃}$ N* $\xrightarrow{90℃}$ Iso.

FIGURE 1 The structure of MHOPOB and phase-transition temperatures.

where the smectic A phase, chiral nematic phase, and isotropic phase are abbreviated to SmA, N*, and Iso, respectively. For IRAS measurements MHOPOB was deposited from acetone solution onto a PVA film precoated on a Pt plate with a high degree of flatness. In the present work, $OCOCH_3$-free PVA (Aldrich Chem. Co.) was mainly used as a substrate material, but $OCOCH_3$-containing PVA was also examined. In transmission measurements MHOPOB was deposited onto a PVA-coated Ge plate in the same manner as above. In any case, the thickness of the MHOPOB film was estimated assuming a bulk density of 1.0 g/cm^3 for MHOPOB. IRAS and transmission spectra reported in this paper were obtained as ratios of data with MHOPOB present to data obtained from the bare PVA substrate.

3. RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the IRAS spectrum for a MHOPOB film of 200 nm thickness formed on a PVA-coated Pt plate. The observed frequencies and assignments for several important bands in the spectrum are given in Table I. In this experiment, *p*-polarized radiation was incident at 70° with respect to the substrate surface normal. According to the normal dipole selection rule in IRAS, the vibrational bands accompanying a change in dipole moment normal to the substrate surface should be observed strongly. It is evident from Figure 2 that on going from the isotropic to the SmC* temperature the bands at 1604, 1508, and 1270 cm^{-1} increase in intensity, while the 1730 and 1080 cm^{-1} bands remain almost unchanged. Taking into account the vibrational assignments for these bands and their transition moment directions with respect to the molecular long axis, the above observations can be explained by the isotropic-homeotropic change in the alignment of MHOPOB molecule. Another support for this is provided by Figure 3 which shows the transmission spectra for a 200 nm-thick MHOPOB film deposited on a PVA-coated Ge plate. We

TABLE I

Observed Band Frequencies, Assignments, and Values of $I\pi/I\sigma$ and β for MHOPOB at the SmC* Phase Temperature (60°C)

Wavenumber (cm^{-1})	Assignment	$I\pi/I\sigma$	β^a/degrees
1730	C=O str.	0.78	60
1604	phenyl-ring str.	3.00	26
1508	phenyl-ring str.	2.96	26
1270	C—O—C (ether) asym. str.	2.64	30
1190	C—O—C (ester) asym. str.	2.22	35
1080	C—O—C (ether) sym. str.	1.35	47
1020	C—O—C (ether) sym. str.	–	–
830	phenyl C—H wag.	0.34	90[b]

[a] The angle between the direction of transition moment and the molecular long axis, calculated by assuming the tilt angle (α) to be 32.0° (see text).

[b] Assumed.

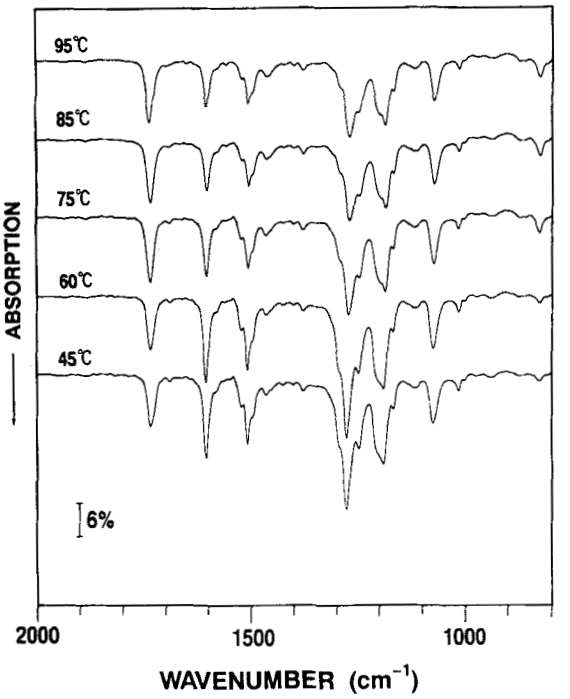


FIGURE 2 IRAS spectra of 200 nm-thick MHOPOB film on a PVA-coated Pt plate as a function of temperature.

