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Effect of Aggregation on the Excited-State Electronic Structure of Perylene Studied by Transient Absorption Spectroscopy

Akihiro Furube, Miki Murai, Yoshiaki Tamaki,† Sadayuki Watanabe, and Ryuzi Katoh*

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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The effect of aggregation on the excited-state electronic structure of perylene was studied through transient absorption measurements of isolated molecules, excimers, monomeric crystals (β-perylene), and dimeric crystals (α-perylene). Changes of electronic state were clearly identified from the changes in transient absorption spectra. A detailed investigation was made by combining the obtained results with previous measurements of ground-state absorption and fluorescence spectra. The energy level of the ion-pair state in α-perylene crystals was estimated, and the results are compared with previous photoconductivity results. Moreover, the relaxation processes of excited states in α-perylene crystals were studied by femtosecond transient absorption measurements.

1. Introduction

Optoelectronic devices based on organic molecular crystals, such as electroluminescence devices and solar cells,[1] have recently been attracting much interest. To achieve high performance in such devices, molecules with suitable optical and electronic properties, such as the absorption coefficient, fluorescence lifetime, and redox potential, must be examined. Extensive data are available in databases, and there are computational techniques that can help us evaluate these properties. Information about molecular properties is useful, but it is insufficient for designing actual devices because device performance is often controlled by properties that arise from aggregation of the molecules. For example, electronic band formation through intermolecular interaction plays an important role in charge carrier transport and exciton diffusion properties and the photoinduced charge generation properties of phthalocyanine films are sensitive to the crystal structure.[2,3]

Property changes caused by aggregation are difficult to evaluate by computational techniques; therefore actual developments of optoelectronic devices have been examined with the help of empirical knowledge. Thus, the change of electronic structure by aggregation from isolated molecules to crystals currently has been attracting much interest. The aggregation effect has been studied in gas-phase clusters through photoelectron spectroscopy.[4] Although these studies have yielded much information about the aggregation effect, comparison with structures has often been inconclusive because of the experimental difficulties involved with determining the structure.

Perylene is typical of molecules that can be used to study changes in electronic excited-state properties caused by the aggregation of isolated molecules into densely packed crystals. Figure 1 shows a schematic drawing of various aggregates of perylene molecules. In dilute solutions, perylene molecules remain isolated. In concentrated solutions, perylene molecules form excimers (excited-state dimers),[5] and therefore such solutions can be used to study the dimeric structure. In the crystalline phase, two crystal structures have been reported: monomeric (β-perylene) and dimeric (α-perylene).[6,7] The absorption spectra of α-perylene and β-perylene crystals differ from the spectrum of isolated molecules in solution,[6] which suggests that intermolecular interactions affect the excited-state electronic structure. Some crystals of perylene derivatives show various colors, whereas in solution the absorption spectra are similar. In other words, the crystal color can be controlled by the aggregation,[8] and thus perylene-derivative crystals are used as practical pigments. The excited-state electronic structure can be studied by using conventional spectroscopic techniques, such as fluorescence and transient absorption spectroscopies.

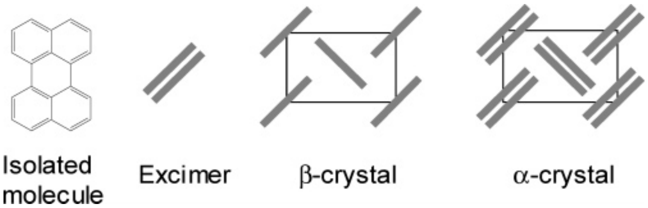

Figure 1. Schematic diagram of various aggregation forms of perylene.

Fluorescence spectroscopy is used to study electronic excited states. Orange fluorescence (E-fluorescence) has been observed in α-perylene crystals,[6,9] whereas blue fluorescence is observed in a dilute solution of perylene.[5] The spectrum of E-fluorescence is similar to that of excimers from a concentrated solution,[5] which indicates that the E-fluorescence is due to the excimer state in the crystal. This similarity is expected because the α-perylene crystal has a dimeric structure (Figure 1). At low temperature ($<$50 K)[6,7,10,11] or high pressure ($>$5 kbar),[12] green fluorescence (Y-fluorescence) is observed instead of E-fluorescence. Y-fluorescence has been explained as originating from crystal defects with a monomeric structure[6,7,13] or a less-relaxed excimer.[10,11] In β-perylene crystals, green fluorescence has been observed, which is similar to Y-fluorescence, and it has been attributed to fluorescence from weakly trapped excited states.[6,12]

Transient absorption spectroscopy can detect all excited species including charge-separated states, whereas fluorescence spectroscopy can detect only fluorescent states. Transient

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* Address correspondence to this author. E-mail: r-katoh@aist.go.jp.
† NEDO Fellow.

