



Solid-state photodimerization via [2+2] cycloaddition in metal complexes and CPs[†]

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Coordination polymers (CPs) are made by the metal ions connecting the organic molecules at regular intervals in the polymer chain. CPs have high crystallinity, multi-dimensional structures, and are made by self-assembly. For last few decades, this active research area has become very much attractive to materials researchers due to the modular design, interesting properties and potential applications of CPs in catalysis, gas storage, ion exchange, separation, polymerization, magnetism, conductivity, optics, etc.

Of these, controlling the reactivity of the CPs is a challenging task, but has potential applications in green synthesis of organic compounds with regio- and stereoselectivity. However, it is now possible to design a reactive solid and conduct a reaction in the solid-state with ease using crystal engineering principles. For the past few years, our research group is actively involved in designing reactive CPs that can undergo structural transformation by [2+2] cycloaddition reactions under UV light as well as sunlight in the solid-state. Here, we present some of the recent results obtained at our laboratory. In addition, the photosalient effect, where crystals leap when exposed to light, is considered a very rare phenomenon. Here, with a one-dimensional (1D) CP that undergoes [2+2] photocycloaddition, we present the evidence of photosalient effect where the crystals undergo popping like popcorn under exposed to UV light as well as sunlight.

Keywords: [2+2] Cycloaddition, metal complexes, solid-state reactions, Stacking interactions, topochemistry.

Introduction

Reactivity is a fundamental chemical property of molecules. Molecules can undergo various types of reactions in all the three states of matter; however, reaction in the solid state differs from other two phases in terms of molecular dispositions and freedom of movement¹⁻³. In addition, postsynthetic approaches have been developed recently as another promising way to introduce useful functional groups^{4,5}. Solid-state structural transformations through single-crystal to single-crystal (SCSC) attains an environmentally benign green concept, because it is devoid of using ecologically harmful organic solvents⁶⁻⁸. Single crystal X-ray crystallography is the only tool currently available to characterize unequivocally the final products of these transformations in the solid state⁹. Hence understanding this SCSC phenomenon to create a stress-free structural transformation in confined coordination space is essential for further advancement in this area. In this regard, topochemical [2+2] photodimeri-

zation has attracted immense interests among the researchers working in the field of solid-state chemistry¹⁰⁻¹⁴. The key factor of photodimerization reaction is to align the olefinic double bonds following the Schmidt's criteria¹⁵⁻¹⁸. This can be achieved by several factors, such as $\pi\cdots\pi$ stacking interaction, aurophilic and argentophilic interactions, counter anion effects etc.¹⁹⁻²³. MacGillivray *et al.* developed an elegant method to align the olefinic double bonds in co-crystals for the synthesis of tailor-made cyclobutanes or ladderanes via photochemical [2+2] cycloaddition reaction²². Vittal and co-workers employed crystal engineering principle to align olefin bond pairs in CPs for topochemical photodimerization.

However, only in limited cases do these dimerization reactions occur in a SCSC manner, and such SCSC transformations involving one-dimensional (1D) or two-dimensional (2D) CPs are still rare. Recently, successful attempts have been made by many groups to utilize this photodimerization reaction in various potential applications²⁴⁻²⁸. In regard to

[†]Invited Lecture.

the application, the impact of photochemical structural transformation on the electrical conductivity of a 1D CP²⁹. Photochemical [2+2] cycloadditions have been considered as a promising route to achieve photoswitchable structures³⁰ and a wide variety of frameworks have been reported³¹.

[2+2] Cycloaddition reaction leading to 0D→1D transformation

A metal-organic compound [Cd(quin)₂(4-nvp)₂] (**1**; Hquin = quinoline-2-carboxylic acid and 4-nvp = 4-(1-naphthylvinyl)pyridine) synthesized³², which undergoes topochemical [2+2] cycloaddition by sunlight irradiation to generate a 1D CP. This reaction is thermally reversible, and switching between two crystalline forms can be monitored by conductivity measurements. Most of the photochemical [2+2] cycloaddition reactions have been carried out using harmful UV radiation. On the basis of green synthesis, dimerization reactions using solar radiation have rarely been explored³³. Complex **1** undergoes sunlight-induced topochemical [2+2] cycloaddition and generates a one-dimensional (1D) CP via crystal-to-crystal transformation. However, the structure of the dimerized product [Cd(quin)₂(*rctt*-4-pncb)]_n (**1'**; *rctt*-4-pncb = *rctt*-1,3-bis(4'-pyridyl)-2,4-bis(naphthyl)cyclobutane) confirmed by a single-crystal X-ray crystallographic experiment of the crystal obtained by keeping the reactor in sunlight. Because of this structural change, there has been a significant effect on the electrical property of the material. The conductivity becomes notably low after dimerization. Most importantly, compound **1'** reverts back to **1** during heating of the crystals at 200°C for 6 h, as is evident from the complete disappearance of cyclobutane protons and the emergence of olefinic protons in the ¹H NMR spectrum in DMSO-*d*₆. This reversible reaction accompanied by switching of the conductivity leads to the development of an electronic device based on molecular switches. Compound **1** undergoes extensive π...π stacking interactions among the aromatic rings of the quin ligands, with the centroid-centroid distances in the range of 3.843–3.848 Å, to fabricate a two-dimensional supramolecular layer structure (Fig. 1).

