

Photochemical Reaction of *p*-hydroxycinnamic-thiophenyl Ester in the Microcrystalline State[†]

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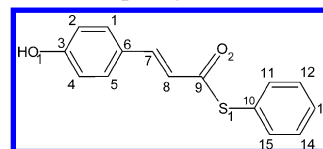
We have studied the photochromic reaction of *p*-hydroxycinnamic-thiophenyl ester in the microcrystalline state. We attributed the fluorescence spectral evolution of the microcrystal, under UV irradiation, to the photoinduced trans-to-cis isomerization. The photocyclic behavior of the chromophore was demonstrated by cis-to-trans back reaction under a subsequent visible light irradiation. In addition, the [2 + 2] topochemical photocyclodimer was observed as another photoproduct. It is considered that the cooperative photoisomerization is initiated at the local lattice distortion and free spaces around the [2 + 2] cyclodimer near the crystal surface, and the photoisomerization induces larger lattice deformation and further photoisomerization in the interior of the crystal.

1. Introduction

Photochromic molecules, whose reversible two isomeric structures with different physical properties in absorption, emission, and vibrational spectra can be controlled by external perturbation light, have been attracting great interest from the viewpoints of both fundamental scientific bases, such as elucidation of the photochemical reactions and their potential applications into optical memories and devices.^{1–3} The studies on a variety of the photochromic reactions have revealed that the photoreaction dynamics is dependent on the polarity and viscosity of the solvent medium, and can be strongly affected when the medium is changed from solution to polymer networks or viscous surrounding matrixes.^{4,5}

In nature, photochromic reactions of chromophores bound to proteins belonging to photoreceptor families are key processes in determining the photochemical properties and biological functions of the proteins.⁶ For instance, the signal transduction of photoactive yellow protein (PYP), a photoreceptor protein for the negative phototactic response of the bacterium *Halorhodospira halophila*, bound covalently to *p*-hydroxycinnamic thioester, involves a photocycle consisting of the trans-to-cis isomerization of the chromophore and proton transfer from and restoring back to the protein pocket.^{7,8} Photoexcitation dynamics of free molecules related to the PYP chromophore has also been systematically explored by using femtosecond transient spectroscopies in efforts to elucidate the intrinsic photochromic reaction of the PYP chromophore.^{9–19} Among the free chromophores studied, *p*-hydroxycinnamic-thiophenyl ester (PCT)

SCHEME 1: Chemical Structure of *p*-Hydroxycinnamic-thiophenyl Ester (PCT)



(Scheme 1) has been probably the most attractive to reproduce the electronic transition and Stokes shift of the PYP chromophore, since its deprotonated form shows a massive absorption and emission spectral shift depending on the solvent polarity.¹⁷ In the solutions, however, the deprotonated PCT does not show photoinduced isomerization in a significant amount.^{10–12,17} On the other hand, we have recently found that protonated PCT shows photoisomerization in solid microcrystal, but the reaction mechanism remains to be fully understood.²⁰ It is generally accepted that the photochemical trans–cis isomerization process involves large-amplitude motions of a rotation around a molecular axis. Therefore, such a large molecular rearrangement in the PCT crystal lattice is rarely observed because of limited free volume and restricted molecular motions compared to those if the compound is in the solution. Moreover, it should be emphasized that this finding is in contrast to other well-known solid state photochromic reactions, which involve either small molecular movements in bulk crystals, such as photoinduced ring-closing and ring-opening reactions for diarylethenes^{2,21,22} and bicycle-pedal motion for salicylideneanilines,^{3,23–25} or large molecular motions on the crystal surface for the trans-to-cis isomerization of azobenzene.²⁶ Important work dealing with intermolecular free volume in the crystal lattice is the introduction of a bulky group into the aromatic rings of salicylideneanilines, expecting that the bulky group opens a space allowing the photochromic reaction.²⁴ Another intriguing observation of the solid state photochromism is cooperative photochemical

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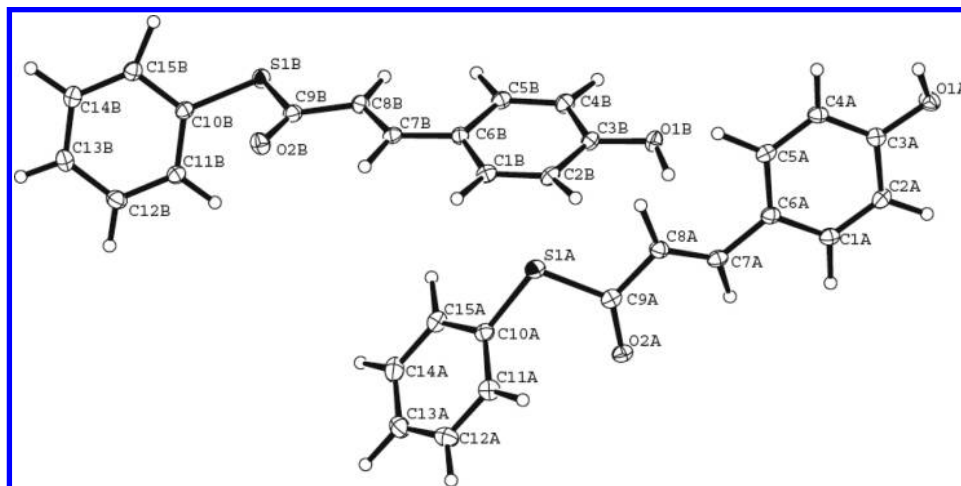


