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# Excited-State Dynamics in an $\alpha$ -Perylene Single Crystal: Two-Photon- and Consecutive Two-Quantum-Induced Singlet Fission

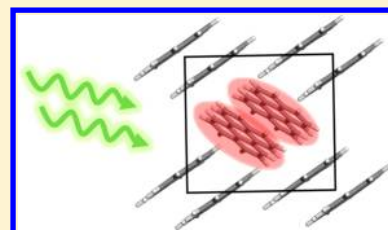
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## S Supporting Information

**ABSTRACT:** Excited-state dynamics in  $\alpha$ -perylene single crystals is studied by time-resolved fluorescence and transient absorption techniques under different excitation conditions. The ultrafast lifetimes of the “hot” excimer (Y) state were resolved. Three competing excited-states decay channels are observed: excimer formation, dimer cation generation, and singlet fission. The singlet fission induced by two-photon and consecutive two-quantum absorption is reported for the first time in an  $\alpha$ -perylene crystal.



## INTRODUCTION

Perylene and its derivatives are widely used in organic field effect transistors,<sup>1</sup> light-emitting diodes,<sup>2</sup> and photovoltaics.<sup>3</sup> Perylene belongs to a monoclinic crystal system and exists in two forms,  $\alpha$  and  $\beta$ .<sup>4</sup>  $\beta$ -Perylene is monomeric, with two molecules per unit cell;  $\alpha$ -perylene is dimeric, with four molecules in a unit cell. The excited-state relaxation in  $\alpha$ -perylene is complicated due to its dimeric structure. A two-step excimer formation mechanism was proposed by Walker et al. when studying the temperature-dependent fluorescence;<sup>5</sup> the excited monomeric state first relaxes to the unrelaxed excimer state (Y state), and then, the Y state relaxes to the relaxed excimer state (E state). Dimer cations were also observed by transient absorption (TA) spectroscopic study by Tamai et al.<sup>6</sup> Moreover, singlet fission, which generates two triplet states by consuming one excited singlet state, was also observed in an  $\alpha$ -perylene crystal with a threshold 3.51 eV by a magnetic field effect study.<sup>7,8</sup>

In the present work, the excited-state electronic structure and dynamics are studied by use of time-resolved fluorescence and TA spectroscopy under one- and two-quantum excitation conditions. With a femtosecond fluorescence upconversion technique, the ultrafast lifetimes of the sublevels of the hot excimer (Y state) are resolved. By applying the TA measurements, dimer cation and excimer formation as well as singlet fission were studied.

## EXPERIMENTAL SECTION

Perylene commercial powder purchased from Sigma-Aldrich was purified by sublimation. Single crystals of perylene were grown from the gas phase by use of the physical vapor transport (PVT) method.<sup>9</sup> The perylene single crystals were characterized by powder XRD using a Bruker AXS D8 Advance XRD.

The peak positions of the experimental powder XRD spectrum match those of the XRD spectrum reported by Trotter et al.,<sup>10</sup> indicating that the crystal is  $\alpha$ -phase.

All optical characterizations are done at room temperature, 20 °C. Steady-state absorption spectra were obtained by a UV–vis spectrophotometer (Cary 100Bio, Varian) at 1.0 nm resolution, and the steady-state fluorescence and excitation spectra were recorded by the spectrofluorometer (Fluorolog-3, HORIBA Jobin Yvon).

Time-resolved fluorescence was measured by a time-correlated single-photon counting (TCSPC) technique with a resolution of 10 ps (PicoQuant PicoHarp 300). The second harmonic of a titanium sapphire laser (Chameleon, Coherent Inc.) at 400 nm (100 fs, 80 MHz) was used as the excitation source. The kinetics of fluorescence from 460 to 750 nm were recorded, and the time-resolved fluorescence spectra were constructed.

A femtosecond fluorescence up-conversion spectrometer (FOG100, CDP) was used to measure the ultrafast fluorescence decay signals with a 400 nm excitation femtosecond laser source (100 fs, 80 MHz). The fluorescence (480–630 nm) was collected by a parabolic mirror and focused into a 0.5 mm BBO crystal (cut angle 38°, ooe interaction) together with the fundamental radiation (800 nm). The resulting sum-frequency radiation (300–352 nm) after passing through a double monochromator (CDP2022D) was detected by photomultiplier-based photon counting electronics.