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absorption has been measured in perylene solutions, and absorption bands due to monomer excited states and excimer states have been identified.[5,14,15] A characteristic absorption band due to an excimer state appears in the near-IR wavelength range. This band can be assigned to a charge-transfer absorption band, the optical transition from an excimer state to an ion-pair state.[5,14] From detailed analyses of peak positions, band profiles, and absorption intensities, intermolecular interactions in the excimer state can be examined.[5]

Although transient absorption spectroscopy is a common technique for studying electronic excited states in solution, few such studies have been carried out for organic crystals because large transparent crystals are not always available. Transient absorption spectra have been reported for an anthracene crystal,[16] which is a prototype crystal for the study of optoelectronic functions, and the transient absorption spectra are similar to the solution spectrum. This similarity suggests weak intermolecular interactions in the excited state. Similarity between crystal and solution spectra has been reported for several other molecules, for example, *p*-terphenyl,[17] *trans*-stilbene,[18] and benzophenone.[19] In these crystals, two constituent molecules are oriented nearly perpendicular in a unit cell so that interaction between the molecules is weak. In contrast, for crystals with a dimeric structure, such as pyrene and α-perylene crystals, the transient absorption spectra differ significantly from the spectra in dilute solution, and this difference suggests strong intermolecular interaction.[20] This spectral change is due to excimer formation in the crystals.

We carried out a systematic study of the transient absorption of perylene in various aggregation forms: isolated molecules, excimers in solution, monomeric crystals (*β*-perylene), and dimeric crystals (α-perylene). We also evaluated the formation rate of the excimer state in α-perylene crystals through femtosecond transient absorption spectroscopy. On the basis of these results, we examined the change of excited-state electronic structure of perylene induced by aggregation.

2. Experimental Section

For measurement of solution spectra, perylene (Wako, GR-grade) was used after purification by recrystallization. Toluene (Wako, GR-grade) was used as the solvent without further purification. A single crystal of α-perylene was grown from melted perylene by the Bridgman method after purification by extensive zone refining. Single crystals (typically 8 × 5 × 1 mm^3) cleaved from ingots were used as sample specimens. A single crystal of *β*-perylene was grown from toluene solution after being purified by recrystallization. The size of the crystals was typically 1.5 × 1 × 0.2 mm^3. The formation of the *β*-crystal was confirmed by fluorescence spectroscopy.

For the nanosecond transient absorption measurements, 505-nm pulses from an optical parametric oscillator (Spectra Physics, MOPO-SL) excited by a Nd^{3+}:YAG laser (Spectra Physics, Pro-230-10) were used for the pumping light. The pulse duration of the laser was about 8 ns. A Xe flash lamp (Hamamatsu, L4642, 2 μs pulse duration) was used as the probe light source. In the visible range, the spectrum of the probe light transmitted through the sample was recorded with a gated CCD camera (Roper Scientific, ICCD-MAX) after being dispersed with a monochromator (Roper Scientific, SP-308) controlled by a computer. In the near-IR range (900−2700 nm), the probe light was detected with a photodiode after passing through a monochromator (Ritsu, MC-10N). An InGaAs photodiode (Hamamatsu, G3476-05) and an MCT photodetector (Dorotek, PDI-2TE-4) were used for the 900−1600- and 1200−2700-nm ranges, respectively. Signals from these detectors were amplified with an amplifier (NF Electronic Instruments, BX-31A) and were processed with a digital oscilloscope (Tektronix, TDS680C).

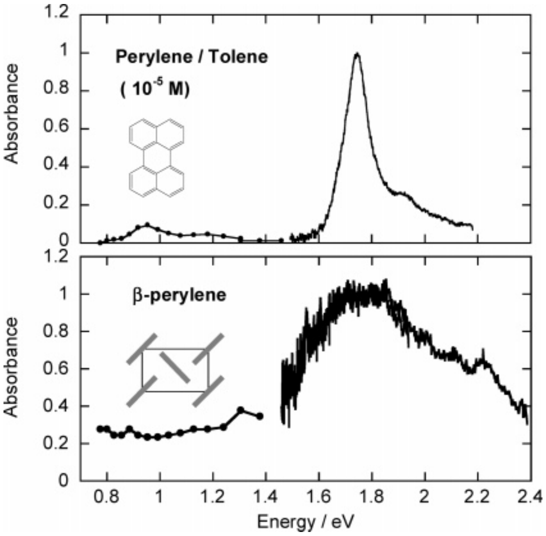

Figure 2. Transient absorption spectra of a dilute solution of perylene (10^{-5} M) and of *β*-perylene crystals.