Figure 1. ORTEP drawing of two independent PCT molecules in the asymmetric unit showing 50% probability displacement ellipsoids.

reaction for spirooxazines and spiropyrans induced by high light intensity excitation, where some free volume in the crystal lattice can be generated by the photochemical reactions of the plural transient species in the high density formation of excited states. The generated free volume allows photoisomerization of the spirooxazines and spiropyrans leading to trans-planar photomerocyanines.^{27–29}

In the present paper, we describe that the protonated PCT in the solid crystal shows a new type of solid state photochromic reaction, involving [2 + 2] topochemical cyclodimerization and trans–cis isomerization, in which the formation of the [2 + 2] cyclodimer provides dynamic free volume in the crystal lattice. This interpretation is evidenced by experimental data concerning X-ray diffraction, NMR spectroscopy, and diffuse reflectance in addition to the fluorescence and infrared spectroscopies. We also demonstrated that, by analyzing the photoexcitation dynamics upon different intensity of light excitation, the cooperative photochemical reaction model is applicable for the PCT crystal.

2. Materials and Methods

2.1. Materials. PCT was synthesized and purified following the procedures reported by Duran et al.³⁰ The chemical structure of the PCT was confirmed using UV–vis absorption, ¹H NMR spectrum, and melting point measurement, where the data were in agreement with those reported earlier.^{10,30} Bulk single crystals of PCT were obtained from slow evaporation of dichloromethane (CH₂Cl₂) solution, whereas needle-like microcrystals (2–15 μm in width and up to 100 μm in length) were grown from evaporation of the same solution on a quartz substrate. After complete drying, the bulk and microcrystals were obtained and used for measurements.

2.2. X-ray Diffraction and Structure Determination. X-ray diffraction data of the bulk single crystal were collected using a Rigaku R-AXIS RAPID X-ray diffractometer with two-dimensional area detector and graphite monochromated Cu Kα radiation (λ = 1.541 87 Å). Lattice parameters were obtained by a least-squares analysis from the reflections for three oscillation images. Molecular and crystal structures of the PCT were solved by direct methods and refined by a full matrix least-squares procedure. All non-H atoms were refined anisotropically. The H atoms were attached geometrically in idealized positions, and were refined isotropically. Details on X-ray structural determination, refinement, atomic coordinates, bond lengths, and bond angles are provided in the Supporting Information.

2.3. Fluorescence, Diffuse Reflectance, and IR Spectroscopies.

Steady state fluorescence, diffuse reflectance, and IR spectroscopies have been employed to monitor the photochromic reactions of PCT microcrystal. The fluorescence spectra of a single microcrystal were measured on an inverted microscope (Olympus IL70) with a halogen lamp as a light irradiation source. The wavelength and power of the light were selected using a dichroic mirror and a neutral density filter, respectively. Diffuse reflectance was recorded on a single beam spectrophotometer (Hitachi F-4500) equipped with a Xe lamp. In this measurement, PCT crystal was mixed with sodium chloride (NaCl) with a 1:125 weight ratio, and was crushed into powder. The diffuse reflectance spectra of PCT before and after light irradiation were referred to the spectrum of pure NaCl. IR spectra of PCT microcrystals before and after UV irradiation were measured by the ATR method on a FTIR spectrophotometer (Horiba FT720).

3. Results

3.1. PCT Structure. PCT crystallizes in the monoclinic *P*2₁/*n* space group [*a* = 16.564(1), *b* = 7.514(1), *c* = 20.842(1) Å, β = 99.496(1)°, *Z* = 8, *V* = 2558.5(1) Å³]. The crystal packing consists of two crystallographically independent PCT molecules, A and B, in the asymmetric unit, as shown in Figure 1. Intermolecular OH⋯O bonds between the hydroxyl and carbonyl oxygen atom interconnect 2-fold rotation-symmetry-related molecules into columns along the crystallographic *b* axis. The molecules are arranged in antiparallel configurations related by inversion symmetry. The center-to-center distance between the ethylenic C=C bonds is 4.08, 4.38, 5.43, and 5.67 Å with the angle between the translation axis and the ethylenic C=C bond being 62, 65, 64, and 38°, respectively (see Figure 2). There are four intermolecular weak interactions involving both the centroids of phenol and phenyl moieties with H⋯π distances being in the range 2.6–2.9 Å. A considerable static free volume or void in the tight crystal packing is not observed. The crystal structure of PCT single crystal after long-time UV irradiation, however, cannot be solved. We found that the photoreaction is not observed in all over the bulk crystal, but only for the surface layer of a few μm, which is much shorter than the crystal dimensions. We also found that the photoexcitation resulted in some fractures on the surfaces of the crystal.

