Crystallographic Snapshots of the Interplay between Reactive Guest and Host Molecules in a Porous Coordination Polymer: Stereochemical Coupling and Feedback Mechanism of Three Photoactive Centers Triggered by UV-Induced Isomerization, Dimerization, and Polymerization Reactions

Shi-Yao Yang,*,[†] Xi-Ling Deng,[†] Rui-Fang Jin,[†] Pance Naumov,*,[‡] Manas K. Panda,[‡] Rong-Bin Huang,[†] Lan-Sun Zheng,[†] and Boon K. Teo[§,∥]

[†]State Key Laboratory of Physical Chemistry of Solid Surface and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

[‡]New York University Abu Dhabi, P.O. Box 129188, Abu Dhabi, United Arab Emirates

[§]iChEM, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

[∥]College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China
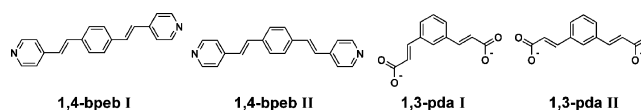
S *Supporting Information*

ABSTRACT: We carried out photopolymerization by [2 + 2] dimerization of a photoreactive guest molecule in the channels of a photoreactive porous coordination polymer. The photoreactions of the guest and two host ligands were monitored by single-crystal X-ray crystallography, providing snapshots of the interplay between the reactive centers. By correlating the structures of these three photocenters, a strong synergism was discovered among three reaction (quasi)equilibria and three types of photochemical reactions (isomerization, dimerization, and polymerization). This result indicates a strong coupling and feedback mechanism among the photocenters moderated by the coordination backbone.

Scheme 1

S olid-state synthesis is increasingly being recognized as an excellent approach for specific synthetic targets because the regularly ordered arrangement of the reactive molecules in a crystalline solid provides a platform for environmentally benign, solvent-free, quantitative, and regio-/stereospecific synthetic access.[1] The desired control over the outcome of any solid-state synthetic procedure requires detailed understanding of the related mechanistic facets. The reaction progress and, desirably, the details of the mechanisms in the solid state can be monitored throughout the entire reaction course in a single-crystal-to-single-crystal (SCSC) transformation.[2] The SCSC reactions have fascinated chemists for over half a century, because they provide an unmatched approach to direct observation of molecular rearrangement or transformations of the reactants to generate desired products.[3]

The SCSC photoreactions normally necessitate extensive preliminary investigations to fine-tune the reaction conditions in a manner that is not detrimental to the crystal. However, these reactions are still quite rare, owing to the fact that the integrity of the crystals is often compromised whenever the perturbation caused by the product overweighs the threshold strain that the crystal lattice can withstand.[4] In addition to small organic molecules in organic crystals,[5] SCSC photosynthesis has already been achieved in organic hosts[6] and in coordination cages.[7] In most of the studied cases, however, the host cavities are relatively small, and thus, only products of low molecular weight can be generated. Indeed, *in situ* photosynthesis of large organic molecules or polymers places serious steric requirements and constraints on the cavities of the host lattice.

Porous coordination polymers are emerging as new promising materials that have attracted intense research interest, in part because they can be utilized as photosynthetic nanovessels to prepare molecules of high molecular weight.[8] Although examples of photodimerization and polymerization in organic molecular crystals and in coordination polymers are known,[9] to our knowledge, regioselective SCSC photopolymerization *via* [2 + 2] photodimerization in a cavity of a porous coordination polymer has not been reported to date.

Our earlier attempts to prepare a photoreactive coordination polymer by bridging metals with the ditopic ligand 1,3-phenylenediacrylic acid (H$_2$(1,3-pda), Scheme 1) by exhaustive hydrothermal procedures ended with crystallization of six solid forms (polymorphs and solvates) of the pure acid.[10] Subsequent synthetic efforts gave rise to a self-assembly of coordination polymer of 1,3-pda with multiple photoreactive centers.

