Stacking of double bonds for photochemical [2 + 2] cycloaddition reactions in the solid state†

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trans-1,2-Bis(4-pyridyl)ethylene (bpe), containing a C=C bond, has been extensively studied for solid-state photochemical [2 + 2] cycloaddition reactions, in discrete molecular and metal complexes, hydrogen bonded and coordination polymeric structures. The challenges in orienting a pair or more of bpe molecules in the solid-state using crystal engineering principles, and their photochemical behaviour and implications, based on Schmidt's postulates, are discussed.

1. Introduction

Solid-state photochemical [2 + 2] cycloaddition reaction is a unique solvent-less and a green way of synthesizing *regio*- and stereospecific highly strained cyclobutane derivatives.[1–10] Systematic studies by Schmidt and his co workers inevitably led to the introduction of topochemical postulates—the specific geometric criteria for the solid-state photochemical [2 + 2] cycloaddition reactions.[6] Due to the existence of a stream of molecules whose photochemical behaviour could not be accounted by this topochemical principle, Schmidt highlighted the limitations of this rule three decades ago and urged the need for detailed investigation and new techniques to study the reaction mechanism.[1,6] This provokes the study of the mechanistic pathway of the reaction, and dependence of the course of the reaction on the crystal texture in addition to the packing principles of the monomers that either obey the topochemical principle or not.[1–2,11–14] Microscopic techniques such as atomic force microscopy (AFM), scanning near field optical microscopy (SNOM) have unraveled the mysteries behind these topochemically defective reactions and resulted in extended solid-state mechanisms from Kaupp and his co-workers.[11] Attempts to investigate the detailed mechanism of solid-state transformations through (i) vibrational spectroscopy which monitors the topotactic nature, (ii) solid-state NMR which deals with the conformational details of possible intermediate states, (iii) AFM techniques which is only a surface study, and (iv) theoretical studies, revealed that the success of all these techniques is possible only with the combination of single-crystal X-ray crystallography.[6–15] It is well known that maintaining single crystallinity during topochemical reactions and the respective single-crystal to single-crystal transformation (SCSC) are rare phenomena.[15] Hence, the inability to retain single crystalline nature hampered the development of topochemical studies. Though

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these days 3D structures can be deduced from powder X-ray diffraction data, this has its own limitations and there is a need for new tools to deduce the structure and packing patterns for this purpose.[16]

A number of review articles have appeared on solid-state photochemistry exclusively on organic systems.[1,10] There are also reports dealing with the facts and findings on the locus of the reaction and discussion on the pathways for the defective systems to be effective for photodimerization upon UV irradiation.[1,11–12] Crystal engineering principles have been utilized to orient the $C{=}C$ bonds in a position suitable for photodimerization by the judicious choice of donor and acceptor groups with respect to the starting material.[10] Though these recent review articles highlight on the use of metal organic systems in addition to the organic molecules, they deal mainly with the construction of defect-free photoactive systems with 100% photodimerization.

Our research started with a focus on crystal engineering of olefin containing ligands in coordination polymeric structures and their photochemical activity with respect to topochemical principles.[17] Our recent reports on enforcing partially photodimerizable systems to 100% photodimerizable systems by inducing desolvation,[18] dehydration[19] and by accelerating the reaction using mechanical forces such as grinding[20] have further increased the need and utility to study the solid-state photochemical reactions. Detailed investigation on the crystal packing and locus of the reaction resulted in resolving and improving the product formation which deals with the molecular movements, pedal-like motion, *etc*. Despite the fact that thousands of photodimerization reactions have been carried out using Schmidt's topochemical criteria, this has not been used as a tool to study the mobility of molecules in solid-state reactions. Only recently it has been demonstrated that it is possible to deduce the solid-state transformations and the most probable 3D structure after transformation using Schmidt's topochemical criteria in crystals that cannot retain the single crystallinity during the reaction.[19] Also photochemical [2 + 2] cycloaddition reactions in higher dimensional systems have not been investigated so far.

2. Strategies for the alignment of olefinic bonds

Kohlschutter's topochemical postulate in 1916 has been reformulated by Schmidt in his seminal work on photochemical [2 + 2] cycloaddition which states that *solid state reactions are topochemically controlled with a minimum amount of atomic or molecular movement*. Hence it is hypothesized that photodimerization reaction is strongly dependent on the nonbonding $C\cdots C$ distance (<4.2 Å) and the parallel alignment of the olefinic bonds of the two reacting molecules.[1,6] This also ensures that the p_z orbitals of the double bonds are nearly collinear and overlap sufficiently to react.

Although the geometric criteria for photochemical reaction in crystals have been well studied, still it is a challenge to align the double bonds in the solid state. Hence, for further advancement of the solid-state photochemical [2 + 2] cycloaddition chemistry, it is a pre-requirement to understand the crystal engineering principles that have been utilized so far to orient the $C{=}C$ bonds suitable for this reaction. Since our work is concerned with *trans*-1,2-bis(4-pyridyl)ethylene or 4,4′-bipyridylethylene (bpe), we limit our discussions only to bpe systems.

Up to now most of the photochemical [2 + 2] cycloaddition reactions in the solid state deal with the alignment of a pair of olefinic bonds in a discrete and serial fashion.[6–8,10] Investigations on the alignment of more than two double bonds in a parallel manner is still in its infancy.[9,20–23] This might be due to the inherent complications during photodimerization reactions, the difficulty in the isolation of 100% photodimerized product and the probable loss of single crystallinity during the reaction. First the discussion will be focused on stacking a pair of $C{=}C$ bonds of bpe in discrete systems, then in a serial manner and finally, in a parallel fashion. While searching the Cambridge Structural Database (CSD) we could also extract many hits with well positioned $C{=}C$ bonds of bpe satisfying Schmidt's topochemical postulate but their photoreactions are yet to be studied.[24] Here we also include some of these examples in our discussion.

The dimerization of bpe molecules can potentially yield a tetrakis(4-pyridyl)cyclobutane (tpcb) derivative with four possible regioisomers, *rctt*, *rtct*, *rcct* and *rccc*, as shown in Fig. 1. Of these the most favorable *rctt*-tpcb isomer has been isolated in the majority of cases. Here *rctt*, for example, means regio *cis*,*trans*,*trans* and the geometrical isomers are described with reference to a single pyridyl group, in a clockwise manner.

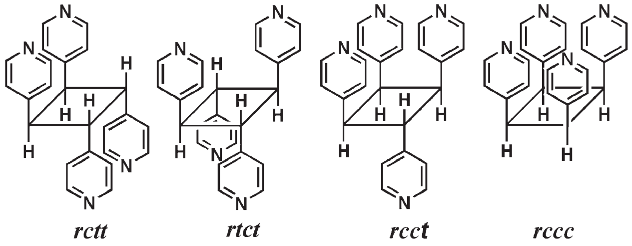

Fig. 1 Pictorial representations of the possible regioisomers of tpcb.

3. Alignment of a pair of olefinic bonds

A number of non-covalent interactions such as hydrogen bonds, charge transfer, chlorine$\cdots$chlorine and $\pi\cdots\pi$ interactions have been successfully exploited to orient the double bonds suitable for photoreactions.[1,8,9,25] A typical alignment of double bonds involving benzene–perfluorobenzene systems are shown in Fig. 2.[9] Interestingly [2 + 2] photopolymerization was also achieved on irradiation of *trans*,*trans*-1,4-bis(2-phenylethenyl)-2,3,5,6-tetrafluorobenzene but the single crystallinity was not maintained (Fig. 2(b)).

