



Exploration of [2+2] photodimerization of coordination polymers in various applications[†]

Basudeb Dutta^{a,b}, Chittaranjan Sinha^{*b} and Mohammad Hedayetullah Mir^{*a}

^aDepartment of Chemistry, Aliah University, New Town, Kolkata-700 160, India

^bDepartment of Chemistry, Jadavpur University, Jadavpur, Kolkata-700 032, India

E-mail: crsjuchem@gmail.com, chmmir@gmail.com

Manuscript received online 10 November 2020, revised and accepted 23 December 2020

The exploration of coordination polymers (CPs) composed of metal ion and organic ligand has been incipient at an astonishing pace. The promising applications and essential diversity in structure of these materials are the driving forces behind the extensive research of such kind. Actually, inorganic metal ions and organic ligands (carboxylate, sulphate etc.) or neutral molecules (N, S donor ligands) are contented to formulate these polymeric compounds. These are the leading accessories to the advancement of solid-state coordination chemistry which is termed as 'crystal engineering' presented by Schmidt. Although, the terminology has been used in regard to the solid-state photochemical [2+2] cycloaddition reaction for first time, subsequently, this [2+2] cycloaddition reaction has been unveiled within the CPs and resulting structural transformation promotes different potential applications: gas sorption, magnetism, sensing, dielectric property, isolation of new organic ligand, electrical conductivity, photo salient effect, flexibility and elasticity of materials. Herein, we discuss on the impact of [2+2] cycloaddition reaction of CPs for various potential applications.

Keywords: Coordination polymers, crystal engineering [2+2] cycloaddition, solid-state reactions, post synthetic modifications.

Introduction

Coordination polymers (CPs) are highly desirable candidates to upgrade the flag of scientific revolution in materials chemistry¹⁻⁵. They have a wide spectrum of applications due to their tailor-made tunable architectures. To depict the desirable structure judicious choices of building block is a reputed tool. However, in the modern days, post synthetic modifications, such as single-crystal to single-crystal (SCSC) conversion, photo and thermo-chemical cycloaddition, *trans*-metallation, functional group derivatisation, coupling reaction etc. have received immense interest⁶⁻⁸. Off these, the photochemical [2+2] cycloaddition is distinctive due to its green in nature, high percent of yield, simple technique, small time consumption etc. Researchers have done enormous work on [2+2] cycloaddition in coordination polymeric system⁹⁻¹¹. This in really helps the chemistry community to upgrade the synthetic strategy and variation in structural architecture. Recently, few groups have been inspired with the previous work of [2+2] cycloaddition on CP system and utilized it for various potential applications. Again, due to its

simple structural tenability, one can easily recover the structure according to asking property. Here the most important factor is the judicious selection of organic ligands and their functionality¹²⁻¹⁴. Keeping this concept in mind, researchers have mainly focused on 'C=C' within the ligand moiety. Among 'C=C' based ligands, *trans*-1,2-bis(4-pyridyl)ethane (bpe), 4-styrylpyridine (4-spy), 4-(1-naphthylvinyl)pyridine (4-nvp), 4,4'-stilbenedicarboxylic acid (sbd), fumaric acid and muconic acids are there. If the arrangement of these ligands are such a manner that 'C=C' bonds are within 4.2 Å (for most of the cases), then they can readily experience [2+2] cycloaddition reaction. After [2+2] cycloaddition (Fig. 1), the obtained photo-product may believed to be the post-synthetic modification (PSM) of CPs for introducing desired properties. This article mainly focuses on the recent development of [2+2] cycloaddition reaction in CPs accompanied by tuning of their desired properties in regard to the applications in gas sorption, magnetism, sensing, dielectric property, isolation of new organic ligand, electrical conductivity, photo salient effect, flexibility and elasticity of materials.

[†]Invited Lecture.

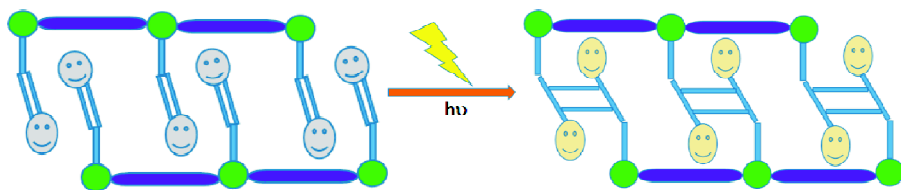


Fig. 1. Pictorial representation of [2+2] cycloaddition reaction in CPs.