can see in Figure 3 that the spectrum taken at 95 °C resembles the IRAS spectrum at the top of Figure 2, but at any other temperature the transmission spectrum differs from the corresponding IRAS spectrum. This arises from the difference in direction of the polarization of radiation between these two methods; in the transmission experiment, the oscillating electric field is naturally polarized parallel to the PVA substrate surface, whereas it is normal to that surface in the IRAS experiment. Accordingly these two methods give complementary information about the molecular alignment. Actually, a more quantitative alignment of MHOPOB on the average can be drawn from Figures 2 and 3, as described below.

We now consider a local alignment of the molecule in the SmC* phase, as shown schematically in Figure 4. In this model, the AB plane is taken to be the substrate surface and the optical axis is normal to that plane. Moreover, α designates the tilt angle, defined by the direction of the molecular long axis with respect to the surface normal and β is the angle between the long axis and the vibrational transition moment of a band of interest. Assuming that the long axes of the molecules in the SmC* phase are inclined at a common angle α, the following relation can be derived for each absorption band.

$$\frac{I_\pi}{I_\sigma}\frac{1}{N} = \frac{4\cos^2\alpha\cos^2\beta + 2\sin^2\alpha\sin^2\beta}{2\sin^2\alpha\cos^2\beta + \sin^2\beta(1+\cos^2\alpha)}$$

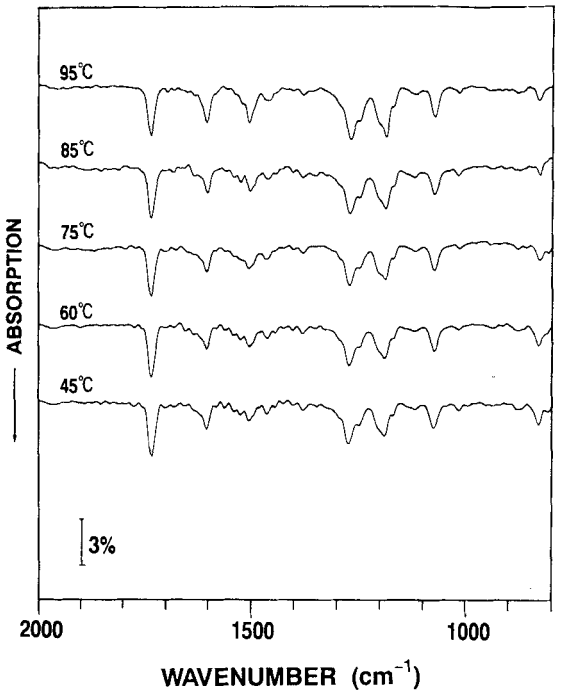


FIGURE 3 Transmission spectra of a 200 nm-thick MHOPOB film on a PVA-coated Ge plate at indicated temperatures.

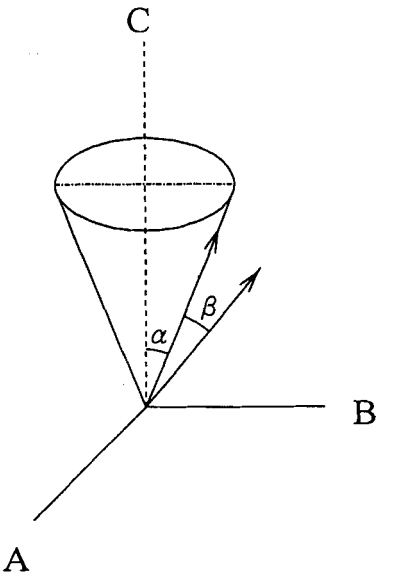


FIGURE 4 Molecular alignment with respect to the substrate surface as defined by angles α and β (see text).