Addition of a secondary ligand, 1,4-bis[2-(4-pyridyl)ethenyl]-benzene (1,4-bpeb, Scheme 1) to the reaction of 1,3-pda with Mn(II) facilitated reproducible crystallization of a porous coordination polymer {[Mn(1,4-bpeb)(1,3-pda)]·(1,4-bpeb)}$_n$
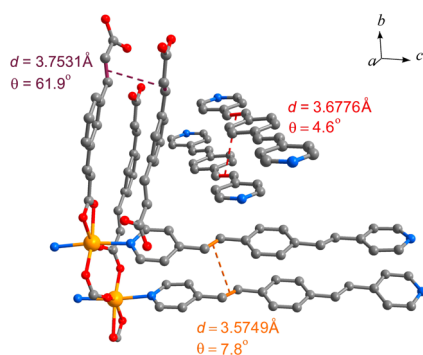
Figure 1. Fragments of the structure of **1** (**0h**) and the relevant metrics for [2 + 2] photoreactions of the guest and ligand molecules.

Figure 2. Space-filling diagram of the crystal packing of **1** (crystal **0h**) as viewed along the crystallographic *a* axis. Each 1D channel accommodates two rows of the guest 1,4-bpeb molecules.

(**1**), in which 1,4-bpeb plays the role of a ligand as well as that of a guest. The resulting coordination polymer is a complex photoreaction system—both ligands and the guest are photo-reactive, and in addition to photodimerization, both reactive components (1,3-pda and 1,4-bpeb) can also undergo conformational pedal-like motion (Scheme 1). To unravel the intricate interplay between the stereochemical and thermodynamic factors on one hand, and the reactivity and kinetics effects of the parallel photoreactions on the other, we studied the action of both intrinsic (molecular geometry and packing) and external (excitation wavelength and irradiation time) effects by monitoring the progress of both photoreactions *in situ* by X-ray crystallography. The results, reported herein, present compelling evidence that the coordination polymers are not rigid; rather, they are capable of providing the necessary flexibility required to sustain the integrity of the crystal in a dynamic, intricate structural environment where not only the guests but also the ligands are transformed during the reactions.

1 was prepared hydrothermally, by reacting 1,3-pda and 1,4-bpeb with Mn^{2+} at 180 °C. The single crystal X-ray structure determination revealed that the product contains 2D nets of coordination polymers. The basic building block of the structure is a binuclear manganese Mn_2 center with two Mn^{2+} ions bridged by two bridging carboxyl groups from two separate 1,3-pda ligands; each Mn^{2+} ion is further chelated by the carboxyl group from a 1,3-pda ligand as well as by two nitrogen atoms from two separate 1,4-bpeb ligands (Figure 1). In this manner, the Mn_2 unit acts as a four-connecting node, linked by two pairs of 1,3-pda along the crystallographic *b* axis and two pairs of 1,4-bpeb ligands along the crystallographic *c* axis to four adjacent Mn_2 units to give a (4,4) net. Finally, the 2D nets stack along the crystallographic *a* axis to complete the crystal structure, leaving 1D channels along the same axis which are sufficiently large to accommodate two rows of guest 1,4-bpeb molecules (Figure 2). A similar coordination polymer without guest molecules has been reported.[11]

The bridging 1,3-pda ligand exists in a single conformation, 1,3-pda I (Scheme 1). The 1,4-bpeb ligand adopts the 1,4-bpeb I conformation (Scheme 1). The guest molecule 1,4-bpeb is also disordered; however, in contrast to the 1,4-bpeb ligand, it exists in two distinct conformations with different occupancies. Two 1,4-bpeb guest molecules reside in the same pore: 79% of which adopts the 1,4-bpeb I conformation and the remaining 21% adopts the 1,4-bpeb II (Scheme 1; Figure S13 in the Supporting Information [SI]). As we will see later, the disposition, conformation, and orientation of these ligand and guest
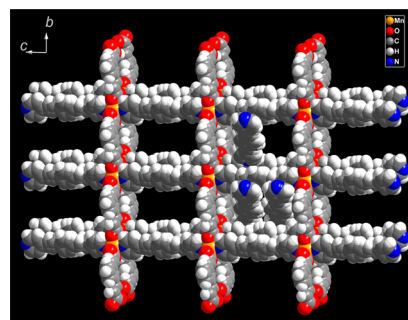
molecules are crucial in the understanding of their photo-reactivities and the corresponding mechanistic details.