Critical discussion

In this section, we will discuss various strategies how [2+2] cycloaddition reaction impacts the properties of CPs for potential applications. In recent years, CPs showing electrical conductivity have attained significant attention among the scientists working in the field of electronic and opto-electronic devices^{15–17}. There are different approaches under consideration for charge transportation: charge transportation through bond and charge transportation through space. It is quite normal to promote the transportation of charge via bond within a compound. Therefore, judicious selection of component building block of CP is a very important factor. Overlap of metal and ligand orbitals can also pave the way for charge carrier. Again, the charge transportation through space is activated via supramolecular interactions. In recent trend, $\pi \cdots \pi$ interactions play the pivotal role for charge transfer. Dincă *et al.* have designed some tetrathiafulvalene (TTF) based metal-organic frameworks (MOFs)^{18,19} to obtain through space charge transportation via $\pi \cdots \pi$ and S \cdots S non-covalent interactions within the network resulting the electrical conductivity of the materials. The electrical conductivity values span in the range from 10^{-6} Scm^{-1} to 10^{-4} Scm^{-1} . Banerjee *et al.* also considered the $\pi \cdots \pi$ interactions in their In(III) MOFs²⁰ to exhibit a better charge carrier mobility ($4.6 \times 10^{-3} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$) (Fig. 2).

To extend the above mentioned approach, our group is also able to explore some compounds for charge transportation which are discussed below.

(a) A Cd(II) based complex $\text{Cd}(\text{quin})_2(4\text{-nvp})_2$ (**1**; Hquin = quinoline-2-carboxylic) undergoes [2+2] photodimerization under sun light to get $\text{Cd}(\text{quin})_2(\text{rctt-4-pncb})_n$ (**1'**; *rctt-4-pncb* = *rctt-1,3-bis(4'-pyridyl)-2,4-bis(naphthyl)cyclobutane*). Here, the deep insight into the structural architectures reveals that

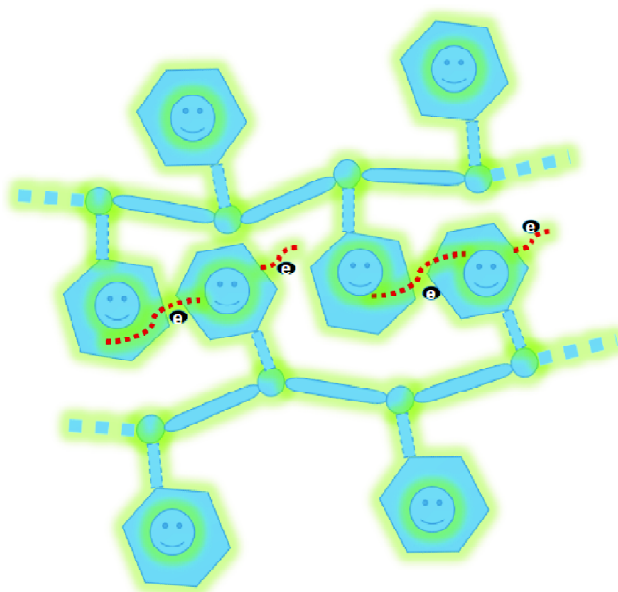


Fig. 2 Probable mechanism for the charge transportation in CPs via $\pi \cdots \pi$ interactions.

$\pi \cdots \pi$ stacking interactions disappears and as a result the electrical conductivity also decreases²¹.

(b) A Cd(II) based one-dimensional (1D) CP, $\{\text{Cd}(\text{bpe})(p\text{-brba})\}_n$ (**2**; *p-Hbrba* = *para*-bromobenzoic) has been converted to $\{\text{Cd}(\text{rctt-tpcb})_{1/2}(p\text{-prba})_2\}_n$ (**2'**; *rctt-tpcb* = *rctt-tetrakis(4-pyridyl)cyclobutane*) via (2+2) photochemical dimerization under UV light. Here, dimerization leads to the reduction of extent of $\pi \cdots \pi$ interactions among aromatic rings, which results the decrease in electrical conductivity²².

(c) Another 1D CP $\{\text{Cd}(\text{adc})(4\text{-nvp})_2(\text{H}_2\text{O})\}_n$ (**3**; H_2adc = acetylenedicarboxylic acid) has undergone topochemical [2+2] photodimerization to generate two-dimensional (2D) CP $[\text{Cd}(\text{adc})(\text{rctt-4pncb})_{1/2}(\text{H}_2\text{O})]$ (**3'**) (Fig. 3). In this case, in this case $\pi \cdots \pi$ stacking interactions have been increased

with respect to the starting material resulting an increase in electrical conductivity.²³ In summary, electrical conductivity of (a) and (b) has been decreased due to absence of $\pi \cdots \pi$ interactions after dimerization, whereas the conductivity increases for (c) owing to the enhancing of $\pi \cdots \pi$ stacking interactions. Interestingly, all these materials (**1**, **1'**, **2**, **2'**, **3** and **3'**) have used to fabricate electronic devices at laboratory level. These findings may be utilized to design electrical conductive CPs and resolve the energy crisis issue.

