

## Spectral blue shift via intermolecular interactions in the B2 and B4 phases of a bent-shaped molecule

Fumito Araoka, Taketo Otani, Ken Ishikawa, and Hideo Takezoe  
*Department of Organic and Polymeric Materials, Tokyo Institute of Technology,  
 2-12-1-58-42 O-okayama, Meguro-ku, Tokyo 152-8552, Japan*

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A set of precise measurements of UV-Vis absorption spectrum for the classical bent-shaped molecule, P-12-OPIMB, revealed that molecular exciton interactions exist even in the mesophases of this system, as manifested as an obvious and abrupt change in the positional and spectral shape at phase-transition points. Based on Kasha's molecular exciton model, we successfully conducted a quantitative analysis of the spectral shift and could determine the local structure of the B4 phase. To the best of our knowledge, such a spectroscopic analysis for the liquid crystals has not been connected with the local structure.

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### I. INTRODUCTION

Already more than a dozen of years have past since the discovery of the polar and switchable bent-core liquid crystalline molecules [1]. The first species of the bent-shaped molecules, P-*n*-PIMB and P-*n*-OPIMB, have exhibited quite new types of polar and chiral phases, such as B2 and B4 phases—the former is one of the most intensively investigated phases of the bent-shaped molecules ever since the beginning because of its ferroelectricity or antiferroelectricity and the latter shows a smooth and vivid blue texture of spontaneously optically segregated domains, which is currently considered as “helical nanofilament phase” [2]. Although the nature of these standard bent-shaped molecules and their phases are getting understood, still “bent shaped” delivers plenty of unique characteristics never seen before in the conventional liquid crystals [3]—emergence of new types of mesophases such as polar smectic A phases [4–6], biaxial nematic phases [7,8], and blue phases [9], huge flexoelectric constants [10], large optical nonlinearity [11], anomalous chirality enhancement in mixtures [12,13], etc. Already, introducing the bent-shaped into mesogenic cores has become one of the standard approaches of molecular synthesis to bring about something new in liquid crystals since the bent-shaped molecules can be expected as a carrier material in a rather new field of research.

Optical features in the ultraviolet-visible (UV-Vis) region can often be traced to the excitation of specific types of electrons in a material. Since the most of liquid crystalline compounds contain an extended conjugated aromatic moiety, spectroscopic measurements such as UV-Vis absorption are considered to be necessary as routine to get the structural information which influences on the desired electronic or optical properties in the bulk liquid crystalline phases of synthesized materials. However, in most cases, the resulted spectra are not sufficient to discuss their electronic structures because of saturated absorption. That is, since sandwich-type cells of several micron thick are often used for such measurements, the absorption from the bulk becomes too strong, so that the resulted absorption saturation makes the important information hidden. This could be the reason why UV-Vis spectra have never essentially been used for structural analyses in liquid crystals.

Recently, we successfully demonstrated a correct measurement of circular dichroism (CD) spectra for the mixtures of the conventional rod-shaped and bent-shaped molecules by means of ultrathin cells that reduce such strong bulk contribution and thus allow us to discuss their spectral shapes even for the near-UV region [13]. In this paper, we again adopted the same kind of ultrathin cell for UV-Vis measurements in one of the standard bent-shaped molecules, P-12-OPIMB, to obtain its correct spectral shape in the near-UV region and obtained an unusual spectral change never reported so far in this system. This fact suggests an existence of intermolecular interactions in the mesophases of this material, similarly to the molecular aggregates of pigments. By a quantitative analysis, we could unambiguously determine the local structure of the B4 phase.

### II. EXPERIMENTAL

P-12-OPIMB, the sample compound used in this study, takes a direct transition between the B2 and B4 phases as given in a phase sequence measured with DSC (Diamond DSC, Perkin Elmer): Iso 168.2 °C B2 138.5 °C B4 (on cooling); B4 148.3 °C B2 171.5 °C Iso (on heating). The sample cell was a sandwich-shaped one consisting of two smooth fused-silica substrates without any spacer. Its thickness was estimated as about 400 nm by optical simulation (SCOUT, W. Theiss Hard- and Software) upon transmittance measurement with a monochromator (USB4000, Ocean Optics) and a polarizing microscope (OPTIPHOT-POL, Nikon). The sample material was injected into the cell with capillary action in the isotropic temperature. Temperature-dependent UV-Vis spectra were measured under precise control of the temperature of the cell using a specially designed oven settled in a UV-Vis spectrometer (V-560, Jasco).

