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Phototriggered Guest Release from a Nonporous Organic Crystal: Remarkable Single-Crystal-to-Single-Crystal Transformation of a Binary Cocrystal Solvate to a Ternary Cocrystal

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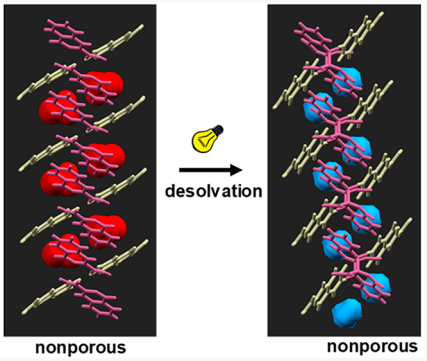
ABSTRACT: The development of organic solids for applications in materials science requires a fundamental understanding of how close packing of molecules can affect structure and function. We report here nonporous organic crystals that release entrapped guest molecules upon application of UV light. We show components of binary cocrystal solvates to undergo an intermolecular photoreaction to generate ternary cocrystals that results in release of entrapped solvent molecules. The phototriggered guest release occurs in a single-crystal-to-single-crystal transformation that is in the absence pores and channels in the solid. The cocrystals are composed of a tetratopic hydrogen-bond-acceptor molecule synthesized in the solid state. The UV-light results in [2 + 2] photodimerization of an isocoumarin to generate a ternary cocrystal with cyclobutane molecules that support guest release.

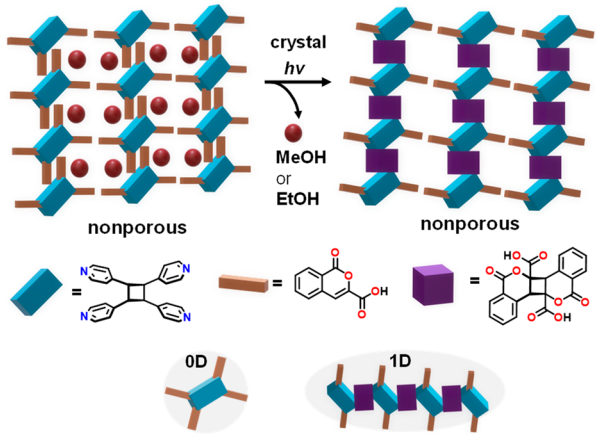


INTRODUCTION

Efforts to increase the structural diversity of molecular solids are important in the design of smart materials.[1−5] A major route to increase structural diversity is to utilize principles of supramolecular chemistry to dictate spatial arrangements of molecular building blocks in solids. Functional groups of the building blocks provide opportunities to tailor solid-state behavior (e.g, reactivity, dynamics) based on composition. In this context, nonporous organic solids that facilitate diffusion of guest molecules while retaining crystallinity are of great interest. The solids enable the intriguing property of guest movement and release in the absence of pores (i.e., intrinsic porosity) and are highly promising for applications in areas[6] such as separations,[4,7,8] energy storage,[9−12] guest transport.[3,13,14] Nonporous solids that release guests, however, remain at a nascent stage of development compared to porous solids (e.g., metal−organic frameworks, coordination polymers, zeolites).[15−17] To date, removal of guests from nonporous solids purely organic in composition has involved very limited approaches other than heat (e.g., pressure, supercritical CO_2).[18,19] In principle, light can be used as an external stimulus to transform or modify the internal molecular and supramolecular structures to facilitate guest release, although such lines of investigation have, to our knowledge, not been pursued for purely organic solids.[19,20]

Here, we describe the application of light to trigger the release of guests from nonporous organic solids (Scheme 1). The light induces an intermolecular [2 + 2] photodimerization[21−25] that modifies the interior crystalline structure to support guest release. Both the photodimerization and guest loss occur in a rare single-crystal-to-single-crystal (SCSC) transformation with the single-crystallinity remaining intact. In

Scheme 1. 0D to 1D Photocycloaddition of Hydrogen Bonding Accompanied by Guest Release from Nonporous Single Crystals