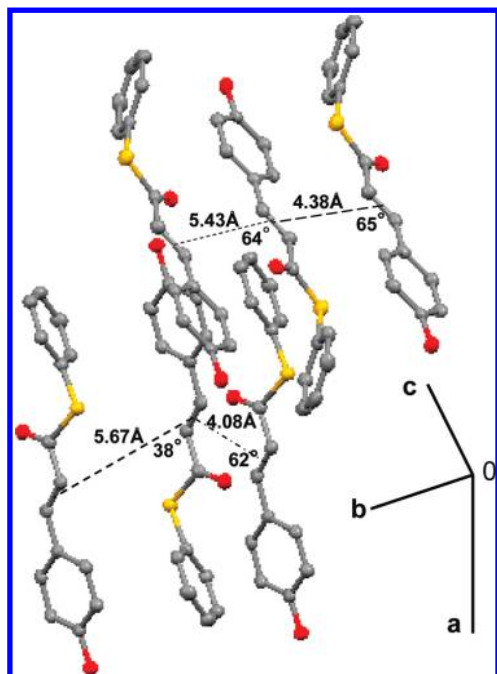


Figure 2. The inversion-symmetry related PCT molecules in antiparallel (head-to-tail) arrangement with various ethylenic C=C distances. All H atoms have been omitted for the sake of clarity.

3.2. Fluorescence Spectra of PCT Microcrystal. We considered the absorption coefficient of the crystal at 405 nm to be the same as that of the CH_2Cl_2 solution ($\epsilon_{405} = 1500 \text{ mol}^{-1} \text{ L cm}^{-1}$). With the molecular density of PCT crystal being $5.19 \times 10^{-3} \text{ mol cm}^{-3}$, we can calculate the light penetration depth of the 405 nm irradiation to be 1.2 μm . We observed that the emission color of the PCT microcrystal is visibly changed from blue to greenish yellow upon continuous UV irradiation,^{20,31} and the emission spectrum is red-shifted as displayed in Figure 3. Emission with a maximum at 490 nm from the trans-PCT shows the intensity increase, in early time irradiation, without any changes in peak position and spectral shape. The intensity of this emission band then gradually decreases following the rise of a new broad emission with a peak at 564 nm, and the latter band continuously increases up to the saturated intensity with the irradiation time. The two emission bands are strongly overlapped without any isoemissive point. The temporal profiles of the emission intensity at 490 and 564 nm upon 8 mW UV irradiation are depicted in Figure 4A. The emission intensities were globally fitted with a two-exponential decay function with time constants of 18.8 ± 0.7 and $140 \pm 1 \text{ s}^{-1}$. The same global fit procedure to the data at lower irradiation power resulted in longer time constants, i.e., 75 ± 1 and $151 \pm 1 \text{ s}^{-1}$ at 4 mW and 104 ± 1 and $150 \pm 1 \text{ s}^{-1}$ at 2 mW. Figure 4B shows the emission at 490 nm at different irradiation powers. This result indicates clearly that the temporal profile is dependent on the irradiation power but not linearly correlated with each other, suggesting that the photoexcitation dynamics of PCT in the crystal lattice is power-dependent and may involve many transient and photoproduct states, which will be addressed in section 4. The emission intensity at 490 nm can be partially recovered by a subsequent visible light irradiation. We demonstrate partial recovery of the emission intensity by over 10 cycles of alternating UV and visible irradiation. However, each cycle shows degradation, which tends to saturate at a high number of cycles (Figure 5).

3.3. Diffuse Reflectance and Infrared Spectra. Upon UV irradiation, the diffuse reflectance spectrum of the crystal shows a red-shift from 398 to 410 nm, a decrease in the intensity, and an increase of the shoulder above 430 nm which extends to around 500 nm (see Figure 6). The reverse photoinduced process, upon subsequent visible light irradiation, is revealed by the reshift from 410 to 398 nm, the reincrease in the intensity, and the decrease of the shoulder above 430 nm. We also demonstrate the alternation of the diffuse reflectance spectrum by several cycles of alternating UV and visible irradiation with intensity degradation of the 398 nm band at each cycle (see Figure 7), and we note that the initial spectrum was not reproduced. This supports evidently the similar observation on the presence of reversible and irreversible photoprocesses shown by the fluorescence spectroscopy.

The IR spectrum in the fingerprint region before and after UV irradiation is shown in Figure 8 (top panel). In the different spectrum between before and after the irradiation (Figure 8, bottom panel), we observed bleaching vibrational bands at 1050, 1273, 1291, 1322, 1572, and 1639 cm^{-1} , shifting bands from 1169, 1435, 1513, 1595, and 1658 cm^{-1} to 1178, 1448, 1517, 1590, and 1672 cm^{-1} , respectively, and new bands at 973, 994, 1283, and 1613 cm^{-1} . In addition, some localized vibrational modes at 1067, 1108, and 1476 cm^{-1} remain unchanged.

4. Discussion

4.1. Molecular Structure of PCT. First, we must assume that the molecular structures, molecular arrangement, intermolecular $\text{OH}\cdots\text{O}$ bonds, and $\text{CH}\cdots\pi$ weak interactions of PCT in the microcrystal are identical to those in the bulk crystal. The presence of two PCT structures in the crystal in general could be addressed by the stabilization by van der Waals force, intermolecular interactions, and H-bonds in the densely packed crystal lattice. The carbonyl oxygen atom of the two PCT molecules is twisted out of the thiocinnamate plane with a $\text{C}_7=\text{C}_8-\text{C}_9=\text{O}_2$ torsion angle of 8.2° (molecule A) and 12.0° (molecule B). In many crystal structures of hydroxycinnamic acids, the $\text{C}=\text{O}$ group is twisted out of the aromatic plane by $4\text{--}6^\circ$,^{32,33} and the torsion angle increases to be around 11° when the π -electron density is increased either by ionization of the carboxylic group or by introducing an electron-rich substituent in the cinnamate moiety.³⁴ Therefore, we suggest that the twisting $\text{C}=\text{O}$ group is the typical feature of the cinnamic derivative due to repulsion between the localized π -electrons at the ethylenic $\text{C}=\text{C}$ and at the $\text{C}=\text{O}$ group. In consistency with the feature of hydroxycinnamic acids in the crystals, the $\text{C}=\text{O}$ group of PYP chromophore is similarly rotated 11.2° .^{35,36}