### III. RESULTS

Figures 1(a) and 1(b) show the UV-Vis spectra at various temperatures on cooling and heating processes, respectively. First, in the isotropic phase on cooling, the spectral curve shows almost the same shape as that in dilution [inset of

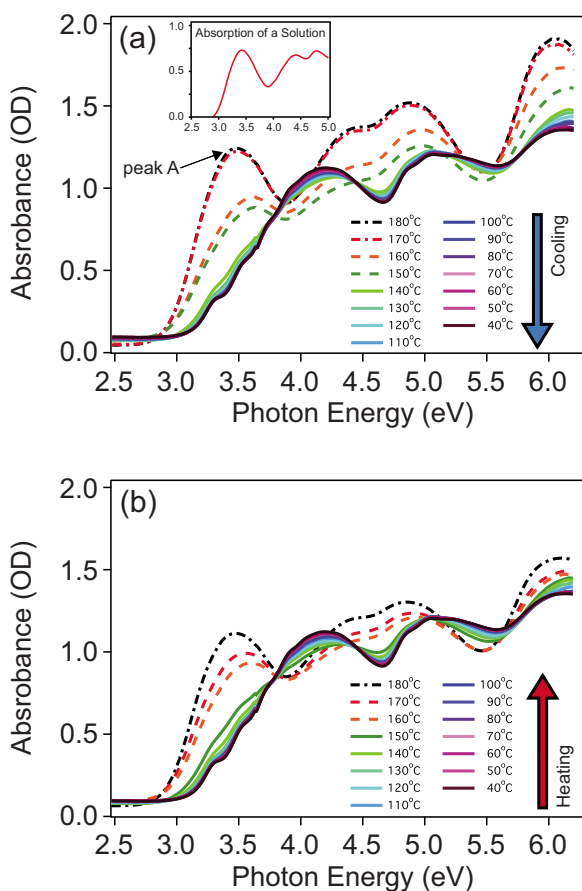


FIG. 1. (Color online) Temperature dependent absorption spectra of P-12-OPIMB in an ultrathin cell on (a) cooling and (b) heating processes. The broken, dashed, and solid lines represent spectra in the isotropic, B2, and B4 phases, respectively. An inserted spectrum in (a) is from P-12-OPIMB dissolved in chloroform.

Fig. 1(a)]. Therefore, this shape can be attributed to absorption of isolated molecules. When the sample is gently cooled down from the isotropic phase, an abrupt change in the spectral shape coincides with the Iso-B2 transition. This change is not so clear, but the lowest-energy peak around 3.5 eV (peak A, hereafter) obviously blue shifts by about 0.15 eV. By further cooling, more drastic spectral change occurs at the B2-B4 transition temperature, which gives a huge blue shift (by about 0.74 eV for peak A), as well as peak broadening. Besides, small periodic fringes appear on the spectrum and gradually get clearer with further cooling in the B4 phase. This spectral transformation process is reversible in heating process as shown in Fig. 1(b), indicating that such a spectral change is attributed to some kind of intermolecular interactions in these phases.