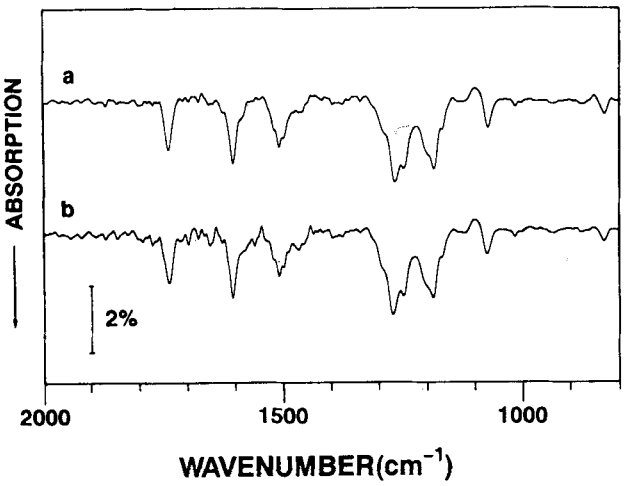


FIGURE 5 As in Figure 3, but for a 20 nm thick MHOPOB film.

Here, I_π and I_σ are the absorption intensities in the SmC* phase measured by the IRAS and the transmission method, respectively and N is the quantity I'_π/I'_σ where I'_π and I'_σ represent the corresponding absorption intensities in the isotropic phase. Based on the assumption that the phenyl C–H wagging mode produces a dipole-moment change approximately perpendicular to the molecular long axis, an α value of ca. 32.0° is obtained from the experimental I_π/I_σ value for that vibration. If this α value is used, values of β for the remainder of the vibrational bands can be estimated from the corresponding I_π/I_σ and I'_π/I'_σ ratios. The β values thus obtained are given in Table I, together with the experimental I_π/I_σ values. It is clear that the β values are quite consistent with the band assignments and the molecular structure of MHOPOB shown in Figure 1. As a result, it may be concluded that for 200 nm thickness the molecules are aligned perpendicular rather than parallel with respect to the PVA substrate surface.

Figure 5 shows the IRAS spectra of a 20 nm-thick MHOPOB film in the Iso and SmC* phases on a PVA substrate. A molecular alignment, similar to that in the 200 nm-thick film, can be deduced for the 20 nm-thick film by comparison with Figure 3. However, the detailed alignment is different, since in Figure 5 the relative intensities of the 1510 and 1270 cm^{-1} bands are weaker than those in Figure 3. Of particular interest in Figure 5 is the fact that no remarkable difference is seen between the Iso (a) and SmC* (b) phase spectra in contrast to the 200 nm-thick film. This persistent alignment at the isotropic temperature of the bulk liquid crystal is most likely attributed to interactions between the PVA and MHOPOB molecules. In other words, this observation can be interpreted as a result of the decreased film thickness and increased interaction with the PVA substrate.

There are many possible factors which are responsible for the perpendicular alignment observed above; presumably we should take into account the various parameters of the PVA substrate such as its anisotropy, surface chemical structure, imperfections, etc., in considering the alignment mechanism. In an attempt to look at

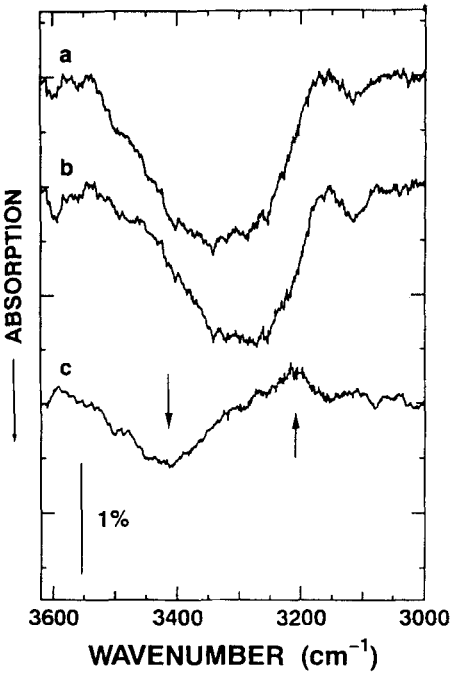


FIGURE 6 Polarization modulation IRAS spectra; (a): PVA, (b): PVA and MHOPOB, and (c): difference spectrum; (b)–(a).

