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Electroabsorption study of ordered polyfluorene thin films: Origin of oscillatory structure near the bottom of the continuum state

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The excited-state structure of ordered (β-phase) poly(9,9-dioctylfluorene) (F8) thin films has been investigated by electroabsorption (EA) spectroscopy. The EA spectra of a number of π conjugated polymers, including disordered (glassy) F8, are well explained by a theoretical essential-state model, which consists of three characteristic excited states and the ground state [Y. Kawabe *et al.*, Phys. Rev. B **44**, 6530 (1991)]. However, it is found that the essential-state model fails to explain the EA spectrum of β-phase F8 because of the appearance of an oscillatory EA signal near the bottom of the continuum state. From the applied electric-field dependence and the directional dependence of the field and polarization of the light, it has been revealed that the oscillation results from several intrachain excited states, some of which are not observed in glassy F8 because of considerable inhomogeneous broadening. To reproduce the EA spectrum of β-phase F8 by a sum-over-states calculation, at least seven excited states, in addition to the ground state, have to be taken into account.

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I. INTRODUCTION

π conjugated polymers have received a great deal of attention as a new class of semiconducting materials due to their flexibility and solution processability.[1–3] They have also served as a model system to study the optical properties of one-dimensional systems with electron-electron and electron-phonon interactions. In spite of enormous effort, however, it is still impossible to obtain single crystals of π conjugated polymers except for polydiacetylene (PDA) derivatives.[4] As a result, samples of almost all such materials inevitably contain significant structural disorder, such as bending and torsion of main chains. Therefore, they show considerable inhomogeneous broadening, which makes it difficult to deduce detailed information concerning excited-state structure from their broad absorption spectra. By means of nonlinear optical (NLO) spectroscopy, rather narrow spectra of π conjugated polymers can be obtained and are used to determine the positions of the "essential states"; utilizing theoretical calculations taking into account electron-electron interaction, Mazumdar and co-workers revealed that there exist three characteristic excited states that primarily contribute to the NLO properties of π conjugated polymers.[5,6] These excited states are referred to as the essential states and consist of the lowest dipole-allowed ($1B_u$) state, the bottom of the continuum (nB_u) state, and the dipole-forbidden (mA_g) state, which is coupled strongly with both the $1B_u$ and nB_u states. The nature of the excited states of π conjugated polymers is well modeled by these essential states, and a number of NLO spectra, especially the electroabsorption (EA) spectra, of thin films have been successfully reproduced by numerical calculation based on the essential-state model.[7–10] However, even in NLO spectra, contributions from the rest of the excited states are masked by residual inhomogeneous broadening. To understand further the excited-state structure of π conjugated polymers beyond the essential-state model, thin films with much less inhomogeneous broadening are required.

Poly(9,9-dioctylfluorene) (F8), which is well known as an efficient blue emitter, shows relatively narrow absorption and emission bands when it adopts a planar conformation (β phase).[11–16] Thin films of the β-phase F8 can be obtained by a solution process, such as drop casting[15] and exposing spin-coated glassy thin films to the vapor of a good solvent.[13] This is in contrast to PDA single crystals, which are prepared by solid-state polymerization from single crystals of diacetylene monomers.[4] It is also known that PDA and its derivatives are nonemissive because of the dipole-forbidden (A_g) state lying below the $1B_u$ state.[17] On the other hand, in π conjugated polymers with aromatic rings, such as F8 and poly(p-phenylene vinylene), a large bond alternation effect results in the appearance of the $1B_u$ state as the lowest excited state and consequent efficient fluorescence.[18] In fact, β-phase F8 thin films have a high fluorescence quantum efficiency (η=70%)[15] and can be used as an emitting layer in efficient organic light-emitting diodes.[19] In glassy F8 thin films, the main chains adopt random-coil conformations as in solution, and its EA spectrum can be explained by the essential-state model.[9,10] In our previous work,[20] we have reported that as the transition from glassy phase into β phase proceeds, a more complex EA spectrum appears that cannot be explained by the essential-state model. The EA spectrum of β-phase F8 has an oscillatory feature below the nB_u state in glassy F8 (see Fig. 2). It is still unclear whether the oscillatory feature is attributable to several intrachain excited states, some of which are not resolved in glassy F8. It might be a Franz-Keldysh (FK) oscillation, which has only been observed in the electroreflectance of PDA single crystals,[21–23] among π conjugated polymers, and is unambiguously regarded as evidence of the formation of a continuum band in which the excited states have large coherence lengths. Another possibility is that the oscillation results from the formation of charge-transfer (CT) states, as observed in polycrystalline thin films of small molecules.[24,25]