MacGillivray *et al.* designed a Ag-based metal-organic compound $[\text{Ag}_2(4\text{-stilbz})_4][\text{CF}_3\text{SO}_3]_2$ (**4**; 4-stilbz = *trans*-1-(4-pyridyl)-2-phenylethylene-N and $\text{CF}_3\text{SO}_3\text{H}$ = trifluoromethanesulfonic acid) which undergoes [2+2] cycloaddition to generate 1D CP $[\text{Ag}_2(4\text{-pyr-ph-cb})_2][\text{CF}_3\text{SO}_3]_2$ (**4'**; 4-pyr-ph-cb = μ -2,3,4-diphenylcyclobutane-1,2-bis(4-pyridyl)-N,N)²⁴. At this point, the conductivity of **4'** rises by 40% in comparison to **4** which is attributed to the $\pi \cdots \pi$ stacking of the stilbazoles sustained by $\text{Ag} \cdots \text{Ag}$ interactions. Lang *et al.* described a 1D CP $\{[\text{Zn}_2(3\text{-bpep})_2(2,5\text{-FDC})_2] \cdot 1.5\text{H}_2\text{O}\}_n$ (**5**; 3-bpep = 2,9-bis-(2-pyridine-3-yl-vinyl)-[1,10]phenanthroline and 2,5-H₂FDC = furan-2,5-dicarboxylic acid that exhibits photochemical cycloaddition to produce $\{[\text{Zn}_2(3\text{-bpep})(\text{trans},\text{rctt-3-bppbpycb})_{0.5}(2,5\text{-FDC})_2] \cdot \text{H}_2\text{O}\}_n$ (**5'**; *trans*,*rctt*-3-bppbpycb = 1,3-bis-(8-(2-pyridine-3-yl-vinyl)-[1,10]phenanthroline)²⁵. This conversion changes the space

between centroid to centroid of criss-cross fashioned double bonds from 3.761 Å to 5.313 Å, which reduces the secondary interactions and impacts the dielectric property of the compound. The relaxation peak strength corresponding to electrical measurement decreases in **5'** sharply. By lowering of $\pi \cdots \pi$ communication, the value of mean dipole fluctuation process decreases and follows the drop of dielectric relaxation peak strength from 0.078 (for **5**) to 0.035 (for **5'**).

Detection of ions or molecules is a significant application in the recent scenario of human civilization and environmental contamination. So far, various detection methods have been achieved to enrich sensing application; among them fluorescence technique is one of the promising and advantageous because of its simple technique, rapid response, effortlessness, real-time, high selectivity and operability. The judicious selection of sensor moiety helps to develop a better sensor. In this regard, CPs have been found to exhibit satisfactory performance in sensing hazardous chemicals with profound selectivity and sensitivity^{26–28}. Mechanism of detection is also described in some cases to get proper understanding structure-property relationship. To get insight into the mechanistic aspects various post synthetic modifications (PSM) have been employed among which [2+2] photodimerization is a well discussed method. Recently, some CPs have been reported to show [2+2] cycloaddition, where changing or improvement of their photo-physical or chemical properties took place. A Cd(II) based CP $\{[\text{Cd}(\text{ppene})(1,4\text{-BDC})] \cdot \text{MeCN}\}_n$ (**6**; ppene = 4-pyr-poly-2-ene, 1,4-H₂BDC = benzene-1,4-dicarboxylic acid) undergoes [2+2] photodimerization to generate $\{[\text{Cd}_2(4\text{-tp-3-lad})(1,4\text{-BDC})_2] \cdot 2\text{MeCN}\}_n$ (**6'**; 4-tp-3-lad = 2,3,5,6-tetra(pyridin-4-yl)bicyclo[2.2.0]hexane). Here, both the CPs have been found to be fluorescence sensors for sensing nitroaromatics in water. However, dimerized product **6'** shows better selectivity and sensitivity with respect to starting material **6** with a lower detection limit (0.12 ppm) for 2,4-DNP in water²⁹. Besides, **6'** is also employed for sensing Hg^{2+} in aqueous medium. Another Cd(II) based 2D CP, $\{[\text{Cd}_2(5\text{-F-1,3-bpeb})(1,3\text{-BDC})_2] \cdot 0.5\text{DMF} \cdot 2\text{H}_2\text{O}\}_n$ (**7**; 5-F-1,3-bpeb = 5-fluoro-1,3-bis[2-(4-pyridyl)ethenyl]benzene; 1,3-H₂BDC = 1,3-benzenedicarboxylic acid) undergoes [2+2] photodimerization to generate $\{[\text{Cd}_2(\text{syn-dftpmcp})(1,3\text{-BDC})_2] \cdot 0.5\text{DMF} \cdot \text{H}_2\text{O}\}_n$ (**7'**; *syn*-dftpmcp = *syn*-3,4,12,13-tetrakis(4-pyridyl)-8,17-bisfluoro-1,2,9,10-diethano[2.2]meta-

