

Communication

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Molecular Interactions Control Quantum Chain Reactions toward Distinct Photoresponsive Properties of Molecular Crystals

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Supporting Information Placeholder

ABSTRACT: In this work, we fabricated four diphenylcyclopropenone (DPCP) crystals, which involved various molecular interactions encoded in individual molecular structures **1-4**. Based on crystalline structural analysis and photoresponsive characterization of the resultant single-crystal microribbons **1-4**, we demonstrated that the magnitude of molecular interactions could effectively control the quantum chain reaction and the photoresponsive property of the DPCP crystals. The microribbons **1** and **2** having weak molecular interactions exhibited an efficient chain reaction and large mechanical photoresponses (i.e., photomelting and photodeforming), while the microribbons **3** and **4** with strong molecular interactions exhibited no chain reaction and mechanical morphology change. Our work presented a new way to achieve molecular crystals with enhanced mechanical photoresponses.

Photoresponsive molecular crystals have attracted intensive attention over the last decades because of the potential application as actuators.¹⁻²³ Many impressive advances have been made in this area, particularly the development of materials based on the photoisomers (e.g., azobenzene¹¹⁻¹⁴ and diarylethene¹⁵⁻¹⁹) and photoreactions²⁰⁻²³. It is still a great challenge, however, to use the photochemical reactions to fully transform the molecular conformational changes into the macroscopic morphology changes of a molecular crystal. This is because photoirradiation of a molecular crystal only gave rise to partially reacted regions within the crystal and some unreacted regions always remained.¹⁻²³ Garcia-Garibay and coworkers made the pioneering work on recognizing a quantum chain reaction of solid-state photo-decarbonylation that resulted from efficient energy transfer in the solid state.^{24,25} This may offer the opportunity to achieve a complete transformation of molecular conformation changes into enhanced mechanical photoresponses. Nonetheless, the information of control over quantum chain reactions toward mechanical photoresponses of molecular crystals is very limited.

In this work, we report that the magnitude of molecular interactions could effectively control the quantum chain reaction toward distinct photoreaction-induced responsibility of diphenylcyclopropenone (DPCP) crystals. Four DPCP single-crystal microribbons 1-4 were fabricated through engineering various molecular interactions encoded in individual molecular structures 1-4 (Figure 1). Specifically, when photo-triggering the DPCP microribbon terminal with a length of 10 μ m, microribbon 1 with a length of ca. 100 μ m quickly and totally melted while microribbon 2 achieved a photodecarbonylation migration of ca. 40 μ m. This directly revealed the quantum chain amplification factors of 9 and 4 for microribbons 1 and 2, respectively. By contrast, microribbons 3 and 4 with strong H-bonding interactions exhibited no quantum chain reactions even at elongated irradiation time and only underwent the photodecarbonylation at the photoirradiated terminals. These results provided valuable information to control quantum chain reactions toward the enhanced mechanical photoresponses of molecular crystals.



Figure 1. (a-d) Molecular structures **1-4** and single-crystal XRD structures of the resultant microribbons **1-4**.

The synthesis of molecules 1-4 bearing different substituents on the same molecular backbone and the preparation of corresponding single-crystal microribbons 1-4 were described in the supporting information. Single-crystal X-ray structures and crystal parameters of DPCP microribbons 1-4 are shown in Figure 1 and Table S1. Microribbon 1 belonged to a triclinic system, space group of P n a 21, in which molecules 1 stacked along c axis with a d-spacing value of 4.03 Å (Figure 1a). This large intermolecular distance suggested the relatively weak interactions between neighbor molecules. Microribbon 2 belonged to a monoclinic system, space group of $P2_1/n$, in which molecules 2 stacked along b axis with the d-spacing value of 4.04 Å, as shown in Figure 1b. Although the intermolecular distance of microribbon 2 along b axis was similar to that of microribbon 1 along c axis, the oxygen atom in the methoxy group was very close to the phenyl in microribbon 2 (i.e., 3.56 Å), indicating the presence of a lone-pair electrons- π interaction in microribbon 2. Compared to microribbon 1, such an accessorial interaction in microribbon 2 could offer better resistance for the single crystal to the phase transition or chemical reaction. In the microribbons 3 and 4, a more molecular interaction of H-bonding (the bond length of ca. 1.8 Å) was introduced (Figures 1c-d). Particularly in the microribbon 4, an H-bonding network was formed (Figure 1d), which could greatly augment the magnitude of the molecular interactions. The differential scanning calorimetry (DSC) measurements verified the magnitude trends of the molecular interactions in microribbons 1-4. As shown in Figure S1, the endothermic peaks were observed at 83 °C, 168 °C, 238 °C, and 253 °C for microribbons 1-4, assignable to their respective phase transition temperature. This indicated the magnitude of molecular interactions followed the order of microribbon 1 < microribbon 2 < microribbon 3 < microribbon 4.