The light source for the femtosecond pump−probe transient absorption measurements was a regenerative amplifier system consisting of a Ti:sapphire laser (800 nm wavelength, 160 fs fwhm pulse width, 1.0 mJ pulse intensity, 1 kHz repetition, Spectra Physics, Hurricane) combined with two optical parametric amplifiers (OPA, Quantronix, TOPAS). One OPA output at 510 nm with an intensity of several microjoules per pulse was used for the pump pulse, and the other OPA output from 1170 to 1560 nm was used for the probe pulse. The probe beam transmitted through the sample specimen was detected by an InGaAs photodetector after passing through a monochromator (Acton Research, Spectra Pro 300). Details of the apparatus have been described elsewhere.[21]

3. Results and Discussion

3.1. Transient Absorption Spectra of Monomer Excited States in Solution and in *β*-Crystals. Figure 2 shows the transient absorption spectrum of a dilute solution of perylene (10^{-5} M) in toluene and the spectrum of a *β*-perylene single crystal recorded with the nanosecond time-resolved transient absorption spectrometer. The spectra were recorded just after excitation so that the contribution of long-lived species, such as triplet excited states, was effectively eliminated from the spectra. Although transient absorption spectra have been reported previously,[5,14,15] there have been no results in the near-IR wavelength range. Thus, we measured in this wavelength range very carefully. For the dilute solution, a strong peak is observed at 1.75 eV (710 nm), which is identical with those of reported spectra.[5,14,15] An additional weak absorption peak can be seen at 0.95 eV (1300 nm). The decay time constant of these absorption peaks is similar to the fluorescence lifetime, and therefore these peaks can be attributed to absorption from the lowest singlet excited state to higher singlet excited states (S−S absorption). For the *β*-perylene crystal, an absorption peak in the visible range is observed at around 1.75 eV. The peak position is similar to that of the dilute solution, but the shape is much broader. In the near-IR wavelength range (<1.4 eV), the absorbance is small, and no apparent structure is seen.

Figure 3 shows schematic diagrams of the electronic structure of isolated molecules and of *β*-perylene crystals. For the isolated

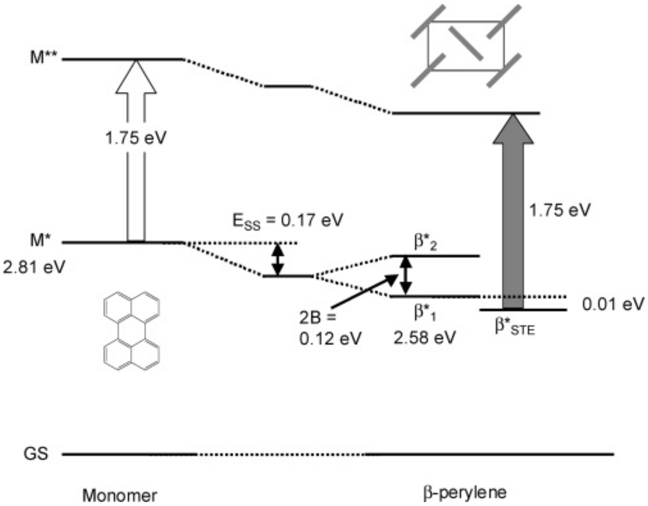

Figure 3. Schematic energy diagrams of perylene monomer and β-perylene crystals.

molecules, the first excited (M*) state is located 2.81 eV above the ground state, as determined from the absorption spectrum edge (440 nm) in solution.[5] In the *ab*-plane of a β-perylene crystal (Figure 1), there are two molecules in a unit cell, and they are oriented nearly perpendicular to each other, an arrangement that is similar to that of an anthracene crystal. Thus, weak intermolecular interaction is expected. The lowest excited state is split into two states, β^*_1 and β^*_2 (Figure 3), by the interaction between the two molecules in the unit cell. The energy level of the lowest excited state, β^*_1, is estimated to be 2.58 eV from the absorption spectra of β-perylene crystals.[22] The energy difference between the M* and the β^*_1 states consists of two parts (Figure 3): site shift energy, E_{ss}, and the half-width of the exciton band, B. From detailed analysis of the absorption spectra of β-perylene crystals,[22] B is estimated to be 0.06 eV, and therefore E_{ss} is estimated to be 0.17 eV. It should be noted that the width of the exciton band, 2B, corresponds to Davydov splitting, which is known to be an index of intermolecular interaction in organic crystals.[23] The value for β-perylene (0.12 eV) is larger than that for anthracene (0.05 eV[24]), which has a similar crystal structure. This difference in values indicates that the intermolecular interaction in β-form perylene crystals is much stronger than that in anthracene crystals.

Upon photoexcitation of perylene molecules in dilute solution, fluorescence from the lowest singlet excited state (M*) is observed as the mirror image of the absorption band.[5] The fluorescence spectrum of β-perylene crystals appears at a position slightly shifted from the mirror image of the absorption band,[25] which suggests that relaxations occur in the excited state. The relaxation process has been studied, and it is known to involve self-trap exciton formation by the interaction of the excited state with the crystal lattice. The relaxed state is labeled as β^*_{STE} in Figure 3. The stabilization energy of the self-trapped exciton in β-perylene crystals is estimated to be 0.01 eV,[25] which indicates weak coupling with the crystal lattice. Thus, the excited state in β-perylene crystals is apparently in a nearly free state. The weak coupling strength leads to a high diffusion coefficient for the exciton, which is evaluated through the exciton−exciton annihilation rate constant, γ_{ss}.[23] For β-perylene crystals, γ_{ss} has been reported to be 1.2×10^{-8} cm^3 s^{-1}.[10] This value is similar to that of anthracene (10^{-8} cm^3 s^{-1}),[26] in which excitons can move easily in the crystal.