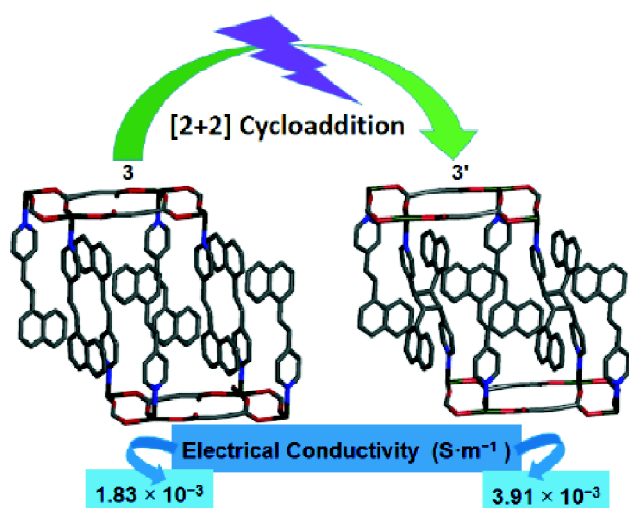


Fig. 3. Topochemical structural transformation of **3** to **3'** via photochemical [2+2] cycloaddition resulting the increase in electrical conductivity.

cyclophane)³⁰. Here, both the compounds have 2D frameworks constructed from linking $[\text{Cd}_2(1,3\text{-BDC})_2]_n$ chains via 5-F-1,3-bpeb or *syn*-dftpmcp bridges. However, after photochemical modification, compound **7'** detects Al^{3+} with much higher selectivity and sensitivity as compared to **7**. The detection limit for **7'** is found to be 183 ppb³⁰. Sensing study reveals that the weak electrostatic interaction between Al^{3+} and F atom of **7** accounts for the profound detection limit. The same observation is also obtained in view of structural architecture; the dihedral angle between two 5-fluorophenyl groups of *syn*-dftpmcp moiety in **7'** is distended as compared to that of **7**, approving better interaction of the Al^{3+} ions with F atom. Such molecular interaction is believed to moderate the energy transfer efficacy of the π - π^* transitions and thus leads to fluorescence quenching of **7'** (Fig. 4). Therefore, it is essential to improve a suitable probe that specifically senses required analytes. In this regard, [2+2] photodimerization is an important PSM to develop such appropriate sensor.

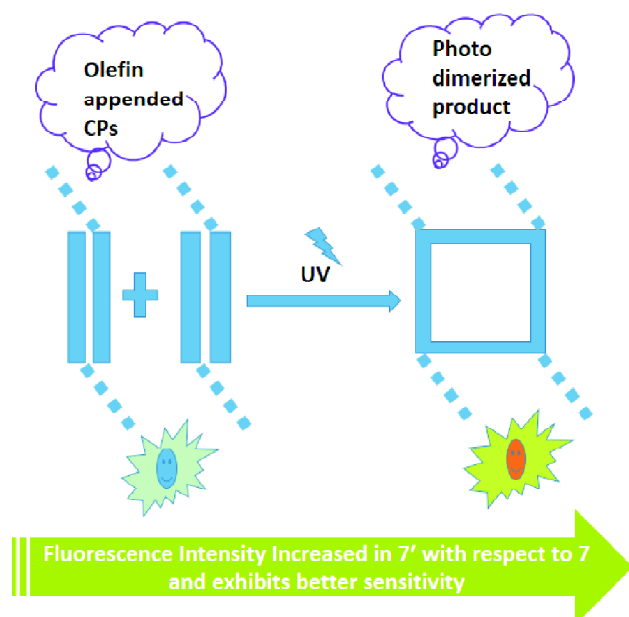


Fig. 4. Photodimerization can be an important PSM to develop an appropriate sensor.