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the single-crystal process, the components of the solid transform from a 0D to 1D hydrogen-bonded structure with guest release occurring at ambient temperature and pressure. While either a photodimerization or guest loss from a single crystal typically results in loss of long-range order and single-crystal character, we are unaware of a nonporous single crystal that survives both a photocycloaddition and loss of guest molecules.[26]

RESULTS AND DISCUSSION

The nonporous solid that supports the phototriggered guest release is the binary cocrystal solvate (**4,4′-tpcb**)·4(**IsoH**)·2(**solvent**) (solvent = **MeOH**, **EtOH**). In the solid, **4,4′-tpcb** acts as a tetrafunctional hydrogen-bond-acceptor, interacting with isocoumarin-3-carboxylic acid (**IsoH**) by O−H···N hydrogen bonds. Half of the **IsoH** acid molecules stack by face-to-face $\pi-\pi$ interactions to undergo the [2 + 2] photodimerization. The components assemble to form 0D seven-component hydrogen-bonded complexes sustained by a combination of O−H···N and O−H···O hydrogen bonds. The guest solvent molecules participate in O−H···O hydrogen bonds to **IsoH**. Overlapping molecules of **IsoH** between nearest-neighbor hydrogen-bonded assemblies undergo the [2 + 2] photocycloaddition reaction that results in guest release.

Reactivity of Pure IsoH. **IsoH**[27,28] was synthesized as reported. We initially determined the photochemical properties of **IsoH** as a pure form. Colorless single crystals of **IsoH** as needles were obtained by slow evaporation of a saturated solution of **IsoH** in ethyl acetate over a period of 2 days.

IsoH crystallizes in the monoclinic space group P $2_1/n$ with two acid molecules in the asymmetric unit (A and B) (Figure 1). The molecules form hydrogen-bonded carboxylic acid

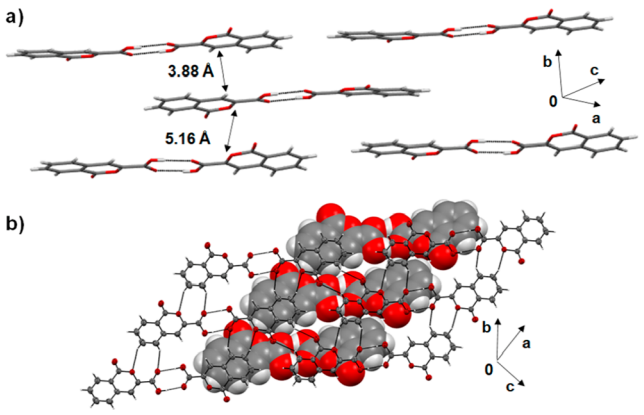

Figure 1. X-ray structure **IsoH**: (a) C=C separations, (b) packing showing network of C−H···O hydrogen bonds within layer.

dimers [O···O separations (Å): O(1)···O(2) 2.672(4), O(3)···O(4) 2.660(3)] (Figure 1a). The best planes of the fused rings of the dimers are twisted slightly from coplanarity (8.2°). The dimers form a layered structure (separation: 3.23 Å) based on ABCD stacking. Adjacent molecules of layers participate in a network of C−H···O hydrogen bonds (C···O separations: 3.317(5)-3.382(4) Å) (Figure 1b). C=C bonds of stacks of molecule A lie parallel and separated by 3.88 Å, with all other C=C bond separations being >5.0 Å. When a powdered crystalline sample of **IsoH** was exposed to UV-radiation (120 h), the solid was photostable. We attribute the photostability of the stacked C=C bonds of **IsoH** to the C−H···O hydrogen bonds "pinning" the acid molecules within the layered structure.[29] The interactions likely provide a rigid environment that suppresses a possible photocycloaddition reaction.