The TA spectra were measured by optical femtosecond pump–probe spectroscopy. The output of the titanium

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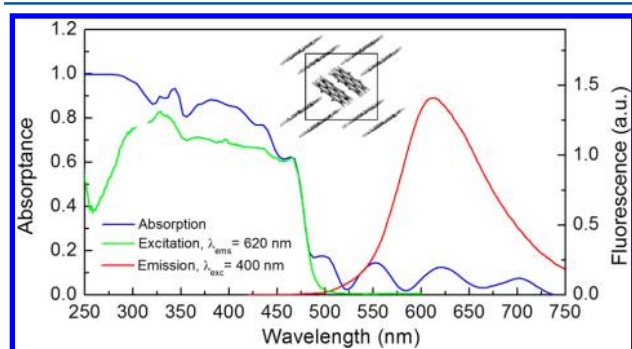
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sapphire (Legend Elite, Coherent) regenerative amplifier seeded by the oscillator (Micra, Coherent) was used as a pulse laser source. The output laser beam was at  $\lambda = 800$  nm, with a pulse width of 65 fs, pulse repetition rate of 1 kHz, and average power of 3.5 W; 90% of the output beam was converted to wavelengths with a range from 250 to 475 nm, which were used for excitation (pump pulse), by use of an optical parametric oscillator (Topas, Light Conversion). The remaining 10% was used to generate a white light continuum in a CaF<sub>2</sub> plate (probe beam).

## RESULTS

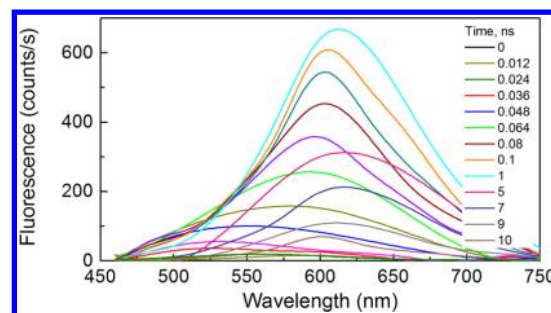
**Time-Resolved Fluorescence Spectra.** Steady-state absorption, fluorescence emission, and excitation spectra of  $\alpha$ -perylene are shown in Figure 1. Absorption is plotted on a



**Figure 1.** Steady-state absorption, fluorescence, and excitation spectra of an  $\alpha$ -perylene crystal.

linear scale of absorbance ( $1 - T$ , where  $T$  is transmittance). The thickness of the sample is estimated from the interference pattern<sup>11</sup> (Figure 1, 500–750 nm),  $L = 1$   $\mu$ m. The fluorescence centered at 615 nm corresponds to the well-known excimer (self-trapped exciton) emission in an  $\alpha$ -perylene crystal.<sup>12</sup> The fluorescence spectrum is invariant under different excitation wavelengths. The discrepancy between the absorption and fluorescence excitation spectra in the wavelength range of 340–465 nm, and even stronger deviation at 250–340 nm, will be discussed in detail below. The fluorescence kinetics of the whole emission range (460–750 nm) in  $\alpha$ -perylene was first studied by the TCSPC technique (Figure S1 in the Supporting Information). The fitting results of the fluorescence kinetics are shown in Table S1 (Supporting Information). In the shorter emission range (460–510 nm), the kinetics were fitted biexponentially, a short time component  $\tau_1 \leq 10$  ps (limited by the instrument response function, IRF), and a long time constant  $\tau_2 = 7$  ns. The amplitude of  $\tau_1$  decreases, while the amplitude of  $\tau_2$  increases with increasing emission wavelength. For the emission from 540 to 750 nm, the short time constant  $\tau_1$  disappears, only leaving  $\tau_2 \approx 20$  ns. The long time component agrees well with the lifetime of the perylene excimer in solution<sup>13</sup> and is in satisfactory agreement with the literature data for the  $\alpha$ -perylene crystal, 42, 80, and 160 ns, reported by Kobayashi,<sup>14</sup> Katoh,<sup>15</sup> and Walker,<sup>5</sup> respectively.

