

Ultrafast Spectroscopic Observation of a Quantum Chain Reaction: The Photodecarbonylation of Nanocrystalline Diphenylcyclopropenone

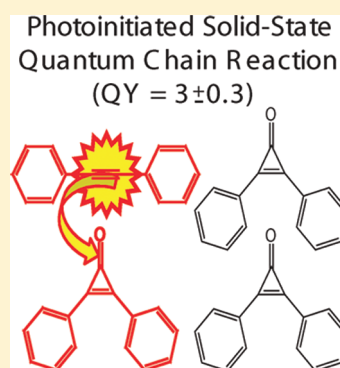
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S Supporting Information

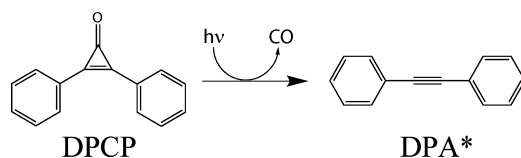
ABSTRACT: Nanocrystalline diphenylcyclopropenone (DPCP) undergoes a photodecarbonylation reaction to form diphenylacetylene (DPA) with a quantum yield of ~ 3 , presumably the result of a quantum chain reaction (QCR). We have performed an ultrafast spectroscopic investigation of this process, and found direct evidence that, following photoexcitation of solid DPCP, DPA product molecules appear in a sequential manner over a ~ 30 ps time scale. We also see spectroscopic evidence for an excited state of DPCP that is optically inaccessible from the ground state; this state can be populated via short-range energy transfer from excited DPA product molecules, providing a mechanistic explanation of the sequential re-excitation and decarbonylation of DPCP and constituting a direct observation of a QCR.

SECTION: Kinetics, Spectroscopy



Diphenylcyclopropenone (DPCP) is a highly strained and reactive molecule with a high-energy content and a remarkably efficient photochemical reactivity.^{1–6} Upon absorption of a UV photon, DPCP molecules in solution undergo a photoinduced decarbonylation reaction with a quantum yield of unity,⁷ producing electronically excited molecules of diphenylacetylene (DPA) plus carbon monoxide (Scheme 1).

Scheme 1. Photodecarbonylation Reaction of DPCP to Form DPA



Despite the apparent simplicity of this photoreaction, there has been controversy over the detailed nature of the electronic states that are involved. In 2004, Takeushi and Tahara⁷ provided support for earlier suggestions^{8–10} that in solution, population created in the second excited state of the reactant, S_2 -DPCP*, with $\lambda_{\text{ex}} = 267$ nm leads adiabatically to the rapid (~ 200 fs) formation of S_2 -DPA* in a vibrationally excited *cis*-bent structure. They also argued that the latter undergoes internal conversion to its first excited state, S_1 -DPA* in ~ 8 ps, which eventually decays on much longer time scales via the triplet. Shortly after, Poloukhine and Popik expressed concerns that the rapid and efficient formation of DPA in this reaction

could lead to experimental artifacts because the DPA photoproduct has a stronger absorption cross-section at the $\lambda_{\text{ex}} = 267$ nm excitation wavelength than the DPCP reactant.¹¹ To address this issue, these workers analyzed the photophysics of a methoxy-DPCP derivative that they proposed diminished this complication; they also studied two naphthyl-DPCP analogues that could be selectively excited with a $\lambda_{\text{ex}} = 400$ nm. Poloukhine and Popik noted that the transient spectra obtained upon excitation of these DPCP derivatives were consistently different from those obtained by the direct excitation of the corresponding DPA, and in combination with quantum mechanical calculations, they interpreted their data as suggesting that the reaction proceeds in terms of an excited-state intermediate (INT*) that loses CO before producing the DPA product exclusively in its ground state, S_0 -DPA.