Photoreactivity of Binary Cocrystal Solvate. **IsoH** is photoactive in the binary cocrystal solvate (**4,4′-tpcb**)·4(**IsoH**)·2(**MeOH**). The cyclobutane **4,4′-tpcb** was formed by a hydrogen-bond-directed solid-state [2 + 2] photodimerization (Scheme 2a).[30] When **IsoH** and **4,4′-tpcb** were cocrystallized (ratio: 4:1) in **MeOH** and the solution was allowed to slowly evaporate, colorless plates of (**4,4′-tpcb**)·4(**IsoH**)·2(**MeOH**) formed after 1 day (Scheme 2b). The formulation of (**4,4′-tpcb**)·4(**IsoH**)·2(**MeOH**) was confirmed by SCXRD analysis and ^{1}H NMR spectroscopy.

The components of (**4,4′-tpcb**)·4(**IsoH**)·2(**MeOH**) crystallize in the triclinic space group $P\bar{1}$ with half of a molecule of **4,4′-tpcb**, two molecules of **IsoH**, and one molecule of **MeOH** in the asymmetric unit (Figure 2). The components form four O−H···N and two O−H···O hydrogen bonds to generate a 0D seven-component complex (Figure 2a). Four molecules of **IsoH** interact with **4,4′-tpcb** via O−H···N [O···N separations (Å): O(1)···N(1) 2.569(1), O(2)···N(2) 2.547(1)] and two molecules of **MeOH** interact with two molecules of **IsoH** [O···O separations (Å): O(2)···O(3) 2.922(3)] via O−H···O hydrogen bonds. The cyclobutane **4,4′-tpcb**, thus, serves as a central hub of four radially oriented **IsoH** molecules. The O−H···O hydrogen bonds occur across the diagonal of the cyclobutane (Figure 2). The **MeOH** molecules account for 116.8 Å^3 or 8.2% of the unit cell volume. The packing means there are no channels running throughout the structure.

The packing of the hydrogen-bonded assemblies results in two of four (i.e., half) of the **IsoH** molecules engaged in head-to-tail (**ht**) face-to-face stacks with adjacent acid molecules (Figure 2b). C=C bonds of the stacked molecules lie parallel and separated by 3.62 Å. The arrangement conforms to the criteria for [2 + 2] photodimerization.

Photoreactivity and Generation of Ternary Cocrystal. When powdered crystalline (**4,4′-tpcb**)·4(**IsoH**) ·2(**MeOH**) was placed between two glass plates and subjected to UV-radiation (450 W medium pressure Hg lamp) for 80 h, the stacked alkenes underwent conversion to a photocyclodimer (Scheme 2c). The formation of the dimer was evidenced by the emergence of a cyclobutane signal at 4.88 ppm and decrease in signal intensity of the olefin at 7.70 ppm in the ^{1}H NMR spectrum (see SI). The position of the cyclobutane peak was consistent with the stacked C=C bonds of **IsoH** converting completely to **IsoH-ht**.[31,32]

Phototriggered Guest Release. The application of the UV-light to (**4,4′-tpcb**)·4(**IsoH**)·2(**MeOH**) resulted in release of the **MeOH** guests from the solid. Specifically, when single crystals of (**4,4′-tpcb**)·4(**IsoH**)·2(**MeOH**) were studied by thermogravimetric analysis, a 5.36% mass loss (calculated: 5.40%) for two **MeOH** molecules occurred up to 161 °C. When single crystals were allowed to sit at ambient temperature and pressure for up to 15 days and in the absence of UV-light, the **MeOH** was retained within the solid. A ^{1}H NMR spectrum following UV-irradiation of the single crystals for 60 h revealed relatively small amounts (ca. 12%) of **MeOH** in the solid. We conclude that the application of the UV-radiation and ensuing photodimerization facilitated the loss of the **MeOH** molecules from the crystal lattice.