Synthetic organic chemistry always pays special attention due to generation of potentially applicable molecules. However, it is really difficult to develop a desire molecule because it takes lot of complicated reaction circumstances

and schemes. Therefore, the time consumption and percentage yield of reaction product are also the vital issues. Moreover, syntheses of highly strained cyclobutane ring derivatives are further difficult using conventional synthetic routes. Hence, engineering a new procedure is every time welcome. In this aspect, Vittal, MacGillivray and other researchers are able to design some cyclobutane based organic compounds by the assistance of template directed syntheses³¹⁻³³; where secondary interactions support to align the C=C bonds within allowable topochemical distance (4.2 Å) and [2+2] photodimerization takes place to synthesize new cyclobutane derivatives. Han and the group³⁴ stretched the concept and contributed some cyclobutane derivatives by the photodimerization of some coordination moieties. Recently, our research group also described an elusive cyclobutane derivative *rcft*-4pncb isolated from the photo-cycloaddition of a 1D CP $[\text{Zn}(\text{glu})(4\text{-nvp})]_n$ (**8**; H_2glu = glutaric acid)³⁵. The compound exhibits photo salient effect and disintegrates in to powder trash. After recrystallization of the powder product, cyclobutane derivative has been isolated (Fig. 5). This compound is a stereo-selective novel organic ligand and may be advantageous for the scheming different coordination architectures and impending applications.

CPs have been documented as potential catalysts in heterogeneous catalysis owing to their adaptable inorganic and organic components, and the structural architectures. Metal-organic compounds comprising catalytically active metal centers, functional organic linkers, or loaded with vigorous catalysts have been designed and utilized in heterogeneous catalysis. The progress of efficient catalyst schemes for the selective oxidation reaction has been captivated incredible fascination to the synthetic chemists³⁶. Wu *et al.* established a unique contribution to design a Mn(II) based 2D CP $[\text{Mn}_2\text{L}_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**9**; H_2L = *E*-5-(2-(pyridin-4-yl)vinyl)isophthalic acid) which undergoes [2+2] cycloaddition to form three-dimensional (3D) CP $[\text{Mn}_2\text{L}'_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**9'**; $\text{H}_2\text{L}'$ = 5,5'-(3,4-diphenylcyclobutane-1,2-diyl)diisophthalic acid)³⁷. Both the compounds exhibit selective oxidation of phenylmethanol to benzaldehyde; which is an important organic transformation. However, the photodimerized compound **9'** gives better yield of oxidation product 97% at 333 K for 18 h, whereas same for the compound **9** is 64%. The variation of catalytic activities of compounds may corre-

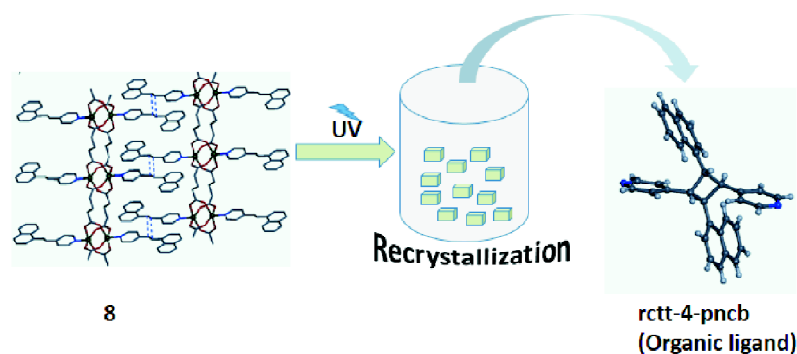


Fig. 5. Isolation of the elusive organic compound from **8** through the recrystallization of photodimerized product.

spond to their diverse in cavity sizes, which effects the diffusion of the substrate. Thus, photochemical structural modification can be a path to adjust the catalytic activity.