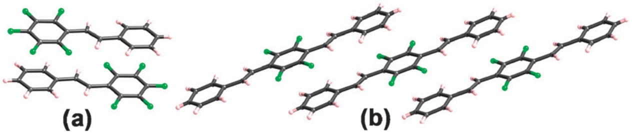

Fig. 2 Packing diagrams of (a) *trans*-pentafluorostilbene and (b) *trans*,*trans*-1,4-bis(2-phenylethenyl)-2,3,5,6-tetrafluorobenzene.

3.1 Hydrogen bond driven discrete molecular assembly

Hydrogen bond driven molecular assemblies developed in MacGillivray's laboratory are donor–acceptor molecular complexes stabilized by the hydrogen bonds to align a pair of double bonds.[10] For example, if hydrogen-bond acceptors such as pyridine are used as part of the olefin containing molecule, then the molecule with hydrogen-bond donor groups, called an anchor or clip, is used to bind a pair of double bonds using the directional properties of the X–H$\cdots$N bonds. Actually the anchors can either act as a donor or acceptor with respect to the olefin system.[26–30]

Using this principle, the C=C bonds in a pair of bpe molecules have been successfully aligned in parallel using 1,3-dihydroxybenzene (resorcinol), and its derivatives or 1,8-naphthalenedicarboxylic acid (1,8-nap) as bifunctional clipping agent (Fig. 3 and 4(a)).[26–29] This resulted in many interesting hydrogen-bonded donor–acceptor molecules with a pair of C=C bonds closely positioned *via* four O–H$\cdots$N hydrogen bonds favoring SCSC photodimerization.[10,26]

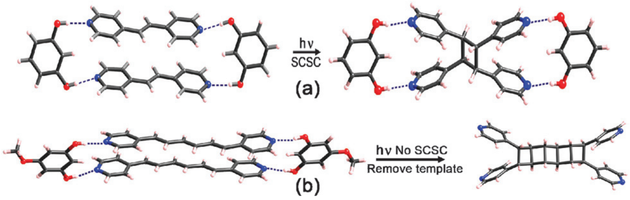

Fig. 3 Resorcinol and methoxyresorcinol as hydrogen bond donors.

On increasing the number of reactive C=C bonds from one to three in the dipyridyl derivative, ladderanes (as shown in Fig. 3(b)) and cyclophanes have been successfully isolated which were otherwise very tedious and laborious to be synthesized by traditional methods.[27] The robustness of molecular clips such as resorcinol derivatives in positioning the double bonds to fulfill Schmidt's geometric criteria has gained entry in undergraduate research laboratory reactions.[28]

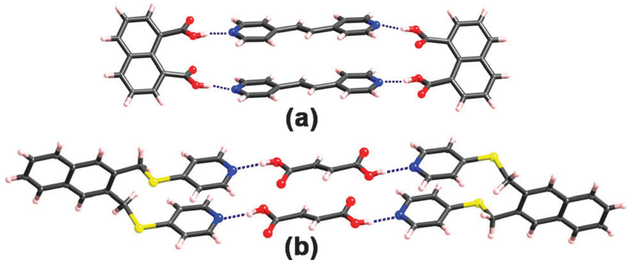

Fig. 4 Representation of code reversal by different clipping agents: (a) 1,8-nap as the hydrogen-bond donor, (b) pyridine derivative as hydrogen-bond acceptor.

The hydrogen-bond donor–acceptor groups in the four-component molecular complex (Fig. 4(a)) satisfying Schmidt's criteria can also be reversed by introducing pyridine units as a part of the clipping agent to anchor a photoactive dicarboxylic acid as shown in Fig. 4(b). Although the donor–acceptor code of an existing template-directed solid-state synthesis has been successfully reversed, only about 70% of the double bonds could be cyclized even after 10 days of irradiation. However, this transformation has been observed to proceed *via* a partial SCSC manner.[30]

3.2 Coordination driven discrete molecular assembly

Metal assisted or metal catalyzed solid-state dimerization, oligomerization and polymerization reactions are well known in the literature.[31–34] The reactive C=C bonds in bpe may well be aligned in the metal complexes by making use of the predictable coordination number and geometry of the metal ions.[31,35] Dinuclear complexes formed by metallophilic interactions and/or bridging ligands, in principle, can be employed to orient a pair (or more) of bpe molecules.[31,36–38]

The dinuclear zinc complex $[Zn_2(L^1)(OH)]$ (L^1 = 2,6-bis[*N*-(2-pyridylethyl)formimidoyl]-4-methylphenol) with a metal–metal distance in the order of 3.5 Å has been used to align a pair of C=C bonds of bpe.[36,38] Reaction of bpe with $[Zn_2(L^1)(OH)]^{2+}$ resulted in tetranuclear molecular rectangle $[Zn_4(L^1)_2(OH)_2(4,4'\text{-bpe})_2]^{4+}$ (**1**) as shown in Fig. 5, in which the C=C bonds in the bpe ligands are aligned at 3.64 Å and the SCSC photodimerization has also been demonstrated effectively.

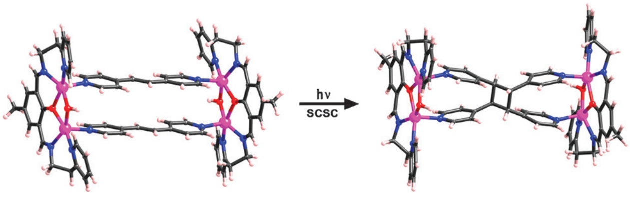

Fig. 5 Schematic representation of the photoreactivity of **1**.

The argentophilic interaction has been utilized to organize the double bonds in the 4-stilbz molecule (4-stilbz = *trans*-1-(4-pyridyl)-2-(phenyl)ethylene) in the silver complex $[Ag_2(4\text{-stilbz})_4](CO_2CF_3)_2$, **2** (Fig. 6).

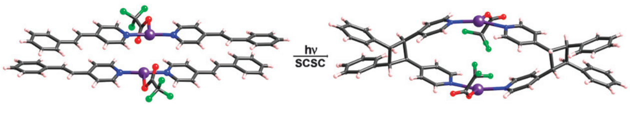

Fig. 6 Schematic representation of the photoreactivity of **2**.

Surprisingly the criss-cross alignment of C=C bonds in this molecule undergoes pedal motion under UV radiation and resulted in 100% isolation of single *rctt*-1,2-bis(4-pyridyl)-3,4 bis(phenyl)cyclobutane isomer instead of the expected *rtct* isomer.[39] Such pedal motions have been well-documented in the literature.[40]

On introducing an organometallic clip, $Cp^*_2M_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2O_4)\text{-}Cl_2]$ (M = Rh, Ir) to anchor the double bonds of bpe, resulted in $[Cp^*_4M_4(\mu\text{-bpe})_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2O_4)](OTf)_4$ [M = Rh **3**, Ir **4**], as shown in Fig. 7.[41,42] The photoreactivity of the tetranuclear rectangular boxes is shown in Fig. 7.[42]

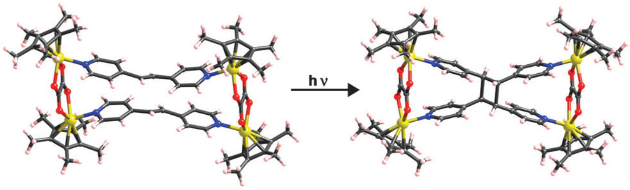

Fig. 7 Schematic representation of the photoreaction of **3**.