Time-resolved fluorescence spectra constructed from decay kinetics are shown in Figure 2. The evolution of fluorescence spectra can be clearly seen. At early times (within 50 ps), the fluorescence spectra are centered at  $\sim 520$  nm. The intensity of the shorter range emission decreases rapidly with time. At 100 ps, the peak position of the fluorescence spectrum shifted to

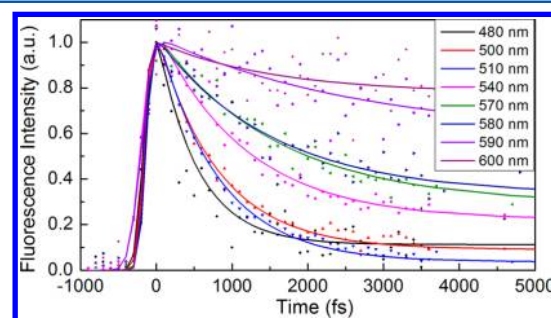


**Figure 2.** Time-resolved fluorescence spectra in an  $\alpha$ -perylene crystal, measured by TCSPC,  $\lambda_{\text{exc}} = 400$  nm.

612 nm, which corresponds to the steady-state fluorescence spectrum.

Our time-resolved fluorescence data agree well with the previous temperature-dependent fluorescence studies.<sup>5,16,17</sup> The fluorescence spectrum of the  $\alpha$ -perylene crystal shows strong temperature dependence; at temperatures  $T > 50$  K, the fluorescence spectra are broad and structureless, dominated by the emission from the relaxed excimer state (E state) with the maximum at 620 nm. At temperatures below 50 K, the E state emission is suppressed, and a blue-shifted emission appears with a maximum at 530 nm. This new emission band was assigned to the unrelaxed hot excimer (Y state) emission.<sup>5,16,17</sup> Moreover, the Y state emission exhibits fine structure, which is indicative of vibronic sublevels. On the basis of the above, we conclude that in our time-resolved fluorescence measurements at 20  $^{\circ}$ C, the short-lived fluorescence spectra (at  $t < 50$  ps) correspond to Y state emission, while the long-lived ones are due to the emission from E state.

In order to resolve decay of the ultrashort Y state, the fluorescence upconversion technique was applied. The results are shown in Figure 3. The same trend as that with TCSPC is

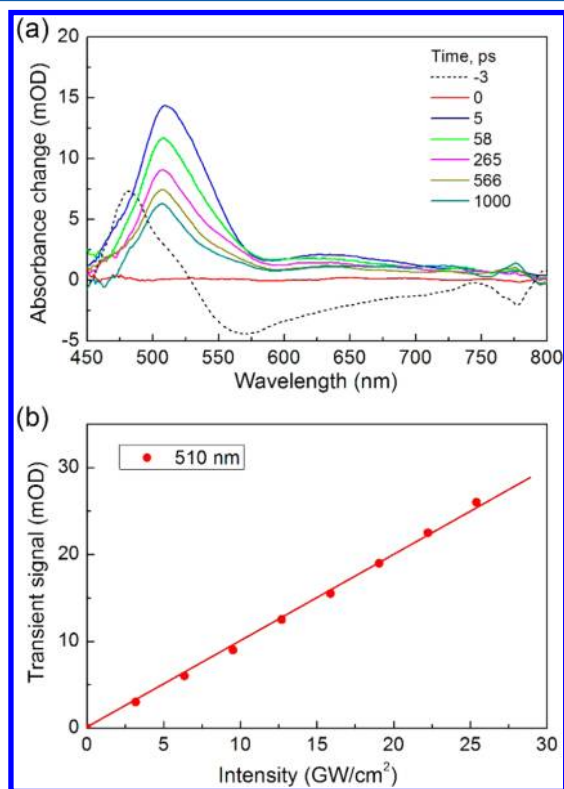


**Figure 3.** The fluorescence kinetics in an  $\alpha$ -perylene crystal, measured by fluorescence upconversion,  $\lambda_{\text{exc}} = 400$  nm.

observed; the fluorescence lifetime becomes longer with increasing emission wavelength. At 460 nm, 92% of the fluorescence decays with a time constant of  $\tau_1 = 500$  fs, while at 630 nm, fluorescence decays mainly with  $\tau_2 > 1$  ns. The wavelength-dependent fluorescence lifetime indicates that the Y state has a fine structure and includes many sublevels, with lifetimes ranging from 500 fs to 3 ps. We should notice that no rise time was detected for all of the fluorescence kinetics due to the strong spectral overlap between Y and E states. As shown in Figure 2, within the first 50 ps, the Y state emission covers the range from 450 to 700 nm; after 50 ps, only the E state emission was observed from 450 to 750 nm. Absence of a rise

component in Y state kinetics indicates that the excited monomeric state relaxation proceeds faster than 100 fs.