One of the valuable aspects of the sustainable growth of our humanity is connected with the eco-friendly and economically favourable capture, separation and storage of gas molecules, e.g. H_2 , N_2 , H_2O , CO_2 , CH_4 , etc. Off these, CO_2 is one of the main components of green house gases and would generate rigorous world-wide climate change if it is accumulated to a high level. Besides, CO_2 is also a necessary intermediate in most of the hydrogen production procedures. Hence, separation and storage of CO_2 from the flue exhaust of plants is progressively significant in the upcoming world. The designing of CPs that can modify its sorption process via tunable channel structure or the pore environment remains a challenge. In this aspect, Kitagawa *et al.* have produced a photo-responsive 2D-CP, $[Zn_2(\text{moip})_2(\text{bpe})_2(\text{DMF})_2]$ (**10**; $H_2\text{moip}$ = 5-methoxy-isophthalic acid) that participates [2+2] cycloaddition as a method to adjust the pore structure and accessible surface area causing an on-demand gas sorption activity³⁸. The olefinic bonds present in the 2D CP maintained the Schmidt's topochemical principle and displayed [2+2] cycloaddition under UV light to generate $[Zn_2(\text{moip})_2(\text{rctt-tpcb})(\text{DMF})_2]$ (**10'**). This process leads to the enhancement in size of the channel due to the formation of cyclobutane. Wu *et al.* have reported a 2D CP, $[\text{Mn}_2L_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**11**; H_2L = *E*-5-(2-(pyridin-4-yl)vinyl)isophthalic acid) which quantitatively undergoes [2+2] cycloaddition reaction into a 3D porous framework, $[\text{Mn}_2L'_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**11'**; H_4L' = 5,5'-(3,4-diphenylcyclobutane-1,2-diyl)diisophthalic

acid)³⁹. This structural modification also caused in increased cell volume (24 to 27%) and enlarged channel size. Both the compounds showed uptake of N_2 at 77 K. These results indicate that photocycloaddition in CPs may result in changes of the space, thereby change in the adsorption behavior.

Every molecule wants to get stabilized via lowering its energy. To minimize the energy, the molecules react and convert energy from one to another. In crystalline solid, the molecules are organized in a regular fashion and their kinetic motions become restricted. Therefore, there remains a possibility of mechanical motion while introduction of external stimuli. Recently, Vittal and coworkers have reported some CPs which are able to undergo [2+2] photocycloaddition along with photo salient effect i.e. crystalline material shatters violently during photochemical conversion similar to popping of popcorn^{40,41}. This light induced mechanical motion of crystalline material attracts the researchers due to promising applications in the fields of engineering and technology in regard to photo and electrochemical study, smart medical and memory devices, molecular and electronic sensors, artificial muscles, photo actuators, and probes⁴²⁻⁴⁴. Reddy and the group have reported some materials where elasticity has altered through photochemical transformation^{45,46}. Naumov *et al.* designed few innovative compounds where photo salient effect revealed excellently during light induced conversions^{47,48}. Inspiring from the exciting activity, our group has also invented a 1D CP, $[\text{Zn}(\text{glu})(4\text{-nvp})]_n$ (**8**) which exhibits photo salient effect (Fig. 5)³⁵. Interestingly, this compound popped with the exposure of UV light as well as the sunlight; although sun light induced popping is little slower. Recently,

Vittal *et al.* reported a Pb(II) based 1D CP, which reveals photo salient effects triggered by [2 + 2] cycloaddition of coordinated olefinic ligands. Here, the rod-shaped crystals display numerous mechanical effects such as jumping, rolling, splitting and breaking upon UV light irradiation⁴⁹.

The inevitability for smart materials is growing swiftly among the material scientists due to the wide diversity in their applications. Photoactuators are type of smart constituents that efficiently adapt external governable stimuli into the mechanical process⁵⁰. In this regard, Lang *et al.* have produced a Zn(II) based compound, [Zn(bdc)(3-F-spy)] (**12**; 1,3-F-spy = 4-(3-fluorostyryl)pyridine; H₂bdc = 1,4-benzenedicarboxylic acid) that is converted to [Zn(bdc)(*rctt*-ppcb)_{0.5}] (**12'**; *rctt*-ppcb = *rctt*-1,3-bis(4-pyridyl)-2,4-bis(3-fluorophenyl)-cyclobutane) via [2+2] cycloaddition reaction and exhibits photomechanical behavior⁵¹. This process indicates that photochemical cycloaddition can cover the route towards the production of consistent devices such as rewritable optical memory storage and smart medicinal memory devices^{52,53}.

Conclusion

In summray, we have described a small overview of current progress of [2+2] cycloaddition within CPs in regard to the impression in various potential applications. This [2+2] dimerization is a striking and highly efficient PSM where the unsaturated double 'C=C' bonds in coordination moieties are transformed into cyclobutane correspondents. The process is demonstrated to be attractive methodology with environmentally benign, regio-selective, facile reaction and high yield. Through this photodimerization, CPs are found to tune their physical, chemical and electronic properties. These correlations will fetch a paradigm shift in our comprehension of the macroscopic materialization of the photodimerizations for exclusive applications. This discussion also displays that [2+2] cycloaddition in CPs may lead to the progression of smart materials. This fashionable alteration of hybrid materials may open up a new path for the efficacy of these compounds and advancement of modern materials chemistry.