Cambridge Structural Database (CSD) search reveals that a few molecular rectangles[37] such as $[\{L^1(\mu\text{-OH})Cu_2\}_2\{\mu\text{-bpe}\}_2](ClO_4)_4\cdot 4H_2O$, (**5**) and $[\{L^2CuZn\}_2\{\mu\text{-bpe}\}_2]$ $(ClO_4)_4\cdot 4.5CH_3OH$, (**6**) generated from dinuclear copper complex $[Cu_2L^1(OH)]^{2+}$, and heterodinuclear $[CuZnL^2]^{2+}$ (L^2 = bis-[2,6-{*N*,*N*′-(1,2-diaminoethyl)(diethylenetriamine) formimidoyl}-4-methylphenol]) with well aligned C=C of bpe ligands are suitable for photocyclization reaction, but may or may not have SCSC transformation due to the presence of lattice water. These molecular rectangles are similar to the Zn(II) analogue which readily undergoes SCSC photodimerization.[38] Some further complexes, namely $[Ag_4(\mu\text{-dppm})_2(\mu\text{-bpe})_2](O_2CCF_3)_4$ (**7**) and $[Au_4(\mu\text{-dppe})_2(\mu\text{-bpe})_2](O_2CCF_3)_4$ (**8**) (where dppm = diphenylphosphinomethane and dppe = diphenylphosphinoethane) synthesized in Puddephatt's laboratory also satisfy Schmidt's geometric criteria.[43] The alignment of C=C bonds in these 'molecular rectangles' prompted us to investigate their photoreactivity.[44] Here the dinuclear Ag(I)/Au(I) complexes derived from the phosphino metal precursors as shown in Fig. 8 have been used as an anchor to align the double bonds of bpe ligands.

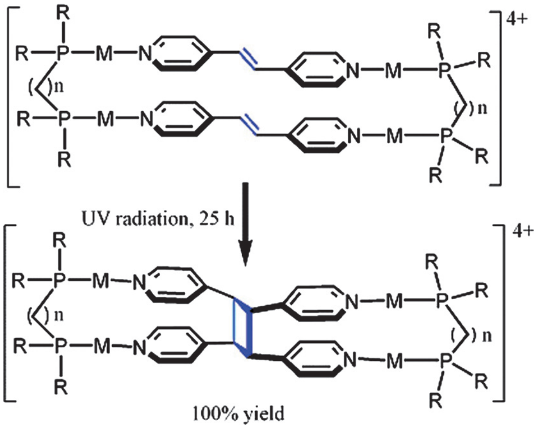

Fig. 8 Schematic representation of photoreaction of the complexes **7** (M = Ag, *n* = 1) and **8** (M = Au, *n* = 2) R = Ph.

Though SCSC was not achieved, the ^1H NMR spectra clearly reveal complete photo-conversion of these complexes after irradiating the compounds under a UV lamp for 24 h. To our surprise, the Au(I) complex undergoes 100% photodimerization also in solution and ^1H NMR indicates the formation of stereo-specific single product *rctt*-tpcb in quantitative yield implying the robustness of the Au(I) complex cation in solution.[44]

4. Alignment of a pair of olefinic bonds in serial fashion

4.1 Hydrogen-bond driven infinite molecular assembly

Fig. 9 shows the 1D hydrogen-bonded tapes formed by co-crystallizing the multifunctional clipping agent 1,2,4,5-benzenetetracarboxylic acid (bta) with bpe. On UV irradiation, the powdered crystalline sample, bta·2bpe (**9**) containing the well-aligned bpe pairs in between the bta clips resulted in 100% photodimerized product as expected.[21]

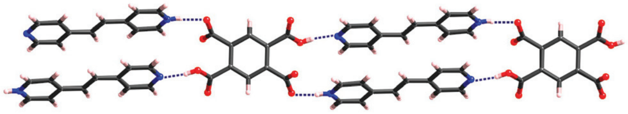

Fig. 9 Packing pattern of bta·2bpe, **9**.

4.2 Halogen-bond driven infinite molecular assembly

Apart from the hydrogen bonds, weaker non-covalent interactions have also been elegantly exploited to preorganize the olefinic bonds of bpe in order to facilitate photochemical [2 + 2] cycloaddition reaction in the solid state. For instance, 1D ribbon-like structures are formed between pentaerythritol ether and bpe pairs (**10**) through N···I interactions (Fig. 10). The well-aligned bpe pairs arranged in a serial fashion furnished 100% photodimerized product, *rctt*-tpcb.[45]

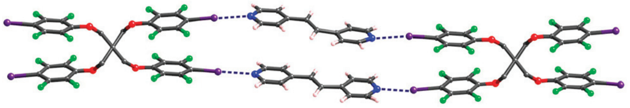

Fig. 10 Packing pattern of the N···I bonded 1D tape of **10**.

4.3 Hydrogen-bond driven infinite coordination complexes

Though the strength and directionality of the hydrogen bonds have been sophisticatedly exploited to align the double bonds, hydrogen-bonded metal complexes have rarely been utilized for this purpose. Such studies on flexible hydrogen-bonded metal complexes provide an opportunity to isolate other stereoisomers of the cyclobutane derivative which have not been encountered in organic systems.

Briceño *et al.* have synthesized two hydrogen-bonded isomeric complexes **11** and **12** of $[Mn(NCS)_2(OH_2)_4]\cdot 4(\text{bpe-2})$ (bpe-2 = *trans*-1,2-bis(2-pyridyl)ethylene) both having two thiocyanate ligands in *trans* fashion.[23] In one isomer, of the four lattice bpe-2 molecules which are sustained by O–H···N interactions, only a pair of bpe-2 molecule is related by a twofold rotation axis which resulted in a criss-cross arrangement of olefinic bonds and also shows the shortest distance of 3.23(2) Å between them. The other two bpe-2 molecules were not expected to be photoreactive due to unfavorable distance and geometry. These criss-cross olefinic bonds undergo cycloaddition under UV light to produce the *rtct*-tpcb isomer quantitatively. It has been found that the bpe-2 molecules held by O–H···N bonds do not undergo pedal motion as observed in other organic systems (*vide infra*), probably due to very strong interactions between the olefinic bonds. On the other hand, in the second isomer, which has parallel disposition of double bonds separated by 3.39(3) Å, the expected *rctt*-tpcb was produced upon UV irradiation.

In the process of employing different metal systems with carboxylates group to anchor the bpe ligands, the reaction of lead(II) acetate in CF_3CO_2H with bpe resulted in an interesting hydrogen-bonded coordination complex.[46] The 1D hydrogen-bonded zwitterionic Pb(II) complex, $[Pb(bpe\text{-}H)_2(CF_3CO_2)_4]$, (**13**) has parallel disposition of bpe-H^+ ligand pairs with an ethylenic C···C distance of 3.87 Å stabilized by the π···π interactions between the pyridyl rings as shown in Fig. 11. The coordinated bpe pairs easily undergo photocyclization under UV irradiation quantitatively to give the anticipated *rctt*-tpcb isomer. The colorless block-like crystals turned into a gel in 1–15 h and became a powder after 25 h of UV irradiation. It may be noted that only one of the nitrogen atoms of the bpe-H^+ is coordinated to Pb(II) and the other protonated pyridyl nitrogen is hydrogen bonded to the neighbouring oxygen atom of the $CF_3CO_2^-$ ligand. During photodimerization, two CF_3CO_2H are eliminated due to the proton transfer from bpe-H^+ to $CF_3CO_2^-$ ligand bonded to the Pb(II), resulting in $[Pb(rctt\text{-}tpcb)(CF_3CO_2)_2]_n$. The photodimerized Pb(II) complex undergoes acid catalyzed isomerization reaction in solution to give *rtct* and *rcct*-tpcb isomers. One of these isomers has been isolated as $[Pb(rcct\text{-}tpcb)(CF_3CO_2)_2]$ which has a zigzag folded 2D coordination polymeric sheet-like structure along with 1D coordination polymeric $[Pb(rctt\text{-}tpcb)(CF_3CO_2)_2]$. It appears that the protonation of two uncoordinated pyridyl nitrogen atoms in the tpcb ligand and residual CF_3CO_2H are responsible for the isomerization of the cyclobutane derivatives in solution. Such isomerization does not occur in complexes which do not have free pyridyl nitrogen, on addition of CF_3CO_2H.