For the isolated molecule, as shown in the transient absorption spectrum in a dilute solution (Figure 2), the energy of the higher excited (M**) state is estimated to be 1.75 eV above that of the M* state. For β-perylene crystals, the transient absorption peak position is similar to that of the isolated molecule, but the peak is much broader (Figure 2). As mentioned above, the exciton in β-perylene crystals interacts weakly with the crystal lattice. The initial state for the transient absorption can be considered to be a localized state, β^*_{STE}, below the exciton band. The final state of the optical transition is a higher exciton band having substantial bandwidth because of Davydov splitting in the higher excited state. This may be the reason for the broad spectral shape of β-perylene crystals.

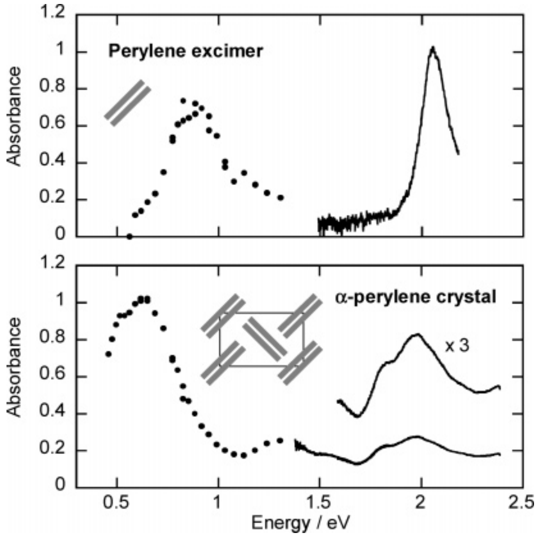

Figure 4. Transient absorption spectra of excimers of perylene and of an α-perylene crystal.

3.2. Transient Absorption of Excimers in Solution and of α-Crystals. Figure 4 shows the transient absorption spectrum of excimers of perylene in a toluene solution and the spectrum of an α-perylene single crystal recorded with the nanosecond time-resolved transient absorption spectrometer. To obtain the absorption spectrum due to excimers in solution, the contribution of the monomer excited state obtained in a dilute solution (Figure 2) was subtracted from the spectrum observed in a concentrated solution.[5] In the solution spectrum, absorption peaks are observed at 2.04 (605 nm) and 0.9 eV (1400 nm). In the solid-state spectrum, absorption peaks are observed at 1.98 (625 nm), 1.38 (900 nm), and 0.65 eV (1900 nm). In addition, there are shoulders at 1.8 (690 nm) and 0.5 eV (2400 nm).

Figure 5 shows schematic diagrams of the electronic structures of isolated molecules, excimers, and α-perylene crystals. As shown in Figure 1, two molecules form a dimmer and there are two dimmers in a unit cell. Each dimer is packed in the unit cell. Thus, we can examine the electronic structure of α-perylene crystals in excited states by comparison with excimers. For excimers in solution, the lowest singlet excited state of the monomer (M*) is separated into two states (E^*_1 and E^*_2) by exciton interaction, which arises from the delocalization of excited states between two molecules. Another important intermolecular interaction is the charge-transfer (CT) interaction. For many aromatic hydrocarbon crystals, an ion-pair (IP) state is known to locate above the lowest excited state[23] and therefore for α-perylene crystals, we put the IP state above the lowest excited (E^*_1) state that mixes with the E^*_1 state by CT interactions. These intermolecular interactions are more pronounced in the excimer, and therefore the electronic structure of the excimer differs significantly from that of the monomer. For α-perylene crystals, there are two dimers in the unit cell, so the interaction between dimers is also important. As a result

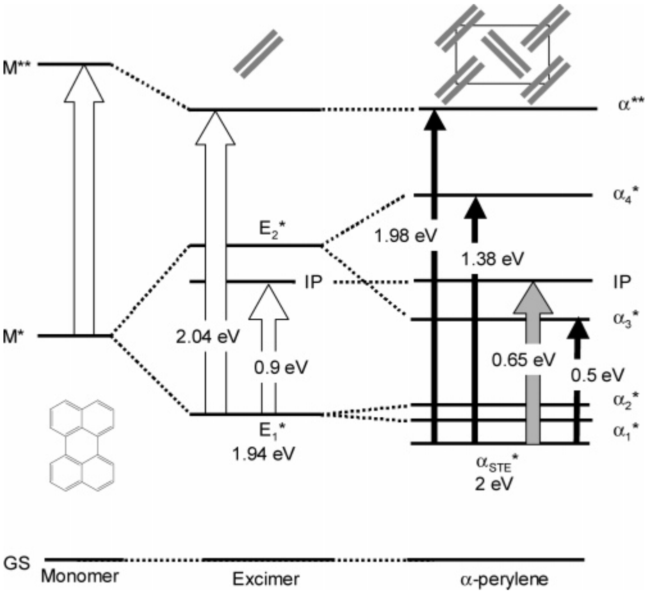

Figure 5. Schematic energy diagram of perylene monomer, perylene excimer, and α-perylene crystals.

of Davydov splitting, the E^*_1 and E^*_2 states split; the split states are depicted in Figure 5 as α^*_1, α^*_2, α^*_3, and α^*_4. In the crystal, the charge-transfer interaction is also important, and the IP state exists above the lowest excited state. The IP state is known to be a CT state,[23] which is a precursor state for charge carriers.