the PVA/MHOPOB interface more closely, an IRAS experiment by polarization modulation[13] was conducted using an extremely thin PVA film as the substrate, the results of which are illustrated in Figure 6. In this figure, spectrum (a) was obtained from the PVA film on a Pt surface. The broad band centered at 3335 cm^{-1} is assigned to the stretching of the PVA O–H bonds. Spectrum (b) is for the PVA film coated with a small amount of MHOPOB. The subtraction of (a) from (b) yields spectrum (c), in which a large negative band appears at 3415 cm^{-1} while a small positive band appears at 3215 cm^{-1}. Thus, it is most likely that the OH stretching band was shifted to 3215 cm^{-1} by the environmental influence of MHOPOB. It is generally known that the amount of the OH-frequency shift upon formation of the OH···O bond is correlated with the O···O distance, the smaller the distance, the larger the shift. As described above, MHOPOB tends to align perpendicular on the PVA substrate and it is then very probable that the alkyl chains of MHOPOB are in contact with the PVA substrate surface. In this situation the repulsion forces between the PVA OH or CH and the MHOPOB CH_3 groups can influence the intramolecular hydrogen bonds and in turn change the O···O distance. Within the scope of short-range molecular interactions, this is a possible cause of the frequency shift of the 3335 cm^{-1} band with the deposition of MHOPOB. In liquid crystals the forces between molecules are presumably of van der Waals type and then of course dipole–dipole and dipole–induced dipole interactions must be taken into account in the present case too.

Within our IRAS measurements of MHOPOB on $OCOCH_3$-free PVA, no positive evidence has been found for the formation of hydrogen bond between the PVA OH group and MHOPOB. However, the situation is rather different when a 20 nm-thick MHOPOB was in contact with PVA containing $OCOCH_3$ residue due to the imperfect hydrolysis of polyvinylacetate. In this case, the C=O stretch band was broad compared to that observed in Figure 5 and tailed to the low frequency side. These features can most probably be explained by assuming the overlapping with at least another C=O stretch band, which was shifted to lower frequencies as a result of the hydrogen bond formation between the C=O bond of MHOPOB and the PVA OH group. The formation of the hydrogen bond is also supported by a higher frequency shift of the band peak due to the ester C—O—C asymmetric stretch vibration. Additional fact of interest is that the molecules were aligned parallel rather than perpendicular to the PVA surface even at the isotropic temperature, the result of which is explained by the hydrogen bonding at the interface.

It is generally recognized that nematic liquid crystal molecules tend to align with their long axes parallel to the direction of rubbing of the cell walls. Indeed, this was also demonstrated in our transmission experiment on a MHOPOB film of ca. 1 μm thickness sandwiched between two BaF_2 plates. The BaF_2 plates were previously coated with PVA followed by rubbing unidirectionally by a lint-free cloth.[14] The spectra taken by radiation with the electric vector polarized parallel and perpendicular to the rubbing direction are shown in Figure 7. The resulting dichroic ratios $k_{\parallel}/k_{\perp}$ for typical vibrational bands are given in Table II, where $k_{\parallel}$ and $k_{\perp}$ are relative absorption