Although the difference between reaching the product along a pathway that includes an excited-state intermediate (INT*) or via the second excited state of the product (S_2 -DPA*) may be considered subtle, we recognized that the energetics and dynamics of this reaction have important consequences when it is carried out in the crystalline state rather than in solution.^{12,13} In particular, we considered that excitation to S_2 -DPCP* could lead to the formation of an excited-state product (DPA* or INT*) that might be able to transfer its energy exothermically

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to a neighboring ground-state reactant. If the reaction and energy transfer steps could be repeated for a number of cycles, excitation could lead to more than one product molecule per photon. Indeed, it was shown that the quantum yield for the solid-state reaction is 3.3 ± 0.3 following excitation to S_2 -DPCP*, confirming that a sufficiently energetic species is able to propagate a quantum chain.^{14–20}

In this Letter, we present the results of a detailed investigation of the photodecarbonylation of DPCP in the solid state using ultrafast transient absorption spectroscopy. With optimized experimental conditions, we find direct spectroscopic evidence that the decarbonylation of multiple DPCP molecules in the solid state occurs by a sequential mechanism that takes up to ~ 30 ps to complete. Our evidence points to energy transfer from excited DPA* product molecules to nearby ground-state S_0 -DPCP molecules as being the key feature explaining the greater than unity quantum yield. Once complete, the energy transfer process places the DPCP acceptor molecules into an excited state that is optically inaccessible from the ground state, from which they can undergo decarbonylation. The energy transfer process can repeat, producing a quantum chain.

Before beginning our investigation into the quantum chain reaction (QCR) in the solid state, we first revisited the ultrafast spectroscopy of the DPCP photodecarbonylation reaction in solution. In our initial studies, which are described in more detail in the Supporting Information, we photoexcited DPCP molecules at 266 nm, and obtained results similar to those in ref 11. We also repeated the experiments exciting at 310 nm, a wavelength at which ground-state S_0 -DPCP can still be promoted to its optically allowed S_2 state, but at which there is very little allowed absorption for ground-state S_0 -DPA. In this way, we were able to avoid interference from directly excited ground-state S_0 -DPA product molecules while studying the excited DPA molecules produced via photodecarbonylation of DPCP. The results of these experiments are described in detail in the Supporting Information and summarized in Figure 1. In

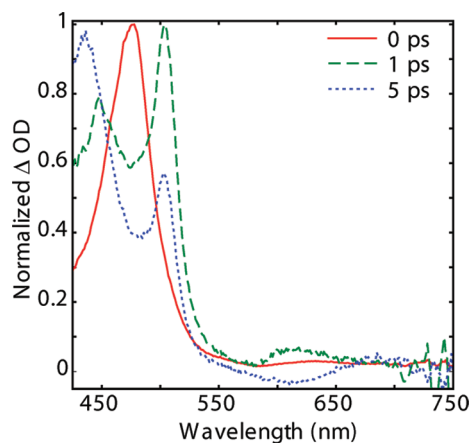


Figure 1. Ultrafast transient absorption spectra of the photodecarbonylation reaction of DPCP following excitation at 310 nm in cyclohexane. The normalized signal at time zero (red solid curve) is attributed to the S_2 excited state of DPCP, at 1 ps the S_2 excited state of DPA is apparent (green dashed curve), and at 5 ps it is clear that the S_2 excited state of DPA decays to the S_1 excited state (blue dotted curve).

agreement with Takeushi and Tahara,⁷ we see clear evidence that the DPA photoproduct is produced in its S_2 excited state.

At time zero (red solid curve), absorption from the excited state, S_2 -DPCP, dominates the transient spectrum at ~ 480 nm. After 1 ps (green dashed curve), the absorption from excited S_2 -DPCP has largely decayed, and has been replaced by a new absorption to the red of 500 nm, which can be assigned to the S_2 -DPA excited state.⁷ This state then undergoes a decay over the next few ps, producing a new state that absorbs near 450 nm (5 ps, blue dotted curve). The logical assignment for this interconversion is the production of the S_1 -DPA state via internal conversion from the S_2 state. Thus, we have strong evidence that the DPA product from the photodecarbonylation of DPCP is produced with a significant amount of excess electronic energy.