Single-Crystal-to-Single-Crystal Photodimerization and Guest Release. The photodimerization of **IsoH** occurred in a rare SCSC transformation (Figure 3).[33,34]

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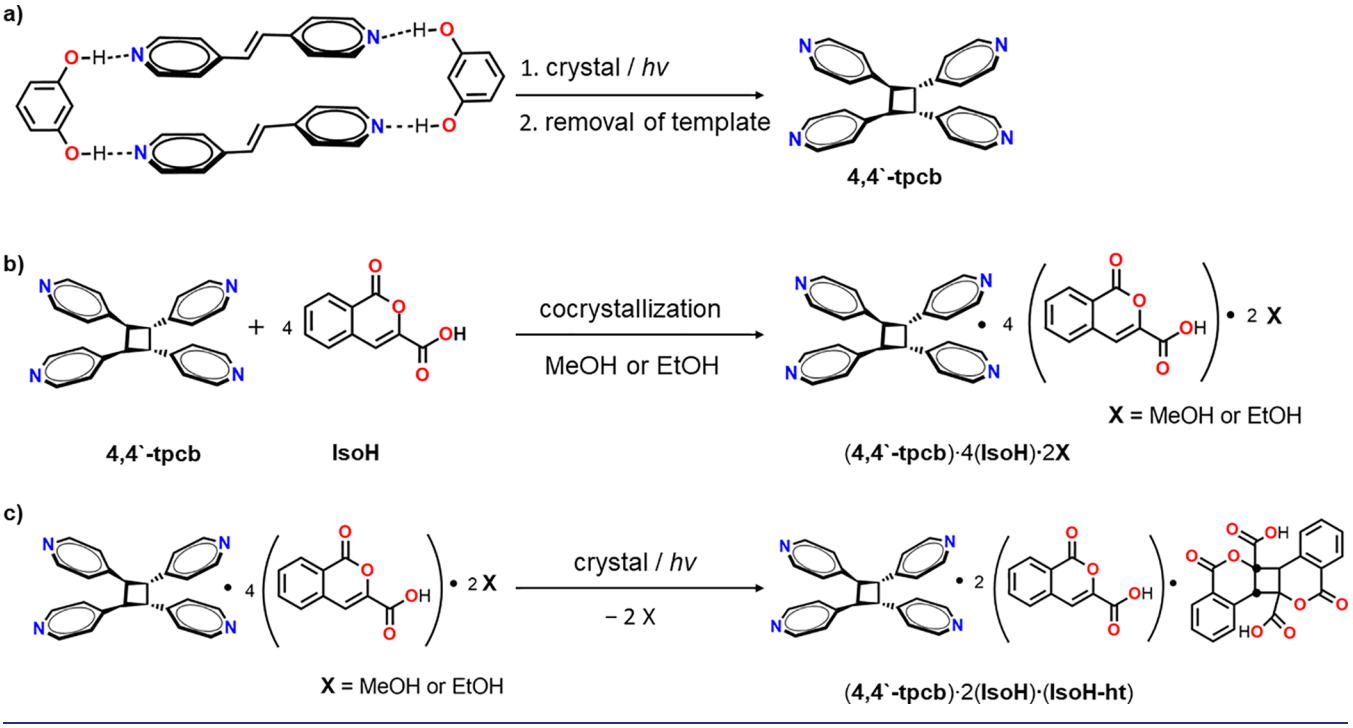
Scheme 2. (a) Solid-State Synthesis of 4,4′-tpcb, (b) Synthesis of Binary Cocrystal Solvate (4,4′-tpcb)·4(IsoH)·2X, and (c) Photoreaction to Form Ternary Cocrystal (4,4′-tpcb)·(IsoH-ht)·2(IsoH)