Acknowledgements

One of the authors BD is grateful to Dr. Samim Khan, Department of Chemistry, Aliah University and Ms. Sukanya Pal, Department of Chemistry, Jadavpur University for their inspiration and kind help throughout the manuscript preparation.

References

1. S. R. Batten, S. M. Neville and D. R. Turner, "Coordination Polymers: Design, Analysis and Application", Royal Society of Chemistry, London, 2009.
2. M.-C. Hong and L. Chen, "Design and Construction of Coordination Polymers", John Wiley & Sons, Inc., Hoboken, New Jersey, 2009.
3. G. R. Desiraju, J. J. Vittal and A. Ramanan, "Crystal Engineering. A Textbook", World Scientific, Singapore, 2011.
4. B. Dutta, C. Sinha and M. H. Mir, *J. Indian Chem. Soc.*, 2018, **95**, 1535.
5. P. Ghorai, A. Dey, A. Hazra, B. Dutta, P. Brandão, P. P. Ray, P. Banerjee and A. Saha, *Cryst. Growth Des.*, 2019, **19**, 6431.
6. A. J. Nuñez, L. N. Shear, N. Dahal, I. A. Ibarra, J. Yoon, Y. K. Hwang, J. S. Chang and S. M. Humphrey, *Chem. Commun.*, 2011, **47**, 11855.
7. Z. Wang and S. M. Cohen, *Chem. Soc. Rev.*, 2009, **38**, 1315.
8. M. Kalaj and S. M. Cohen, *ACS Central Science*, 2020, **6**, 1046.
9. S. Khan, B. Dutta and M. H. Mir, *Dalton Trans.*, 2020, **49**, 9556.
10. D. Liu, Z. G. Ren, H. X. Li, J. P. Lang, N. Y. Li and B. F. Abrahams, *Angew. Chem. Int. Ed.*, 2010, **49**, 4767.
11. I. E. Claassens, L. J. Barbour and D. A. Haynes, *J. Am. Chem. Soc.*, 2019, **141**, 11425.
12. I. H. Park, H. Ju, K. Kim, S. S. Lee and J. J. Vittal, *IUCrJ*, 2018, **5**, 182.
13. Li, N. Y., Liu, D. and J. P. Lang, *Chem. Asian J.*, 2019, **14**, 3635.
14. R. Medishetty, I. H. Park, S. S. Lee and J. J. Vittal, *Chem. Commun.*, 2016, **52**, 3989.
15. L. Sun, M. G. Campbell and M. Dincă, *Angew. Chem. Int. Ed.*, 2016, **55**, 3566.
16. B. Dutta, R. Jana, C. Sinha, P. P. Ray and M. H. Mir, *Inorg. Chem. Front.*, 2018, **5**, 1998.
17. B. Dutta, A. Dey, S. Maity, C. Sinha, P. P. Ray and M. H. Mir, *ACS Omega*, 2018, **3**, 12060.
18. T. C. Narayan, T. Miyakai, S. Seki and M. Dincă, *J. Am. Chem. Soc.*, 2012, **134**, 12932.
19. S. S. Park, E. R. Hontz, L. Sun, C. H. Hendon, A. Walsh, T. Van Voorhis and M. Dincă, *J. Am. Chem. Soc.*, 2015, **137**, 1774.
20. T. Panda and R. Banerjee, *Proc. Natl. Acad. Sci. India, Sect. A*, 2014, **84**, 331.
21. B. Dutta, A. Dey, C. Sinha, P. P. Ray and M. H. Mir, *Inorg. Chem.*, 2019, **58**, 5419.
22. S. Islam, J. Datta, S. Maity, B. Dutta, S. Khan, P. Ghosh, P. P. Ray and M. H. Mir, *Cryst. Growth Des.*, 2019, **19**, 4057.
23. B. Dutta, A. Dey, C. Sinha, P. P. Ray and M. H. Mir, *Inorg. Chem.*, 2018, **57**, 8029.
24. K. M. Hutchins, T. P. Rupasinghe, L. R. Ditzler, D. C. Swenson, J. R. G. Sander, J. Baltrusaitis, A. V. Tivanski

Dutta *et al.*: Exploration of [2+2] photodimerization of coordination polymers in various applications