We recall that the PCT molecules in the crystal packing are in the antiparallel configuration with the center-to-center distance between the ethylenic $\text{C}=\text{C}$ bonds being 4.08, 4.38, 5.43, and 5.67 Å. It is known that the two neighboring trans ethylenic $\text{C}=\text{C}$ bonds in the crystal lattice in parallel, antiparallel, or even crisscrossed arrangement with the distances between the centers in the range of 3.5–4.2 Å are favorable to form a [2 + 2] cyclodimer upon photoirradiation, as shown for trans-cinnamic or cinnamamide derivatives.^{37–41} Thus, we should consider that there is a [2 + 2] photodimerization taking place in the PCT crystal lattice; especially the molecules with a center-to-center distance as short as 4.08 Å meets the criterion.³⁷ In cases where the distances between the centers are above the limit, such a [2 + 2] photodimerization will fail to proceed.

4.2. Photoinduced [2 + 2] Cyclodimerization. In order to quantify the [2 + 2] photodimerization, we first evaluate the emission properties of PCT microcrystal. In the excited state,

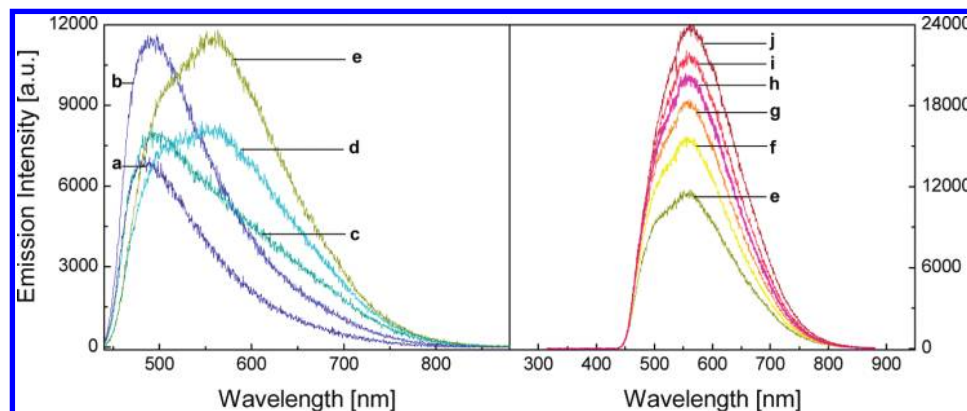


Figure 3. Fluorescence spectra of a single microcrystal of PCT under UV irradiation ($\lambda = 405$ nm, 8 mW) at 1.6 (a), 4.8 (b), 16 (c), 64 (d) 100 (e), 150 (f), 200 (g), 250 (h), 300 (i), and 400 s (j).

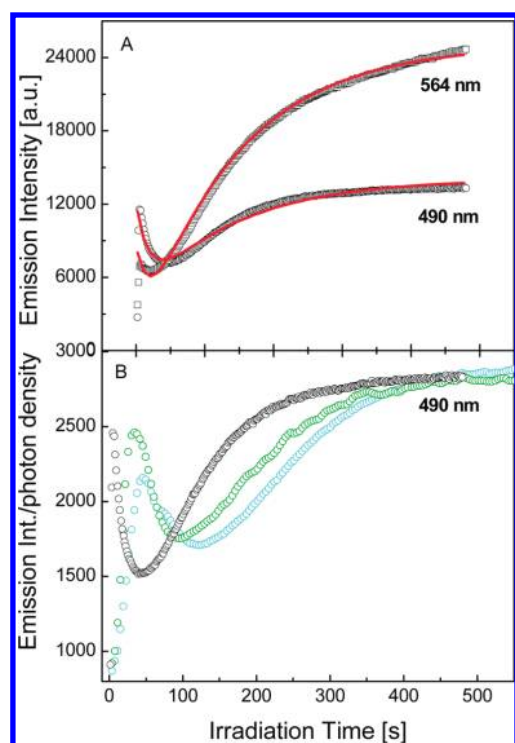


Figure 4. (A) Time-dependent emission intensity at 490 and 564 nm under 8 mW 405 nm light irradiation. The lines are calculated fits with two-exponential decay functions. (B) Time-dependent emission intensity at 490 nm at different irradiation power (black, 8 mW; green, 4 mW; cyan, 2 mW).

before any conformational changes take place, a PCT molecule is considered to loosen or break its intermolecular OH \cdots O bonds and CH \cdots π weak interactions with neighboring molecules in the crystal. This loosening of intermolecular interactions results in an enhancement of emission efficiency, by which the emission intensity at 490 nm is enhanced in the early time irradiation. The new emission at 564 nm, however, must be associated to the emission of distinctly different species, that is, a structure converted from the trans configuration. This emissive species should not be the [2 + 2] cyclodimer which absorbs in the far UV region. The backward reaction by visible light irradiation also indicates that the species is a reversible photoproduct state. The degradation of the emission intensity upon alternating UV and visible irradiation (Figure 5) indicates a reduction of the conversion from the trans form to the reversible photoproduct state in each photocycle. This is indicative of branched relaxation pathways, and one of the pathways should be the irreversible [2 + 2] cyclodimer.