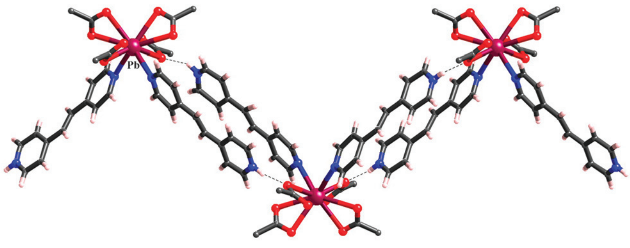

Fig. 11 A portion of the 1D hydrogen-bonded **13** (the disordered atoms and fluorine atoms are not shown for clarity).

Hill and Briceño reported $Mn(2,4\text{-}bpe)_2(OH_2)_4](ClO_4)_2\cdot 2(2,4\text{-}bpe)\cdot 2H_2O$ (**14**) and $[Mn(2,4\text{-}bpe)_2(NCS)_2(OH_2)_2]$ (**15**) hydrogen-bonded metal complexes (2,4-bpe = *trans*-1-(2-pyridyl)-2-(4-pyridyl)ethylene) in which the coordinated and free 2,4-bpe in the lattice have been found to align in parallel through hydrogen bonding and both produced the *rctt* stereoisomer quantitatively.[47] However a mixture of *rctt* and *rcct* isomers were formed in 1 : 1 ratio with a total conversion of 91% by refluxing **15** in H_2O–CH_2Cl_2 but not **14**. It may be noted that both **14** and **15** have free uncoordinated pyridyl groups, and the inertness towards isomerization of **14** may be presumed to be due to lack of acidity in the solution.[47]

4.4 Coordination driven infinite molecular assembly

For coordination polymeric structures, 1D coordination polymers with ladder structures are the simplest and most suitable to closely orient the double bonds in the spacer ligands such as bpe.[48,49] The distance between the double bonds can be controlled by judicious combinations of the metal ions and bridging ligands. The major challenge in this methodology is to get the appropriate experimental conditions to isolate the desired ladder structures.[17,48,49] Anchoring pairs of bpe ligands in an infinite serial fashion has been accomplished by using simple zinc carboxylate salt which resulted in the desired 1D coordination polymers, $[\{(CH_3CO_2)(\mu\text{-}O_2CCH_3)Zn\}_2(\mu\text{-}bpe)_2]_n\cdot$(**16**) and $[\{(CF_3CO_2)(\mu\text{-}O_2CCH_3)Zn\}_2(\mu\text{-}bpe)_2]_n$ (**17**). Though complete photodimerization of the coordination polymer, **16** could be achieved the crystals were cracked upon irradiation. When 50% of the acetate ions were replaced by $CF_3CO_2^-$ ions, the resultant **17** (shown in Fig. 12) undergoes 100% topochemical photodimerization in a SCSC manner.[17] The fluorine atoms in the molecule allow the crystal to withstand the strain generated during photodimerization.

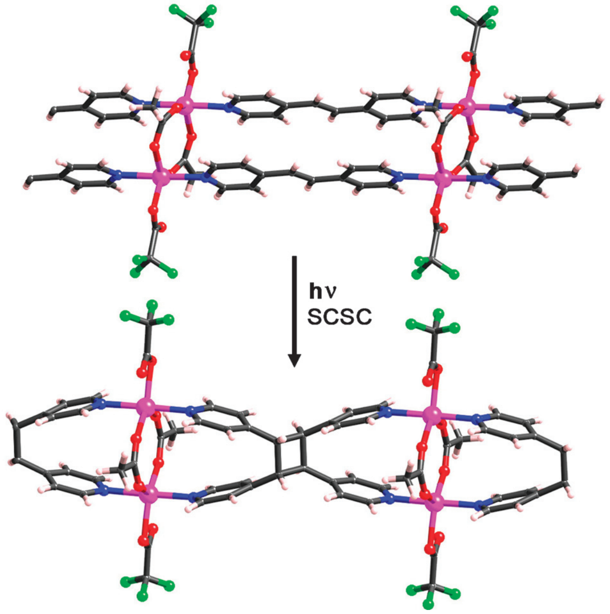

Fig. 12 Representation of the SCSC photoreactivity of **17**.

The dinuclear complex cation $[Zn_2(L^1)(OH)]^{2+}$ described in section 3.2 for orienting a pair of bpe have also been used to align infinite pairs of bpe ligands in the 1D coordination

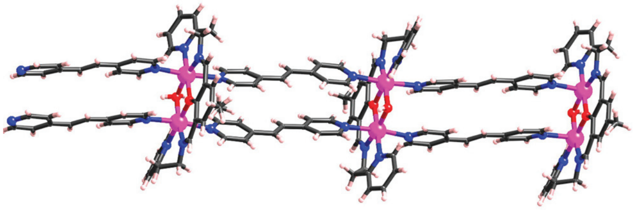

Fig. 13 Perspective view of the 1D ladder coordination polymer, **18**.

polymer, $[Zn_2(L^1)(OH)(\mu\text{-bpe})_2](ClO_4)_2\cdot 4H_2O$, (**18**) shown in Fig. 13.[50] The photoconversion has been found to be 100%, however, no SCSC transformation could be observed due to the loss of lattice water and hence the single crystalline nature in the process.

The use of metallophilic interactions in the alignment of a pair of bpe ligands in discrete metal complexes has been discussed in section 3.2. The same principle can be extended to align infinite pairs of bpe ligands in 1D coordination polymers. A number of Ag(I) containing coordination polymers with ladder structures have been extensively studied by Schröder's group.[49] The solid-state structure of the Ag(I) coordination polymer, $[\{(\mu\text{-}CF_3CO_2)Ag\}_2(\mu\text{-bpe})_2]\cdot H_2O$, **19** (Fig. 14) was found to contain the expected well-aligned infinite bpe ligand pairs stabilized by Ag···Ag interactions, carboxylate bridging, and π···π interactions but the solid-state structure was heavily disordered.[18] Nevertheless, this compound undergoes 100% photodimerization under UV light as confirmed by ^{1}H NMR of the UV irradiated product. Due to the loss of water molecules during irradiation, the SCSC transformation was not observed.

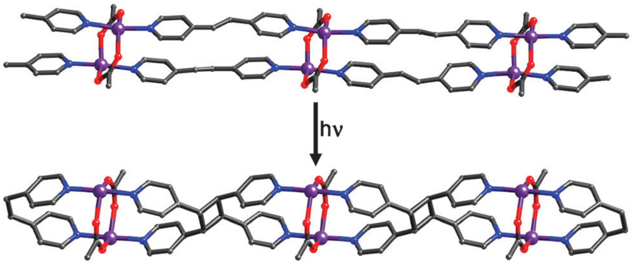

Fig. 14 1D ladder coordination polymer **19** (where hydrogens are omitted for clarity) and the probable photodimerized product.