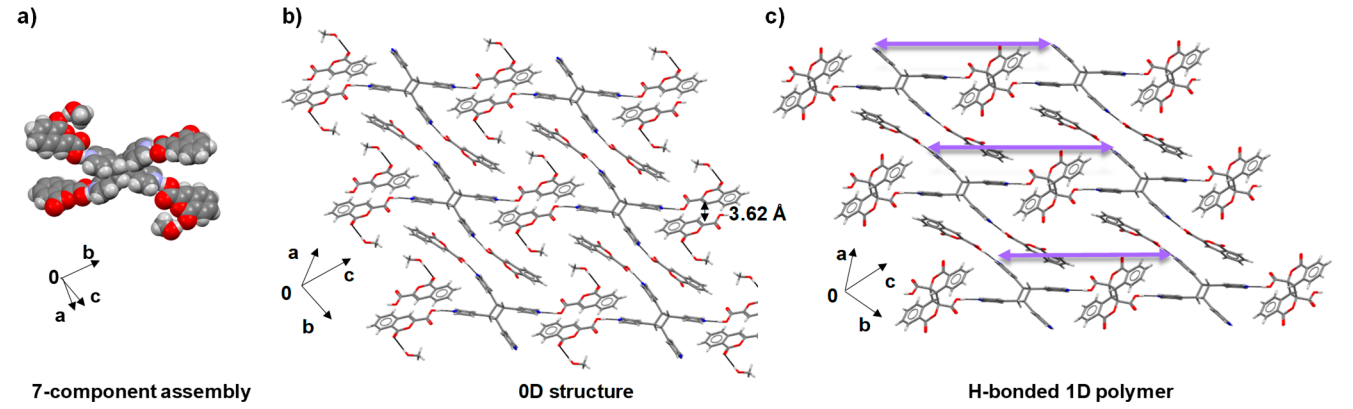


Figure 2. X-ray structure of (**4,4′-tpcb**)·4(**IsoH**)·2(**MeOH**): (a) space-filling view of 0D assembly, (b) packing highlighting overlap of C=C bonds, and (c) photoreaction leading to hydrogen-bonded 1D assembly.

When single crystals of (**4,4′-tpcb**)·4(**IsoH**)·2(**MeOH**) (Figure 3a–c) were exposed to UV-radiation for 60 h, the isocoumarin photodimer formed in approximately 89% conversion. Optical microscopy confirmed the crystals to remain intact. A single-crystal X-ray diffraction analysis revealed the photodimerization to proceed in a SCSC transformation to form **IsoH-ht** (Figure 3d,e). The cyclobutane **IsoH-ht** and **4,4′-tpcb** in the resulting photoreacted solid interact via O–H···N hydrogen bonds (O···N: 2.528(6) Å) stronger than the unreacted alkene **IsoH** (O···N 2.566(5) Å). Virtually all of the **MeOH** molecules were lost from the single crystals as evidenced by the difference Fourier map for the **MeOH** solvent (occupancies: 0.10, cavities: 26.7 Å^3 or 1.9% of unit cell volume).

Phototriggered guest release was also realized using **EtOH** as the included solvent (see SI, Figure S5B). Colorless lath-like crystals of (**4,4′-tpcb**)·4(**IsoH**)·2(**EtOH**) were determined to form that are isostructural to **MeOH**, with the difference reflected by unit cell volumes 1416.9(2) versus 1470.7(3) Å^3, respectively. When exposed to UV-light, (**4,4′-tpcb**)·4(**IsoH**)·2(**EtOH**) was quantitatively converted to solvent-free (**4,4′-tpcb**)·(**IsoH-ht**)·2(**IsoH**) (Figure 4). It is notable that the final photoreacted solids exhibit comparable cell volumes (V = 1393.1(4) Å^3 and 1407.9(2) Å^3), with the originally reacted **EtOH** solid possessing stable cavities (45.2 Å^3 or 3.2% of unit cell volume) with the absence of channels.

Phototriggered Single-Crystal Guest Release. The single-crystal guest releases of **MeOH** and **EtOH** are remarkable. Lattices of crystals that experience either photodimerizations or losses of guest often result in damage to the solid state with single crystals cracking, falling apart, and losing crystallinity.[18] A loss of single crystallinity is attributed to a build-up and release of stress and strain.[35] Cracking and destruction is considered a consequence of an inability of a lattice to allow stress to be efficiently released.[36] By contrast, the single-crystals reported here are robust, maintaining the