The host−guest system **1** represents a complex photochemical system that comprises a multitude of photoreactive centers which, in addition to the dimerization and polymerization, can also undergo conformational isomerization around the double bonds. Thus, it is of interest to discern the relationship and interplay between the ligands (1,3-pda and 1,4-bpeb) of the host and the guest (1,4-bpeb) molecules, as well as between the two conformers of the guest (1,4-bpeb) molecules, in terms of their photochemical responses. Based on the stereochemistry of the crystal structure of **1** before UV irradiation (crystal **0h**), there are four possible geometric relationships between every two nearest C=C bonds in the crystal structure:

(1) For the major component of the guest molecules, in the 1,4-bpeb I conformation, the C=C bonds are juxtaposed for polymerization by head-to-tail [2 + 2] photodimerization at $d =$ 3.6776 Å and $\theta = 4.6°$ (θ is the angle between two C=C bonds and d is the distance between the midpoints of the two C=C bonds). On the other hand, the corresponding parameters of the minor component in the 1,4-bpeb II conformation, $d = 3.6201$ Å and $\theta = 73.7°$, are unsuitable for photodimerization.

(2) In the case of the two 1,4-bpeb ligands, for the major orientation $d = 3.5749$ Å and $\theta = 7.8°$, so the photodimerization is feasible. On the other hand, for the minor orientation, the corresponding values of $d = 3.6285$ Å and $\theta = 17.6°$ suggest that photodimerization is not possible.

(3) In the 2D coordination polymer, the distance between the two 1,3-pda ligands is 6.5861 Å, far beyond the limiting topochemical distance of 4.2 Å.

(4) The distance between the two 1,3-pda ligands from adjacent 2D nets is 3.7531 Å. The θ angle of 61.9° also prohibits photodimerization.

The photoreactivity of **1** was studied by IR spectroscopy of powder samples exposed to UV light of different wavelengths under ambient conditions at different exposure times (SI Figures S4−S7). The weak IR band at *ca.* 1540 cm^{-1} is due to C=C stretching of 1,4-bpeb I, typically observed for a *trans*-conjugated double bond. The stronger bands at 960 and 826 cm^{-1} are assigned to the out-of-plane bending mode of the C=C—H group of the 1,4-bpeb I ligand. These values are in agreement with the theoretical stretching frequencies based on DFT calculations (see Figures S10 and S11 in the SI).

After irradiation with UV LED light (365 nm), the IR spectra remained unaffected. However, when the sample was exposed to UV light from a low-pressure mercury lamp (254 nm) for 48 h, the intensities of the bands from 1,4-bpeb decreased and the
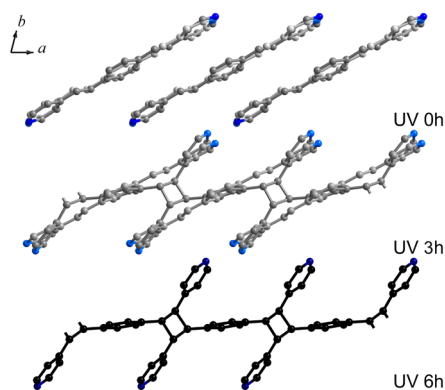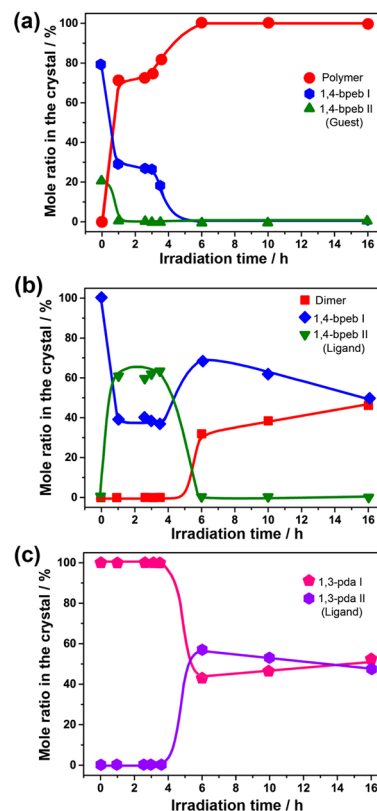
Figure 3. Polymerization of 1,4-bpeb guest molecules in single crystals of **1** at different UV irradiation times. The shade of the structure represents its yield, with darker shade for higher occupancy.