Single-crystal X-ray structure determination of **1'** exhibits quantitative dimerization along with topochemical structural transformation from a monomeric coordination compound to a 1D polymeric chain (Fig. 2). However, the solid-state structure of **1'** reveals the disappearance of π...π stacking arrangements because of the formation of a strained

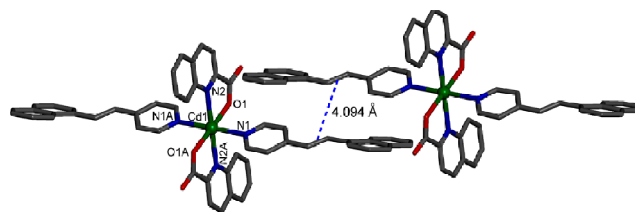


Fig. 1. X-Ray crystal structure of compound **1** showing the alignment of 4-nvp ligands. Hydrogen atoms are not shown for clarity.

cyclobutane ring. From the above discussion, a mononuclear cadmium(II) compound and its dimerized product was obtained in sunlight irradiation. The monomer undergoes [2+2] cycloaddition to form dimer in sunlight via crystal-to-crystal transformation, and the dimer can be reverted back with heating. Here, the dimerized product has been able to obtain in a green process by avoiding ecologically harmful UV irradiation. Interestingly, this structural transformation is accompanied by switching of the conductivity between the monomer and dimer, which might lead to the development of electronic switching devices.

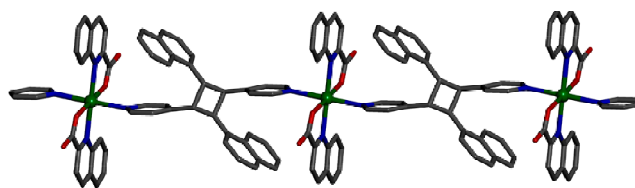


Fig. 2. View showing a portion of the 1D polymeric chain of **1'**. Hydrogen atoms are not shown for clarity.

[2+2] Cycloaddition reaction leading to 1D→1D' transformation

An interesting 1D CP [Cd(bpe)(*p*-brba)₂]_n (**2**) has been synthesized using 1,2-bis(4-pyridyl)ethylene (bpe) spacer and monodentate *para*-bromobenzoic acid (*p*-brba) ligand³⁴. The 1D chains are aggregated via Br...π and π...π stacking interactions to fabricate 3D network. Interestingly, the compound **2** is photoreactive and undergoes SCSC photochemical [2+2] cycloaddition to form dimerized 1D CP [Cd(*rctt*-tpcb)_{1/2}(*p*-brba)₂]_n (**2'**) [*rctt*-tpcb = *rctt*-tetrakis(4-pyridyl) cyclobutane]. Due to this solid-state structural transformation, π...π stacking interactions among *p*-brba ligands of adjacent chains have remained absent in the dimerized product, which leads to the reduction in electrical conductivity value after photodimeri-

zation. Here, the nonbonding distance between the double bonds of a pair of bpe ligands are congenial for photochemical [2+2] cycloaddition in the solid-state following the Schmidt's criteria ($< 4.2 \text{ \AA}$). UV irradiation of single crystals of **2** for half an hour reveals the formation of 100% dimerized products as evident from $^1\text{H NMR}$ spectra. The $^1\text{H NMR}$ spectrum in $\text{DMSO-}d_6$ shows the complete disappearance of peak corresponding to olefinic protons ($\delta = 7.53$) and appearance of cyclobutane protons ($\delta = 4.65$) of *rctt*-tetrakis(4-pyridyl)cyclobutane. Hence, irradiated single crystal of **2** was selected for single crystal X-ray data collection. The X-ray crystallographic analysis of photodimerized product of **2**, $[\text{Cd}(\text{rctt-tpcb})_{1/2}(\text{p-brba})_2]_n$ (**2'**) exhibits the formation of a new bond across the olefinic bonds. As a result, two pyridyl rings become no more parallel and diverge from the cyclobutane ring. From the above results, it has been concluded that conductivity value enhances upon photo-dimerization due to the increase in the extent of $\pi\cdots\pi$ interaction. Since, the structural transformation eradicates the $\pi\cdots\pi$ stacking interactions present among the adjacent layers, leading to the reduction of conductivity value after photodimerization. Thus the material follows 'box open-box close' rule during the electrical conductivity; which is a useful concept for material applications.

