

Photoluminescence and photoconductivity studies of oriented polyfluorene thin films

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Abstract

Photoluminescence and photoconductive properties of poly(9,9-dioctylfluorene) (F8) on rubbed polyimide (PI) alignment layers have been studied. The F8 thin films are highly oriented, which is manifested from polarized absorption, fluorescence, and photoconductivity spectra (the order parameter of F8 is 0.86). The ratio of photocurrent parallel to perpendicular directions to the rubbing direction (photoconductivity anisotropy) is 18 at 2.9 eV for F8. Effects of C₆₀ addition to F8 on the optical properties are also studied. C₆₀ addition to F8 significantly increases photoconductivity but decreases the order parameter (0.67) and the photoconductivity anisotropy (7 at 2.9 eV). Both F8 and C₆₀ doped F8 thin films exhibit similar photoconductive response and similar photoconductivity anisotropy (3–4) above 3.8 eV.

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1. Introduction

Aligned conjugated polymers have technological importance for the fabrication of polymeric photoelectronic devices, such as light-emitting diodes, field-effect transistors and photosensors. It is expected that the alignment of polymer backbones significantly improves charge-carrier mobilities, and induces polarized photoluminescence and polarized photoconductivity in these devices. In general, the alignment of polymer backbones is achieved by stretching [1], rubbing [2,3], photoalignment [4,5] and a friction transfer method [6]. Attractive method for alignment of polymer backbones is based on the utilization of liquid crystalline phase of the polymers on mechanically rubbed polyimide thin films, as employed in liquid-crystal display industries.

poly(9,9-dioctylfluorene) (F8) is a π -conjugated polymer and a thermotropic liquid crystal above 443 K [7,8]. It is expected that F8 can be applied to polarized light sources for integrated optics and to detection of polarized light because conjugate organic systems often exhibit a pronounced anisotropy of the electric structure, induced by alignment technique

for liquid crystals [3,5,7,8]. It is thus important to study quantitative data on the orientational characteristics and their effects on the optical properties of F8 thin films.

In this work, we report the study of the orientational characteristics of F8 on polyimide (PI) alignment layers using polarized optical absorption, fluorescence, and photoconductivity spectroscopies. The photoconductivity of aligned F8 thin films is measured with coplanar Au electrode configuration. This electrode configuration is suitable for the study of photoconductivity because the photoconductivity spectra (either sybatic or antibatic response) are influenced by internal filter effects in sandwiched electrode configuration with asymmetric electrode materials [4]. It is shown that photoconductive anisotropy of F8 aligned thin film is large (the ratios of photocurrent parallel to perpendicular directions to the rubbing direction are 18 at 2.9 eV for F8) and hence the materials are applicable to polarization sensitive devices. C₆₀-doping effects of polarized photoconductivity in aligned F8 thin films are also shown.

2. Experimental

Alignment layers of PI-C obtained from Nissan Chemical Co., Ltd. were coated onto quartz substrates and the PI-C layers

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were rubbed unidirectionally with a nylon cloth after baked at 353 K for 5 min and then at 453 K for 60 min. The thin film samples of F8 whose thicknesses were ~ 100 nm were prepared by spin-coating from toluene solution on quartz substrates that had been precoated with rubbed PI-C alignment layers (the chemical structures of PI-C and F8 are shown in Fig. 1). These samples were found to be optical isotropic. The F8 thin films were subsequently heated to 473 K followed by slow cooling to room temperature in N_2 atmosphere and after the heat treatment the F8 thin films were highly oriented. For the steady-state photoconductivity measurements, coplanar structures with Au electrodes spaced about 600 μm apart were subsequently vacuum deposited onto the F8 surfaces. C_{60} doped F8 thin films aligned on PI-C were also prepared. The purity of C_{60} was 99.98% and C_{60} doping was done by adding C_{60} to F8 toluene solution. The optical absorption spectra of as-coated and aligned F8 thin films were measured with a JASCO V-570 spectrophotometer having a PFH-507 polarizer. For polarized fluorescence measurements at 298 K, an He–Cd laser (Kinmon IK3301 R-G) was used as a polarized excitation source, and the fluorescence spectra were measured using a UV polarizer and a CCD detector (Hamamatsu PMA-11). For the steady-state photoconductivity spectra measurements, the light passed through a monochromator from a 500-W Xe lamp (USHIO UXL-500D-O), was focused onto the gap area of the coplanar structures. The signal derived from a silicon photodiode was fed to a lock-in amplifier and the resulting photoconductivity spectra were normalized to the equal number of incident photons.