To clarify the origin of the oscillatory signal, this study presents EA measurements associated with the third-order, as well as higher-order optical nonlinearity of β-phase F8 thin films. We also investigated the directional dependence of the applied electric field and polarization of the light on oriented β-phase F8 thin films. From these detailed EA measurements and considerations including a numerical calculation, we conclude that the oscillation results from several intrachain excited states separated by small energy intervals.

II. EXPERIMENT

We used F8 synthesized via Suzuki coupling. Samples of β-phase and glassy F8 thin films with a thickness of 100 nm were prepared by drop casting and spin coating from toluene solutions, respectively. For the EA measurements, we used quartz substrates on which interdigitated aluminum electrodes spaced 10 μm apart had been photolithographically patterned. Oriented β-phase F8 thin films were fabricated on an aligned polyimide layer prepared on the aluminum interdigital electrodes. The detailed fabrication process for oriented β-phase F8 thin films with excellent dichroic ratios is described elsewhere.[26,27]

The EA measurements used monochromatic light from a 500 W xenon lamp as the light source and a silicon photodiode as the photodetector. A function generator (NF, DF1906) and an ac power amplifier (NF, 4020) were utilized to apply an electric field modulated at a frequency of 1 kHz to the samples. The amplitude of the applied electric field F was varied from 50 to 175 kV/cm. The changes in the intensity of transmitted light at twice and four times the modulation frequency ($\Delta T_{2\omega}$ and $\Delta T_{4\omega}$) were detected by a lock-in amplifier (NF, LI5640), while the transmittance T was monitored by a digital voltmeter (Keithley, 617). As will be shown below, $\Delta T_{2\omega}/T$ within the weak-field regime depends on the third-order optical nonlinearity, whereas $\Delta T_{2\omega}/T$ within the strong-field regime and $\Delta T_{4\omega}/T$ involve contributions from higher-order optical nonlinearity. In this paper, we mainly discuss the EA signals detected at twice the modulation frequency ($\Delta T_{2\omega}/T$) unless otherwise specified. All EA measurements were performed at 10 K. Optical absorption spectra of the thin films were recorded with a spectrophotometer (JASCO, V-570). We also performed photoconductivity (PC) yield measurements to identify the character of a specific excited state. For these measurements, monochromatic light chopped at a frequency of 87.3 Hz illuminated the same samples used for EA measurements; the samples were biased by a dc electric field of 5 kV/cm, and the photocurrent generated at the same frequency was detected by the lock-in amplifier. The PC yield spectrum is obtained by dividing the photocurrent spectrum by the corresponding absorption spectrum.[28,29]

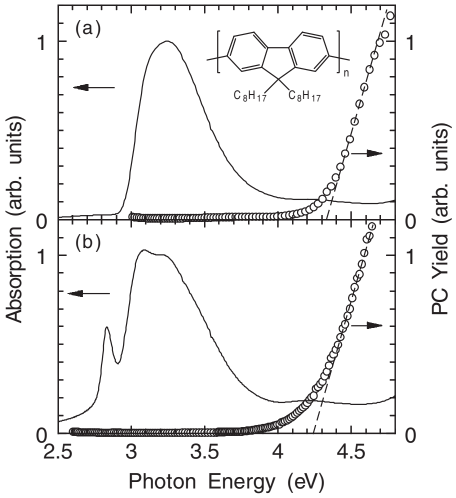

FIG. 1. Optical absorption (solid lines) and PC yield (open circles) spectra of the (a) glassy and (b) β-phase F8 thin films at room temperature. The broken lines are guides for the eyes. Inset: the chemical structure of F8.