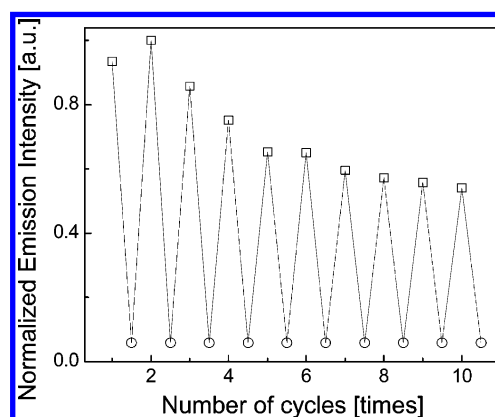


Figure 5. Emission intensity at 605 nm against the number of subsequent UV and visible irradiations; the rectangular and circular data points are the intensity after UV ($\lambda = 405$ nm) and visible irradiations ($\lambda = 546$ nm), respectively.

The formation of such a [2 + 2] cyclodimer was detected using ^1H NMR spectroscopy for the PCT microcrystals after long-time UV irradiation and then dissolved in CDCl_3 . Indeed, the ^1H NMR spectrum contains the [2 + 2] cyclodimer (around 10%) and trans PCT. The chemical shifts of [2 + 2] cyclobutane were in the range 4.00–4.70 ppm, as shown in Figure 9, and were in accordance with the assignment of the other photocyclodimerization in crystal lattice reported by Hasegawa et al.³⁸ The chemical shifts assigning the protons of phenol and thiophenyl of the [2 + 2] cyclodimer were nearly overlapped with those of the trans PCT at 6.81–6.87, 6.92–6.96, and 7.21–7.31 ppm. This suggests that either the amount of cis isomer is much smaller than the [2 + 2] cyclodimer or a twisted or a cis isomer relaxes into the trans form if the trans configuration is energetically favorable, similar to its parent molecule, *p*-hydroxycinnamic acid,⁴² because the steric constraints and mutual interactions between the [2 + 2] cyclodimer and the formations of a twisted or a cis isomer become weaker upon dissolution.

4.3. trans-cis Photoisomerization. The bleaching bands in the IR spectrum (Figure 8) must be related to the vibrational modes of trans-PCT, and the new bands should be attributed to those of the photoproducts. Part of the new bands should be assigned to the vibrations of the [2 + 2] cyclodimer. However, the marker modes of its [2 + 2] cyclobutane vibrations are expected to appear at lower frequency positions below the fingerprint region, and they should be very weak due to either the low quantum yield or low IR extinction absorption coefficient. An indirect marker band is the frequency upshift of the carbonyl $\nu\text{C}=\text{O}$ mode at 1672 cm^{-1} .

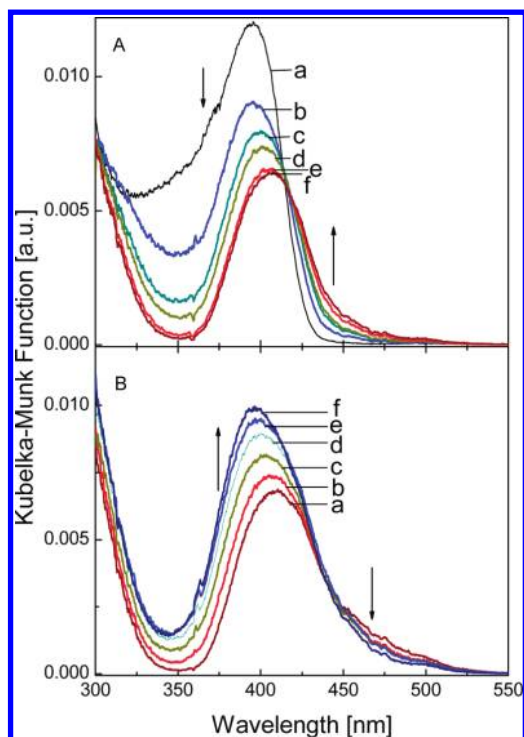


Figure 6. (A) UV-vis diffuse reflectance of powdered PCT before (a) and at 30 (b), 60 (c), 90 (d), 150 (e), and 180 min (f) under low intensity UV irradiation ($\lambda = 400$ nm). (B) UV-vis diffuse reflectance of the sample after 180 min of UV irradiation (a) and then at 30 (b), 60 (c), 90 (d), 150 (e), and 270 min (f) under low intensity visible ($\lambda = 480$ nm) irradiation. The arrows indicate the rise and decrease of the diffuse reflectance.