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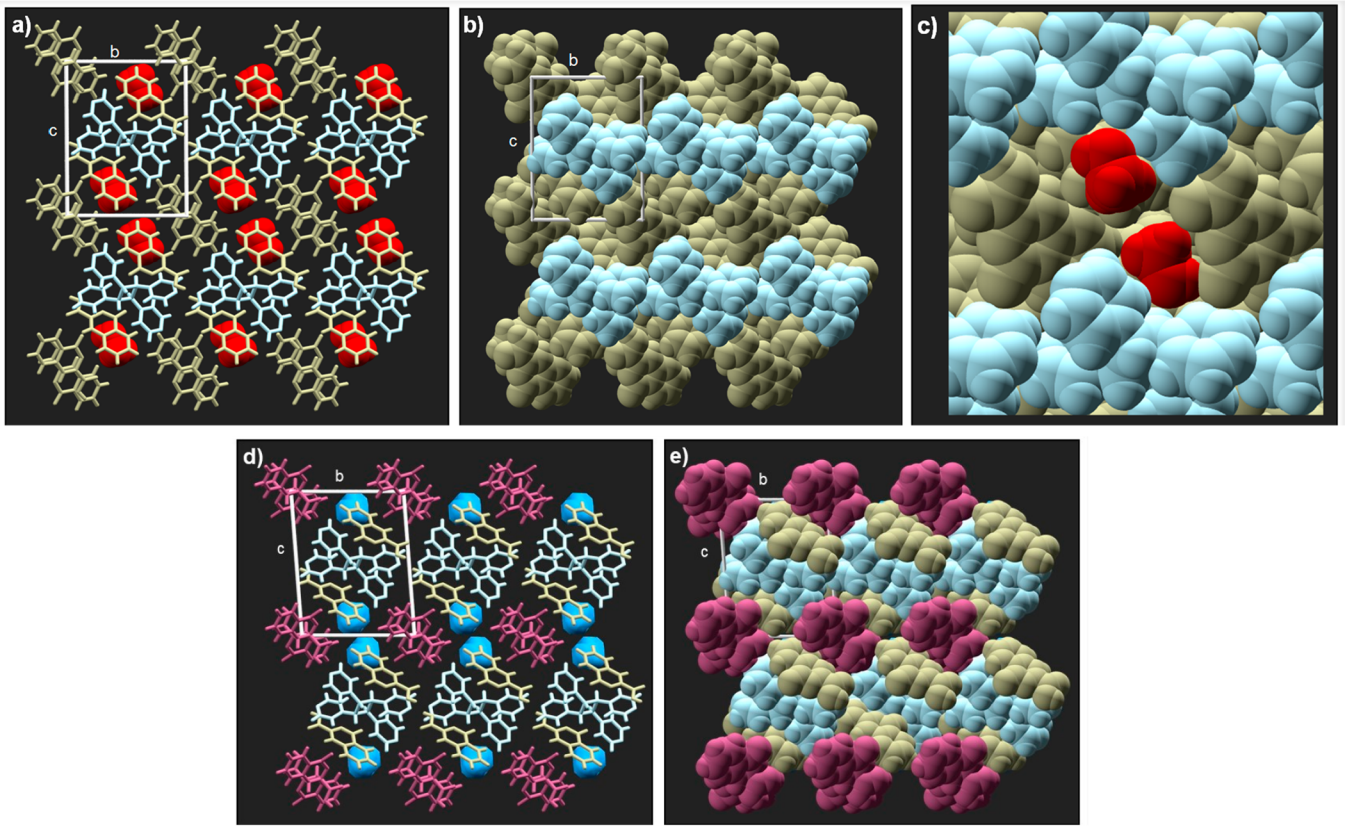

Figure 3. X-ray structures: (**4,4′-tpcb**)·4(**IsoH**)·2(**MeOH**). (a) **MeOH** (red) in close packed environment, (b) space-filling showing absence of pores (**MeOH** not visible), (c) extended packing showing **MeOH** encapsulation, and photoproduct (**4,4′-tpcb**)·(**IsoH-ht**)·2(**IsoH**)·0.2(**MeOH**): (d) desolvated cavities (blue) and (e) space-filling view (**4,4′-tpcb** = blue).

