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A study of α- and β-phase poly(9,9-dioctylfluorene) by electroabsorption spectroscopy

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Abstract

The excited-state structure of β-phase poly(9,9-dioctylfluorene) (F8) is investigated by means of optical absorption and electroabsorption spectroscopies in order to reveal the effect of β-phase formation on the excited-state structure in F8. The excited-state structure of β-phase F8 consists of six essential states, where two new B_u states are formed on the four essential states of α-phase F8. The two additional B_u states result from the energy splitting of the B_u states of α-phase F8, caused by intermolecular interaction in β-phase F8.

Keywords: Poly(9,9-dioctylfluorene) (F8); β-phase; Electroabsorption; Intermolecular interaction

1. Introduction

Poly(9,9-dioctylfluorene) (F8), one of blue-emitting polymers, has attracted considerable interest because of its high hole mobility and high photoluminescence (PL) quantum efficiency [1–3]. In addition to these important properties, F8 exhibits complex phase behavior (α, β, and crystallized phases) [4–6]. F8 thin film shows different optoelectronic properties dependent on its phases: α-phase F8 is the glassy phase where the polymer backbones do not form a particular conformation with long-range order, and can be prepared simply by spin coating, and crystallized-phase F8 is highly ordered phase obtained after thermal treatment above the nematic melting point followed by slow cooling to room temperature. β-phase F8 is a metastable phase characterized by the planar polymer backbone [4]. β-phase F8 thin film can be fabricated by several ways, such as drop casting [6,7], exposure of α-phase thin film to certain solvent vapors [8], and thermal treatment of α-phase thin film at around glass transition temperature [9]. β-phase F8 shows the most red-shifted absorption and PL spectra and the highest PL quantum efficiency among the three phases [6]. Although several studies of β-phase F8 from physical points of view have been reported, the change in the excited-state structure caused by β-phase formation is still unclear.

In general, electroabsorption (EA) spectroscopy has been employed to investigate the excited-state structures of conjugated polymers. EA spectroscopy detects not only optically allowed (B_u) states but also forbidden (A_g) states. Using EA spectroscopy with a sum over states (SOS) calculation, the excited-state structures of several conjugated polymers have already been determined. For example, Liess et al. have found that EA spectra of a variety of conjugated polymers can be modeled by using the SOS calculation based on the excited-state structures consisting of three essential states ($1A_g$, $1B_u$, and mA_g) [10]. We have reported that the excited-state structure of α-phase F8 is determined by fitting the SOS calculation to the experimental EA spectrum; the determined excited-state structure consists of four essential states ($1A_g$, $1B_u$, mA_g, and nB_u) [11].

In this work, we determine the excited-state structure of β-phase F8 by means of optical absorption and EA spectroscopies, and SOS calculation. We then compare the excited-state

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structures of β-phase and α-phase F8 in order to reveal the effect of β-phase formation on excited-state structure in F8.

2. Experimental

The chemical structure of F8 is shown in the inset of Fig. 1(a). α-phase F8 thin films were fabricated by spin coating from 1.5 wt.% F8/toluene solution onto quartz substrates, whereas β-phase F8 thin films were prepared by drop casting from 0.15 wt.% F8/toluene solution, which is the best way to fabricate high-quality β-phase thin film [6,7]. The thickness of the thin films was about 100 nm. For EA measurements, interdigital electrodes with finger spacing of 20 μm were fabricated on quartz substrates and then the F8 thin films were coated onto the quartz substrates.

Optical absorption spectra were measured with a JASCO V-570 spectrophotometer. EA measurements were performed as follows: excitation light from a 500-W Xe lamp through a monochromator was focused onto the sample, and the transmitted light was detected by a Si photodiode. 5-kHz sinusoidal electric field of 10^5 V/cm was applied to the samples, and lock-in technique was employed to detect changes ΔT in the transmission T. For sufficiently thick films ($d \geq 100$ nm), the change in the optical density $\Delta\alpha$ can be approximately calculated from $-\Delta T/T = \Delta\alpha d$. All EA measurements were performed at 10 K.