**TA Spectroscopy of an  $\alpha$ -Perylene Crystal.** TA was studied by use of a pump–probe technique. The TA spectra under 340 nm excitation are shown in Figure 4a. After the



**Figure 4.** (a) TA spectra for an  $\alpha$ -perylene crystal thin film at different delay times;  $\lambda_{\text{exc}} = 340$  nm. (b) The intensity dependence of the 510 nm TA signal at 5 ps.

baseline correction (the signal at negative delay times is subtracted), the TA spectrum has a pronounced peak at 505 nm, accompanied by a broad absorption band ranging from 600 to 800 nm. We assign the 505 nm TA band to the absorption of the dimer cation; in perylene solution, it is located at 503 nm.<sup>18</sup> The intensity dependence of this TA signal is linear, indicative of a one-photon process (Figure 4b). It is in agreement with the location of an ion pair (IP) state (precursor of the charge carriers) at 2.65 eV (468 nm).<sup>19</sup> According to the literature, the excimer of the  $\alpha$ -perylene crystal has a broad absorption with a maximum at 620 nm.<sup>6,19,20</sup> Therefore, we assign the 600–800 nm TA band to the excimer absorption, that is, hot Y and relaxed E states.

It should be mentioned that at negative delay times, a pronounced positive TA band located at 480 nm together with a broad negative TA signal (560–750 nm) was observed. The negative delay time means that the probe beam comes earlier than the pump beam. However, because the repetition rate of our laser is 1 kHz, we can consider that the observed signal is generated by the previous pulse, that is, the actual time delay between pump and probe pulses is 1 ms. The negative transient signal is independent of the delay time. Therefore, we assign this signal to the fluorescence emitted by the sample after excitation by the pump. We can also call this fluorescence steady-state, even though it is excited by a pulsed source. This steady-state fluorescence is integrated over 150 ms and

averaged over the measuring time (several seconds) and is reflected on the TA spectra because our TA software is not subtracting the fluorescence. The blue shift of the negative transient signal peak relative to the steady-state fluorescence may be due to the overlap of the positive triplet state absorption and the negative fluorescence. The positive TA signal is indicative of a long-lived species. Under the assumption of the first-order decay, we estimated the lifetime of the 480 nm TA band,  $\tau = 1.8$  ms. However, we cannot fully exclude the contribution of the exciton–exciton annihilation because high excitation powers are applied. Therefore, the actual lifetime should be faster than our estimated 1.8 ms.

In perylene solution, the triplet state TA band was reported to have a maximum at 485 nm.<sup>21–23</sup> The only measurement on the triplet TA in the crystal was performed by Katoh et al.;<sup>15</sup> the maximum is at wavelengths shorter than 520 nm. The lifetime of  $T_1$  in solution was reported to be 4.8 ms,<sup>21–23</sup> whereas it was 0.4 ms in the crystal.<sup>24</sup> It agrees well with our estimation for the lifetime of the 480 nm band. On the basis of the above, we assign the 480 nm TA band to triplet state absorption.

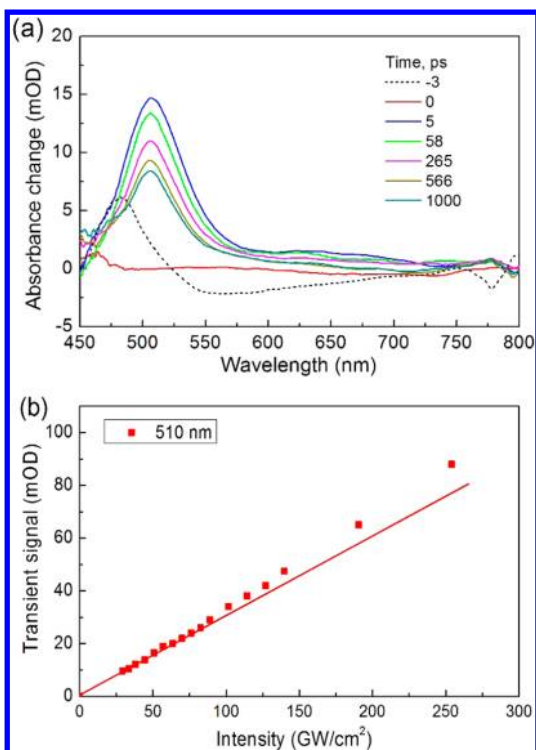
The TA spectra in perylene solution are given in the Supporting Information (Figure S2); the 700 nm band is assigned to singlet–singlet absorption, in agreement with refs 13 and 19. No triplet state TA was found due to the low triplet yield ( $\phi_{\text{isc}} = 0.01$ ).<sup>23</sup> Only in the highly concentrated solution at delays longer than 5 ns was the triplet band (490 nm) observed. Therefore, the triplet states observed in the  $\alpha$ -perylene crystal (Figure 4) are *not* generated by intersystem crossing. We conclude that efficient triplet formation in the crystal is due to singlet fission.