#### IV. ANALYSIS AND DISCUSSION

Before performing an analysis on these experimental data, molecular orbital (MO) calculation (complete neglect of differential overlap/S method) was carried out to obtain knowledge on the electronic transitions concerning the monomeric absorption spectrum. Figure 2(a) is a calculated absorption

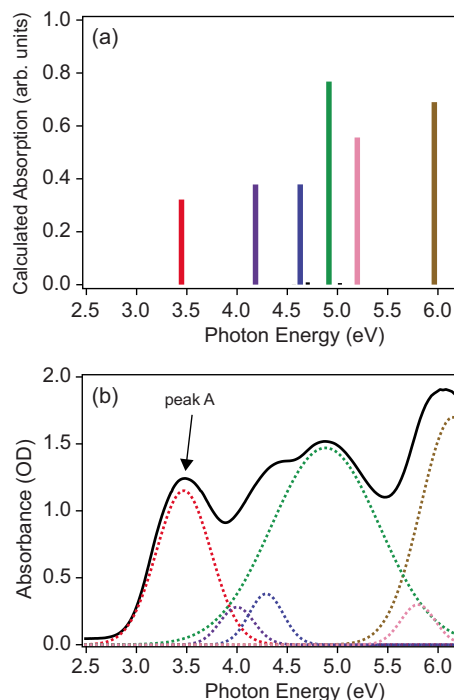


FIG. 2. (Color online) (a) Theoretical UV-Vis absorption spectrum as given by MO calculation. (b) The absorption spectrum in the isotropic phase (solid line) decomposed into six Gaussian peaks (dashed lines) by taking account of six calculated absorption peaks in (a).

spectrum obtained for the core of the bent-shaped molecules in an optimized conformational state in which the two molecular wings are twisted oppositely with respect to the central aromatic plane. This result is quite consistent with the experimental one except for inhomogeneous broadening. According to this calculation, the above peak A can be assigned as of the first exciton transition, mainly corresponding to the motion of  $\pi$  electrons in the aromatic rings along one of the arms of the molecule. We also conducted some calculations for nontwisted or more twisted conformations, but there was no obvious blue shift as much as that observed in the experimental result. This fact strongly indicates that the spectral change obtained experimentally is not due to the molecular conformation change but due to the intermolecular effect in the condensation state.

First for the analysis, we conducted peak decomposition for the monomeric spectrum (here in this study, the spectrum for Iso phase at 180 °C) by adopting a Gaussian function on the photon energy domain to each peak to take account of its inhomogeneous broadening. Figure 2(b) shows the decomposed peaks whose sum well reproduces the original spectrum. The maximum absorbance, peak energy, and full width at half maximum (FWHM) of the Gaussian for peak A were 1.15 optical density (OD), 3.47 eV, and 0.6 eV, respectively. Then, we can evaluate the transition dipole moment  $\mu$  by using these values.

In general, the molar extinction coefficient  $\epsilon$  is known as given in Lambert-Beer's law,

$$\log_{10}T(\lambda) = -\epsilon cl = -\epsilon\rho\frac{1000}{M}l, \quad (1)$$

where  $T(\lambda)$  refers to transmittance at a wavelength  $\lambda$  and  $c$ ,  $l$ , and  $M$  are the molar concentration, the light path length in the sample media, and the molecular mass, respectively. For the bulk molecular density  $\rho$ , we assume just one for the sake of simplicity. Actually,  $\epsilon$  in Eq. (1) just gives information at a single wavelength, which does not give a true identification of the total intensity of the transition. Usually, the real measure of the transition peak is given by the integral molar absorption of the single peak over reciprocal wavelength  $\omega$  in  $\text{cm}^{-1}$ , and then its dipole strength  $M_d$  can be derived as the following equation [14]:

$$M_d = 9.18 \times 10^{-3} \int_{\omega} \frac{\epsilon}{\nu} d\nu. \quad (2)$$

Since the dipole strength and transition dipole moment in Debye have the relationship

$$\mu = \sqrt{M_d}, \quad (3)$$

we obtain  $\mu$  for a certain absorption peak. In this study,  $\mu=6.72$  D was obtained for peak A in the isotropic phase.

