

## Surface studies of polyimide thin films via surface-enhanced Raman scattering and second harmonic generation

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**SUMMARY:** Two polyimides having the same backbone chemical structure and different pendant side groups at the 2- and 2'-positions of the diamine, the six methylene units capped with 4-cyanobiphenyl end groups and trifluoromethyl, were synthesized (6FDA-6CBO and 6FDA-PFMB). Surface-enhanced Raman scattering and surface optical second harmonic generation measurements show that after rubbing the major change in 6FDA-PFMB surface appears in the orientation of the dianhydride, which was originally planar, but becomes tilted with respect to the surface plane. In the case of 6FDA-6CBO, rubbing also causes the originally planar 4-cyanobiphenyls to tilt away from the surface and assume an azimuthally anisotropic distribution.

### Introduction

Uniform and unidirectional liquid crystal (LC) alignment, which is essential for liquid crystal display (LCD) technology, is often realized by using rubbed polyimide films as alignment layers<sup>1</sup>. Therefore, it is important that we understand the mechanism responsible for this surface-induced LC alignment, including the possibility of controlling the pretilt angle. It is generally believed that molecular interactions between LC and polyimide surfaces<sup>2–7</sup> rather than the micro-groove<sup>8</sup>) plays the key role in affecting the LC alignment. This suggests the importance of knowing the molecular orientation and chemical structure of the polyimide surfaces. Most of the studies rely on bulk-sensitive methods such as infrared dichroism and optical retardation<sup>9–15</sup>. Recently, some surface-sensitive measurements using electron spectroscopy for chemical analysis<sup>16</sup>) and X-ray scattering to obtain molecular orientation and structure<sup>17,18</sup>) of polyimide surfaces have been reported. A clear understanding of the correlation between polyimide surface structure and bulk LC alignment is still missing, suggesting the need of further investigation with other sensitive experimental techniques.

In this paper, we report the study of a polyimide specially designed for high pretilt LC alignment with two unusually surface-sensitive techniques, surface-enhanced Raman scattering (SERS) and surface optical second harmonic generation (SHG). We found that the molecular alignment at the surface of such polyimide thin films can be significantly changed by rubbing. These changes are

presumably responsible for inducing the high pretilt of the LC alignment.

Vibrational spectroscopy is known to be an effective probe to assess the nature of chemical bonding, interactions, conformations and even orientation of molecules. However, normal infrared or Raman vibrational spectroscopy to polymer films generally is not surface-specific. It was found in 1974 that the intensity of Raman scattering from molecules adjacent to a roughened silver surface can be enhanced by as much as  $10^6$  times<sup>19,20</sup>). The enhancement decreases rapidly as a function of distance away from the silver surface, making this Raman scattering particularly surface-sensitive. SERS is now considered as one of the major techniques in the area of surface characterization. Here we report, to the best of our knowledge, the first application of SERS to the study of effect of rubbing on polyimide surfaces.

The other surface probe we employed was SHG, which is a second-order nonlinear optical process. Under the electric dipole approximation, it is forbidden in media with inversion symmetry, but allowed at surfaces or interfaces where such symmetry is necessarily broken. Consequently, it is intrinsically surface-sensitive. The polarization dependence of SHG allows the determination of surface molecular orientation<sup>6,7</sup>). The SHG process is governed by a surface nonlinear susceptibility tensor  $\bar{X}^{(2)} = N\langle\bar{\alpha}^{(2)}\rangle$ , where  $N$  is the surface density,  $\bar{\alpha}^{(2)}$  is the hyperpolarizability tensor, and  $\langle\rangle$  denotes the average over the orientational distribution of the molecules. From SHG,

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one can measure  $\bar{X}^{(2)}$  from which the approximate orientational distribution can be determined assuming  $\bar{\alpha}^{(2)}$  is known. The situation is greatly simplified if the molecules are rod-like. In such a case,  $\bar{\alpha}^{(2)}$  is dominated by a single element  $\alpha_{\xi\xi\xi}^{(2)}$ , with  $\xi$  along the long molecular axis, and the orientational distribution can be more readily obtained from  $\bar{X}^{(2)}$ . The sample we used in this study belongs to this category.