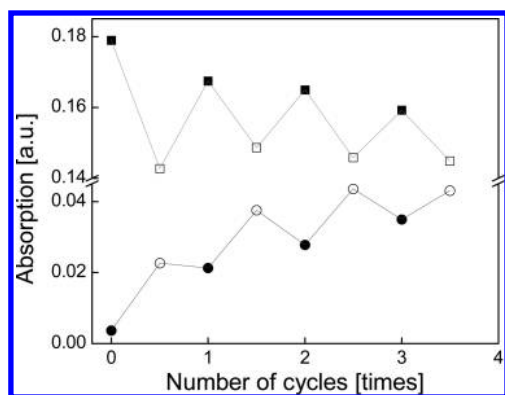


Figure 7. Diffuse reflectance intensity at the 398 nm band (upper data) and at the 468 nm shoulder (bottom data) against the number of subsequent UV and visible irradiations; the filled and open data points are the intensity of the bands after UV ($\lambda = 400$ nm) and visible ($\lambda = 480$ nm) irradiations, respectively.

Important marker bands are the bleaching band at 1050 cm^{-1} together with the new bands at 973 and 995 cm^{-1} . These bands have been assigned to the specific $\nu\text{C}_7\text{H}=\text{C}_8\text{H} + \nu\text{C}_8-\text{C}_9$ mode of the trans and cis form of thiocinnamic ester, respectively.^{17,18,43} We note that the trans-to-cis conversion of the PYP chromophore clearly exhibits similar bleaching/new bands of the $\nu\text{C}_7\text{H}=\text{C}_8\text{H} + \nu\text{C}_8-\text{C}_9$ mode of the chromophore at $1058/994\text{ cm}^{-1}$.⁴⁴⁻⁴⁸ This finding may indicate that the UV photoirradiation also induces trans-to-cis isomerization, and that the reversible product state, mentioned in section 4.2, is the cis PCT isomer. Further support for the trans-to-cis isomerization is the bleaching/new bands at $1639/1613\text{ cm}^{-1}$, which have been assigned to mainly the ethylenic $\nu\text{C}_7=\text{C}_8$ bond of trans and cis configuration, respectively, and the similar mode of the protonated cis

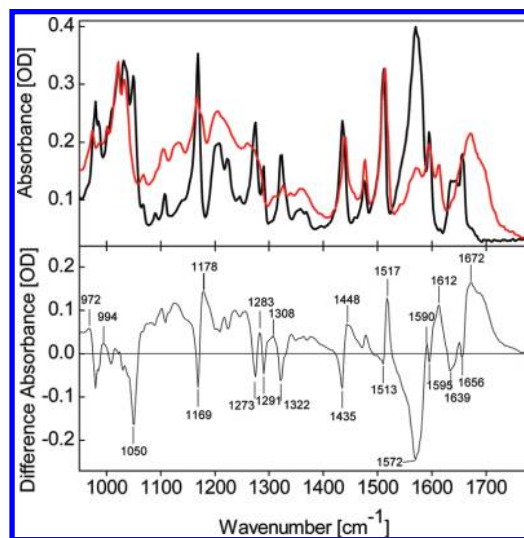


Figure 8. IR spectrum of PCT before (black) and after long time UV irradiations ($\lambda = 405$ nm) (red) (top panel) and the difference IR spectrum between before and after irradiations for 750 s (bottom panel).

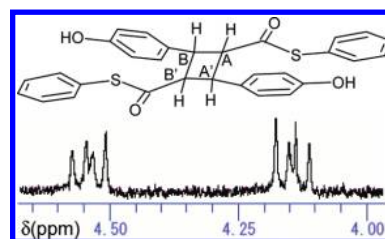


Figure 9. ^1H NMR spectra (270 MHz) of PCT after UV irradiations for 750 s showing the presence of the [2 + 2] photocyclodimer with the assignment of [2 + 2] cyclobutane protons. Coupling constant: $J_{AA'} = 7.02$ Hz, $J_{BB'} = 7.02$ Hz.

intermediate of the PYP chromophore is located at 1599 cm^{-1} .⁴⁴⁻⁴⁸ The bleach of the ethylenic mode from the trans $\delta\text{C}_7\text{H}=\text{C}_8\text{H}(\text{B}_u)$ at 1291 cm^{-1} and a new mode of cis $\nu\text{C}_3-\text{O} + \delta\text{C}_7\text{H}=\text{C}_8\text{H}(\text{A}_1)$ at 1283 cm^{-1} are also in agreement with a recent IR study on trans *p*-hydroxycinnamic acid, which has a related pair of bleaching/new bands at $1294/1288\text{ cm}^{-1}$ upon trans-to-cis isomerization.⁴⁶ In the cis intermediate PYP chromophore, the $\delta\text{C}_7\text{H}=\text{C}_8\text{H}(\text{A}_1)$ mode has been assigned to the band at 1286 cm^{-1} .^{47,48}

A frequency shift of the carbonyl $\nu\text{C}=\text{O}$ mode from 1656 cm^{-1} to a broadband at 1672 cm^{-1} can also provide a direct insight into the trans-to-cis isomerization, since by twisting or flipping of the thioester bond the carbonyl group has less substantial couplings with other nuclear vibrations, resulting in higher frequency position of the $\nu\text{C}=\text{O}$ mode. A similar frequency upshift of this mode was observed from 1631 to 1653 cm^{-1} in PYP,⁴⁴⁻⁴⁸ and from 1700 to 1722 cm^{-1} in *p*-hydroxycinnamic acid methyl ester, upon trans-to-cis photoisomerization.⁴⁹

In addition to those isomerization marker modes, the frequency positions of the phenolic moiety^{17,44-46} are also slightly shifted from 1169 , 1435 , 1513 , and 1595 cm^{-1} to 1178 , 1448 , 1517 , and 1590 cm^{-1} , respectively, due to most probably couplings with minor contributions of other nuclear motions, although the phenolic moiety is structurally unchanged. On the other hand, localized vibrational modes of the thiophenyl moiety¹⁷ at 1067 , 1108 , and 1476 cm^{-1} should remain unchanged. These findings provide evidence that the vibrational motions of these two moieties are not significantly altered upon the conformational changes in the crystal lattice.