The fact that the photodecarbonylation reaction leaves significant electronic energy in the DPA product is consistent with the idea that this energy could be used in a QCR to initiate decomposition of nearby DPCP molecules in the solid state. To investigate this process, we turned our attention to unravelling the detailed mechanism of the QCR that takes place in the solid state. Unfortunately, the irreversibility of the photodecarbonylation of DPCP, combined with the much stronger excited-state absorption cross-section of DPA than that of DPCP, effectively eliminates any possibility of studying this reaction spectroscopically in a single crystal. Thus, we chose to study the solid-state reaction using nanocrystalline suspensions of both DPCP and DPA in water^{12,13} that were prepared via a reprecipitation method.²¹ By using such suspensions, we were able to employ a one-way laminar flow jet (~ 100 μm thick) for our samples,²² allowing us to use solution-phase techniques to study the irreversible solid-state photochemistry.²³ In this way we could flow the samples fast enough to ensure a fresh sample volume on each laser shot at the 1 kHz repetition rate of our laser system, but slow enough that the samples are effectively motionless on the sub-nanosecond time scales being probed in the experiment. We then measured the transient absorption spectrum following excitation of nanocrystalline DPCP using pump and broadband probe laser pulses derived from an ultrafast Ti:sapphire amplifier (Coherent, Legend Elite) seeded with a broadband Ti:sapphire oscillator (Coherent, Mantis) that produces ~ 40 fs pulses of light with ~ 3 mJ of energy centered at ~ 800 nm. The 266-nm pump light was created by tripling a portion of the 800-nm output of the amplifier. The visible broadband probe pulses were created by focusing another portion of the 800-nm light into a sapphire plate to generate a white-light continuum. We prepared the nanocrystalline DPCP suspensions in the dark and handled the samples only under red light to avoid the formation of any DPA product before the introduction of the UV pump pulse.

In the course of our experiments, it became clear that it was critical to also study the photodynamics of a nanocrystalline DPA control sample as well as the nanocrystalline DPCP sample of interest. This is because the reaction in Scheme 1 produces DPA in an electronic excited state, and it is important to compare the dynamics of excited DPA produced following photodecarbonylation of DPCP to those produced by direct excitation of solid-state DPA. Figure 2 shows transient absorption spectra of nanocrystalline suspensions of both DPCP (red curves) and DPA (blue curves) as a function of time delay following excitation at 266 nm. Photoexcitation of solid-state DPCP clearly produces a short-lived excited state that absorbs near 500 nm; the decay of this state leads to the formation of a broad peak at redder wavelengths that strongly resembles the spectrum of directly photoexcited solid-state

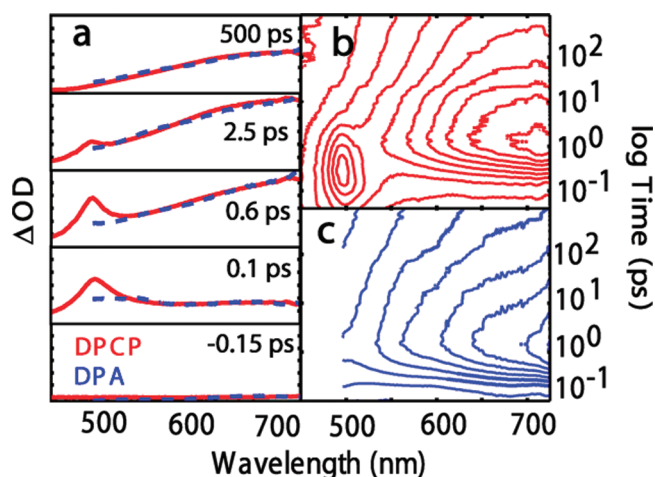


Figure 2. Ultrafast transient absorption spectra of the photodecarbonylation of nanocrystalline solid DPCP to form DPA as well as the direct photoexcitation of solid DPA. The transient spectrum following photoexcitation of solid DPCP is presented at various times in panel a as the solid red curves and contour plot in panel b. The transient spectrum following photoexcitation of solid DPA is shown as the dotted blue curves in panel a and in the contour plot in panel c.