III. RESULTS AND DISCUSSION

The absorption spectra of glassy and β-phase F8 thin films are shown in Figs. 1(a) and 1(b), respectively. In the glassy phase, a featureless broad absorption band corresponding to the $1B_u$ state is observed at 3.2 eV. In the β phase, an additional narrow band appears at 2.84 eV and is attributed to the $1B_u$ state when π conjugation is extended along the whole planar polymer backbone. An absorption peak at 3.08 eV in the β phase is assigned to a vibronic satellite of the $1B_u$ state. The absorption band at 3.22 eV has been traditionally attributed to random-coil portions of β-phase F8. However, recent studies using single-molecule spectroscopy have suggested that β-phase F8 exists to a much greater extent in an extended planar conformation than was previously thought.[30] Thus, we have assigned the absorption band also to a vibronic satellite. In contrast to the obvious differences in the low-energy region (2.7–3.1 eV) of the two absorption spectra, the high-energy regions (3.8–4.4 eV) are very similar. In glassy F8, the nB_u state (the bottom of the continuum state) is located around 4.2 eV, as estimated from PC yield in Fig. 1(a).[9]

Figure 2 reveals dramatic changes in the high-energy region of the EA spectra of the two forms of F8: the broad positive peak around 3.9 eV in glassy F8 splits into two in the β phase, resulting in the complex oscillatory feature previously observed.[20] In the spectrum of the β phase in Fig. 2(b), an oscillatory feature is also observed in the low-energy region; it can be interpreted simply in terms of a Stark shift of the $1B_u$ state because the first energy derivative of the absorption spectrum mirrors the low-energy oscillation in the EA spectrum. On the other hand, the oscillatory feature in the β-phase high-energy region has a negative peak at 3.75 eV that is not reproduced by the first or even the second energy derivatives of the broad absorption spectrum in the same spectral region.

An oscillatory feature in EA spectrum is reminiscent of the FK oscillation (or the FK effect) observed near the band

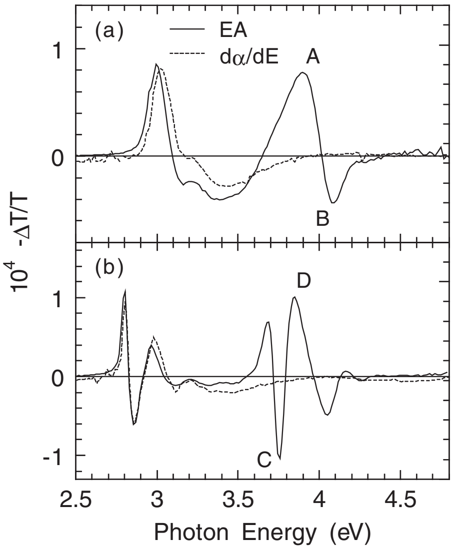

FIG. 2. EA spectra (solid lines) and the first energy derivative of the absorption spectra (broken lines) of the (a) glassy and (b) β-phase F8.

edge of inorganic semiconductors, which was extensively studied more than 40 years ago.[32] Theoretically, the FK oscillation can be described by using an Airy function and it has been shown that in the ideal case, i.e., without inhomogeneous broadening, the amplitude and period of the oscillation increase with $F^{1/3}$ and $F^{2/3}$, respectively. This behavior is in striking contrast to EA signals due to discrete excited states, whose spectral shape is independent of F and the amplitude follows an F^2 dependence in a weak-field regime. More recently, an analytic expression for the FK effect in a one-dimensional system with inhomogeneous broadening has been derived by Pedersen and Lynge.[31] Although the expression is too complicated to understand the nature of the oscillation intuitively, the authors have demonstrated that the oscillation period still follows the $F^{2/3}$ dependence. Unfortunately, the F dependence of the amplitude in such systems was not shown. Experimentally, an oscillatory electroreflectance signal observed in PDA single crystals 0.5 eV above the lowest exciton state has been attributed to the FK effect in a one-dimensional system with a small amount of inhomogeneous broadening.[21–23] The oscillation in this case clearly shows the spectral broadening with the $F^{2/3}$ dependence and a transition from an F^2 dependence in a weak-field regime to an $F^{1/3}$ dependence in a strong-field regime.[21–23] In the spectral region where the oscillation appeared, no absorption band with appropriate intensity could be found; this fact is also considered as a characteristic feature of a one-dimensional FK effect because in one-dimensional systems the oscillator strength concentrates in the lower exciton states rather than the band states.