A quick search of the CSD reveals an interesting acetate-bridged coordination polymeric cation in $[\{Cu(CH_3CO_2)(H_2O)\}_2(\mu\text{-bpe})_2][Cu_2(nta)_2(bpe)]_2$ (**20**) shown below in Fig. 15 which was obtained from the self-assembly reaction of $Cu(CH_3CO_2)_2\cdot 2H_2O$, nitrilotriacetic acid (nta, $N(CH_2COOH)_3$) and bpe.[51]

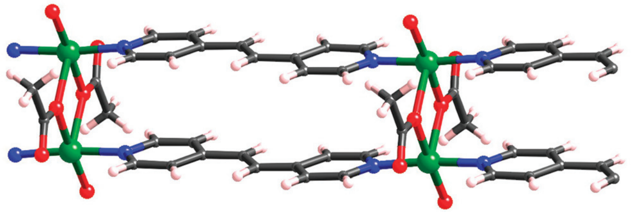

Fig. 15 A portion of the 1D coordination polymer of the cationic fragment in **20**.

Though bpe ligands in the above coordination polymer satisfies Schmidt's geometric criteria, their photo-reactivity is yet to be evaluated.

All the above results indicate that it is possible to orient the C=C bonds of the bpe units using metal carboxylates. Alignment of double bonds of the bpe ligands using various supramolecular interactions in organic, metal complexes and metal–organic frameworks (MOFs) have not only enhanced our knowledge in solid-state photochemistry but also help us to generalize the crystal engineering principles to assemble molecules at will in the solid state.

5. Alignment of more than two olefinic bonds

To date, major interest has been focused on (i) the alignment of photoactive molecules congenial for the photochemical [2+2] cycloaddition reactions in organic and coordination complexes and (ii) quantitative isolation of a single stereo-specific photodimerized product in the solid state. This could, most probably, be achieved successfully in the systems with a pair of aligned double bonds satisfying Schmidt criteria. To the best of our knowledge the photoreactivity has not been much investigated in solids containing more than a pair of aligned double bonds in a parallel or criss-cross orientation and maintaining Schmidt's distance criterion. It will be of immense interest to investigate the structural changes and the nature of products formed in these systems on exposure to UV light. The following sections are categorized with respect to the number of double bonds in the crystal structures irrespective of the type of supramolecular interactions responsible for the alignment of C=C bonds.

5.1 Alignment of three olefinic bonds in a parallel fashion

Co-crystallization of the trifunctional clip, tricarballylic acid (tca) with bpe resulted in a 1D hydrogen bonded tapes, **21** (bpe·tca) in which three bpe molecules are aligned in parallel (as shown in Fig. 16) with C=C distance of 3.82 Å and meet the criteria proposed for photodimerization reaction.[21]

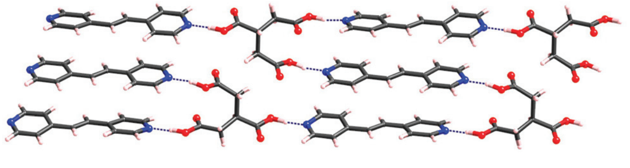

Fig. 16 Packing pattern of the 1D hydrogen bonded tape, **21**.

It has been reported that UV irradiation of the co-crystals resulted in 90% photodimerized product. In a three-layer arrangement of bpe where two thirds of the bpe can only undergo photodimerization, the observed percentage conversion is surprisingly much greater than expected. The SCSC conversion is not observed and suggests that the 90% photodimerization can only be achieved through reactions with the neighboring hydrogen-bonded strands. A detailed analysis of the packing revealed that the C=C bonds from the adjacent tapes are indeed closer to one another with an inter-tape

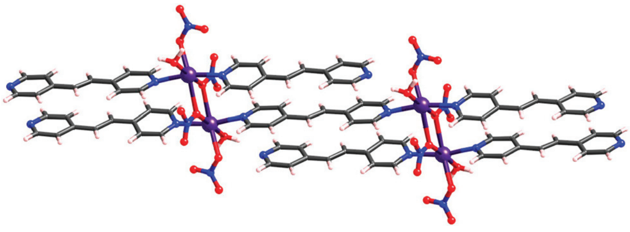

Fig. 17 View of a the 1D zigzag coordination polymer, **22**.

distance of 3.59 Å. Sliding motion of these molecules can account for the observed high yield.

Fig. 17 shows an interesting crystal structure that contains a 1D zigzag coordination polymer $[\{Cd(NO_3)_2(H_2O)(bpe)\}_2(\mu\text{-}bpe)]_n$ (**22**) with three bpe ligands aligned parallel, satisfying Schmidts geometric criteria but its photoreactivity has not been studied.[52] This molecule will be a good candidate to rationalize the movements of molecules, if any.

5.2 Alignment of six olefinic bonds in parallel and criss-cross fashion

The 1D hydrogen-bonded $[Zn(bpe)_2(H_2O)_4](NO_3)_2\cdot 8/3H_2O\cdot 2/3bpe$ (**23**) is isotypical to the Co(II) complex reported in the literature.[53] In the solid state, each Zn(II) cation in $[Zn(bpe)_2(H_2O)_4]^{2+}$ has two uncoordinated pyridyl rings which form complementary O–H···N hydrogen bonds with one of the hydrogen atoms of the neighboring coordinated water molecules resulting in a hydrogen-bonded 1D polymer as shown in Fig. 18.[20] The hydrogen-bonded strands are stacked in the (101) plane such that six bpe ligands have been found aligned in the distance range of 3.548–3.884 Å as shown in Fig. 18. The nitrate anions, lattice water and free bpe molecules are sandwiched between the $[Zn(bpe)_2(H_2O)_4]^{2+}$ cationic layers alternately. This is the first time that six olefins in a row has been found in a crystal structure to satisfy Schmidt's distance criterion, of which four lie in criss-cross fashion (around Zn2) and two have parallel orientation (bonded to Zn1).

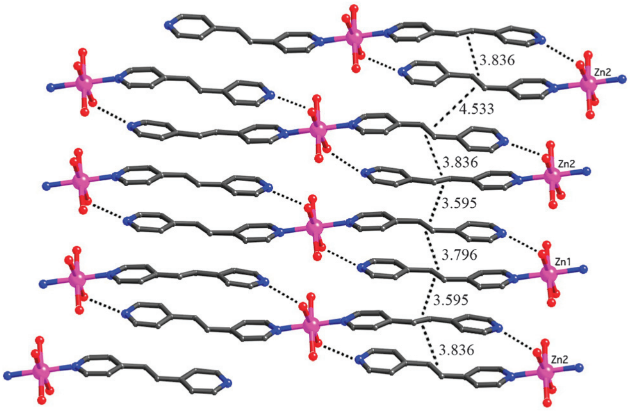

Fig. 18 A view from the *a*-axis showing the details of the alignments of double bonds in the hydrogen-bonded 1D polymeric structures present in **23**. The hydrogen atoms have been omitted for clarity.

Although criss-cross alignments of the C=C bond pairs have been studied for their photoreactivity,[54,55] both parallel and criss-cross arrangement of double bonds in a single compound has not been tested before for this purpose. The assembly of olefins in this hydrogen-bonded metal complex offers a unique possibility for the regiocontrolled access in the solid state.