As mentioned above, the energy level of the lowest excited state (M*) in the monomer can be evaluated from the absorption spectrum. In the dimer configuration, however, it is impossible to estimate the energy level of the lowest excited state from the absorption spectrum because the optical transition from the ground state to the lowest excited state (E^*_1) is symmetrically forbidden. On the other hand, optical transition from the ground state to the second excited state (E^*_2) is allowed. Ferguson reported on the absorption spectra of perylene dimers;[27] he estimated the energy level of the E^*_2 state to be 3.35 eV.

Upon photoexcitation of perylene dimers, the E^*_2 state is primarily populated; then relaxation from the E^*_2 to the E^*_1 state occurs rapidly, and weak fluorescence from the E^*_1 state can be observed at 640 nm.[27] Thus, we estimated that the E^*_1 state is located 1.94 eV above the ground state. This fluorescence is known as excimer fluorescence, which has a long lifetime and low quantum yield. It has been reported that the lifetime of perylene excimers in solution is 17.6 ns and the quantum yield is 0.02.[5] This is because the fluorescence from the forbidden E^*_1 state arises by vibronic coupling.

Optical transition from the lowest excited state to higher excited states in perylene excimers in solution is also observed (Figure 4). The peak at around 2.04 eV (600 nm) is assigned to the transition from the E^*_1 state to a higher excited (E**) state. In the near-IR wavelength range, optical transitions reflecting intermolecular interaction are expected to appear. The peak observed at 0.9 eV (1400 nm) is assigned to the transition from the E^*_1 state to the IP state; this assignment is based on comparison with the absorption spectrum of several aromatic excimers.[5,14] Although from a detailed analysis of the spectrum[5] absorption to the E^*_2 state is expected to appear at around 1.07 eV (1150 nm), there is no corresponding absorption band in the spectrum. The absence of this band may be due to overlapping of the band with the strong CT absorption band.

The E^*_1 and E^*_2 states are both split into two electronic states, α^*_1 and α^*_2, and α^*_3 and α^*_4, respectively. Absorption spectra of the ground state in α-perylene crystals have been observed,[28] and the energy levels of the α^*_3 and α^*_4 states were found to be 2.67 and 3.31 eV above the ground state, respectively. Optical transition from the ground state to the α^*_1 and α^*_2 states is symmetry forbidden.

Fluorescence from the lowest excited state, α^*_1, can be observed. The excited state (free excitons) interacts with the crystal lattice; self-trapped excitons (STEs) then form, and fluorescence from the state (E-fluorescence) can be measured. The relaxed state is depicted as α^*_{STE} in Figure 5. The spectrum from the α-perylene crystal is similar to that of excimers in solution because free excitons interact mainly with the nearest molecules. Thus, the STEs can be considered to be excimer states in the crystal. The excimer state (STE) is localized at the bottom of the exciton band. The stabilization energy of STEs in α-perylene crystals is estimated to be 0.08 eV.[27] It has been reported that the lifetime of the excimer fluorescence is 110 ns and that the quantum yield is 0.2 at room temperature.[27] From these values, the radiative lifetime of the STEs is estimated to be 550 ns, which is similar to the lifetime of the isolated excimers (880 ns). This long lifetime also indicates that the fluorescent state of α-perylene crystals can be considered to be an excimer state. Since excitons in α-perylene crystals interact with the lattice, slow exciton motion is expected. In fact, two values for the exciton−exciton annihilation rate constant, γ_{ss}, of α-perylene crystals have been reported: 2.4×10^{-10} cm^3 s^{-1}[10] and 8×10^{-14} cm^3 s^{-1}.[28] In any case, both of these values are much smaller than that of β-perylene (1.2×10^{-8} cm^3 s^{-1}[10]). The energy level of the lowest excited α^*_{STE} state has been estimated to be 2.0 eV from the peak of the excimer fluorescence.[26]