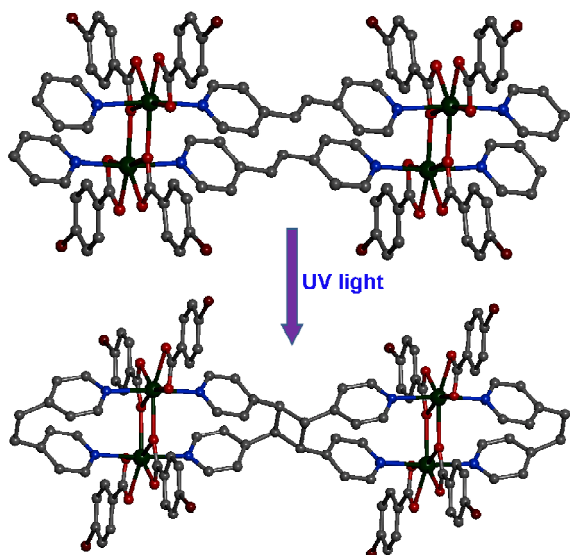


Fig. 3. A schematic diagram showing solid-state structural transformation of **2** to dimerized product **2'**. Carbon: gray; Nitrogen: blue; Oxygen: red; Cadmium: green. The hydrogen atoms are omitted for the clarity.

[2+2] Cycloaddition reaction leading to 1D→2D transformation

A pair of 4nvp ligands has been successfully aligned in head-to-tail fashion in a 1D double chain ladder polymer $[\text{Cd}(\text{adc})(4\text{-nvp})_2(\text{H}_2\text{O})]_n$ (**3**; H_2adc = acetylenedicarboxylic acid). The compound **3** that undergoes a photochemical [2 + 2] cycloaddition to form $[\text{Cd}(\text{adc})(\text{rctt-4-pncb})_{1/2}(\text{H}_2\text{O})]_n$ (**3'**) reaction accompanied by single-crystal to single-crystal (SCSC) structural transformation from a 1D chain to a 2D layer structure²⁹. These structural changes on photodimerization have an significant impact on the conductivity and Schottky nature of the compound. Interestingly, 4-nvp ligand of one ladder is exactly aligned parallel in a head-to-tail fashion to the 4-nvp ligand of the adjacent ladder. There are $\pi\cdots\pi$ stacking interactions between pyridine and naphthalene groups with a centroid-centroid distance of 3.60 \AA . The bond distance between the center of the adjacent C=C bonds is 3.67 \AA , which indicates the possibility of photochemical [2+2] cycloaddition. However, of a pair of 4-nvp ligands of a dimeric unit, only one ligand undergoes alignment with that of the adjacent ladder, indicating 50% of 4-nvp ligands have the possibility of photodimerization.

Herein, a linear 1D CP undergoes photochemical [2+2] cycloaddition accompanied by SCSC topochemical structural transformation from a 1D double chain to a 2D layer structure, leads to a decrease in distance between the adjacent chains as well as $\pi\cdots\pi$ stacking interactions resulting in an increase in conductivity. This appears to be a rare example, where [2+2] cycloaddition has an impact on electrical conductivity and the Schottky nature of the CP. Therefore, this kind of material can be used as a promising candidate for future device application.

[2+2] Cycloaddition reaction leading to photosalient effect

'Photosalient effect' of crystals is rare mechanochemical phenomena, in which single crystals shatter violently during photoreaction resembling to popping of popcorn. Recently, this light induced motility of crystals attracted special attention for potential future applications in photochemical actuators for electrochemical, smart medical and memory devices, artificial muscles, sensors, and probes. There have been very few reports on such phenomena happened by photochemical [2+2] cycloaddition reaction. However, they are limited to