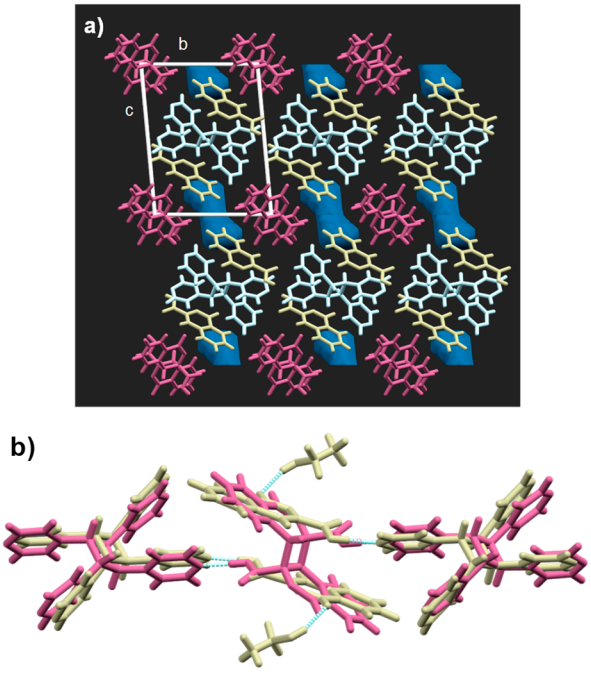

Figure 4. X-ray structure (**4,4′-tpcb**)·(**IsoH-ht**)·2(**IsoH**). (a) After SCSC photoreaction depicting formation of cyclobutane (pink) that defines the 1D hydrogen-bonded structure and (b) overlay of reacting molecules before (pale green) and after (pink) SCSC transformation.

single-crystal character in the wake of both a covalent-bonding forming reaction and release of guests. We attribute the robustness of the single crystals to the discrete, or 0D, nature of the hydrogen-bonded assemblies. Feldman has noted that localizing hydrogen bonding into a discrete structure enables "dependent-site" control of the [2 + 2] photodimerization.[37] The discrete nature allows for the hydrogen bonding to effectively isolate movements of molecules during a photoreaction in a way independent of long-range packing. Consequently, negative impacts that molecular motion may have on long-range order that can result in, for example, loss of C=C proximity and alignment, can be minimized. Here, in addition to supporting quantitative conversion of the stacked C=C bonds of **IsoH**, it is likely that the zero-dimensionality of the hydrogen-bonded structures allows accumulated stress and strain generated by not only the photodimerization but also the losses of guests to be dissipated[35] locally so as to not significantly interfere with long-range packing and preserve single-crystal character. In our own work, we have reported a number of cases where discrete hydrogen-bonded structures allow for both quantitative yield and SCSC reactions.[21,38−42] While we are unsure of an exact mechanism, it is likely that the localized hydrogen bonding in combination with the weaker interactions (e.g., van der Waals forces) that dictate the packing of the discrete structures effectively serve to absorb shock created by molecular movement, thereby providing a measure of "crystal fluidity" to allow for single-crystallinity to be maintained.[43]

CONCLUSIONS

In conclusion, we have described a nonporous solid that supports phototriggered guest release. UV irradiation induced

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a [2 + 2] photodimerization that occurred in a SCSC transformation and with SCSC loss of guests. We are expanding the material to larger guests and exploring the possibility of guest capture. Studies are underway to elucidate the mechanism of guest release, which likely occurs owing to cooperativity[9] of crystal packing and originates from the zero-dimensionality of the hydrogen-bonded structures. Selective capture, storage, and controlled release using UV light as a stimulus can aid in the development of solid-state materials for applications in guest storage.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c09732.

Materials, methods, synthesis, and analysis; characterization data from ^{1}H NMR spectroscopy, TG-IR data; powder X-ray diffraction data; single-crystal X-ray diffraction data (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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