Figure 2. (a) Schematic representation and (b) bright-field optical microscopic images of the photomelting of microribbon 1 after UV irradiating the microribbon terminal (10 μ m). (c) Schematic representation and (d) bright-field optical microscopic images of the photo-deforming of microribbon 2 after UV irradiating the microribbon terminal (10 μ m).

Given that the molecular interactions could hinder the molecular volume changes of DPCP to diphenylacetylene (DPA) in molecular crystals and thereby yield an energy barrier for the photoreactions, we envisioned that distinct chain reaction amplification should be observed over microribbons **1-4**. To confirm this, we utilized a confocal laser scanning microscopy (CLSM) to directly compare the chain reaction amplification. As illustrated in Figures 2a and 2b, the microribbon terminal with 10 μ m in length was irradiated by a 375 nm scanning laser (18 W mm⁻², 4 μ s per

pixel, 200×200 pixels per frame) for 15 s to initiate the reaction. Surprisingly, microribbon 1 with a length of 100 µm rapidly melted in 15 s after photo-triggering, indicating a highly efficient propagation of the chain reaction where the excited products (DPA*) transferred energy to neighboring molecules of unreacted areas. This result also meant the quantum chain amplification factor of microribbon 1 was more than 9. Here the weak molecular interactions in microribbon 1 should facilitate both the photoreaction and the breakdown of the crystal structure. The melting behavior could even be transferred between the microribbons that stacked each other (Figure S2), again indicating the high propagation efficiency of the chain reaction. The photo-triggered chain reaction was also observed on microribbon 2 after the photoirradiation of its terminal (Figures 2c and d). However, the migration length of the chain reaction in microribbon 2 was much shorter (ca. 40 µm) and the reacted area didn't melt but became darker. Scanning electron microscopy (SEM) imaging of the darker area revealed that the smooth microribbon granulated after the photodecarbonylation (Figure S3). The distinct propagation ability of the chain reactions over microribbons 1 and 2 should be correlated with the different molecular interaction magnitude. In microribbon 2, the stronger molecular interactions yielded a higher energy barrier for the changes of molecular volume needed in the photodecarbonylation and thereby decreased the propagation distance of the chain reaction.



Figure 3. (a) Bright-field and (b) fluorescence-mode optical microscopic images of the photodecarbonylation of microribbon 3 after UV irradiating the microribbon terminal (10 μ m). (c) Bright-field and (d) fluorescence-mode optical microscopic images of the photodecarbonylation of microribbon 4 after the UV irradiating microribbon terminal (10 μ m).

The chain reaction could be completely blocked when the magnitude of the molecular interactions in molecular crystals was largely increased. As shown in Figure 3, microribbons 3 and 4 with strong molecular interactions (e.g., H-bonding) exhibited no propagation of the chain reaction when the microribbon terminal was irradiated even for elongated time (e.g., 2h). Interestingly, no apparent changes were observed over microribbons 3 and 4 under the bright-field CLSM. However, the photodecarbonylation of DPCP into DPA at the terminal with irradiation could be revealed by fluorescence-mode CLSM, where the emission of the photoirradiated area became much weaker than that of the rest area

(Figures 3b and 3d). Notably, compared to microribbon **3**, microribbon **4** exhibited a much slower photochemical reaction that took ca. 2 h to finish the emission changes (Figure 3d). To further compare the photodecarbonylation rate in microribbons **1-4**, we used Fourier-transform infrared (FT-IR) spectroscopy to real-time monitor the vibration intensity changes of O=C- group under the UV irradiation (5 mW/cm²). As shown in Figure S4, for microribbons **1** and **2**, the adsorption peak of O=C- group at 1840 cm⁻¹ quickly disappeared after 9 s and 16 s, respectively. For microribbons **3** and **4**, however, this characteristic peak slowly disappeared after 10 min and 120 min, respectively. These observations consisted well with the aforementioned photoresponses observed under CSLM.



Figure 4. (a, b) Bright-field optical microscopy image of the photomelting of microribbon 1 (a) and the photodeforming of microribbon 2 (b) upon the UV light irradiation. (c, d) Fluorescencemode optical microscopy image of the photoresponse of microribbons 3 (c) and 4 (d). Scale bar represented 10 μ m.