In case of β-phase F8, the oscillatory EA signal also appears in the spectral range where there is no characteristic absorption band. Moreover, a deviation from the F^2 dependence of the amplitude is apparent in Fig. 3(a), where the F dependences of amplitudes between the points marked by A and B in glassy F8 and by C and D in β-phase F8 in Fig. 2 are plotted. It should be noted that in the same field regime, such a deviation from an F^2 dependence was not observed around 2.9 eV in the β phase. In Fig. 3(b), we show plots of EA intensity divided by F^2 for various F values to emphasize any spectral broadening and deviation from an F^2 dependence. In this figure, the deviation of the amplitude as well as a slight blueshift near 3.8 eV can be seen. However, this spectral change is different from that observed in PDA single crystals[21–23] and that expected from the analytic expression for one-dimensional FK effect.[32] For one-dimensional systems, the first negative peak of the FK oscillation appears at the band gap energy E_g, above which spectral broadening should be observed. In other words, in the case of an FK oscillation, the amount of blueshift increases with increasing spectral distance from E_g. However, the blueshift observed around 4.1 eV in the β phase is rather smaller than that around 3.8 eV. Furthermore, as shown in Fig. 1(b), the onset of the PC yield in the β phase is located at higher than 3.75 eV, indicating that the first negative peak does not correspond to the band gap of the β phase. In addition to these differences, the oscillatory feature in β-phase F8 thin films was observed even at room temperature (not shown here). The FK oscillation is sensitive to the degree of structural disorder so that it is expected to disappear at room temperature.[22] Therefore, we conclude that the oscillatory feature in β phase is not an FK oscillation.

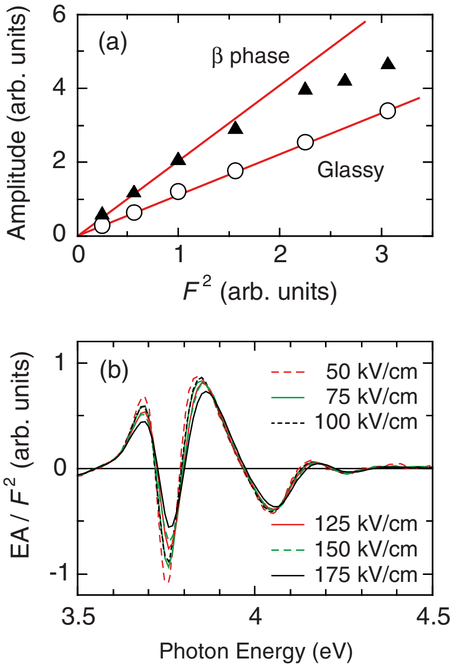

FIG. 3. (Color online) (a) Field-strength dependence of EA signals. Open circles and filled triangles are the data taken from the amplitude between the positions marked by A and B in Fig. 2(a) and marked by C and D in Fig. 2(b), respectively. The solid lines represent the F^2 dependence. (b) Field-strength dependence of the EA oscillation observed in β-phase F8. All the spectra were divided by F^2 to emphasize the deviation from the F^2 dependence.

The F-dependent spectral shape and the deviation of the amplitude from an F^2 dependence in Fig. 3 result from contributions from higher-order optical nonlinearity of β-phase F8 thin films. As well known, in the strong-field regime, the