Single crystals of 1D hydrogen-bonded complex **23** have been found to undergo photochemical [2 + 2] cycloaddition reactions and furnished tpcb in up to 46% yield in 25 h of UV irradiation, of which 39% is *rctt*-tpcb, and 7% is the *rtct*-tpcb isomer as monitored by ^{1}H NMR spectroscopy. However the percentage of *rtct*-tpcb formed is much lower than the expectation based on the presence of more anti-parallel orientation of the double bonds. These C=C bonds aligned in criss-cross fashion are well-known to undergo pedal motion prior to photodimerization in the solid-state[40,54,55] and such pedal motion in C=C bonds of *trans*-stilbene has been well studied by Ogawa and co-workers.[40] Further, the light-induced pedal-like motion of the double bonds to parallel dispositions have also been studied by Ramamurthy and others.[55] Hence, it may be concluded that the formation of more *rctt* isomer observed here may be attributed to this motion.

Mechanical grinding has been found to accelerate the pedal motion of the criss-crossed olefins to parallel alignment as well as the movements of free bpe in the lattice. For example, 5 min ground single crystals of **23** yielded 100% photocyclized product tpcb, when exposed under UV light for 25 h. This product still contains 11–13.4% of the *rtct* isomer which is likely to have originated from the free uncoordinated bpe molecules in the lattice. Molecular movements of these lattice bpe molecules are expected to produce both *rtct* and *rctt* in equal ratio, *i.e.*, 12.5% *rctt* isomer in the overall yield.[56,57] In other words, all the criss-cross bpe pairs attached to Zn2 were converted to parallel pairs during the grinding process whereas only ~50% of the free bpe molecules have undergone rotation during molecular movements, to account for the observed ~88% *rctt* isomer. The 100% photoreactivity confirms the movements of the free uncoordinated bpe molecules in the lattice which were separated by more than 7.2 Å. Such mechanically induced molecular migrations in the crystal lattice have been studied by Kaupp *et al.*[11]

6. Photochemical [2 + 2] cycloaddition reaction to study solid-state reactions

Based on Schmidt's criteria, a number of crystal structures containing olefinic double bond pairs have been found to be suitable for photochemical [2 + 2] cycloaddition reactions.[1,10] However, there are many examples where Schmidt's distance criterion was not met, still found to be photoreactive.[1,11] According to Kaupp, the photodimerization can occur in these solids after the molecules are displaced or rearranged to meet Schmidt's geometric criteria.[11] Hence Schmidt's criteria for photodimerization can be used as a tool to study the movements of molecules in the solid state. Some of the recent examples are discussed below.

6.1 Desolvation assisted anisotropic molecular movements

The hydrogen-bonded 1D coordination polymer $[Ag(\mu\text{-}bpe)(H_2O)](CF_3CO_2)\cdot CH_3CN$, (**24**), shown in Fig. 19, was isolated as a kinetic product when attempting to synthesize the ladder

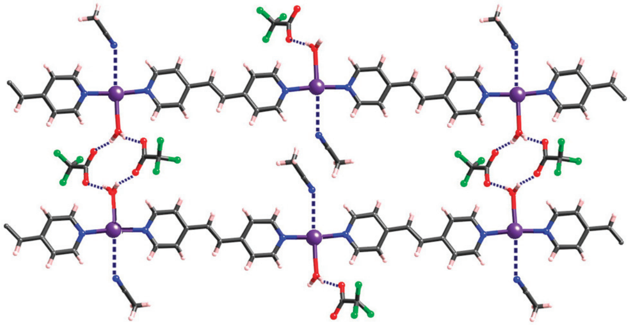

Fig. 19 Packing of the hydrogen-bonded silver complex **24**.

structure similar to **19** but without solvent in the lattice. The bpe ligands in **24** are too far away from each other to satisfy the geometric criteria for photodimerization.[18] The hydrogen atoms of the coordinated water molecules from the two adjacent linear 1D coordination polymeric $[Ag(\mu\text{-bpe})(H_2O)]_n$ chains are hydrogen bonded to the oxygen atoms of the two uncoordinated $CF_3CO_2^-$ ions to form a 12-membered hydrogen-bonded ring [O–H···O, d = 1.87 Å, D = 2.74 Å, θ = 162°]. This connectivity creates a 2D hydrogen-bonded brick wall-like structure approximately in *ac* plane. As per the topochemical principle, this coordination polymer is not expected to undergo photochemical [2 + 2] cycloaddition.[18]

However, the ^1H NMR spectrum of the irradiated product reveals 100% photodimerization which contradicts the topochemical principle. A careful examination of the precursor crystals reveals that desolvation occurs readily which leads to the anisotropic movements of 1D polymers within the crystal. This, in turn, results in the transformation of the 1D coordination polymer to a thermodynamically more stable coordination polymer with ladder structure, where the X-ray powder diffraction pattern of the desolvated complex matched well with the simulated powder pattern of the ladder polymer (**19**). Here 100% photodimerization reaction has been used as a direct evidence for the formation of a ladder structure from the hydrogen-bonded 1D coordination polymer (**24**). Such solid-state structural transformation due to desolvation and subsequent molecular movements in 1D coordination polymers would have been otherwise unnoticed, if the photoreactivity of desolvated **24** were not tested.[18] This clearly supports the extended solid-state mechanism proposed by Kaupp, that crystals which do not obey Schmidt's requirements for [2 + 2] photodimerization reaction can also undergo cycloaddition reaction if the molecules are not interlocked.[11] Though these molecular movements can be induced within the crystal lattice as well as in the solid-state reactions by grinding (mechanochemical reactions), and irradiation, this anisotropic cooperative molecular movements which lead to *chemical reaction* discovered in this system through desolvation have not been realized before. Hence a simple dehydration or desolvation observed in MOFs cannot always be viewed as a *physical phenomenon*.

Reaction of bpe with $Cd(CH_3CO_2)_2{\cdot}2H_2O$, resulted in hydrogen-bonded 1D coordination polymer $[Cd(bpe)(CH_3CO_2)_2(H_2O)]_n$ (**25**).[19] These strands are arranged in parallel and hydrogen bonded to each other through O–H···O interactions between coordinated water and neighbouring carboxylato oxygen atoms to render a 2D array as shown in Fig. 20.

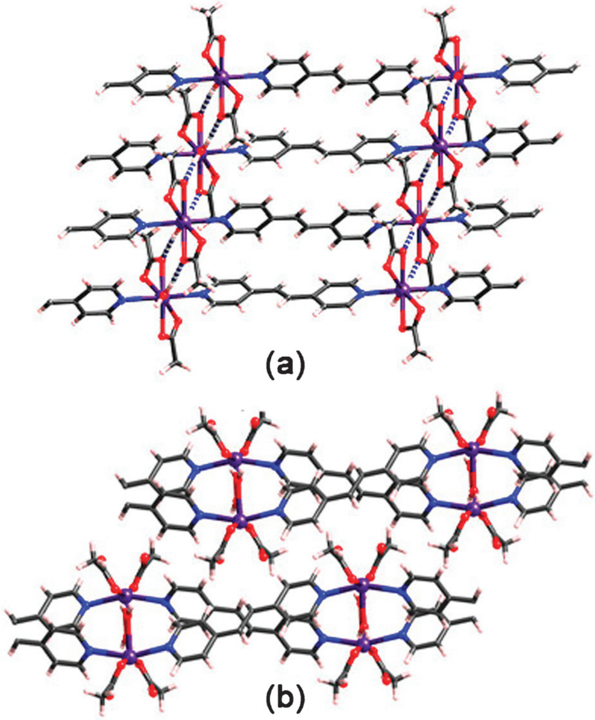

Fig. 20 (a) A view of a portion of the hydrogen-bonded 1D polymer **25**. (b) Another view showing the criss-cross alignment of the ethylenic double bonds and the consecutive layer.