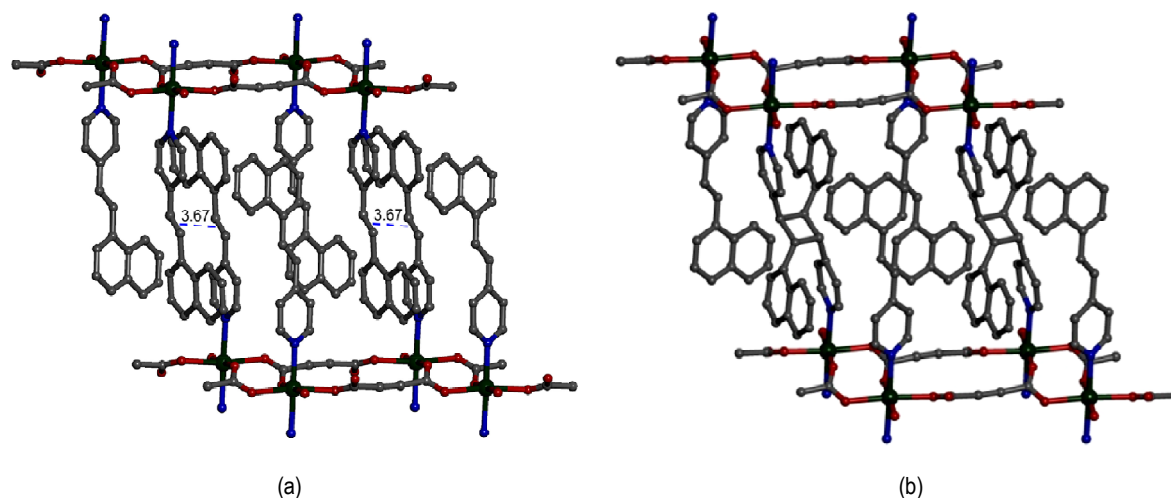


Fig. 4. (a) A perspective view of alignment of 4-nvp ligands between adjacent chains in **3**. Distances are in Å. Only selected atoms are shown for clarity. (b) A perspective view of two adjacent chains in **3'** after UV irradiation.

discrete metal-organic compounds^{35,36}. Here, we report the “photosalient effect” of 1D CP [Zn(glu)(4-nvp)] (**4**) (H_2glu = glutaric acid) with paddle-wheel unit $[Zn_2(O_2CC)_4]$ accompanied by isolation of new cyclobutane ligand *rctt*-4-pncb (**5**) (Fig. 5)³⁷. To the best of our knowledge, herein, we report the first example of 1D CP that shows photosalient effect. Under UV irradiation, the crystals pop so much so that they disintegrate into powder debris. Interestingly, the popping crystals have also been observed in presence of sunlight, although the phenomenon is sluggish. Moreover, while re-crystallization of powder residue from alcoholic solution, an elusive highly strained cyclobutane ligand, *rctt*-4-pncb is isolated. This may be a new way of synthesizing highly strained cyclobutane ligand via post-synthetic modifications of CP. Thus, we report the design and fabrication of CP, observation its photosalient effect and isolation of cyclobutane ligand.

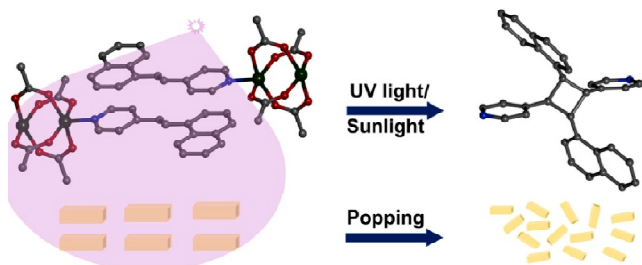


Fig. 5. A schematic diagram showing 1D CP (**4**) exhibiting photosalient effect accompanied by the release of free cyclobutane ligand, *rctt*-4-pncb (**5**).

Conclusion

In this short review, we have presented an overview of reactivity and structural transformations of CPs in the solid-state involving the formation of at least a chemical bond. Herein, using photochemical [2+2] cycloaddition (cause), various types of transformations (effects) have been observed. Interestingly, these structural changes by photo-dimerization have impacts on conductivity properties and Schottky nature of the CPs. CPs exhibit a variety of solid-state reactions that involve changes in coordination spheres by the loss, uptake or exchange of ligands or guest molecules and by external stimuli. The single-crystal X-ray diffraction is the most used technique to follow the solid-state structural changes. However, in the past, many interesting structural transformations, where single crystallinity was lost, have been overlooked or left unexplored due to the lack of modern techniques. We anticipate that with the help of modern structure determining tools, many systems undergoing single crystalline-to-polycrystalline and crystalline-to-amorphous-to-crystalline transformations can be routinely studied; and many new discoveries will be made which will establish new milestones on the path of progress of modern solid-state science.

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