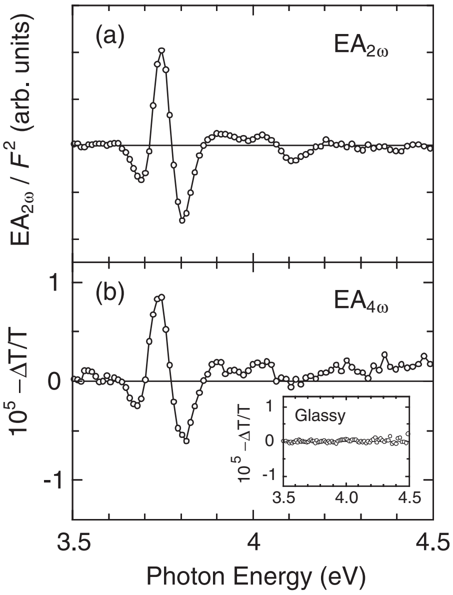

FIG. 4. (a) Difference spectrum between EA$_{2\omega}/F^2$ at 125 kV/cm and EA$_{2\omega}/F^2$ at 50 kV/cm, shown in Fig. 3(b). (b) EA$_{4\omega}$ spectrum of β-phase F8 measured at 125 kV/cm. Inset: EA$_{4\omega}$ spectrum of glassy F8 measured under the same experimental condition.

contribution from higher-order optical nonlinearity must be taken into account. To treat the fifth-order optical nonlinearity explicitly, the change of transmitted light ΔT under the applied electric field $F = F_0 \cos \omega t$ is expanded as follows:[33,34]

$$
\begin{aligned}
-\frac{\Delta T}{T} &\propto 3\,\mathrm{Im}\left[\frac{\chi^{(3)}}{\tilde{n}}\right]F^2 + 5\,\mathrm{Im}\left[\frac{\chi^{(5)}}{\tilde{n}}\right]F^4 + \cdots \\
&\approx 3\,\mathrm{Im}\left[\frac{\chi^{(3)}}{\tilde{n}}\right](F_0 \cos \omega t)^2 + 5\,\mathrm{Im}\left[\frac{\chi^{(5)}}{\tilde{n}}\right](F_0 \cos \omega t)^4 \\
&= \frac{3}{2}\mathrm{Im}\left[\frac{\chi^{(3)}}{\tilde{n}}\right]F_0^2(1 + \cos 2\omega t) \\
&\quad + \frac{5}{8}\mathrm{Im}\left[\frac{\chi^{(5)}}{\tilde{n}}\right]F_0^4(\cos 4\omega t + 4\cos 2\omega t + 5),
\end{aligned} \tag{1}
$$

where $\tilde{n}$ is the complex refractive index and $\chi^{(3)}$ and $\chi^{(5)}$ are the third- and fifth-order optical susceptibilities. Equation (1) indicates that contribution of $\chi^{(5)}$ to the EA signal with an angular frequency of 2ω increases with F and can be measured directly by monitoring the EA signal at an angular frequency of 4ω (EA$_{4\omega}$). In Fig. 4(b), we show the EA$_{4\omega}$ spectrum of a β-phase F8 thin film measured at 125 kV/cm. This EA$_{4\omega}$ spectrum demonstrates that contribution of $\chi^{(5)}$ is significant at this field strength. The contribution of $\chi^{(5)}$ to the EA spectrum at an angular frequency of 2ω (EA$_{2\omega}$) can also be found from two EA$_{2\omega}$ spectra measured at low and high field strengths. Thus, we calculated the contribution of $\chi^{(5)}$ by subtracting EA$_{2\omega}/F^2$ at 125 kV/cm from EA$_{2\omega}/F^2$ at 50 kV/cm. The obtained difference spectrum is shown in Fig. 4(a). The two spectra in Fig. 4 are in good agreement with each other and thus confirm that the deviation from the F^2 dependence is not due to the FK effect but is rather due to contributions from higher-order optical nonlinearity.

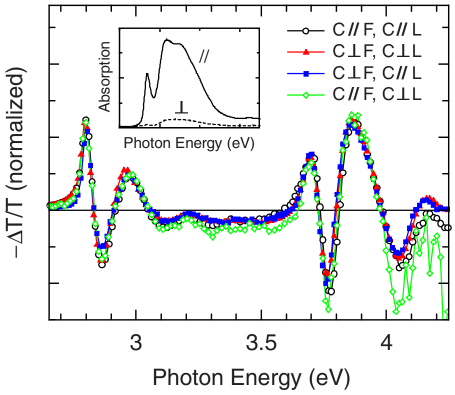

FIG. 5. (Color online) Normalized EA spectra of oriented β-phase F8 thin films measured using polarized light (L) and applied electric field (F) parallel and perpendicular to the chain direction (C). The low signal-to-noise ratio above 4.0 eV results from the large absorbance of the polyimide layer. Inset: polarized absorption spectra of the oriented β-phase F8 thin films.