Transient absorption bands for α-perylene crystals differ significantly from those of excimers in solution. From this difference, the charge-transfer character and intermolecular interactions can be examined. A transient absorption band in the visible range is observed at 1.98 eV (625 nm), which is a position similar to that of excimers in solution (2.04 eV). This band can be assigned to the transition from the α^*_{STE} state to the α** state. According to the energy level diagram (Figure 5), optical transitions from the α^*_{STE} state to higher excited states (α^*_4, α^*_3) and IP states are expected to be observed in the near-IR wavelength range. From its similarity to bands in the transient absorption spectra of excimers, the strong absorption band at 0.65 eV (1900 nm) can be assigned to the transition from the α^*_{STE} state to the IP state. The additional peak at 1.38 eV (900 nm) and the shoulder at 0.5 eV (2400 nm) can be assigned to the transitions from the α^*_{STE} state to the α^*_4 and α^*_3 states, respectively. The energy levels of these states from the ground state are estimated to be 3.38 and 2.5 eV, respectively. These values are similar to the energy levels estimated from the ground-state absorption (3.31 eV for the α^*_4 state and 2.67 eV for the α^*_3 state[29]). This similarity again suggests that the assignments of the observed transient absorption spectra are appropriate. The energy difference between these absorption peaks corresponds to the energy splitting of the E^*_2 state in excimers, and the splitting is estimated to be 0.92 eV.

3.3. Relationship between the Observed Charge-Transfer Absorption Band and the Photoconductive Band Gap. In organic crystals, ion-pair states are known to be CT states. They are an important intermediate for charge carriers,[3,23] and therefore they have been studied extensively. However, the properties of the CT state, such as the energy level and lifetime, are not fully understood. This is because the absorption coefficient of the optical transition from the ground state to CT

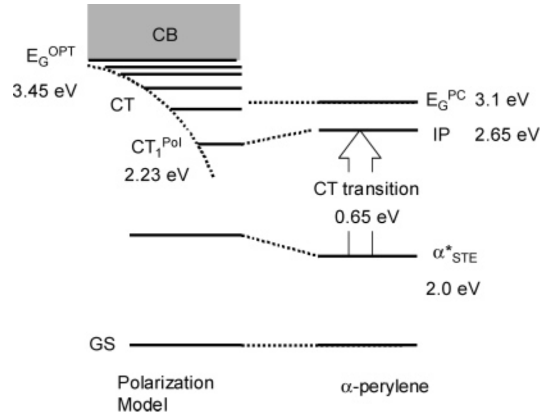

Figure 6. Schematic energy diagrams of CT states based on the polarization model and on α-perylene crystals.

states is weak and is often overlapped by strong absorption due to neutral excited states. Thus, CT states in organic materials have been studied through electric field modulation spectroscopy. Such spectra have been reported for organic crystals such as anthracene,[30] naphthacence,[31] pentacene,[31] and phenothiazine.[32]

Figure 6 shows a schematic diagram of the conduction band and CT states in organic crystals. The intermolecular interaction of organic crystals is not large, so the band gap energy can be estimated by the polarization model[23] and expressed as

$$E_G = I_g - E_A + P_+ + P_- \tag{1}$$

where I_g is the ionization potential of a molecule in the gas phase, E_A is the electron affinity in the gas phase, and P_+ and P_- are the polarization energies induced by a cation and an anion, respectively. According to the Born model,[33] the polarization energy P can be written as

$$P = P_+ = P_- = -\frac{e^2}{8\pi\epsilon_0 R}\left[1 - \left(\frac{1}{\epsilon}\right)\right] \tag{2}$$

where R is the effective radius of the ion, e is the elementary charge, ϵ is the dielectric constant of the medium, and ϵ_0 is the permittivity of the vacuum. The Born formula is known to give reasonable values when the van der Waals radius, R_{vdW},[34] is used as the R value for the ion.[35] Thus, the polarization energy in perylene crystals is estimated to be -1.34 eV for $R = R_{vdW} = 0.378$ nm and $\epsilon = 3.4$. Hence, the band-gap energy is estimated to be $E_G = 3.12$ eV for $I^g = 6.90$ eV,[24] $E_A = 1.10$ eV,[36] and $P_+ = P_- = -1.34$ eV. This value agrees with the band-gap energy, E_G^{PC} (3.1 eV), estimated from photoconductivity measurements.[24]

The CT states are located below the conduction band because of stabilization by the Coulomb interaction between a cation and an anion. Thus, the energy level, E_{CT}, of CT states relative to the ground state can be expressed as

$$E_{CT} = E_G - C \tag{3}$$

$$C = -\frac{e^2}{4\pi\epsilon\epsilon_0 r_{CT}} \tag{4}$$

where C is the Coulomb energy, and r_{CT} is the radius of the CT state. Accordingly, the CT states converge to the energy of the fully charge-separated state, the conduction band, with increasing r_{CT}. Thus, the band-gap energy can also be estimated when the energy levels of the CT states are available.[30,36] It has been reported that the band-gap energy, E_G^{opt}, estimated from the energy levels of CT states is significantly higher than the band-gap energy, E_G^{PC}, estimated from the photoconductive threshold[36] and that the energy difference ($E_G^{opt} - E_G^{PC}$) is 0.3−0.4 eV. The reason for the difference was examined on the basis of molecular (vibronic) polarization.[36] Thus, E_G^{opt} of perylene crystals is estimated to be about 3.45 eV ($E_G^{opt} = E_G^{PC} + 0.35$).