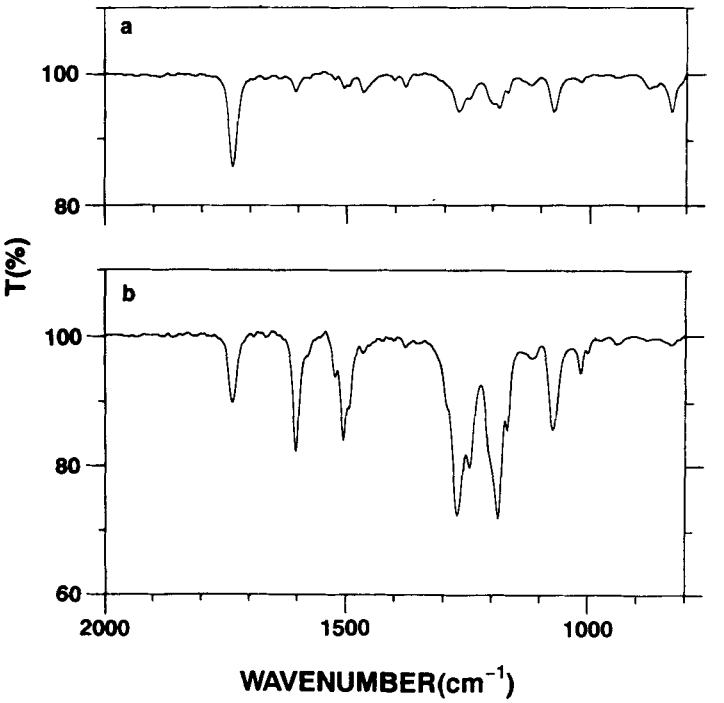


FIGURE 7 The polarized transmission spectra of a MHOPOB film at 60 °C taken with radiation parallel (a) and perpendicular (b) to the rubbing direction.

TABLE II

Observed Band Frequencies, Assignments, and Values of Dichroic Ratio ($k_\parallel/k_\perp$) and a 1 μm-thick MHOPOB Film in the SmC* Phase (at 60°C)

Wavenumber (cm^{-1})	Assignment	$k_\parallel/k_\perp$ [b]	β [c]/degrees
1732	C=O str.	0.75	60
1607	phenyl-ring str.	7.12	10
1510	phenyl-ring str.	7.64	8
1270	C—O—C (ether) asym. str.	5.50	18
1192	C—O—C (ester) asym. str.	6.27	14
1072	C—O—C (ether) sym. str.	2.69	35
830	phenyl C—H wag.	0.22	90 [d]

[a] Rubbed in a single direction.
[b] $k_\parallel$ and $k_\perp$ refer to absorption coefficients parallel and perpendicular to the rubbing direction.
[c] Values based on $\alpha = 26.3°$ (see text).
[d] Assumed.

coefficients for radiation parallel and perpendicular, respectively, to the rubbing direction. Based on the assumption that the molecules are aligned with their long axes uniaxially around the rubbing direction and the transition moment of the 830 cm^{-1} band is oriented perpendicular to the long axis, an α value of 26.3° was obtained. By using this value, the β values for other vibrational bands were calculated in the same manner as described before. The results are presented in Table II.

4. CONCLUSIONS

We used IRAS for the first time to investigate the molecular alignment of MHOPOB in thin films on PVA substrate surfaces. In particular, this technique provided evidence for the interfacial interaction between the LC and PVA substrate surface. However, since IRAS is based on the specular reflection of radiation on a metal surface, it demands extremely thin samples when used for probing such an interface. In this regard, surface enhanced electric field spectroscopy (SEEFS)[15] is better suited, because the species within a range of about 5 nm from the metal surface can be observed strongly.[16] Its practical features have shortly been reported elsewhere.[17]

Acknowledgement

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 04205011) from the Ministry of Education, Science and Culture of Japan. We are grateful to Y. Fukuda, Shimazu Technoresearch Co. for the spectroscopic facility used in this work. We are also obliged to Hitachi Research Laboratory, Hitachi Ltd. for financial support.

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