Next we proceed to examine whether the oscillation could result from a CT transition from one chain to another. In the EA spectra of polycrystalline thin films of small molecules, oscillatory signals whose spectral shape resembles the second energy derivative of their absorption spectra were observed above the Stark shift of the Frenkel exciton.[24,25] In these oscillatory signals, each negative peak corresponds to a CT state transferring from one molecule to a different molecule. When the applied electric field is parallel to this transfer direction, the CT state gives rise to a stronger EA signal than when the field is perpendicular to the transfer direction. Since CT states have different transfer directions in crystalline thin films of small molecules, the observed oscillatory signals due to CT transitions exhibit a complex dependence of their amplitudes on the direction of the applied electric field.[24] Here, to find this directional dependence for β-phase F8, we prepared oriented β-phase F8 thin films on the aluminum electrodes and carried out EA measurements by applying electric fields parallel and perpendicular to the chain direction. However, as shown in Fig. 5, the EA spectra are almost identical to one another except for differences in amplitude, indicating no significant directional dependence. Therefore, CT transitions can be excluded as the origin of the oscillatory feature around 3.8 eV. Note that in studies of π conjugated copolymers, excitations from one monomer unit to neighboring units are also referred to CT transitions,[35] but here such CT transitions are not distinguished from other intrachain transitions.

From the above considerations, we conclude that the observed oscillation results from several intrachain excited states, some of which are not resolved in the glassy phase because of inhomogeneous broadening. Based on a semiempirical quantum-chemical calculation taking into account multireference double-configuration interaction, Beljonne *et al.* revealed that, in addition to the essential states, there may exist some B_u and A_g states that contribute to the NLO response as strongly as the mA_g and nB_u states.[36] The oscillation in β-phase F8 has fulfilled this prediction and thus indicates experimentally that the essential-state model may not be adequate for highly ordered thin films of π conjugated polymers.

From the sum-over-states (SOS) calculation reported by Orr and Ward,[37] it is possible to fit EA spectra of π conjugated polymers. Here, based on an eight-level model consisting of the ground state and the seven excited states, we calculated $\chi^{(3)}$ as well as $\chi^{(5)}$ spectra for β-phase F8 thin films using the following equations:[38]

$$\chi^{(3)}(\omega) \propto \sum_{lmn} \frac{\mu_{gl}\mu_{lm}\mu_{mn}\mu_{ng}}{(\omega_{lg}-\omega-i\gamma)(\omega_{mg}-\omega-i\gamma)(\omega_{ng}-\omega-i\gamma)}, \tag{2}$$

$$\chi^{(5)}(\omega) \propto \sum_{lmnpq} \frac{\mu_{gl}\mu_{lm}\mu_{mn}\mu_{np}\mu_{pq}\mu_{qg}}{(\omega_{lg}-\omega-i\gamma)(\omega_{mg}-\omega-i\gamma)(\omega_{ng}-\omega-i\gamma)(\omega_{pg}-\omega-i\gamma)(\omega_{qg}-\omega-i\gamma)}, \tag{3}$$

where l, m, n, p, and q denote states within the eight-level model, g indicates the ground state, ω is the frequency of the incident light, μ_{ij} is the transition dipole moment (TDM) between two states labeled by i and j, γ is a damping constant, and ω_{ig} is the excitation frequency from states g to i. The best fits are shown in Fig. 6, where excellent agreement between the experimental and calculated results is obtained. Although similar spectra can be obtained from different sets of parameters, to produce a good fit, the A_g and B_u states necessarily must appear near the positive and negative peaks of the oscillation in the $\mathrm{EA}_{2\omega}$ spectrum, respectively.