The lowest CT state (CT$_1$) is a CT state having the nearest distance between molecules in a crystal. For α-perylene crystals, the nearest distance has been reported to be 0.346 nm,[37] which is the face-to-face distance of dimers in the crystals. Using the polarization model, the energy level of the CT state (CT$_1^{pol}$) in this configuration is estimated to be 1.22 eV below the conduction-band edge. Namely, the CT$_1^{pol}$ state is located at 2.23 eV above the ground state (using $E_G^{opt} = 3.45$ eV).

As shown in Figure 4, the strong charge-transfer absorption band in α-perylene crystals is observed at 1900 nm (0.65 eV), and the final state of the absorption is assigned to be the CT$_1$ state. Thus, the energy level of the CT$_1$ state (CT$_1^{NIR}$) above the ground state can be estimated to be 2.65 eV, the sum of the E-state energy (2 eV) and transition energy (0.65 eV). This energy (CT$_1^{NIR}$) is slightly higher than that of the CT$_1^{pol}$ state estimated to be 2.23 eV by the polarization model. This shows that the polarization model is not precise for the estimation of the energy level of the CT$_1$ state, which suggests that other factors should be taken into account. In the polarization model, the energy of the ion-pair state is estimated as the stabilization of a cation and an anion from the bottom of the conduction band by the Coulomb energy (eq 3). For a CT state with a small ion-pair distance, the electronic coupling between a cation and an anion becomes stronger, and therefore the energy level is affected by the charge-transfer interaction. Moreover, the CT$_1$ state becomes unstable if it is strongly coupled with the lowest excited state.

As already mentioned, CT states in organic crystals are important as precursors for charge carriers. This is because CT states are partially ionized (ion-pair) states, and they dissociate into free carriers by the thermal activation process. Because of their large stabilization energy, CT states with small radii cannot dissociate easily. Although higher CT states with large radii can easily dissociate into free carriers, these states are not easy to populate by direct optical transitions, because of the small transition dipole moment. As a result, the efficiency of charge carrier generation is not high; for example, it was measured to be 10^{-3} in anthracene crystals.[16] Turning to α-perylene crystals, the CT states are destabilized by the mixing with the lower excited state, as discussed above. Namely, dissociation energy levels of the CT states decrease by the destabilization, suggesting that charge carrier generation becomes efficient. The destabilization of the CT states could be an important factor in the design of high-performance photoconductive devices. The photoconductive properties of phthalocyanine films have been extensively studied, and they are known to be sensitive to the crystal structure. Yamasaki et al. reported that a film with dimer structure showed high activity,[3] which implies that dimer formation leads to enhanced photoconductive activity through the destabilization of the CT states.

3.4. Formation Dynamics of Excimers in α-Perylene Crystals Through Femtosecond Transient Absorption Spectroscopy. The formation dynamics of excimer states (STE) in α-perylene crystals is summarized as follows. Upon photoexcitation with 510-nm light, which is the absorption edge of the crystals, the α*$_3$ state is directly populated in the crystal, whereas the α*$_1$ and α*$_2$ states are not directly populated because these

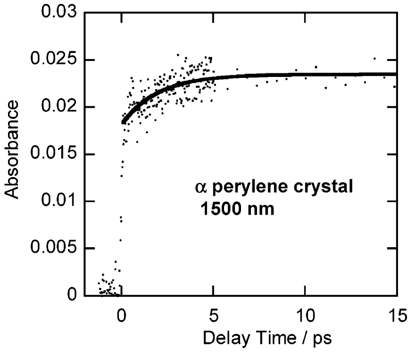

Figure 7. Rise profile of transient absorption observed at 1500 nm in α-perylene crystals.

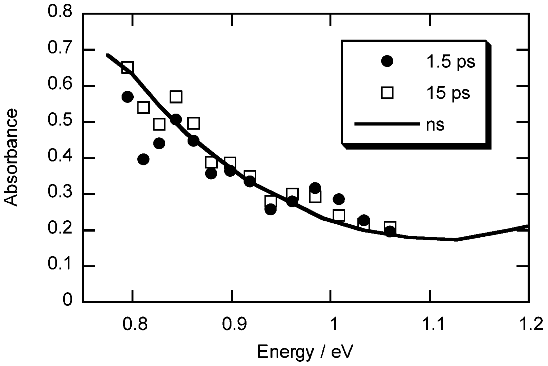

Figure 8. Transient absorption spectra recorded at 1.5 and 15 ps in α-perylene crystals.

transitions are symmetrically forbidden. The α^*_3 states decay rapidly to α^*_1 states through an internal conversion process. Subsequently, these states interact with the crystal lattice and then excimer states (STE) are formed.