DPA. A careful inspection of Figure 2, however, reveals that the dynamics of DPA formed from DPCP are different than those of directly excited DPA, providing a first glimpse into the mechanism of the QCR. In particular, the excited-state absorption spectrum of directly excited DPA appears to be constant with time after the first ~ 1 ps (panel c), whereas the excited-state absorption of DPA produced via Scheme 1 from DPCP shows subtle shifts and changes in shape for many picoseconds following excitation (panel b).

To better understand the subtle spectral differences in the spectra of excited solid-state DPA produced in the two different ways, we employed generalized two-dimensional correlation analysis (2DCoA),^{24,25} a standard technique used in NMR and two-dimensional infrared (2DIR) spectroscopy that can elucidate spectral changes that are difficult to discern in a traditional one-dimensional spectrum. Further discussion of 2DCoA and the way it was applied to the data in Figure 2 is provided in the Supporting Information. Figure 3 shows the synchronous 2D spectra of photoexcited nanocrystalline DPCP samples at ~ 0.7 ps (panel a) and ~ 17.5 ps (panel c); panels b and d show the same analysis for the directly excited solid DPA control sample at the same delay times, respectively. The early time spectrum in panel a clearly shows the peak at 500 nm that is also seen in Figure 2, which we assign to the initially excited S_2 -DPCP*. It also shows that the broad red absorption seen in Figure 2 is actually composed of two overlapping bands, at 625 and ~ 750 nm, both of which we assign to the DPA photoproduct. Panel b shows that direct excitation of solid DPA also leads to a spectrum composed of two overlapping peaks, with a weak band at ~ 600 nm and a stronger band at ~ 700 nm. Perhaps most importantly, the spectra in Figure 3 show unambiguously that the excited-state absorption bands of DPA produced from excitation of solid DPCP shift and change shape in a different manner than those for directly excited solid DPA.

To better elucidate the dynamics of the two overlapping excited-state DPA absorption peaks, we used a least-squares routine to fit the broad DPA transient absorption band to the sum of two Gaussians, whose dynamic peak positions were

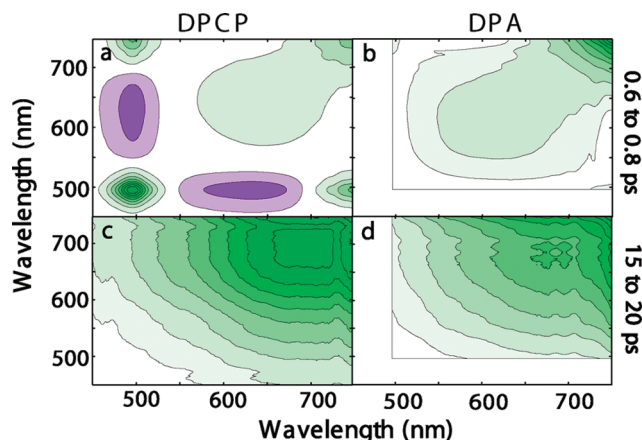


Figure 3. Synchronous 2D correlation spectra of the transient absorption at early time (0.6 to 0.8 ps) of the (a) photodecarbonylation of solid DPCP to form DPA and (b) the direct photoexcitation of solid DPA. Also shown are the synchronous spectra in a window over longer delay times (15–20 ps) for DPA produced via photoexcitation of DPCP (c) and for directly excited DPA (d).

guided by the 2DCoA. We also fit the DPCP excited-state band at 500-nm to a sum of Gaussians whose positions and width did not change with time; the details of our fitting procedure can be found in the Supporting Information. The results of our fits to the transient spectra of both samples are shown in Figure 4. In