- and L. R. MacGillivray, *J. Am. Chem. Soc.*, 2014, **136**, 6778.
25. J.-Y. Sima, H.-X. Li, D. J. Young, P. Braunstein and J.-P. Lang, *Chem. Commun.*, 2019, **55**, 3532.
 26. B. Dutta, R. Jana, A. K. Bhanja, P. P. Ray, C. Sinha and M. H. Mir, *Inorg. Chem.*, 2019, **58**, 2686.
 27. Y. K. Wu, L. Qin, C. Fan, S. L. Cai, T. Zhang, W. H. Chen, X. Y. Tang and J. X. Chen, *Dalton Trans.*, 2019, **48**, 8911.
 28. M. Villa, M. Roy, G. Bergamini, M. Gingras and P. Ceroni, *Dalton Trans.*, 2019, **48**, 3815.
 29. W. J. Gong, Z. G. Ren, H. X. Li, J. G. Zhang and J.-P. Lang, *Crys. Growth Des.*, 2017, **17**, 870.
 30. W. X. Li, J.-H. Gu, H. X. Li, M. Dai, D. J. Young, H. Y. Li, and J.-P. Lang, *Inorg. Chem.*, 2018, **57**, 13453.
 31. G. K. Kole, R. Medishetty, L. L. Koh and J. J. Vittal, *Chem. Commun.*, 2013, **49**, 6298.
 32. E. Elacqua, P. Kaushik, R. H. Groeneman, J. C. Sumrak, D.-K. Buëar and L. R. MacGillivray, *Angew. Chem. Int. Ed.*, 2012, **51**, 1037.
 33. M. A. Sinnwell and L. R. MacGillivray, *Angew. Chem. Int. Ed.*, 2016, **55**, 3477.
 34. L. L. Ma, Y. Y. An, L. Y. Sun, Y. Y. Wang, F. E. Hahn and Y. F. Han, *Angew. Chem. Int. Ed.*, 2019, **58**, 3986.
 35. B. Dutta, C. Sinha and M. H. Mir, *Chem. Commun.*, 2019, **55**, 11049.
 36. A. Gheorghe, T. Chinnusamy, E. Cuevas-Yañez, P. Hilgers and O. Reiser, *Org. Lett.*, 2008, **10**, 4171.
 37. M. H. Xie, X. L. Yang and C. D. Wu, *Chem. Eur. J.*, 2011, **17**, 11424.
 38. H. Sato, R. Matsuda, M. H. Mir and S. Kitagawa, *Chem. Commun.*, 2012, **48**, 7919.
 39. M. H. Xie, X. L. Yang and C. D. Wu, *Chem.-Eur. J.*, 2011, **17**, 11424.
 40. R. Medishetty, A. Husain, Z. Bai, T. Runëevski, R. E. Dinnebier, P. Naumov and J. J. Vittal, *Angew. Chem. Int. Ed.*, 2014, **53**, 5907.
 41. R. Medishetty, S. C. Sahoo, C. E. Mulijanto, P. Naumov and J. J. Vittal, *Chem. Mater.*, 2015, **27**, 1821.
 42. M. A. Garcia-Garibay, *Angew. Chem. Int. Ed.*, 2007, **46**, 8945.
 43. Z. Skoko, S. Zamir, P. Naumov and J. J. Bernstein, *J. Am. Chem. Soc.*, 2010, **132**, 14191.
 44. M. Irie, S. Kobatake and M. Horichi, *Science*, 2001, **291**, 1769.
 45. R. Samanta, D. Kitagawa, A. Mondal, M. Bhattacharya, M. Annadhasan, S. Mondal, R. Chandrasekar, S. Kobatake and C. M. Reddy, *ACS Appl. Mater. Inter.*, 2020, **12**, 16856.
 46. R. Samanta, S. Ghosh, R. Devarapalli and C. M. Reddy, *Chem. Mater.*, 2018, **30**, 577.
 47. P. Naumov, J. Kowalik, K. M. Solntsev, A. Baldrige, J.-S. Moon, C. Kranz and L. M. Tolbert, *J. Am. Chem. Soc.*, 2010, **132**, 5845.
 48. N. K. Nath, M. K. Panda, S. C. Sahoo and P. Naumov, *CrystEngComm.*, 2014, **16**, 1850.
 49. B. B. Rath and J. J. Vittal, *J. Am. Chem. Soc.*, 2020, **142**, 20117.
 50. J. A. Lv, Y. Liu, J. Wei, E. Chen, L. Qin and Y. Yu, *Nature*, 2016, **537**, 179.
 51. Y. X. Shi, W. H. Zhang, B. F. Abrahams, P. Braunstein and J. P. Lang, *Angew. Chem. Int. Ed.*, 2019, **58**, 9453.
 52. P. Hosseini, C. D. Wright and H. Bhaskaran, *Nature*, 2014, **511**, 206.
 53. N. Y. Li, J. M. Chen, X. Y. Tang, G. P. Zhang and D. Liu, *Chem. Commun.*, 2020, **56**, 1984.