## Experimental part

The polyimide samples we studied are denoted by 6FDA-PFMB and 6FDA-6CBO. Their chemical structures are given in Fig. 1. The parent polyimide, 6FDA-PFMB, was

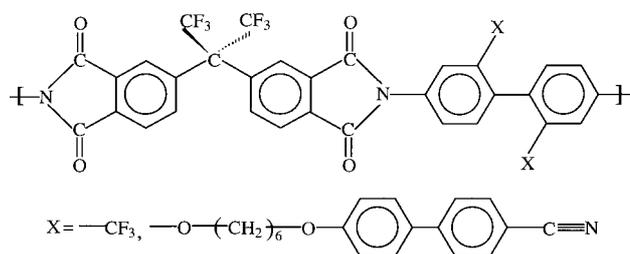


Fig. 1. Chemical structures of two aromatic polyimides studied in this study

synthesized by a one-step polymerization method from 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (PFMB) diamine in refluxing *m*-cresol at 200 °C for at least 4 h<sup>21</sup>. The intrinsic viscosity of the resulting 6FDA-PFMB polyimide was 1.50 dL/g in *m*-cresol at 30 °C, which indicated that it was a high molecular weight material<sup>22</sup>. The polyimide containing side-chain liquid crystals, 6FDA-6CBO, was also synthesized by the same one-step polymerization method from 6FDA and 2,2'-bis(4'-cyanobiphenyl-4-yloxyhexyloxy)-4,4'-diaminobiphenyl. Alkyl side chains containing six methylene units extended with 4-cyanobiphenyl mesogens were introduced onto 2- and 2'- positions of the diamines. The polymerization was also carried out by refluxing in *m*-cresol. The intrinsic viscosity of 6FDA-6CBO was 0.50 dL/g in chloroform at 30 °C<sup>23</sup>. Solution nuclear magnetic resonance and Fourier-transform (FT) infrared spectroscopy results showed that poly(amic acid)s can not be detected in these samples<sup>23</sup>.

Thin films of 6FDA-PFMB and 6FDA-6CBO for SERS measurements were made by spin-coating 2% (w/w) solutions in cyclopentane at 2000 rpm onto indium-tin-oxide (ITO)-coated glass substrates followed by baking at 120 °C for 20 h. Thickness of the films was controlled to a range of 200–600 nm. Thicker films with thickness of 2–5  $\mu$ m were prepared from more concentrated solutions for bulk sample measurements. Thin films for the SHG measurements were prepared by the same solution at 2000 rpm on fused silica substrates followed by the same thermal treatment procedure. Rubbing was carried out with a rotating drum wrapped

with velvet. LC molecules sandwiched between two such substrates gave 6FDA-6CBO a pretilt angle of  $\approx 20^\circ$ . The preparation of SERS-active substrates involved the use of a silver colloidal deposition method via the reduction reaction of AgNO<sub>3</sub> in deionized water<sup>24</sup>. The silver colloids were directly deposited onto the rubbed and non-rubbed surfaces of polyimide thin films simultaneously.

FT Raman experiments were carried out using a back-scattering geometry on a Bruker IFS 100 FT Raman spectrometer equipped with an air-cooled pumped Nd-YAG laser and a ultra-sensitive liquid nitrogen cooled Ge detector. In the SHG experiment, a frequency-doubled Q-switched mode-locked Nd: YAG laser at 532 nm was used as the fundamental input beam and the second harmonic field was detected in the reflection direction after proper filtering. The incidence angle was 67°. Since 532 nm is at the tail of the absorption band of 6FDA-6CBO, the fundamental laser intensity must be kept low enough to avoid optical damage of the sample.

## Results and discussion

Fig. 2a and 2b show normal FT-Raman vibrational spectra from thick films of 6FDA-PFMB and 6FDA-6CBO polyimides. Comparison of these two spectra (Fig. 2c) results in identification of the vibration modes of the *n*-alkyl side chains and 4-cyanobiphenyl mesogens. In addition to a few residual modes from the polyimide backbone, two groups of vibration modes in the spectrum can