However, this arrangement is not favorable for cycloaddition reaction as the nonbonded C···C distance between the ethylenic carbon atoms of the two bpe ligands in the adjacent chains is 4.33 Å and are arranged in anti-parallel fashion (Fig. 20(b)). Still this polymer with criss-cross alignment of bpe in the single crystal or powdered form resulted in 33% photodimerized product, *rctt*-tpcb probably due to pedal motion of the bpe ligands as discussed earlier, which partially reorient the bpe to parallel fashion prior to photodimerization. Thermogravimetry shows the loss of aqua ligand occurs in the range 67–106 °C with crystal disintegration. The dehydrated sample obtained by heating **25** at 110 °C for 3 h, when subjected to UV radiation for 30 h shows 100% conversion to *rctt*-tpcb.[19]

A close examination of the packing revealed that the non-bonding distance between Cd(II) and the oxygen atom of the carboxylate group involved in O–H···O bonding with the adjacent polymeric chain is 4.44 Å. The removal of coordinated aqua ligand below 100 °C is likely to be due to the formation of a new Cd–O bond with this carboxylate oxygen atom after the water loss.[11,15,58] This will give rise to two possibilities; either a 2D coordination polymer or a 1D coordination polymer with ladder structure. However, 100% photodimerization of the dehydrated sample and ^{113}Cd NMR confirm the formation of the ladder structure after dehydration as shown in Fig. 21.[19] The thermal dehydration causes cooperative pedal motion between the adjacent bpe ligands disposed in criss-cross fashion to form a ladder-like structure with well-aligned bpe pairs ready for 100% photodimerization reaction to furnish the *rctt*-cyclobutane ring exclusively.

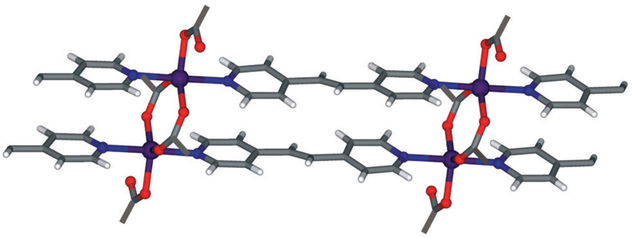

Fig. 21 The proposed structure after dehydration of **25**.

In this work, photodimerization reaction has been used as an invaluable tool to monitor the solid-state structural transformation by thermal dehydration.

7. Alignment of bpe in higher-dimensional networks

The photodimerization ability of the bpe molecules in various hydrogen-bonded 1D polymers, 1D coordination polymers, 2D hydrogen-bonded coordination polymers have been investigated, but in all the cases, the maximum number of bpe molecules aligned in parallel is restricted to six (section 5.2).

Hence it would be of interest to study the movements of bpe molecules which are arranged in an infinite parallel array congenial for photodimerization reactions, under UV radiation. Under these conditions, the bpe molecules may either be held by hydrogen bonds or other relatively weak supramolecular interactions and with enough void space (reaction cavity).[1] This arises a question whether the bpe molecules communicate with each other to undergo 100% cyclization or through a random way to give partial dimerized product.

Photoreactivity of such bpe alignments have not been exploited so far though observation has been made with stilbene. In the co-crystal **26** *trans*-stilbene and *trans*-decafluorostilbene are packed alternately to form an infinite assembly as shown in Fig. 22 with the closest olefin–olefin separation of 3.784 and 3.749 Å and provide 100% photodimerized product on irradiation for 5 h.[9]

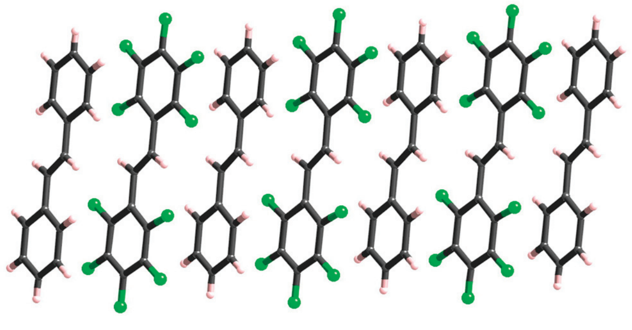

Fig. 22 Molecular packing diagram of the co-crystal, **26**.

According to the authors,[9] the reaction starts from the surface inwardly. The formation of the first dimer causes perturbation of the spacings between the adjacent olefins which resulted in quantitative yield.[9]

The crystal structure of (bpe-H_2)(NO_3)$_2$ (**27**), contains infinite arrangement of bpe-H_2^{2+} cations aligned in parallel along the *b*-axis as shown in Fig. 23.[59] The distance between the centers of the adjacent pyridyl groups is 3.694 Å which is same as the distance between the centers of the adjacent C=C bonds. The nitrate anions are strongly hydrogen-bonded to the pyridinium cations (NO, 2.756 Å, H···O, 1.90 Å, ∠NHO, 160.6°) and several C–H···O interactions are also present to stabilize the crystal structure.

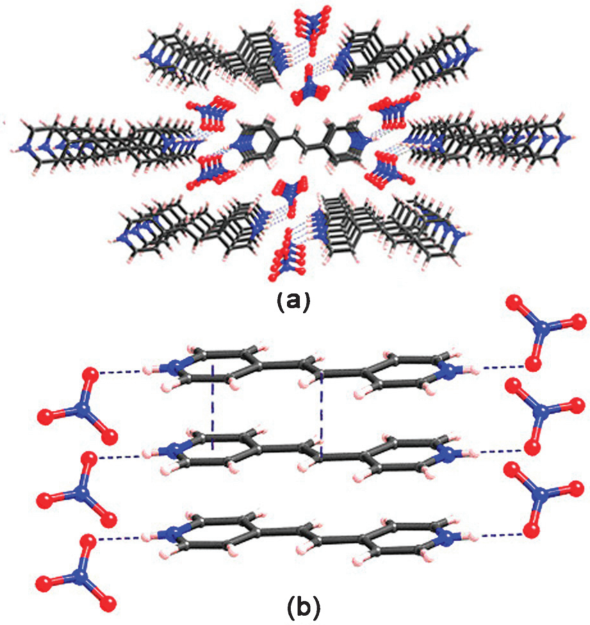

Fig. 23 (a) Perspective view of **27** projected along the *b* axis showing the disposition of nitrate ions and the cation. (b) Clear view of the hydrogen bonding interaction.

This crystalline solid with an interesting infinite array of perfectly parallel alignment of bpe undergoes 100% photodimerization when subjected to UV radiation for 12 h while single crystallinity is not maintained in this process (see ESI†).[44] When the dimerization is initiated, the bpe molecules on the surface presumably first react to form tpcb, which trigger the pairing of bpe molecules in the next and subsequent deeper layers of the crystal and thus guiding the cyclization reaction in harmony leading to quantitative product.

In the recently reported pillared layered MOF, [$Mn_2(HCO_2)_3(bpe)_2(H_2O)_2$]$ClO_4 \cdot H_2O \cdot$bpe, **28** there are two types of bridging bpe ligands.[22] In one type, the bpe ligands are aligned parallel with a large gap in between that is filled by the lattice bpe molecules stabilized by O–H···N bonds (Fig. 24). This arrangement leads to a 1D array of parallel bpe suitable for photodimerization reactions. This compound is expected to give 66% *rctt*-tpcb and indeed 60% conversion has been observed experimentally. The hydrogen-bonded bpe ligands in this system provide the flexibility for photodimerization and the loss of lattice water probably may be responsible for the loss of single crystallinity upon dimerization. Although the alignment of bpe molecules is very similar to the previously described example, **27**, the lower photoconversion may arise from the rigidity of the alternate bpe ligands as

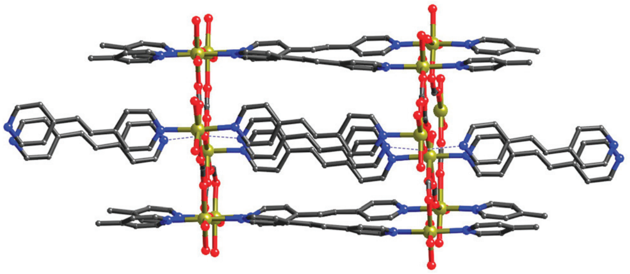

Fig. 24 The packing diagram of **28**, showing the sandwiched hydrogen-bonded bpe array.

well as the anchoring of the hydrogen-bonded bpe molecules in the structure.