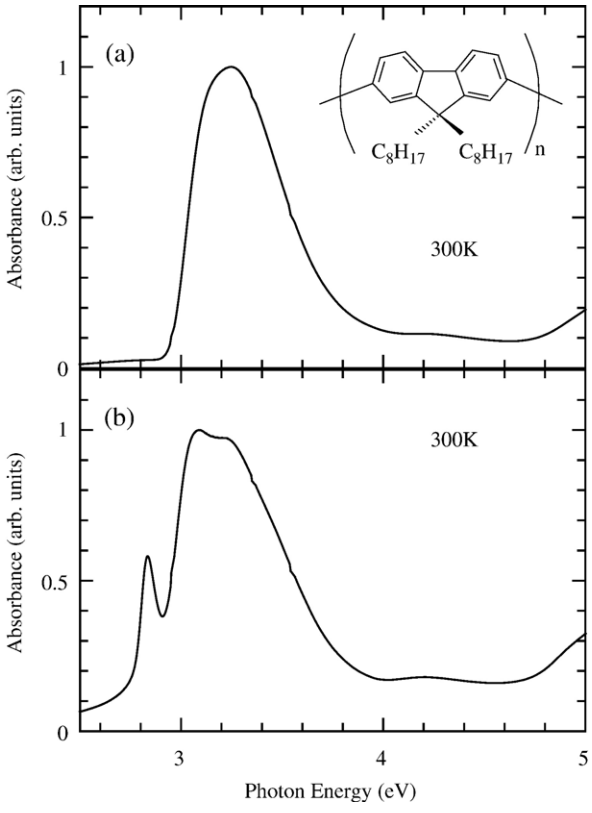

Fig. 1. Optical absorption spectra of (a) α-phase and (b) β-phase F8 thin films. Inset: chemical structure of F8.

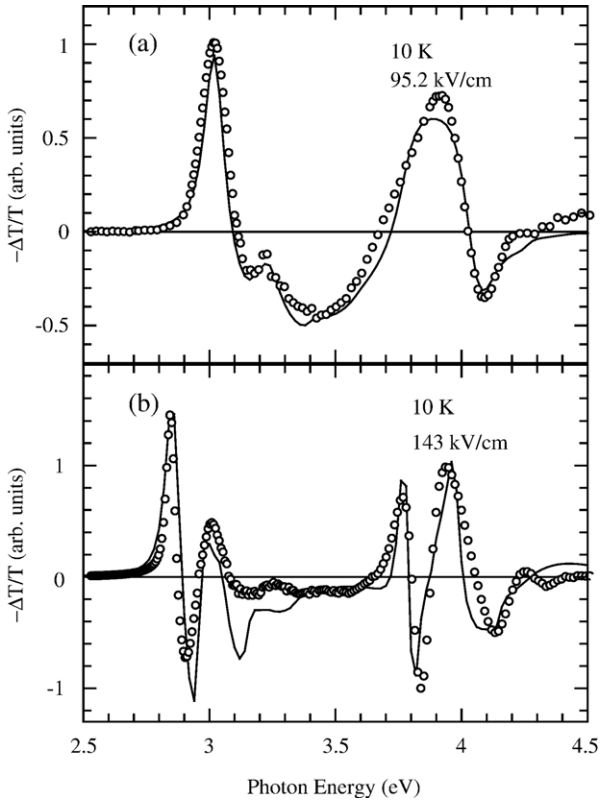

Fig. 2. EA spectra of (a) α-phase and (b) β-phase F8 thin films. Open circles and solid lines indicate experimental and calculated spectra, respectively.

EA signal is related to the imaginary part of the optical third-order susceptibility $\chi^{(3)}$ using the third-order perturbation theory:

$$-\frac{\Delta T}{T} = \Delta\alpha d = \frac{4\pi\omega}{nc}\mathrm{Im}\left[\chi^{(3)}(-\omega;\,\omega,0,0)\right]F^2 d \qquad (1)$$

where ω is the input radiation frequency, n is the refractive index, F is the electric field strength, and d is the film thickness. Orr and Ward showed that $\chi^{(3)}$ can be estimated from SOS calculation, in which all contributions from several essential states are summed up, multiplying their transition dipole moments and inverses of energy intervals between two of the essential states [12]. The SOS calculation enables us to determine excited-state structures of conjugated polymers from EA spectra by taking account of vibrational effects and conjugation length distribution [10,11].

3. Results and discussion

Optical absorption spectra of α-phase and β-phase F8 at room temperature are shown in Fig. 1. The α-phase F8 spectrum has two broad bands at 3.2 eV and 4.2 eV, which are ascribed to $1B_u$ and nB_u absorption, respectively [11]. In β-phase F8 thin film, an additional narrow absorption peak appears, and is well known as a characteristic feature of β-phase F8 [13]. However, the origin of the additional absorption peak is still a controversial issue. It is considered