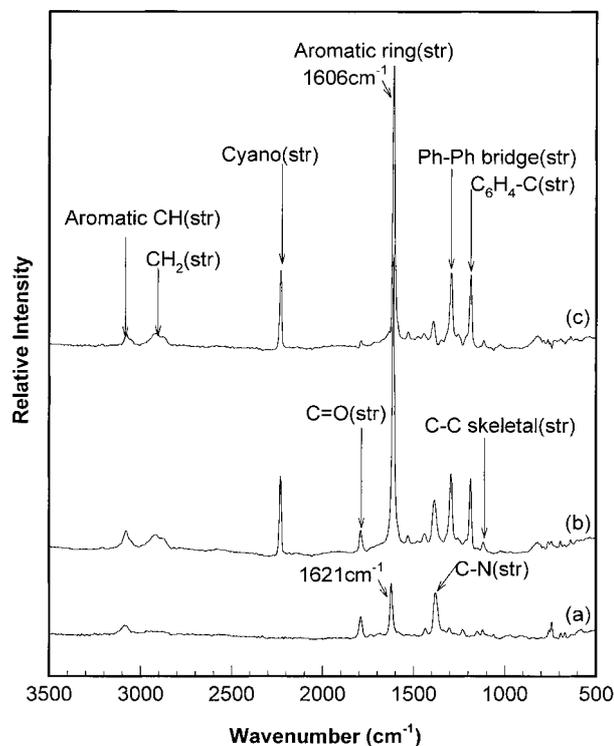


Fig. 2. FT-Raman spectra of the bulk vibration modes in (a) 6FDA-PFMB thick films, (b) 6FDA-6CBO thick films, and (c) difference spectrum between (a) and (b)

be identified for the alkyl side chains and their end groups. For the 4-cyanobiphenyl end groups, the aromatic C—H stretching is at  $3074\text{ cm}^{-1}$ , the C≡N stretching is at  $2227\text{ cm}^{-1}$ , the aromatic in-plane ring stretching is at  $1606\text{ cm}^{-1}$ , the phenylene-phenylene bridge stretching is at  $1291\text{ cm}^{-1}$  and the C<sub>6</sub>H<sub>4</sub>—C stretching is at  $1182\text{ cm}^{-1}$ . The last two may also involve aromatic X-sensitive vibration modes. For the methylene units, the absorption bands at  $2908$ ,  $2860$ ,  $1450$  and  $1112\text{ cm}^{-1}$  are the asymmetric CH<sub>2</sub> stretching, symmetric CH<sub>2</sub> stretching, CH<sub>2</sub> deformation and C—C skeletal stretching, respectively. The presence of the  $1112\text{ cm}^{-1}$  band indicates that at least some of the methylene units in the alkyl side chains adopt a *trans*-conformation<sup>25</sup>. The normal FT-Raman spectra for the rubbed thick films are almost identical to those of the unrubbed films, indicating that rubbing is not strong enough to affect the bulk structures.

For thin-film polyimide samples, normal FT-Raman spectroscopy is not sensitive enough to yield meaningful spectra. With silver colloids deposited on the film surface, however, the SERS spectra of the thin film 6FDA-PFMB and 6FDA-6CBO can be readily observed as shown in Fig. 3a and 3b, respectively. The band frequencies are in fairly good agreement with those shown in Fig. 2 for the bulk samples, although the relative intensities are different because of selection rules associated

with surface enhancement on metals. The difference spectrum between Fig. 3a and 3b is given in Fig. 3c. Comparing the spectra between Fig. 2c and Fig. 3c reveals that the CH<sub>2</sub> symmetric and antisymmetric stretching vibrations around  $2860$ – $2925\text{ cm}^{-1}$  are more strongly enhanced, possibly due to close contact of the side chains with the silver colloids. This band is broad and asymmetric, and the intensity of the CH<sub>2</sub> asymmetric (out-of-phase) stretching mode at  $2925\text{ cm}^{-1}$  is much higher than that of the CH<sub>2</sub> symmetric (in-phase) stretching mode at  $2860\text{ cm}^{-1}$ . Based on the selection rules of SERS for molecules adsorbed on metal surfaces, molecular vibrations involving motions perpendicular to the surface should be enhanced in the spectra, while those involving motions parallel to the surface weakened<sup>26</sup>. Therefore, SERS can be used for qualitative determination of molecular orientation at surfaces<sup>27</sup>. The drastic decrease in the intensity of the aromatic in-plane stretching at  $1606\text{ cm}^{-1}$ , and the nearly complete disappearance of the aromatic C≡N stretching at  $2227\text{ cm}^{-1}$ , the phenylene-phenylene bridge stretching at  $1291\text{ cm}^{-1}$  and the C<sub>6</sub>H<sub>4</sub>—C stretching at  $1182\text{ cm}^{-1}$  (as indicated above, the last two may also involve aromatic X-sensitive vibration modes) indicate that the long molecular axis of the 4-cyanobiphenyl mesogen in the side-chain lies more parallel to the thin film surface. On the other hand, the intensity