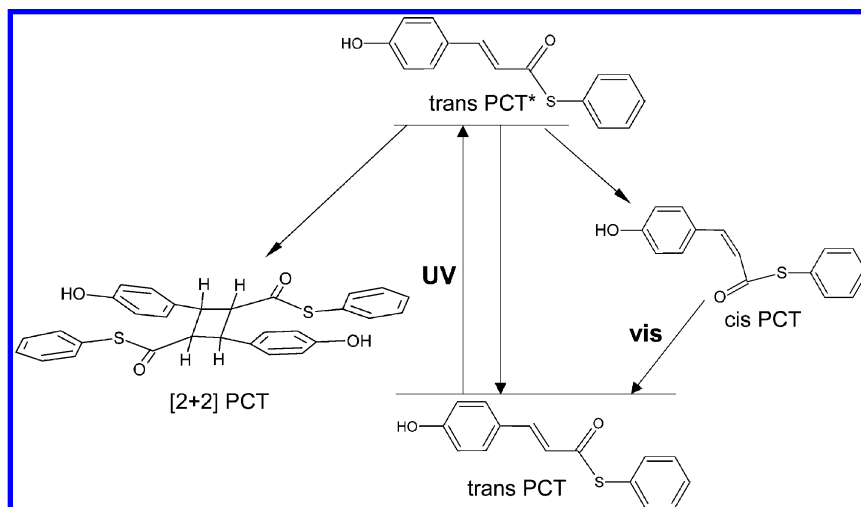


Figure 10. Schematic diagram of photoexcitation dynamics of PCT microcrystal.

4.4. Photochromic Reaction of PCT in the Microcrystalline State.

Here, we propose that photochromic reaction of PCT microcrystal involves the branched photoexcitation dynamics as discussed above. As shown schematically in Figure 10, we consider that photoexcitation of the PCT molecules could induce loosening of intermolecular interactions or an excited state proton shift of PCT*, leading to a charge translocation along the π -conjugation. This charge translocation, which affects the characters of the C=C double and C—C single bonds, has been suggested to be the early intramolecular process for the isomerization.^{6,14,50,51} The PCT in the excited state then relaxes into branched pathways; a photoisomerization by flipping the carbonyl group or a [2 + 2] cyclodimerization by coupling the two adjacent C=C moieties. The quantum yield of the two relaxation pathways is dependent on irradiation power. A higher irradiation power induces a higher ratio between the emission maximum intensity at 490 nm and the saturated intensity at 564 nm (Figure 4B). The increase in the two emission intensities can be ascribed to the increase in the concentration of the excited states of trans and cis PCT in the crystal, respectively. Under the higher intensity of light irradiation, more photons are sent on to the small area of the crystal. We suggest that one photon excites a single molecule, giving rise to generation of defects in surrounding molecules, and the other photons induce more defects within the small area, making a local distortion in the crystal lattice. In the distorted lattice, then, coupling between the photoexcited, transient, and ground state PCT or conformational changes of an excited PCT take place. Thus, all of the processes result in a nonlinear relationship between the temporal profiles of the emission spectra and the number of irradiated photons. Such a nonlinear relationship has also been reported previously for the crystals of spirooxazines and spiroyrans under fs pulse excitation.^{27–29} We should consider that the molecular couplings in the distorted lattice also result in local heating, which induces larger lattice distortion and modifies the center-to-center distance between the ethylenic C=C bonds. Therefore, it is reasonable that the higher power intensity induces larger lattice distortion in the tight crystal packing, leading to a more favorable condition for the [2 + 2] photocyclodimerization rather than for the photoisomerization.

Although a detailed description of the reaction coordinates of the photoisomerization is still an open question, the formation of the [2 + 2] cyclodimer is a clear indication that the photoactive sites are around the ethylenic C=C and two adjacent C—C bonds. Indeed, the cis PCT is produced after a large

molecular motion, which requires some spaces. The isomerization should be prohibited in the densely packed crystal, even though this reaction proceeds via a volume-conserving rotation of the carbonyl group by the hula twist mechanism,^{52,53} such as the conformational motions of the protonated *p*-hydroxycinnamic derivatives in solution phase.⁵⁴