Spectral properties of molecular dimers and aggregates, such as spectral shift, are discussed by their exciton band structure and corresponding selection rules based on the molecular exciton interaction model developed by Kasha [Fig. 3(a)]. In this model, exciton interaction  $E_{ext}$  of a linear chain of an infinite number of molecules is expressed in terms of the molecular interval  $r$  and the angle  $\alpha$  of the transition dipoles with respect to the chain axis as [15]

$$E_{ext} = \frac{\mu^2}{4\pi\epsilon_0 r^3} (1 - 3 \cos^2 \alpha), \quad (4)$$

where  $\epsilon_0$  is the dielectric constant in vacuum. By considering Eq. (4), one may find the important rules as follows. If  $\alpha > 54.7^\circ$ , namely, the molecules rather stack onto each other, then  $E_{ext}$  takes positive, which means blue shift of the absorption spectrum (H aggregate). Oppositely, for  $\alpha < 54.7^\circ$  which gives the structure rather in a head-to-tail configuration, spectral red shift will occur (J aggregate). As we have seen above, spectral blue shift was observed in absorption spectra of mesophases of P-12-OPIMB, suggesting an existence of H-aggregate-like state in these phases. Actually, the B2 phase has been considered as one of tilted smectic phases, in which tilted molecules are packed in polar-ordered smectic layers, so that there cannot be any molecular positional order in each smectic layer because of its fluidity in the layer. However, the emergence of the slight blue shift implies that molecular excitons in the B2 phase are interacting with each other already in this state. Because of its fluidity, spectral peaks still keep showing inhomogeneous broadening like those in the Iso phase.

The B4 phase was ascribed as an assembly of helical nanofilaments, as evidenced by freeze-fracture transmission electron microscopy. Although electron and x-ray diffraction studies clarified the long-range twisted layer of a rectangular lattice with lattice constants of  $a=6.58$  Å and  $b=6.26$  Å

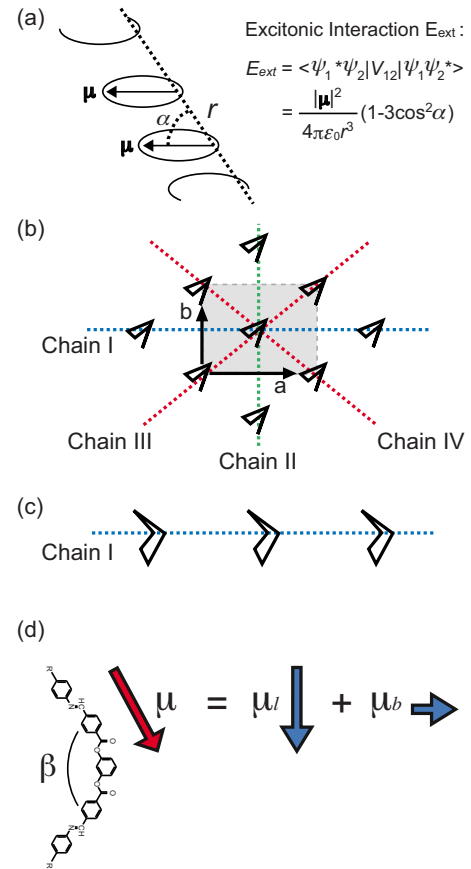


FIG. 3. (Color online) (a) A linear chain with transition-equivalent components inclined at an angle  $\alpha$ . (b) The 2D lattice model as a local structure of the B4 phase and (c) its side view as viewed along chain I. (d) The transition dipole moment  $\mu$  is “nearly” parallel to one of two wings and can be divided into two orthogonal projection dipole moments  $\mu_b$  and  $\mu_l$ .

[2], molecular arrangement in the unit cell has not been identified yet. Considering such a two-dimensional (2D) lattice as a local structure, we can analyze the spectral shift by assuming additivity of the exciton interactions of the following four linear chains in the 2D lattice structure [15]: in the top view of the lattice, two along  $a$  and  $b$  axes (chains I and II) and the other two along the diagonal lines (chains III and IV) as depicted in Fig. 3(b). In the present case, the molecular bent direction was chosen to be in the lattice plane to have a spontaneous polarization along the filament (chain III direction) as evidently indicated by optical second-harmonic generation (SHG) [16]. Figure 3(c) illustrates the side view of the lattice with molecules along chain I. In the top and side views, wide arms stand for the arms toward the readers. For instance, along chain I, molecules are tilted from the lattice plane normal (see side view), and the bent direction is deviated from the chain I direction within the lattice plane (see top view).