bands typical for the cyclobutane ring evolved. Exposure of the samples to UV light from a low-pressure mercury lamp (185 nm) also showed strong changes in the IR signature. Similarly, the samples were irradiated with UV light from a high-pressure mercury lamp, and the bands from 1,4-bpeb decreased significantly. Interestingly, in all cases the peak at 1645 cm^{-1} assigned to 1,3-pda remained unaffected. We conclude from the IR spectroscopic data that while UV light with wavelength $\lambda < 320$ nm induces photoreaction of 1,4-bpeb in **1**, the 1,3-pda ligand is effectively photoinert.

To explore the stereochemical effects and temporal course of the photoreaction, as well as to investigate the relationship between the reactivity and the structure subtleties, we monitored the SCSC photochemical reaction and the corresponding structural transformation upon UV irradiation by single-crystal X-ray analysis. In single crystals excited at 365 nm (crystal **365**, SI Table S2), we could not observe any significant structural changes. This is in line with the IR spectroscopic results, providing unequivocal evidence that the energy of UV light with $\lambda \geq 365$ nm is insufficient to induce photodimerization.

However, when the samples were exposed to unfiltered light from a high-pressure mercury lamp which includes higher energy radiation, significant structural changes were observed with the guest 1,4-bpeb molecules in the channels. The temporal evolution of the major component of the guest molecule as a function of UV irradiation is depicted in Figure 3. After UV exposure of 1 h (crystal **1h**), the ratio of the major component (1,4-bpeb I) decreased from 79% to 29%, while the ratio of the minor conformation (1,4-bpeb II) decreased from 21% to 0% (see **1h** in SI Table S2). More importantly, a new product, the polymer obtained by head-to-tail [2 + 2] photodimerization reaction of the major component of the guest molecules, was generated in a yield of about 71% at **1h**, as determined by structural analysis (see **1h** in Figure 3 and Table S2 in the SI). After 3 h of UV irradiation (**3h**), more 1,4-bpeb I polymerized. The polymerization process was complete at **6h** when the remaining 30% of 1,4-bpeb I was converted into the polymer (see *n***h** for *n* > 6 in Figure 4 and SI Table S2).

Figure 4b depicts the corresponding transformation of the 1,4-bpeb host ligand upon UV irradiation. Upon 1−4 h of exposure, the ligand, originally in the 1,4-bpeb I form, isomerized to the 1,4-bpeb II form, reaching an apparent quasi-equilibrium at ratio 0.39:0.61 (**2h** in SI Table S2). This isomerization is apparently triggered by the polymerization of the guest molecules discussed above (Figure 4a). However, between 4 and 6 h of UV exposure,

Figure 4. Ratio of different components of the reactants and the products vs UV irradiation time: (a) photopolymerization of the guest 1,4-bpeb molecules; (b) photodimerization of coordinated 1,4-bpeb ligands; and (c) photoisomerization of the 1,3-pda ligands.

surprisingly, virtually all of the ligand 1,4-bpeb II was converted back to the 1,4-bpeb I form, half of which immediately dimerized (Figure 4b). As a result, the percentage of the unreacted ligand 1,4-bpeb I increased by 30%, from 38% at **3h** to about 68% at **6h**, while that for the dimer increased from 0 to 30%, respectively. Between **6h** and **16h**, part of the 1,4-bpeb I ligand dimerized until a 1:1 ratio was reached at **16h** (**6h−16h** in SI Table S2). The reason(s) for the survival of a substantial amount (about 50%) of the unreacted 1,4-bpeb ligand may be due to the structural constraints (both molecular and lattice) imposed by the guest polymer (100%), which fills up the cavities, and the ligand dimers (32−50%), which significantly distort the coordination framework, after 6 h of UV exposure.