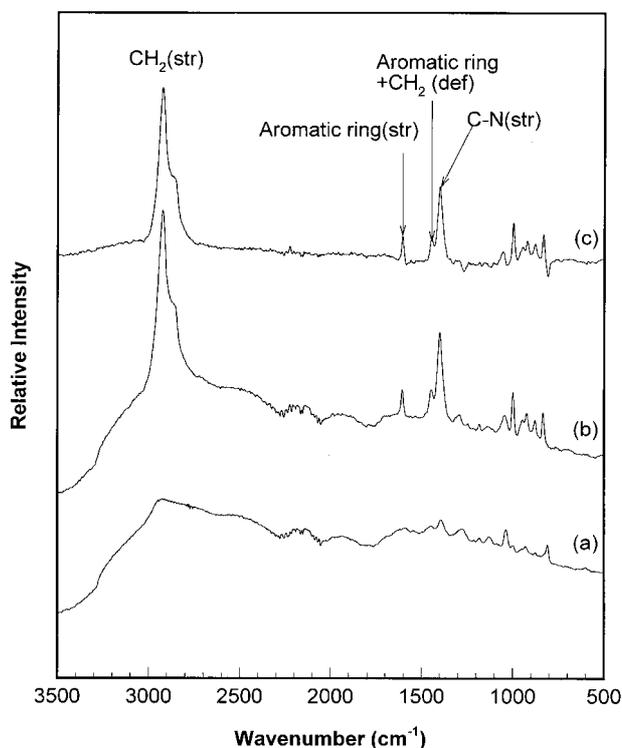


Fig. 3. SERS spectra of the vibrational modes before rubbing in (a) 6FDA-PFMB thin films, (b) 6FDA-6CBO thin films, and (c) difference spectrum between (a) and (b) for unrubbed surfaces

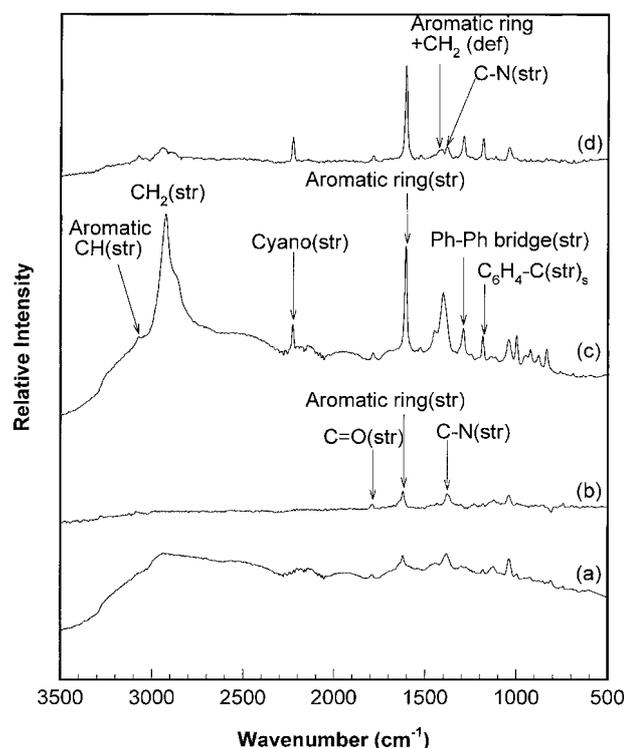


Fig. 4. (a) SERS spectra of the vibrational modes after rubbing in 6FDA-PFMB thin films, (b) difference spectrum between (a) and Fig. 3(a), (c) SERS spectra of the vibrational modes after rubbing in 6FDA-6CBO thin films, (d) difference spectrum between 4(c) and Fig. 3(b)