The robustness of the O–H···N hydrogen bonds to orient bpe molecules in the co-crystal with a brick wall type structure CMCR·2bpe·benzil ethanol (**29**) (CMCR = *C*-methylcalix[4]resorcinarene) is highlighted here in Fig. 25.[60]

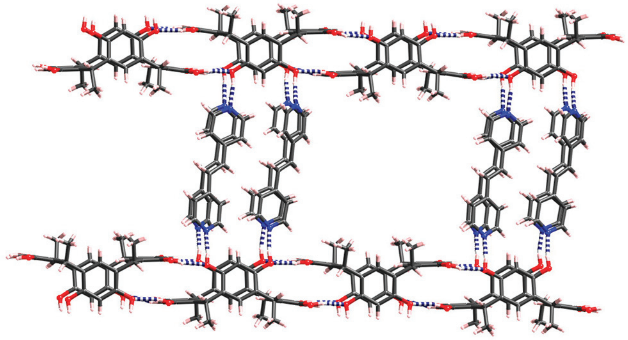

Fig. 25 A portion of the 2D hydrogen bonded brick-wall structure of **29** (benzil dimers in the cavity are removed for clarity).

This is achieved by the multifunctional clip CMCR which adopts a boat conformation and only two of the four resorcinol units in the calixarene align the bpe pairs to obey Schmidt's geometric criteria for photodimerization. Detailed investigation in this system will enhance our understanding of solid-state reactivity in 3D hydrogen-bonded structures.

The supramolecular ladder structures with the bpe molecules occupying the rungs such that face-to-face π–π stacking renders infinite parallel orientations of the bpe molecules, have been observed in the organic two-component system bpe·AP (**30**) synthesized from 3-aminophenol (AP), shown in Fig. 26(a).[61] Fig 26(b) shows another co-crystal, bpe·PBA·H_2O (**31**) with ladder structure, derived from phenyl boronic acid (PBA) and bpe that has an infinite arrangement of bpe molecules conforming the topochemical postulate.[62] A detailed study on the photodimerization of these co-crystals will be useful for better understanding of the mechanistic pathway of their photo-reactvity.

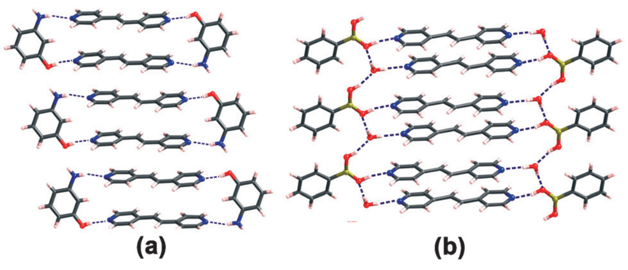

Fig. 26 The packing pattern of (a) **30** and (b) **31**.

Higher dimensional coordination polymers containing perfectly oriented bpe pairs are rare. Usually, the movements of the bridging bpe ligands are restricted in the higher dimensional coordination networks where both sides of the linear spacer are coordinatively bonded to the metal ions. In such cases, although the bpe ligands have been found in parallel arrangements, the solid may not be photoreactive. For example, $\{[Co(bpe)(muco)](DMF)(H_2O)\}_n$ (**32**) (muco = *trans*,*trans*-muconic acid) as shown in Fig. 27 has a 3D interpenetrating structure and $[Ce(bpeo)_{1.5}(NO_3)_3]_n$ (**33**) (bpeo = *trans*-1,2-bis(4-pyridyl)ethene-*N*;*N*′-dioxide) contains a 3D network structure.[63,64] The bpe ligand in **32** and bpeo ligand in **33** have parallel dispositions with the distance between the centers of adjacent double bonds around 3.781 and 3.649 Å respectively. However UV radiation of single crystals of **32** and **33** did not give any cyclobutane product.[44,63] On the other hand, in the photodimerization in pillared layered MOF **28**, the presence of uncoordinated bpe molecules might be the probable reason for the quantitative formation of photodimerized product.

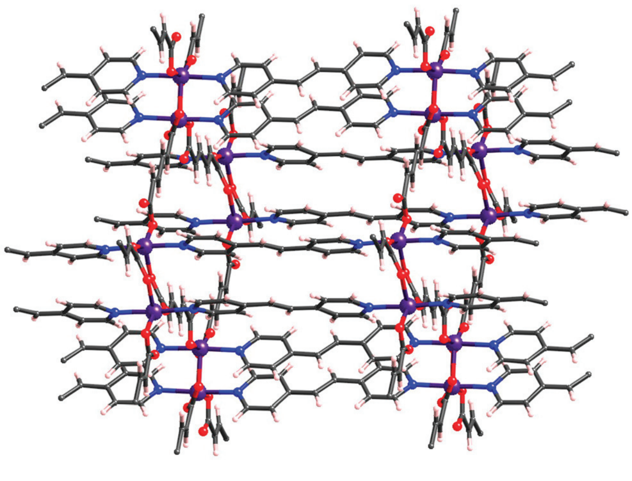

Fig. 27 The 3D packing pattern of **32** showing the parallel alignment of bpe (solvent molecules are removed for clarity).

8. Summary and outlook

The purpose of this brief overview has been to highlight the current trend and advances in the solid-state reactivity with respect to [2+2] photocyclization of C═C bonds in bpe molecules. The detailed investigation on the crystal engineering principles responsible in the photodimerizable compounds reveals that (i) when the bpe molecules are not tightly packed, for example, in the discrete molecular complexes and 1D hydrogen-bonded and coordination polymeric complexes, olefin pairs undergo 100% photodimerization; (ii) if the bpe molecules are interlocked such that the movements are restricted, this may result in only partial or no photochemical reaction; (iii) the quantitative photodimerization in hydrogen-bonded molecular systems and metal complexes of higher dimensionality is also due to the intrinsic structural flexibility afforded by the weak interactions and availability of free void space; (iv) simple dehydration or desolvation in MOFs cannot always be viewed as a physical phenomenon. The intermolecular interactions in the solids carry important information about the molecular movements and reactivity towards external stimuli, and such information has been successfully used in enforcing complete photodimerization in partially photodimerized compounds. Still the mechanistic pathway of the photo-reactivity of bpe molecules forming an infinite parallel array has not been understood completely. This might provide information about how molecules 'communicate' with one another in the reaction process.

A number of crystalline solids containing C=C bonds do not undergo photodimerization despite satisfying Schmidt's criteria. On the other hand, there are equal number of cases where photocyclization is not expected, surprisingly found to be otherwise.[11] Crystal structure analyses of these systems exhibiting unexpected photoreactivity unraveled several pieces of new information about the mobility of the bpe molecules. Although the bpe molecule has been discussed extensively in this review to illustrate the solid-state reactivity, the knowledge gained may well be extended to other systems with or without C=C bonds in other solids.

Acknowledgements

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