Figure 4c shows the corresponding changes of the host ligand 1,3-pda. During UV irradiation for 6 h, 1,3-pda I remained intact, seemingly playing the role of an innocent bystander throughout the photochemical reactions and the subsequent structural transformations as described above. However, upon completion of the polymerization process of the 1,4-bpeb guest molecules (Figure 4a) and the dimerization of the 1,4-bpeb ligands reaching an apparent equilibrium at 6 h of exposure (Figure 4b), the ligand 1,3-pda I also isomerized to 1,3-pda II (*n***h** for *n* ≥ 6 in SI Figure S12 and Table S2), with only minor changes toward equilibrium. It should be noted that dimerization of 1,3-pda could not occur for either forms (I or II) due to the significant deviation of the θ angles from 0° (e.g., θ = 38.4, 35.1, 54.7, and 55.0° for **10h**).

These results indicate that there is a strong interplay and synergism among the three solid-state equilibria, that is, the isomerization of the guest 1,4-bpeb molecule, the host 1,4-bpeb ligand, and the host 1,3-pda ligand. Moreover, the photo-

polymerization of the guest 1,4-bpeb molecules, the photo-dimerization of the 1,4-bpeb ligands, and the photoisomerization of the 1,3-pda ligands are strongly coupled together stereochemically. In other words, once a photochemical reaction is initiated by absorption of a UV photon of sufficient energy, it triggers a chain of structural transformations which enable further photochemical reactions to occur and/or results in the shifts or perturbations of the three solid-state isomerization equilibria described above. We believe that this coupling mechanism is the natural consequence of a complex, intricate, intrinsic "structural feedback" system provided by the somewhat flexible coordination polymer which is capable of adjusting and readjusting itself to the dynamic environment caused by the three types of reactions mentioned previously.

In conclusion, we have carried out polymerization of 1,4-bpeb through SCSC [2 + 2] photodimerization in a "molecular reactor" comprising a 2D porous coordination polymer with three distinct photoreactive centers. The progress of the polymerization was monitored in a step-by-step manner during the photoreaction, and the evolution and the structure of a regular polymer product was characterized by single-crystal X-ray diffraction, thereby producing a series of snapshots of the entire reaction process. By correlating the reactivity of the guest molecules with those of the ligands in the host framework, a synergistic relationship among the three reaction (quasi)-equilibria and the three types of photochemical reactions (polymerization, dimerization, and pedal-like isomerization) was observed. Throughout these reactions and the subsequent structural transformations, the metal−organic framework, although significantly distorted, remained intact. The "communication" between the reaction centers may be indicative of a strong coupling and feedback mechanism moderated by the coordination backbone.

To the best of our knowledge, this is the first instance of a solid-state regioselective [2 + 2] polymerization and the first example of a coordination polymer wherein both ligands and guest molecules photoreact under UV irradiation. Moreover, this work presents a novel synthetic strategy in that an array of polydentate groups can be used as ligands to coordinate to metal ions to form porous frameworks with large nanopores capable of housing guest molecules appropriately positioned to undergo photochemical reaction(s) to produce desired products. This strategy may find applications in a wide variety of systems. In regard to this particular framework (or related systems), it would be interesting to explore the possibilities of cross-photo-dimerizations and copolymerizations to yield synthetically challenging organic polymers (work in progress).

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

syyang@xmu.edu.cn.
pance.naumov@nyu.edu

Notes

The authors declare no competing financial interest.

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561

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