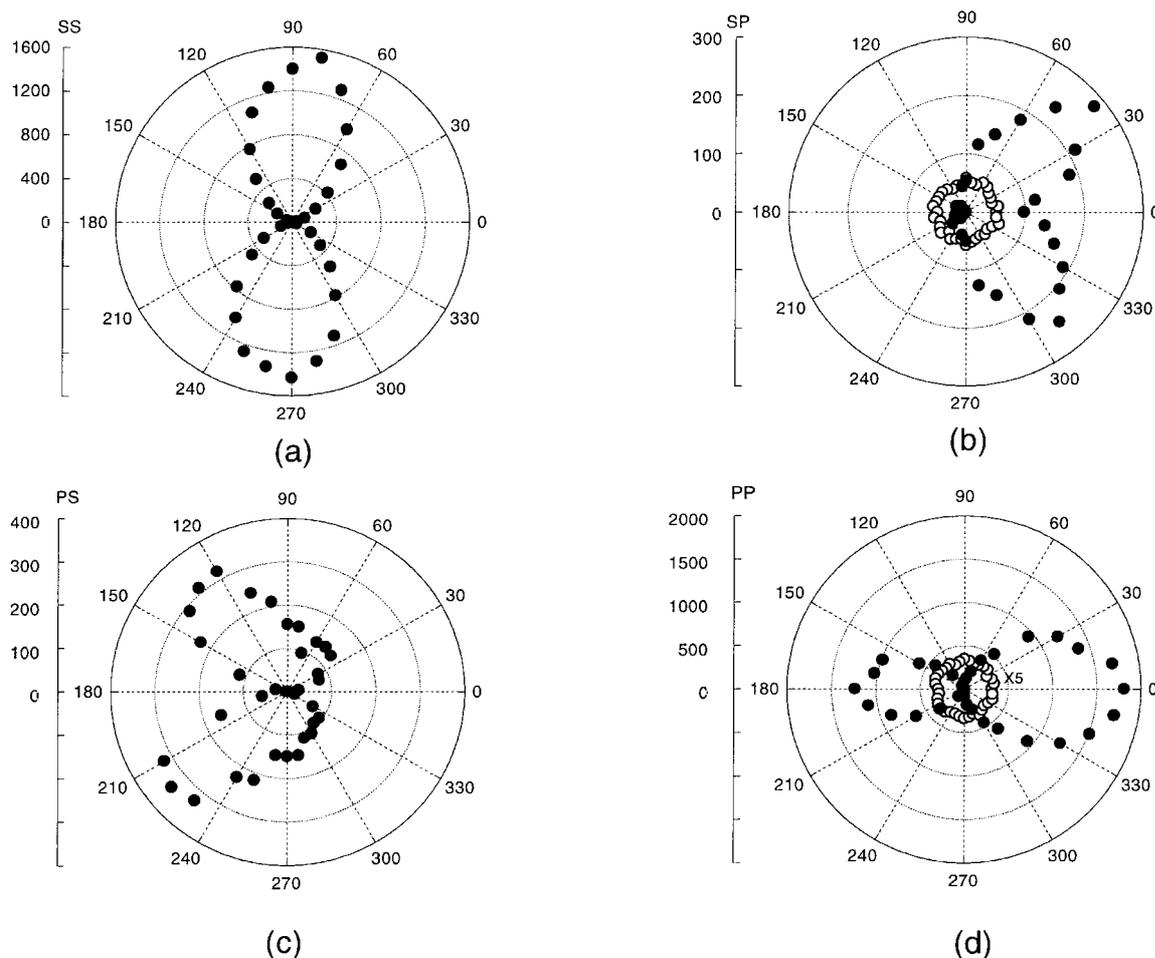


Fig. 5. SHG measurement on unrubbed (opened symbols) and rubbed 6FDA-6CBO thin films: (a) both input and output are s-polarized (s-in, s-out); (b) s-in p-out; (c) p-in s-out; and (d) p-in, p-out. (The SHG signal from the unrubbed sample is enlarged by a factor of 5 in this figure). Note that SHG with s-polarized output from isotropic samples are forbidden by symmetry

of the symmetric C—N stretch of 6FDA at  $1380\text{ cm}^{-1}$  is substantially enhanced. This suggests that the presence of side chains at the thin-film surface substantially distorts the orientation of these bridge bonds, making them tilt away from the surface (see below). Furthermore, the symmetric C=O stretching mode in the imide rings of 6FDA at  $1791\text{ cm}^{-1}$  and the backbone phenylene stretching modes at  $1621\text{ cm}^{-1}$  were not observed, showing that the imide-phenylene conjugated structure adopts a planar conformation nearly parallel to the surface.