The triplet state in perylene solution is located at 1.53 eV. Therefore, in order to generate two triplet states via singlet fission, we need to excite the singlet state with photon energy of 3.06 eV (404 nm). The only measurement on singlet fission in an  $\alpha$ -perylene crystal was done by the magnetic field effect under excitation with a xenon lamp.<sup>7,8</sup> The threshold for singlet fission was estimated to be 3.51 eV (353 nm). The competing reaction was considered to be the fast excimer formation. TA spectra in  $\alpha$ -perylene crystals were also obtained by Tamai<sup>6</sup> and Furube.<sup>19</sup> However, they did not observe triplet transient, most probably because of either thick sample or the limitation in the probe wavelength range.

## DISCUSSION

Comparison of the absorption and fluorescence excitation spectra shows that they are in line above 465 nm (Figure 1). However, below 465 nm, there is a slight drop of the excitation spectrum, indicating a quenching process. This is due to dimer cation formation from the IP; the threshold according to ref 19 is 2.65 eV. At wavelengths below 350 nm, there is a drastic drop of the fluorescence, although the absorption becomes much larger. It is indicative of an efficient singlet fission that proceeds directly from the upper vibrational levels of  $S_1$ . The threshold of this process is 3.51 eV.<sup>7,8</sup> We have also measured the TA spectra with 475 nm excitation, that is, below the threshold for both fission and cation formation. These TA spectra are similar to that for 340 nm excitation (Figure 5a). The TA signals from the dimer cation and excimer still dominate the whole spectra. Moreover, at the negative delay time, the triplet absorption is still the dominant TA peak. However, as mentioned above, neither cation generation nor singlet fission under one-photon absorption at 475 nm should be expected.





**Figure 5.** (a) TA spectra for an  $\alpha$ -perylene crystal thin film at different delay times;  $\lambda_{\text{exc}} = 475$  nm. (b) The intensity dependence of the 510 nm TA signal at 5 ps.

The intensity dependence of the transient signal at 510 nm (dimer cation absorption) at 5 ps (Figure 5b) below 100 GW/cm<sup>2</sup> is linear. However, at higher excitation intensities above 150 GW/cm<sup>2</sup>, this dependence becomes nonlinear. The 480 nm TA signal at negative delays (triplet absorption) shows similar intensity dependence. We explain this nonlinearity in terms of both two-photon absorption (TPA, i.e., simultaneous absorption of two photons) and consecutive two-quantum absorption (TQA, i.e., two-step absorption of two photons via an intermediate state). The schematics for TPA and TQA are shown in Figure 6a. The contribution of TPA and TQA processes was discussed in detail in refs 25 and 26 for the nonlinear crystal KDP.

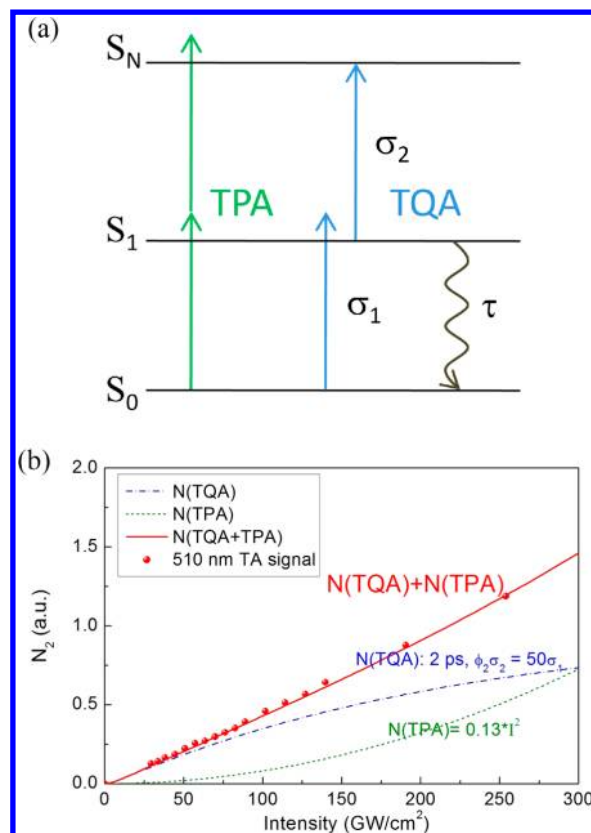
The rate equations for TQA process are<sup>25–27</sup>