In Fig. 7, we illustrate the excited-state structures of β-phase F8 expected from the SOS calculation and of glassy F8 determined from the essential-state model.[9] The oscillation in the $\mathrm{EA}_{2\omega}$ spectrum is apparently characteristic of the β phase and the $\mathrm{EA}_{4\omega}$ signal is only observed in the β phase [see the inset of Fig. 4(b)]. Therefore, we believe that the series of the A_g and B_u states around 3.8 eV required to explain the EA spectra reflects the excited-state structure of β-phase F8. In Table I, we also summarized the TDMs used to obtain the fitting results in Fig. 6(b). These values may change if we carry out the numerical calculation based on a different model, a nine-level or ten-level model for instance. Nevertheless, it must be true that TDMs between the B_u and A_g states leading to the oscillation around 3.8 eV always have extremely large absolute values. This is rationalized from Eqs. (2) and (3) as follows: the magnitude of $\chi^{(3)}$ at the position of an excited state (l) is mainly determined by numerator, $\mu_{gl}\mu_{lm}\mu_{ml}\mu_{lg}$, of one or a few terms involved in the transition between g and l. This is the theoretical explanation

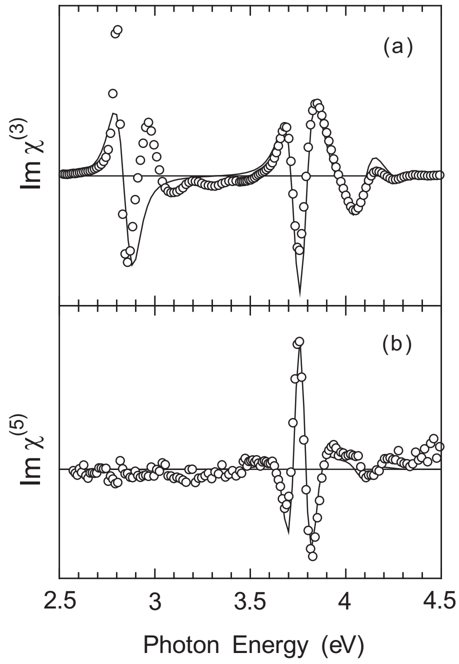

FIG. 6. Open circles give the spectra of (a) Im $\chi^{(3)}$ and (b) Im $\chi^{(5)}$ calculated from the corresponding EA spectra of β-phase F8. Solid lines are the best fits obtained using Eqs. (2) and (3).

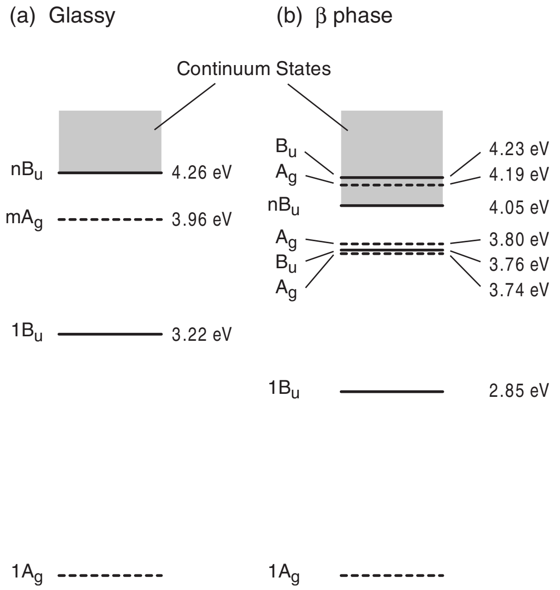

FIG. 7. (a) The excited-state structure of glassy F8 reported in Ref. 9 and (b) one of β-phase F8 expected from the SOS calculation. The solid and dotted lines indicate B_u and A_g states, respectively. The energy intervals between the $1B_u$ and $1A_g$ states are reduced in order to fit in the figure.

TABLE I. TDMs used to obtain the best fit shown in Fig. 6. The TDMs are normalized to that between the $1A_g$ and $1B_u$ states.