Fig. 4a shows the SERS for 6FDA-PFMB after rubbing. The difference spectrum (Fig. 4b) obtained by subtracting Fig. 3a from Fig. 4a reflects the rubbing effect on the polyimide backbone. The vibration mode at  $1621\text{ cm}^{-1}$ , which represents the aromatic in-plane ring stretching in the dianhydrides, is enhanced by rubbing<sup>27</sup>. This suggests that rubbing causes the phenylenes in the dianhydride part of the polyimide backbones to more or less tilt away from the surface. This is consistent with the

appearance of the peak at  $1791\text{ cm}^{-1}$  associated with the symmetric C=O stretching in imide rings that are conjugated with phenylenes in dianhydrides. The symmetric C—N stretching in the bridge between dianhydrides and diamines at  $1380\text{ cm}^{-1}$  also shows enhancement and further confirms the tilting of the dianhydride group.

The SERS spectrum of the rubbed 6FDA-6CBO thin film is shown in Fig. 4c. Subtracting the unrubbed 6FDA-6CBO spectrum in Fig. 3b from the spectrum in Fig. 4c yields the difference spectrum presented in Fig. 4d, which describes the effect of rubbing on the 6FDA-6CBO surface. It is seen that all those 6CBO modes (described earlier with reference to Fig. 2c), which were hardly detectable from the unrubbed surface, become clearly visible after rubbing. This indicates that rubbing has caused a reorientation of the 6CBO side chains at the surface: they have raised from the nearly planar configuration to a tilted configuration on the surface. The spectrum in Fig. 4d also exhibits the 6FDA modes that appear in

Fig. 4b (illustrating the rubbing effect on the 6FDA-PFMB surface). This suggests that the polyimide backbone is similarly distorted or reoriented by rubbing in this case. The side-chain reorientation of the 6FDA-6CBO surface by rubbing is presumably responsible for the observed surface-induced high pretilt in the LC bulk film. The effect has been corroborated by our SHG result. In addition, SHG measurement can provide information on the azimuthal distribution of the side-chain orientation<sup>6,7</sup> as we shall now discuss.

The SHG was mainly generated by the 4-cyanobiphenyl mesogens as seen from the fact that the SHG from 6FDA-PFMB at the same fundamental intensity was negligible. As mentioned earlier<sup>6,7</sup>, the 4-cyanobiphenyl group has a hyperpolarizability tensor  $\bar{\alpha}^{(2)}$  dominated by a single element  $\alpha_{\xi\xi\xi}^{(2)}$ . Thus, its orientation can be deduced from the nonlinear susceptibility tensor  $\bar{\chi}^{(2)}$  which in turn can be determined by measuring the azimuthal variation of SHG with different input/output polarization combinations. Here we only sketch the results qualitatively and leave the quantitative analysis to a future report (in preparation by XZ, YRS, JYG and SZDC). Fig. 5 shows an example of the SHG data on unrubbed and rubbed 6FDA-6CBO surfaces. As seen from the figure, the SHG signal from the unrubbed sample is small and essentially isotropic, while that from the rubbed sample is much larger and considerably anisotropic, indicating a significant rearrangement of the 4-cyanobiphenyl orientation induced by the rubbing process. The 6CBO side chains are aligned more parallel to the rubbing direction. The results also indicate some slight changes in the polar orientation of 6CBO, consistent with the above-mentioned SERS result that the 4-cyanobiphenyl group becomes more tilted from the surface after rubbing. The azimuthally anisotropic and nonplanar alignment of the 6CBO side chain at the surface is presumably the reason why rubbed 6FDA-6CBO surfaces can render a high pretilt in a bulk LC film through orientational epitaxy.

## Conclusion

A polyimide specially designed to give high LC pretilt, 6FDA-6CBO, was synthesized. The surface structure of 6FDA-6CBO thin film before and after rubbing was studied by SERS and SHG. It has been found that the rubbing process significantly rearranges the surface orientational distribution of the side-chains, and slightly changes the alignment of the backbone. These results may shed some light on the understanding of the molecular mechanism responsible for aligning LC by rubbed polyimide and the systematic design of alignment layers for inducing high-pretilt LC bulk alignment.

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