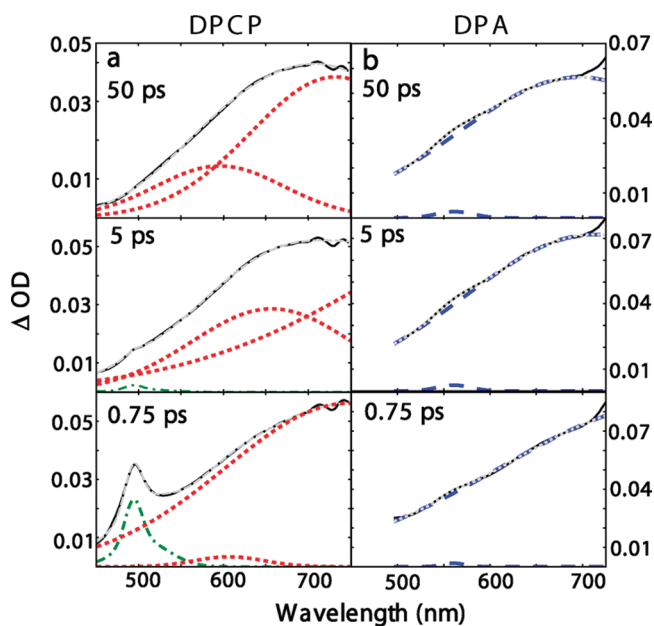


Figure 4. (a) Transient absorption spectrum and fits for selected time slices for the photodecarbonylation of solid DPCP to form DPA; fits to the excited-state absorption of DPCP are the green dot-dashed lines, DPA fits are the red short dashed lines, the total fit is the gray dashed lines, and the raw data is the black solid lines. (b) Time slices of the photoinduced absorption of nanocrystalline DPA. Gaussian fits are the blue long dashed lines, the total fits are the gray dashed lines, and the raw data are the solid black lines.

both panels of this figure, the dashed gray curves representing the total fit show excellent agreement with the experimentally measured spectra (black curves). The green dot-dash curves in panel a represent the sum of the two Gaussians used to fit the excited-state S_2 -DPCP* band, and the red dashed curves

represent the two Gaussians used to fit the DPA photoproduct absorption. In panel b, the blue dashed curves show the two Gaussians used to fit the transient spectrum of the directly excited DPA control sample. Both the data and the fits in Figure 4 show clearly that the two Gaussians that describe the absorption of DPA produced via photodecarbonylation of DPCP have dynamic changes in their peak positions and relative amplitudes, while those that describe the absorption of directly excited DPA are essentially constant with time. Even though the transient spectrum of the DPA control sample could be fit reasonably well with just one Gaussian, as described in more detail in the Supporting Information, we prefer to use two Gaussians to maintain consistency with the DPCP fits and the 2DCoA results.

Figure 5a provides some details of the dynamic changes involved in the solid-state photodecarbonylation reaction by

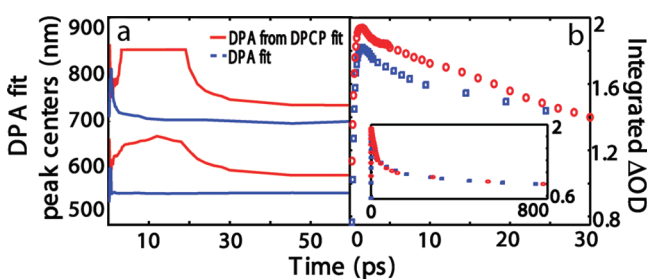


Figure 5. (a) Position of the peak centers of the two Gaussians in Figure 4a used to fit the transient absorption of DPA following the photodecarbonylation of solid DPCP (solid red curves) and directly excited solid DPA (dashed blue curves). (b) Integrated intensity of the DPA transient absorption following the photodecarbonylation of solid DPCP (red circles) and direct photoexcitation of solid DPA (blue squares). The solid curves are multiexponential fits to the integrated spectral data with time constants described in the text. The slower decay dynamics for DPA produced via the photodecarbonylation of solid DPCP provide a direct signature of the QCR.