This formation process can be followed by the ultrafast transient absorption technique. Figure 7 shows the temporal profile of transient absorption signals in α-perylene crystals observed at 0.83 eV (1500 nm) after excitation by 510-nm light. At this probe wavelength, charge-transfer absorption due to excimers is mainly observed. The rise profile can be reproduced by two components: the instantaneous rise component (<100 fs) and the exponential rise component with a time constant of 2 ps (solid line in Figure 7). The relative ratio of these components was found to be 4:1. Figure 8 shows absorption spectra recorded at 1.5 and 15 ps. The temporal change of the spectra appears to be negligible, and these spectra are similar to those of α-perylene crystals recorded in the nanosecond time range (Figure 4). This result indicates that the rise profile shown in Figure 7 is not due to spectral change during excimer formation but directly reflects the population of the excimer state.

The observed rise of the transient absorption signal is not consistent with naive expectations. In fact, 80% of the excimer states are populated very rapidly (<100 fs), and the residual 20% are generated slowly (2 ps). This implies that there are at least two pathways for the excimer population in the crystal: a direct population process from the α^*_1 state to the excimer α^*_{STE} state (direct path) and an indirect process via an intermediate state that is located between the α^*_1 state and the α^*_{STE} state and has a 2-ps lifetime (indirect path). Figure 9 shows these two paths schematically.

The population dynamics of the excimer state (α^*_{STE}) in α-perylene crystals has been studied at low temperature (<100 K) through time-resolved fluorescence spectroscopy.[11,38] Although orange (E-) fluorescence, which is fluorescence from the excimers, is mainly observed at higher temperature (>100 K), green (Y-) fluorescence becomes dominant at lower temperature (<100 K). At lower temperature, the rise time of E-fluorescence is in good agreement with the decay time of Y-fluorescence, which suggests that the excimer states are populated via the Y-state. Y-fluorescence is also observed in α-perylene crystals at room temperature under high pressure.[12] Recently, Fujino and Tahara reported ultrafast fluorescence decay of α-perylene crystals at room temperature.[39] They obtained two decay components with lifetimes of 2.2 and 38.7 ps. Although they assigned the fast component to free exciton fluorescence and the slow one to Y-fluorescence, the 2.2-ps component is similar to the rise time of our transient absorption results (Figure 7). Although the properties of the Y-state at room temperature are not fully understood, the Y-state is one of the possible intermediates of the indirect path in the model shown in Figure 9.

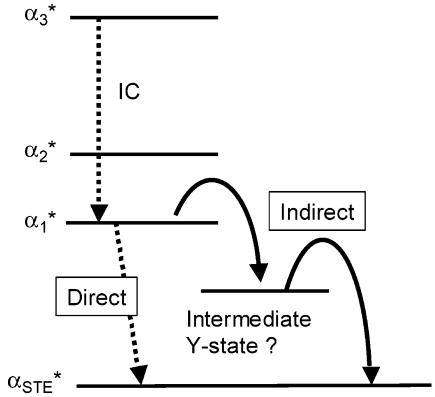

Figure 9. Schematic energy diagram of the relaxation process in α-perylene crystals.

To understand the formation process in detail, the origin of the Y-state must be examined. The origin of Y-fluorescence has been explained by a crystal defect having monomeric structure[6,7,13] or a less-relaxed excimer.[10,11] In the present results, there are two paths for excimer formation. This suggests that the Y-state originates from a defect because the heterogeneous reaction kinetics would not be expected if the Y-state originated from the less-relaxed excimer.

Although the concentration of the crystal defect having monomeric structure would not be high in purified single crystals, the Y-state is populated with relatively high efficiency (20%). The reason for the high efficiency may be due to exciton migration. The α^*_1 state, which is the origin of the Y-state, is not strongly coupled with crystal lattice so that the α^*_1 state can move quickly before relaxation into the α^*_{STE} state. During the exciton migration, the α^*_1 state is efficiently captured by the defect, subsequently the Y-state is populated. The Y-state relaxes to stable excimer states after detrapping by a thermal activation process. Thus, the process becomes much slower than the direct relaxation process from the α^*_1 state to the excimer state. At lower temperature, the detrapping process becomes much slower, and therefore only the Y-fluorescence can be observed. In other words, the Y-state is a localized state in the α-crystals. This is consistent with the observation by Freydorf et al.[10] that the Y-state does not show annihilation behavior.

As shown in Figure 4, there is a shoulder at 1.8 eV (690 nm), which is at an energy level similar to the transient absorption in isolated molecules and in *β*-perylene crystals (1.75 eV). This similarity implies absorption due to defects having a monomeric structure. The concentration of the defects may be sensitive to the crystal perfection and the observed region in the crystal. Therefore, we are now developing a spatial-resolved transient absorption spectrometer.[40]

Conclusion

We studied the effect of aggregation on the excited-state electronic structure of perylene through transient absorption measurements of isolated molecules, excimers in solution, monomeric crystal forms (β-perylene), and dimeric crystal forms (α-perylene). By analyzing the transient absorption spectra, we examined electronic structure changes. Besides neutral excited states, we obtained information about charge-transfer (ion-pair) states. This technique is applicable to many other systems. The collection of information about intermolecular interactions would be useful in the design of new functional devices.

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