$$\frac{dN_0}{dt} = -\sigma_1 I N_0 + \frac{N_1}{\tau} \quad (1)$$

$$\frac{dN_1}{dt} = \sigma_1 I N_0 - \phi_2 \sigma_2 I N_1 - \frac{N_1}{\tau} \quad (2)$$

$$\frac{dN(\text{TQA})}{dt} = \phi_2 \sigma_2 I N_1 \quad (3)$$

where  $N_0$ ,  $N_1$ , and  $N(\text{TQA})$  are the populations of the ground state ( $S_0$ ), intermediate state ( $S_1$ ), and the two quantum excited state ( $S_N$ ).  $\sigma_1$  and  $\sigma_2$  are the absorption cross sections of  $S_0 \rightarrow S_1$  and  $S_1 \rightarrow S_N$  transitions, respectively ( $\sigma_1 = 7.6 \times 10^{-17}$  cm<sup>2</sup> at 475 nm<sup>28</sup>).  $\phi_2$  is the yield of the final product from the two quantum excited state ( $S_N$ ). Assuming a rectangular pulse shape and on the basis of different intermediate state lifetimes and the ratio of  $\phi_2 \sigma_2$  and  $\sigma_1$ , we have obtained the numerical solution of the rate eqs 1–3 as well as the intensity dependence of  $N_2$ ,



**Figure 6.** (a) Schematics of TPA and TQA transitions. (b) The fitting results of the power-dependent population of TQA and TPA excited states.

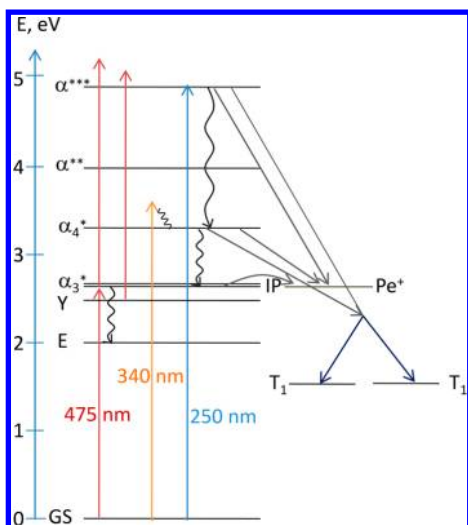
shown in Figure S3 (see the Supporting Information). Taking the TPA process into consideration, the rate eq 3 will become

$$\frac{dN_2}{dt} = \phi_2 \sigma_2 I N_1 + \beta I^2 \quad (4)$$

The best fit is obtained for  $\phi_2 \sigma_2 = 50 \sigma_1$  (Figure 6b). The lifetime of  $S_1$  is taken at  $t = 2$  ps, which corresponds to the hot excimer Y state lifetime. On the basis of the above considerations, we suggest that both singlet fission and dimer cation formation under 475 nm are due to the coexistence of TPA and TQA. The one- and two-photon induced singlet fission has already been reported in our previous publications with a rubrene crystal.<sup>29,30</sup> However, two-quantum singlet fission, to our best knowledge, was not reported in the literature.

In order to study the relaxation kinetics from the upper excited electronic states, TA spectra were recorded under 250 nm excitation (Figure S4, see the Supporting Information). Compared with 340 and 475 nm excitation conditions, the triplet state transient becomes much stronger relative to the amplitude of the dimer cation. It is indicative for efficient singlet fission from upper excited electronic states. The singlet fission schematics in an  $\alpha$ -perylene crystal are depicted in Figure 7.

Under one-photon excitation at 250 and 340 nm, the upper excited states  $\alpha^{***}$  and  $\alpha_4^*$  are directly populated. Upon 475 nm excitation, upper excited state  $\alpha^{***}$  is reached via TPA and TQA. Singlet fission proceeds directly from  $\alpha_4^*$  and  $\alpha^{***}$ , competing with ultrafast relaxation to lower excited states and formation of a dimer cation and excimer. Under all excitation



**Figure 7.** Singlet fission schematic in an  $\alpha$ -perylene crystal.  $\alpha_3^*$  and  $\alpha_4^*$  are symmetry-allowed excited states;  $\alpha^{**}$  and  $\alpha^{***}$  are upper excited states;<sup>19</sup> Y and E are hot and relaxed excimer states, respectively; IP is the ion pair state;  $Pe^+$  is the dimer cation; and  $T_1$  is the lowest triplet state.

conditions, that is, one-photon and two-photon/quantum excitation, no rise time was observed for the triplet state formation. This ultrafast fission ( $\ll 50$  fs) most probably is due to the dimeric structure of  $\alpha$ -perylene.