One possible explanation for the isomerization of PCT in the crystal lattice is a cooperative photochemical reaction model. In this context, the continuous light irradiation generates local lattice distortion and intermolecular couplings as mentioned above, resulting in dynamic free spaces, which allow the surrounding excited PCT molecules to isomerize cooperatively. This should be considered as an extension of our previous cooperative reaction model, where the photoexcited and plural transient species of spiroyrans or spirooxazines generated densely by intense femtosecond light in the crystal lattice are proposed to interact and couple with each other, creating a free volume, and move cooperatively into trans-planar or near-planar photomerocyanines within nanosecond time scales.^{27–29,55} We should note that, although the intermolecular couplings forming the [2 + 2] cyclodimer is the topochemical reaction with minimal disruption of the crystal lattice, the formation of the [2 + 2] cyclodimer provides dynamic free spaces, since the two antiparallel PCT molecules form a cyclobutane ring with the C—C distance turning from around 4 Å apart into within 1.6 Å. The free space allows the closest neighboring excited PCT to accomplish the volume-conserving rotation followed by such rotation of the next neighboring excited PCT. However, the photoisomerization must be initiated near the crystal surface, and the isomerization in turn increases more lattice deformation and induces further photoisomerizations. Since the [2 + 2] cyclodimers are formed periodically, the photoisomerization is further enhanced toward the interior of the crystal. This is in contrast to the trans-to-cis isomerization of azobenzene which only occurs on the crystal surface with a low yield.²⁶ The photodynamics of trans-cis isomerization of PCT in the crystal is even different from that of salicylideneanilines with a bulky group substituent introduced into the aromatic rings, where the bulky group acts as a space opener for static free volume in the crystal lattice.^{3,24}

The temporal profiles of the emission at 490 and 564 nm are well fitted with the two-exponential decay function, except for the two data points at early time irradiation, as shown in Figure 4A. This indicates that the rate of the emission increase at 490 nm is not constant. However, it is useful to note that, from the

photoexcitation dynamics proposed in Figure 10, the concentration of the excited states of trans and cis PCT in the crystal also follows the two-exponential decay functions, pointing out that the photodynamic model is relevant, although we could not calculate the rate constant of each reaction.

In the above proposed photochromic reaction, the cis photoproduct state undergoes a backward reaction to the trans form upon visible light irradiation. We believe that both forward and backward photoisomerizations proceed under the condition in which the crystal lattice is distorted, since the original lattice must have been broken by the first UV irradiation. This is in contrast to the uniform photochromism,^{2,23} photocyclodimerization,⁴¹ or photopolymerization,^{39,56} in which these topochemical reactions occur in a single-crystal-to-single-crystal transformation with the original crystal lattice being almost unchanged throughout the photoreaction.⁵⁷ For the PCT crystal, the lattice deformation, the dynamic voids, and the coexistences of two or more structures in its single bulk crystal after UV irradiation are the reasons for the fractures on the crystal surface and for the difficulty to solve its crystal structure. The powder X-ray diffraction pattern for PCT crystals after UV irradiation, however, does not show a new diffraction peak compared to that before irradiation, regardless of some differences in diffraction peak intensities (data not shown). This finding is an indication that the cis isomer does not form a new crystal lattice. The formation of the cis isomer in the crystal, to some extent, is important, since there are only a few examples of chromophores showing photochromism in the crystalline state due to the fact that the chromophores have unstable photoproduct isomers.^{2,22,27–29,55}

4.5. The Structure of the cis PCT Isomer. It would be interesting to evaluate the structure of the cis PCT. It is useful to recall that the marker band of the phenol group is only slightly shifted from 1513 to 1517 cm^{-1} for the $\nu\text{PhOH}(19\text{a}) + \delta\text{CH}(18\text{a})$ mode and from 1169 to 1178 cm^{-1} for the $\delta\text{CH}(9\text{a}) + \delta\text{OH}$ mode, revealing that the cis isomer remains unambiguously in the protonated state. Interestingly, the latter band is similar to the protonated cis *p*-hydroxycinnamic thioester in PYP at 1174 cm^{-1} .⁴⁵ We also recall that the cis PCT has a 12 nm red-shift in diffuse-reflectance spectrum from the trans form, as shown in Figure 6. The absorption spectrum of the deprotonated cis chromophore in PYP ($\lambda_{\text{max}} = 465 \text{ nm}$), which is a nonrelaxed geometry with a rotated ethylenic group,^{35,36} is red-shifted by 17 nm from the ground state trans configuration ($\lambda_{\text{max}} = 448 \text{ nm}$). From the similar vibrational mode and electronic structure, it might be reasonable to speculate that the cis PCT configuration may adopt a nonrelaxed geometry with a rotated ethylenic group.

5. Conclusion

In the present study, we have succeeded in the demonstration of a new archetype of solid state photochromic reaction of PCT microcrystal, involving [2 + 2] cyclodimerization and trans-to-cis isomerization, in contrast to those of well-known two-state photochromic reactions. We propose that the photoexcitation induces an excited state proton shift of PCT*, which undergoes two relaxation pathways. The formation of the [2 + 2] cyclodimer should be an important supporting factor to facilitate dynamic free spaces in the crystal lattice for the neighboring excited molecules to accomplish cooperatively a volume-conserving trans-to-cis isomerization. A reverse reaction is undergone from cis-to-trans by a visible light irradiation, demonstrating a photocyclic behavior. We also demonstrated that higher power intensity results in higher possibility of

intermolecular coupling, leading to the modification of the center-to-center distance between the ethylenic C=C bonds favorable for the [2 + 2] photocyclodimer.

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Supporting Information Available: Detailed information on X-ray structural determination, bond lengths, bond angles, intermolecular interactions, and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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