We assume that interlayer interactions are sufficiently small and hence negligible. According to the aforementioned MO calculation, the transition dipole moment of the molecular exciton is nearly parallel to one of the two equivalent molecular wings, so that it is necessary to consider two orthogonal projection dipoles along the molecular bent direc-

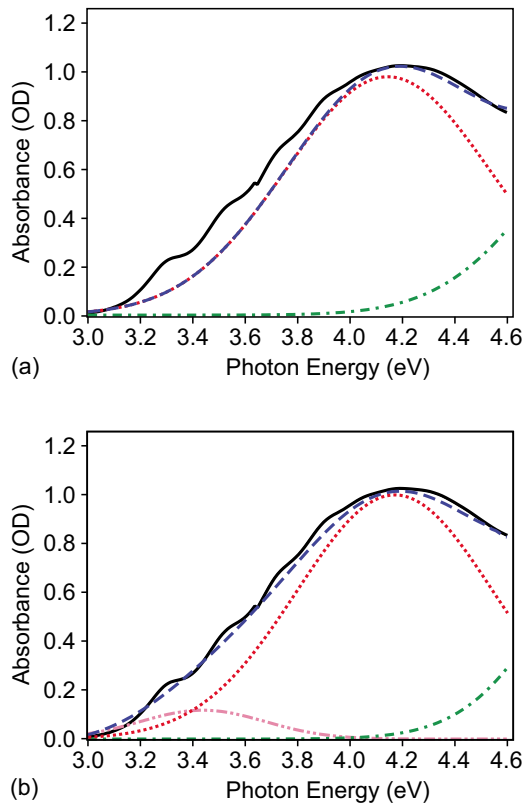


FIG. 4. (Color online) The comparison of the fitting results for peak A in the absorption spectrum at 40 °C (solid curve) by using a single Gaussian (a) and two Gaussian (b) functions. Each dashed curve is a sum of the Gaussian components (broken curves).

tion  $\mu_b$  and the long axis  $\mu_l$ , as shown in Fig. 3(d). In such a case, since each projection dipole independently gives the spectral shift, peak splitting is generally observed (commonly known as the Davydov splitting). In fact, the broadened lowest-energy peak A in the B4 phase cannot be explained only by using a single Gaussian function, as shown in Fig. 4(a). By contrast much better fit can be obtained using a combination of two Gaussian functions, as shown in Fig. 4(b). Thus, the possible peak decomposition into two Gaussian functions is consistent with the occurrence of the Davydov splitting. The peak value, peak energy, and FWHM of these two Gaussian components shown in Fig. 4(b) are 0.1 and 1.0 ODs, 3.43 and 4.18 eV, and 0.54 and 0.81 eV, respectively. Since the center of the Gaussian peak A of the monomeric spectrum in Fig. 2(b) is located at 3.46 eV, we can find that the smaller lower-energy Gaussian peak slightly red shifts by about 0.03 eV, and the larger higher-energy Gaussian peak significantly blue shifts by about 0.72 eV. Moreover, we could estimate the ratio of the dipole moments corresponding to these two Gaussian components as about 3.85 by again adopting Eqs. (1)–(3). As we assigned small and large peaks to  $\mu_b$  and  $\mu_l$ , respectively, we can simply deduce the bent angle as  $\beta=151^\circ$  by taking an arctangent of this ratio. This angle is larger than the bent angle  $\beta=120^\circ-130^\circ$  reported in the literature by means of NMR [17], SHG [18], and infrared spectroscopy measurements [19]. However, we think that our hypothesis is still consistent because the transition moment is not “perfectly” parallel to the wing but is “nearly” parallel.

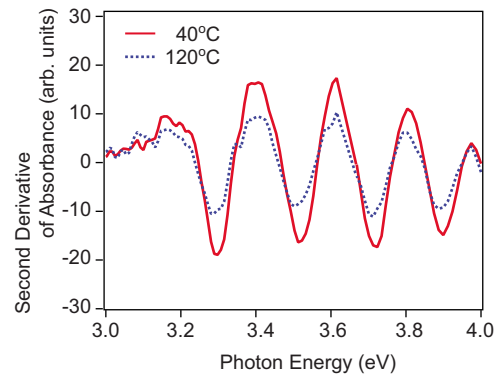


FIG. 5. (Color online) The second derivatives of the absorption spectra of the B4 phase at 40 °C (solid line) and 120 °C (broken line).