showing how the peak centers of the two Gaussians used to fit the DPA excited-state absorption in both samples change as a function of time. The solid red curves show that starting after ~ 2 ps, the two peaks representing the excited-state absorption of DPA produced following photodecarbonylation of DPCP undergo a dramatic shift in their peak positions: these two bands both shift rapidly to the red, reaching their longest wavelength at ~ 10 ps, and then return roughly to their original positions after ~ 20 – 30 ps. In fact, the fit for the peak of the redder of the two bands shifts beyond our spectral window to ~ 1100 nm. We do not believe that the DPA* band actually shifts this far during this time window; instead, it appears that the Gaussian fit shifts to better describe an additional absorption from the tail of a new band that appears during the ~ 2 – 30 ps window. By contrast, the blue dashed curves, which represent the transient spectral dynamics of directly excited nanocrystalline DPA, show no dynamics after a rapid (< 1 ps) initial growing-in period. Thus, the spectral dynamics seen in the photoexcited solid-state DPCP sample must be a direct result of the QCR that produces excited-state DPA via a different mechanism than direct excitation. What is perhaps even more interesting is the fact that there is a ~ 2 ps delay following photoexcitation before the dramatic shift of the excited-state spectrum of DPA produced from the photodecarbonylation of solid DPCP takes place. This demonstrates that the solid-state QCR that produces DPA begins only after

the initially excited S_2 -DPCP population has decayed and excited DPA photoproduct has already appeared.

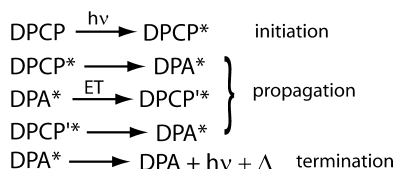
To better understand the sequence of events leading to DPA production from excited solid-state DPCP, and to verify that the dynamics we see do not depend on the way we fit the data, in Figure 5b we show the dynamics of the spectrally integrated DPA transient absorption, which should be proportional to the total DPA population, for both of our nanocrystalline samples. At long times (≥ 30 ps), the inset shows that the decay dynamics of the two samples are identical within the noise, indicating that once the QCR is complete, excited DPA produced from DPCP has dynamics identical to that produced by direct excitation. At early times (~ 2 – 30 ps), however, the main panel makes it clear that the decay of excited DPA produced from solid DPCP (red circles) is slower than that of directly excited solid DPA (blue squares). This suggests that excited DPA is continuing to be produced on the 2–30 ps time scale in the solid DPCP sample, leading to a slower DPA decay relative to direct excitation. This observation effectively eliminates the possibility that the QCR takes place during (or more quickly than) the ~ 2 ps lifetime of DPCP*, since, if it did, the population dynamics of DPA* produced from DPCP and those produced from direct excitation would be identical after this time. Moreover, the fact that the slower decay coincides exactly with the spectral shape changes seen in Figure 4a provides further evidence that the QCR must occur during this 2–30 ps window. Together, all of our analyses indicate that the QCR is sequential, not concerted, and that once it is complete, the DPA produced via photodecarbonylation is no different than that produced via direct excitation.

It is important to note that it is possible that the different spectral dynamics we observe for DPA* produced from DPCP and DPA* produced via direct excitation could be due to differences in the local environment. Indeed, the data in Figure 2 show a very small shift in the position of the DPA* band in the two different samples, suggesting that the spectrum of DPA* surrounded by DPCP molecules is subtly different than that of DPA* surrounded by ground-state DPA molecules. The crystal structures of both DPCP and DPA are known,^{26,27} and neither shows contacts that are shorter than the sum of the van der Waals radii of the atoms on adjacent molecules. Instead, both structures display aromatic edge-to-face interactions with relatively small overlap of the surfaces between neighbors. Moreover, the UV absorption spectra of DPCP in solution and the solid state are quite similar to each other, and those of DPA differ by a red shift of only ~ 35 nm in the nanocrystals. Neither compound's spectrum displays significant broadening or exciton splitting in the solid state. Given all these observations, we believe that environmental differences are unlikely to explain the dynamics we see, particularly since the differences we observe occur only after a ~ 2 ps time delay: if the local environment were responsible for the differing dynamics in the two samples, we would have expected to see the differences start from the very beginning.