## CONCLUSIONS

The excited-state dynamics in an  $\alpha$ -perylene crystal was studied by use of time-resolved fluorescence and TA techniques under various excitation conditions. For the first time, in  $\alpha$ -perylene, the singlet fission (triplet formation) was observed directly by use of TA spectroscopy. The hot excimer (Y) state has various sublevels with lifetimes ranging from 500 fs to 3 ps. Three ultrafast competing decay channels for the excited singlet state are observed, that is, excimer formation, dimer cation generation, and singlet fission. By increasing the excitation photon energy above 4.96 eV, singlet fission becomes more efficient. On the basis of both the experimental data and theoretical calculations, the TPA and consecutive TQA induced singlet fission in  $\alpha$ -perylene is demonstrated.

## ASSOCIATED CONTENT

### Supporting Information

TCSPC results of an  $\alpha$ -perylene crystal, TA spectra of solution, fitting results of TQA, and TA spectra of a crystal under 250 nm excitation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## REFERENCES

(1) Jones, B. A.; Ahrens, M. J.; Yoon, M.-H.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. High-Mobility Air-Stable N-Type Semiconductors with Processing Versatility: Dicyanoperylene-3,4,9,10-bis(dicarboximides). *Angew. Chem., Int. Ed.* **2004**, *43*, 6363–6366.

(2) Angadi, M. A.; Gosztola, D.; Wasielewski, M. R. Organic Light Emitting Diodes Using Poly(phenylenevinylene) Doped with Perylenedimide Electron Acceptors. *Mater. Sci. Eng., B* **1999**, *63*, 191–194.

(3) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. Self-Organized Discotic Liquid Crystals for High-Efficiency Organic Photovoltaics. *Science* **2001**, *293*, 1119–1122.

(4) Tanaka, J. The Electronic Spectra of Aromatic Molecular Crystals. II. The Crystal Structure and Spectra of Perylene. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 1237–1249.

(5) Walker, B.; Port, H.; Wolf, H. C. The Two-Step Excimer Formation in Perylene Crystals. *Chem. Phys.* **1985**, *92*, 177–185.

(6) Tamai, N.; Porter, C. F.; Masuhara, H. Femtosecond Transient Absorption Spectroscopy of a Single Perylene Microcrystal under a Microscope. *Chem. Phys. Lett.* **1993**, *211*, 364–370.

(7) Albrecht, W. G.; Michel-Beyerle, M. E.; Yakhot, V. Exciton Fission in Excimer-Forming Crystal Dynamics of Excimer Build-Up. *J. Lumin.* **1979**, *20*, 147–149.

(8) Albrecht, W. G.; Michel-Beyerle, M. E.; Yakhot, V. Exciton Fission in Excimer Forming Crystal. Dynamics of an Excimer Build-Up in  $\alpha$ -Perylene. *Chem. Phys.* **1978**, *35*, 193–200.

(9) Laudise, R. A.; Kloc, C.; Simpkins, P. G.; Siegrist, T. Physical Vapor Growth of Organic Semiconductors. *J. Cryst. Growth* **1998**, *187*, 449–454.

(10) Camerman, A.; Trotter, J. The Crystal and Molecular Structure of Perylene. *Proc. R. Soc. London, Ser. A* **1964**, *279*, 129–146.

(11) Tanaka, J. The Electronic Spectra of Aromatic Molecular Crystals. I. Substituted Benzene Molecules. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 833–847.

(12) Nishimura, H.; Yamaoka, T.; Mizuno, K.; Iemura, M.; Matsui, A. Luminescence of Free and Self-Trapped Excitons in  $\alpha$ - and  $\beta$ -Perylene Crystals. *J. Phys. Soc. Jpn.* **1984**, *53*, 3999–4008.

(13) Katoh, R.; Sinha, S.; Murata, S.; Tachiya, M. Origin of the Stabilization Energy of Perylene Excimer as Studied by Fluorescence and Near-IR Transient Absorption Spectroscopy. *J. Photochem. Photobiol. A* **2001**, *145*, 23–34.