Now we consider the spectral shifts due to two transition dipoles. First, let us start with the dipole along the bent direction  $\mu_b$ . Since the molecular bent direction is chosen to be in the lattice plane, the parameter required to calculate the spectral shift is only the angle  $\phi$  between the molecular bent direction and the lattice  $a$  axis. The contributions to the shift from  $\mu_b$  along chain directions I, II, III, and IV for  $\phi=0^\circ$  are  $-0.023$ ,  $0.01$ ,  $-0.013$ , and  $-0.013$  eV, respectively. Here, positive and negative signs represent blue and red shifts, respectively. The summation of these values gives the minimum shift of  $-0.039$  eV. The same calculation leads to  $-0.043$  eV at  $\phi=90^\circ$ . In between, the shift value monotonically decreases with increasing  $\phi$ . Thus, the spectral shift due to  $\mu_b$  is not sensitive to  $\phi$  and is limited to a small red shift, being consistent to the small red shift of 0.03 eV obtained by the experimental analysis. For the analysis of the spectral shift due to  $\mu_l$  component, we fixed the bent direction along the lattice  $a$  axis, i.e.,  $\phi=0$ , since this gives the minimum red shift, being most consistent to the experiment. Then the blue shift was estimated by changing only the molecular tilt  $\theta$ . The maximum blue shift was 1.32 eV at  $\theta=0$ . The observed blue shift of 0.72 eV is obtained at about  $\theta=33^\circ$ , which is a summation of all the contributions from chain I (0.019 eV), chain II (0.018 eV), chain III (0.26 eV), and chain IV (0.26 eV). Large and small contributions to the blue shifts can be easily understood from positional relationships of each dipole along four chains. Thus, even in the B4 phase, molecular tilt with respect to the lattice (layer) plane exists and explains the origin of chirality in the B4 phase based on layer chirality [20]. Actually, our result rather prefers the model proposed by Hough *et al.* [2] than the alternative model recently suggested by Martínez-Perdigueró *et al.* [21]. In such a way, we could propose the mechanism of the spectral change in the B4 phase, in which nanofilaments behave similarly to nanocrystals of pigments.

Another typical feature of the aggregate state is a vibronic structure appearing on the spectrum in the B4 phase. Since often in aggregates molecular excitons transfer themselves slowly from one molecule to another so as to stay relatively longer time in one molecule, a vibronic structure often emerges around the corresponding exciton absorption peak. Figure 5 shows a plot of the second derivatives of the absorption spectra of the B4 phase at 40 and 120 °C, confirm-

ing the existence of a vibronic structure as repeating peaks on the photon energy domain. The corresponding wave number to the period of the peaks was  $1700\text{ cm}^{-1}$ , which agrees well with that of the aromatic stretching mode reported in the literature [19]. Since the molecular exciton on the aromatic rings may induce the aromatic vibration, it seems to be natural.

## V. CONCLUSIONS

We measured a set of temperature-depending UV-Vis absorption spectra of the classical bent-shaped molecule, P-12-OPIMB, by means of an ultrathin liquid crystalline cell which enables us to obtain the genuine spectral position and shape of the near-UV absorption. The result revealed the

existence of molecular exciton interactions even in the mesophases, as manifested as an obvious and abrupt change in the spectral position and shape at phase transitions. Such an intermolecular interaction has not been considered to be essential in the conventional fluidic mesophases, as far as we know. We performed a quantitative analysis of the spectral shift in the B4 phase based on Kasha's molecular exciton model and successfully determined the local structure of the B4 phase. This fact proves that the helical nanofilament state behaves like a nanocrystal of pigments from the spectroscopic point of view.

## ACKNOWLEDGMENT

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