3. Results and discussion

Fig. 2 shows the optical absorption spectrum of an as-coated F8 thin film and the polarized optical absorption spectra of an F8 thin film on PI-C prepared by cooling from 473 K. In the aligned F8 thin film, the optical absorption edge is redshifted by ~ 0.10 eV in comparison with that in the as-coated F8 thin film. We determined from the spectra of the aligned F8 thin film the maximum dichroic ratio to be 18:1 and the value of the orientational order parameter $\langle P_2 \rangle$ to be 0.86 [9]. The structures of as-coated and aligned F8 thin films are amorphous and polycrystalline, respectively, confirmed by X-ray diffraction experiments, and the redshift in the optical absorption spectra caused by the alignment is due to the crystallization of F8 [10].

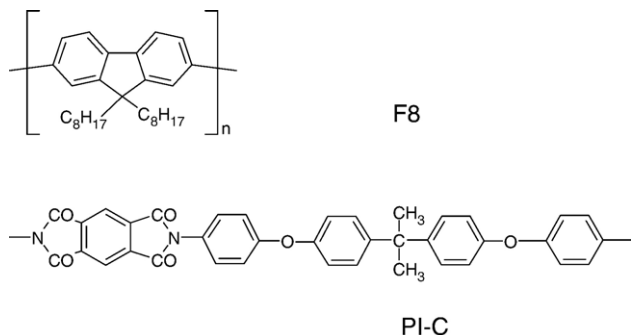


Fig. 1. Chemical structures of F8 and PI-C.

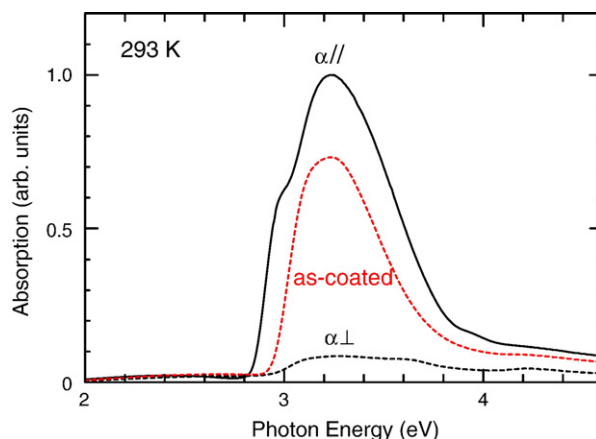


Fig. 2. Polarized optical absorption spectra of an as-coated F8 thin film and an F8 thin film aligned on PI-C.

In steady-state polarized fluorescence measurements, the direction of the polarization of the excitation beam was set to be either parallel (Exc //) or perpendicular (Exc \perp) to the rubbing direction of the samples. Similarly, the linearly polarized fluorescence components oriented either parallel (PL //) or perpendicular (PL \perp) to the rubbing direction were detected. Fig. 3 shows polarized fluorescence spectra of F8 thin film on PI-C prepared by cooling from 473 K. The fluorescence spectra exhibit a clear vibronic structure with peaks at 2.86, 2.70 and 2.54 eV. We determined from the peak intensity at 2.86 eV in Fig. 3 the value of $\langle P_2 \rangle$ to be 0.86 [11]. The value of $\langle P_2 \rangle$ obtained from polarized fluorescence measurements for the aligned F8 thin film on PI-C is in good agreement with that from polarized optical absorption measurements.

In polarized steady-state photoconductivity measurements, the electric field applied parallel to the rubbing direction. Photoconductivity for incident light parallel ($I_{//}$) and perpendicular (I_{\perp}) to the rubbing direction were measured. Fig. 4 shows polarized steady-state photoconductivity spectra of an F8 thin film aligned on PI-C. The photoconductivity spectrum for parallel excitation exhibits a sharp peak and the peak position differs from that for perpendicular excitation. The photoconductivity peak is located at 3.2 eV (the peak of the optical

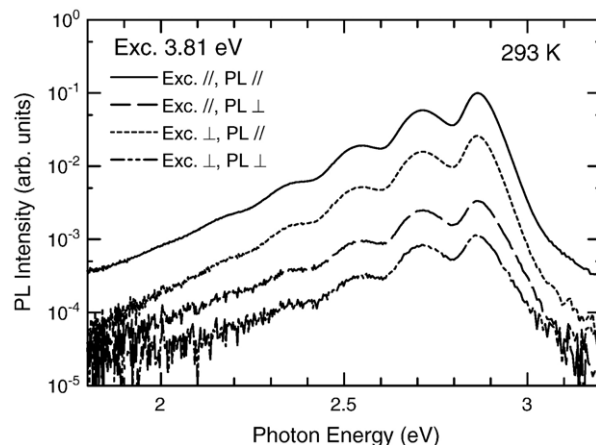


Fig. 3. Polarized fluorescence spectra of an F8 thin film aligned on PI-C.

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