(14) Kobayashi, T. The Observation of the Excimer Formation Process in Pyrene and Perylene Crystals Using a Picosecond Ruby Laser and Streak Camera. *J. Chem. Phys.* **1978**, *69*, 3570–3574.

(15) Katoh, R.; Tamaki, Y.; Furube, A. Transient Absorption Microscopic Study of Triplet Excitons in Organic Crystals. *J. Photochem. Photobiol. A* **2006**, *183*, 267–272.

(16) Auweter, H.; Ramer, D.; Kunze, B.; Wolf, H. C. The Dynamics of Excimer Formation in Perylene Crystals. *Chem. Phys. Lett.* **1982**, *85*, 325–329.

(17) Mizoguchi, R.; Kano, S. S.; Wada, A. Optical Control of Excited States of  $\alpha$ -Perylene Crystal Using Optimized Pulse Shaping Method. *Chem. Phys. Lett.* **2003**, *379*, 319–324.

(18) Kimura, K.; Yamazaki, T.; Katsumata, S. Dimerization of the Perylene and Tetracene Radical Cations and Electronic Absorption Spectra of Their Dimers. *J. Phys. Chem.* **1971**, *75*, 1768–1774.

(19) Furube, A.; Murai, M.; Tamaki, Y.; Watanabe, S.; Katoh, R. Effect of Aggregation on the Excited-State Electronic Structure of Perylene Studied by Transient Absorption Spectroscopy. *J. Phys. Chem. A* **2006**, *110*, 6465–6471.

(20) Ludmer, Z.; Zeiri, L.; Starobinets, S. Nonlinear Fluorescence Reabsorption in Excimer-Forming Crystals by Electronically Excited Molecules. *Phys. Rev. Lett.* **1982**, *48*, 341–344.

(21) Porter, G.; Windsor, M. W. Studies of the Triplet State in Fluid Solvents. *Faraday Discuss.* **1954**, *17*, 178–186.

(22) Porter, G.; Windsor, M. W. The Triplet State in Fluid Media. *Proc. R. Soc. London, Ser. A* **1958**, *245*, 238–258.

(23) Parker, C. A.; Joyce, T. A. Formation Efficiency and Energy of the Perylene Triplet. *Chem. Commun.* **1966**, *4*, 108b–109.

(24) Kotani, M.; Kakinuma, K.; Yoshimura, M.; Ishii, K.; Yamazaki, S.; Kobori, T.; Okuyama, H.; Kobayashi, H.; Tada, H. Charge Carrier Transport in High Purity Perylene Single Crystal Studied by Time-of-

Flight Measurements and through Field Effect Transistor Characteristics. *Chem. Phys.* **2006**, 325, 160–169.

(25) Gurzadyan, G. G.; Ispiryan, R. K. Two-Photon Absorption Peculiarities of Potassium Dihydrogen Phosphate Crystal at 216 nm. *Appl. Phys. Lett.* **1991**, 59, 630–631.

(26) Gurzadyan, G. G.; Ispiryan, R. K. Two-Photon Absorption in Potassium Dihydrophosphate, Potassium Pentaborate and Quartz Crystals at 270 and 216 nm. *J. Nonlinear Opt. Phys. Mater.* **1992**, 01, 533–540.

(27) Shaquiri, Z.; Keskinova, E.; Spassky, A.; Angelov, D. A Picosecond Flash-Photolysis Study of the Biphotonic Ionization of Psoralen Derivatives and Ethidium Bromide. *Photochem. Photobiol.* **1997**, 65, 517–521.

(28) Hochstrasser, R. M. Spectral Effects of Strong Exciton Coupling in the Lowest Electronic Transition of Perylene. *J. Chem. Phys.* **1964**, 40, 2559–2564.

(29) Ma, L.; Zhang, K.; Kloc, C.; Sun, H.; Michel-Beyerle, M. E.; Gurzadyan, G. G. Singlet Fission in Rubrene Single Crystal: Direct Observation by Femtosecond Pump–Probe Spectroscopy. *Phys. Chem. Chem. Phys.* **2012**, 14, 8307–8312.

(30) Ma, L.; Galstyan, G.; Zhang, K.; Kloc, C.; Sun, H.; Soci, C.; Michel-Beyerle, M. E.; Gurzadyan, G. G. Two-Photon-Induced Singlet Fission in Rubrene Single Crystal. *J. Chem. Phys.* **2013**, 138, 184508.