We next investigated the photodecarbonylation and the resulting photoresponses of microribbons 1-4 with entire UV irradiation (365±5 nm) under optical microscopy (Figure 4). As shown in Figure 4a and Movie S1, microribbon 1 deposited on a glass slide rapidly collapsed and melted in ca. 15 s under UV irradiation, indicating that the rapid photochemical decarbonylation in microribbon 1 destroyed the ordered crystal structure. In addition, X-ray diffraction (XRD) characterization of microribbon 1 before and after 15 s UV irradiation confirmed that the single crystal structure of microribbon 1 completely disappeared and the amorphous DPA products were simultaneously formed (Figure S5a). Unlike microribbon 1. microribbon 2 didn't collapse and melt but deformed from the photochemical decarbonylation upon UV irradiation (Figure 4b and Movie S2). XRD characterization of the microribbon 2 before and after the UV irradiation indicated that the volume changes from DPCP to DCA and CO only partially destroyed the crystal structure and part of the ordered structure still remained (Figure S5b). SEM imaging revealed that the smooth surface of microribbon 2 granulated, similar to that in Figure 2d. Apparently, the weak molecular interactions in microribbon 1 was not enough to maintain the ordered structure when large molecular volume changes took place upon UV irradiation, while the relatively strong molecular interactions in microribbon 2 could keep part of original crystal structure under similar conditions.

This hypothesis was again supported by the photoresponsive behavior of microribbons 3 and 4. As shown in Figure S6, no photoresponse was observed under bright-field optical microscopy even upon elongated UV irradiation for both cases. However, fluorescence optical microscopy imaging of microribbons 3 and 4

showed that the blue fluorescence gradually turned into yellow with increasing the UV irradiation time (Figure 4c-d and Movie S3), indicative of the production of DPA from DPCP via the photochemical decarbonylation. Moreover, the rate of the fluorescence change of microribbon 3 was much faster than that of microribbon 4 (Figure 4c-d), similar to those in Figure 3. Interestinglv. XRD characterization of microribbons 3 and 4 before and after the UV irradiation indicated that their crystal structures did not change despite the large changes in molecular volume caused by the photochemical decarbonylation (Figure S7). Furthermore, SEM imaging displayed that the surface of microribbons 3 and 4 remained smooth after UV irradiation (Figure S8). These results indicated that the molecular interactions in 3 and 4 microribbons were strong enough to endure the impact of large molecular volume changes by UV irradiation and maintain their total original ordered structure.

To further demonstrate that the distinctly different photoresponsive properties of single-crystal microribbons 1-4 were attributed by the different intermolecular interactions engineered in crystals but not by the slight difference of molecular structures 1-4 at the molecular level, the photodecarbonylation reaction of molecules 1-4 was investigated in solution phase. Figure S9 shows the time-dependent fluorescence changes of molecules 1-4 acetonitrile solution (5 mM) under UV irradiation (365 \pm 20 nm, 9.6 mW/cm²). Apparently, the solution photodecarbonylation rates of molecules 1-4 were very similar and the photodecarbonylation could be efficiently finished in ca. 11 min for all cases. This strongly indicated that the difference of molecular structures 1-4 with different groups on phenyl groups (ortho versus para, methoxy versus hydroxyl) had no effect on their photodecarbonylation reactions at the molecular level. Resultantly, the comparable photodecarbonylation of molecules 1-4 at the molecular level confirmed that the different photoresponsive properties of single-crystal microribbons 1-4 were attributed by the different intermolecular interactions engineered in crystals. In addition, no apparent fluorescence was observed in Figure S9 for molecules 1-4 acetonitrile solution with UV irradiation less than ca. 8 min. This is because the fluorescence spectra of the photodecarbonylation products partly overlapped with the UV-Vis adsorption spectra of the reactants 1-4 (Figure S10). In this case, the fluorescence of the small amounts of photodecarbonylation products were absorbed by the large amounts of unreacted reactants at the initial stage of the reaction.

In conclusion, we demonstrated that the quantum chain reaction and the photoresponsive property could be effectively controlled by the magnitude of molecular interactions involved in DPCP crystals. Specifically, the weak molecular interactions yielded a relatively low energy barrier for the molecular volume changes in the photoreaction, which facilitated the propagation of the chain reaction and the creation of large mechanically photoresponsive properties, e.g., photomelting for microribbon 1 and photodeforming for microribbon 2. In contrast, the strong molecular interactions in microribbons 3 and 4 hindered the chain reaction and mechanical morphology changes. These findings provided valuable information for crystal engineering of molecular materials with enhanced mechanical photoresponses.

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Notes

The authors declare no competing financial interests.

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Supporting Information Available: Experimental section, Table S1, Figure S1-S10 and Movie S1-S3. This material is available free of charge via the internet at <u>http://pubs.acs.org</u>.

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