	$1B_u$	B_u [a]	nB_u	B_u [b]
$1A_g$	1	−0.1	−0.18	−0.11
A_g [c]	1.1	7.8	−4.4	4.4
A_g [d]	0.22	−8.9	6.7	−0.56
A_g [e]	−0.11	0.22	0	0.22

[a] B_u state at 3.76 eV.
[b] B_u state at 4.23 eV.
[c] A_g state at 3.74 eV.
[d] A_g state at 3.80 eV.
[e] A_g state at 4.19 eV.

for the appearance of a large $\chi^{(3)}$ peak at the position of an excited state with a large TDM from the ground state, $|\mu_{gl}|^2$. In the case of β-phase F8, however, the oscillation with a large amplitude appears in the spectral range where there is no excited state with a large TDM from the ground state, as shown in Fig. 1(b). To compensate for the small TDM of the resonance excited state and induce a large EA signal, it is necessary that the TDM between the excited states, $|\mu_{lm}|^2$, around 3.8 eV should have a large absolute value. The same holds for the $\chi^{(5)}$ spectrum.

In the excited states of π conjugated polymers, the nB_u state is characterized as the bottom of the continuum state. The theoretical studies have revealed that the excited states below the nB_u state have an excitonic character. Above the nB_u state, there are also excited states with a different character; excitation to those excited states has a transition dipole moment perpendicular to the chain axis and a strong contribution to photocarrier generation.[29] In glassy F8, this kind of the excited state lies at 4.2 eV, very close to the nB_u state.[9] In the β phase, this state can still be found at 4.2 eV both from the polarized absorption spectrum perpendicular to the alignment direction[26] and from the onset of the PC yield in Fig. 1(b). However, the PC yield in the β phase gradually rises from a lower energy than does the onset in the glassy phase. This suggests that in the β phase, an excited state with a weak contribution to photocarrier generation exists around 4.0 eV. In poly(2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylene vinylene) (MEH-PPV), the nB_u state is located at 3.0 eV,[8] from which the PC yield rises gently and increases steeply around the second type of excited state (at 3.8 eV).[42] Therefore, we assign the B_u state at 4.05 eV to the nB_u state in β-phase F8. The lower B_u state at 3.76 eV seems to be too low in energy to be identified as the nB_u state since the shift of the $1B_u$ state after the phase transition is only about 0.37 eV.

Finally, we compare the oscillation in β-phase F8 with those reported in regioregular poly(3-hexyl thiophene) (P3HT)[39] and methyl-substituted ladder-type poly(para-phenylele) (MeLPPP):[40] in P3HT the ordered packing is formed in the solid state and in MeLPPP the planarity of the main chain is maintained by the bridging carbon atom between adjacent phenyl rings. The oscillations observed in P3HT and MeLPPP are much smaller than that in β-phase F8. One reason for the difference is that, compared to other π conjugated polymers, F8 has a relatively large TDM between the ground and nB_u states,[9] which enhances the EA signals associated with the nB_u state. Another might be the better oxidative stability of F8. In the case of P3HT, the oscillation is only observed in freshly prepared samples. Österbacka *et al.* proposed that this change results from oxidation or doping by oxygen.[39] Indeed, P3HT is known to be readily oxidized because its highest occupied molecular orbital (HOMO) level is relatively high (4.9 eV).[41] In contrast, the HOMO level of F8 is much deeper (5.7 eV).[41] The oxidative stability of F8 may allow us to observe the large EA oscillation more easily. In fact, the oscillation is also observed in β-phase F8 thin films which were kept in air in the dark for more than one month.

IV. CONCLUSION

We have studied EA spectra of glassy and β-phase F8 thin films and found that the oscillatory EA signal, which appears when the polymers adopt a planar conformation, reflects the presence of intrachain excited states in β-phase F8. To reproduce the EA spectrum of β-phase F8 by a SOS calculation, seven excited states in addition to the ground state have to be considered. This indicates that the essential-state model is not adequate to explain the EA spectra of ordered thin films of π conjugated polymers. On the other hand, the essential-state model explains well the EA spectrum of glassy F8, where the oscillation is not observed due to considerable inhomogeneous broadening or disappears because of mixing of the three excited states forming the oscillation due to structural disorder.

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