Overall, the recurring theme seen in the data is that the QCR takes place over the 2–30 ps time scale. The excited-state absorption bands are broad and strongly overlap, but relatively straightforward analyses provide a way to accentuate the different spectral dynamics of DPA* produced from DPCP and those produced via direct excitation. Not only is it possible to make out the slight differences directly in the raw data (Figure 2b,c), but the slower population decay dynamics in the DPCP sample (Figure 5b), the spectral changes that become more

readily apparent via 2DCoA (Figure 3), and simple Gaussian fitting (Figure 4) show that the QCR has a definite spectral signature. Taken together, the data in Figures 2–5 strongly support a picture of the QCR as occurring via the mechanism proposed in Scheme 2, which is also summarized in the

Scheme 2. QCR of DPCP and DPA



Abstract graphic.¹³ One could consider fitting the kinetics of S₂ DPA formation and decay with assumed rates of energy transfer and decarbonylation according to Scheme 2, but it is known that the local stress that develops in reacting crystals as a function of conversion leads to different absolute rate constants for every subsequent step,^{28,29} so that such an exercise would not provide much insight. Instead, we believe that the DPA molecules created following photodecarbonylation of solid DPCP are formed in a highly excited electronic state, with relatively little loss of energy as the ring strain is lost during the CO release, exactly as we saw with the solution-phase reaction (see Figure 1, the Supporting Information, and ref 7). The proximity of the molecules in the solid allow the newly created excited DPA molecules to undergo energy transfer to a neighboring DPCP molecule. The energy-accepting state of the nearby DPCP, however, must be different than that in the initial optical excitation: there is no sign of additional S₂-DPCP absorption at ~500 nm during the 2–30 ps window, and the spectral red shift seen in Figure 5a suggests that whatever the accepting state is, it does not strongly absorb in the region blue of 750 nm where we can easily probe. Thus, we believe that Dexter energy transfer from excited S₂-DPA* can excite nearby ground-state S₀-DPCP molecules to a state that is optically inaccessible from the ground state. This energy transfer mechanism takes place on a 2–30 ps time scale because the neighboring molecules have relatively poor π-electron overlap in the crystal, as discussed above. Thus, the nanocrystalline structure and the ultrafast data are inconsistent with the possibility that the QCR occurs entirely in the first 2 ps. Despite the fact that the energy-accepting state of DPCP is different from that prepared initially, the newly excited DPCP can undergo excited-state decarbonylation, with the process repeating roughly twice in a chain reaction, resulting in the observed quantum yield of about three.

In summary, we believe that the data presented here provide the first direct spectral signatures of a solid-state QCR. Upon photoexcitation of solid-state DPCP, electronically excited DPA is formed on a ≤2 ps time scale. The excited DPA product can then transfer its energy to a nearby ground-state S₀-DPCP molecule on a 2–30 ps time scale, allowing this new DPCP molecule to also undergo decarbonylation, with the process continuing in a chain-like fashion. The data make it clear that the chain reaction occurs in a sequential and not concerted fashion, with a well-defined chain intermediate that unfortunately absorbs outside of our spectral window. All of these results serve to highlight how dramatically photochemical reactions can change in the proximity of other molecules in the solid state.

■ ASSOCIATED CONTENT

Supporting Information

Solution phase experiments, nanocrystalline suspension preparation, experimental apparatus for ultrafast pump–probe spectroscopy, 2DCoA, and Gaussian fitting. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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