Templated [2 + 2] Photodimerizations in the Solid State

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1 ENGINEERING REACTIVITY IN THE SOLID STATE

Crystal engineering is an area of supramolecular chemistry that relies on the use of intermolecular forces to achieve solid-state frameworks with desired physical and/or chemical properties. The field is undergoing rapid development owing to an awareness that such an approach to synthesis can afford functional solids with unique properties (e.g., reactivity, optical properties, magnetism). In this context, chemists have worked to design olefins that will crystallize, with certainty, in geometries suitable for intermolecular [2+2] photodimerization reactions. The reaction results in the formation of two carbon–carbon single (C–C) bonds in a rigid, yet flexible, environment that can afford products, otherwise, unattainable in solution. That the reaction occurs in a solvent-free environment also means that the approach can provide an entry to the emerging area of green chemistry.

It is with these ideas in mind that we describe here supramolecular approaches to control [2+2] photodimerization reactions in the solid state based on the use of templates. We first describe the use of small organic molecules that act as templates and then move to metal–organic complexes. We end with a treatment of other cycloadditions (e.g., [4+4] cycloaddition, Diels–Alder) that may also be controlled using the template approach.

2 APPROACHES TO CONTROL THE [2+2] PHOTODIMERIZATION

Pioneering work of Schmidt involving cinnamic acids resulted in geometry criteria for a [2+2] photodimerization to occur in the solid state. In particular, it was determined that the cycloaddition reaction is topochemically controlled in solids with minimal molecular movement. The reaction is generally dictated by parallel alignment and overlap of olefinic bonds with a separation distance of < 4.2 Å. Schmidt also revealed that the geometry and positioning of olefins in the solid state are highly sensitive to subtle changes to molecular structure. More specifically, it was demonstrated how the organization of molecules in the solid state can be “unpredictably” influenced by functional groups or substituents. Thus, homologous series’ of cinnamic acids, in contrast to the liquid phase, did not exhibit homologous reactivities in solids. The lack of reaction homology has meant that it has remained difficult
for chemists to synthesize molecules in solids with similar degrees of synthetic “freedoms” that are realized in solution.

3 EMERGENCE OF SUPRAMOLECULAR CHEMISTRY

Since the work of Schmidt, several advances have been made to circumvent problems associated with crystal packing in attempts to reliably facilitate [2+2] photodimerizations in solids. In particular, intermolecular forces from the field of supramolecular chemistry have been exploited to steer the packing of olefins into geometries for reaction. Covalently attached functional groups that employ directing effects based on π–π stacking, charge-transfer complexation, and hydrogen bonding were initially studied to control packing. Despite significant successes, however, somewhat limited control of reactivity, in the context of a general organic synthesis, was achieved since the functional groups lacked an ability to effectively compete with demands of dense packing.

Whereas initial work to control [2+2] photodimerizations in the solid state involved the use of substituents, chemists have recently turned to auxiliaries (Scheme 1). Organic molecules and metal–organic complexes in the form of templates have been used to assemble and organize olefins via hydrogen bonding and metal coordination, respectively, for reaction. The templates preorganize olefins within supramolecular assemblies of molecules with structures largely independent of crystal packing. As a result, the templates have provided a means to construct relatively complex molecules in solids (e.g., ladderanes and paracyclophanes) with high levels of stereocontrol and in up to quantitative yields.

4 TEMPLATED [2+2] PHOTODIMERIZATIONS

4.1 Hydrogen bonds

The first small-molecule templates to control the [2+2] photodimerization in the solid state involved ditopic hydrogen-bond donors. The templates assembled olefins lined with pyridyl groups. The solid-state reactivity was, consequently, achieved within a cocystal or a “structurally homogeneous crystalline material that contains two or more neutral building blocks present in definite stoichiometric amounts.”

More specifically, MacGillivray and coworkers demonstrated that photostable trans-1,2-bis(4-pyridyl)ethylene (4,4′-bpe), on cocrystallization with 1,3-dihydroxybenzene or resorcinol (res), forms a discrete four-component molecular assembly sustained by four O–H · · · N hydrogen bonds. The C=C bonds of 4,4′-bpe were aligned within the 0D assembly parallel and separated by 3.65 Å (Figure 1). On UV irradiation, the olefins reacted to afford rctt-tetrakis-(4-pyridyl)cyclobutane (rctt-4,4′-tpcb) stereospecifically and in quantitative yield.

A template based on a crown ether was subsequently employed to organize C=C bonds within a 0D complex in a solid for a [2+2] photoreaction. Specifically, Garcia-Garibay, Stoddart, and coworkers demonstrated that reaction of a bisparaphenylene-34-crown-10 (bpp-34-crown-10) with a bis(dialkylammonium)-substituted stilbene (amm-stilb) produced the four-component complex 2(bpp-34-crown-10)·2(amm-stilb) held together by eight N+–H · · · O hydrogen bonds (Figure 2). The cavity of the crown ether was filled with the ends of the two reactants, with the olefinic bonds being parallel and separated by ~4.20 Å. UV irradiation resulted in a dimerization of amm-stilb to give a single diastereomer in ~80% yield.

[Diagram of strategy to control reactivity in the solid state using a template.]

[Diagram of synthesis of 4,4′-tpcb using res as an organic template.]
Templated $[2 + 2]$ photodimerizations in the solid state

Figure 2 Capped-stick model of the photoactive assembly 2(bpp-34-crown-10)-2(amm-stilb).

MacGillivray and coworkers also described a dicarboxylic acid that acted as a template (Figure 3). Cocrystallization of 1,8-naphthalenedicarboxylic acid (1,8-nda) with either 4,4'-bpe or 2,2'-bpe produced four-component assemblies sustained by four O–H···N hydrogen bonds (Figure 3a). The olefins were parallel and separated by a distance of 3.73 and 3.91 Å, respectively, which rendered 4,4'-bpe and 2,2'-bpe photoactive. UV irradiation of each solid produced the corresponding $rctt$-cyclobutanes in quantitative yield. In a related work, Jones demonstrated the ability of a triacid to act as a template. Specifically, cocrystallization of tricarballylic acid (tca) with 4,4'-bpe afforded a 1D hydrogen-bonded tape wherein the C=C bonds of 4,4'-bpe were parallel and separated by 3.8 Å (Figure 3b). UV irradiation produced 4,4'-bpe in 90% yield.

In addition to symmetrical hydrogen-bond donors, MacGillivray and coworkers introduced unsymmetrical Rebek’s imide (Reb-im) as a template (Scheme 2). Cocrystallization of Reb-im with 4,4'-bpe produced a discrete four-component assembly with olefins parallel and separated by 3.78 Å. The assembly was sustained by a combination of O–H···N and N–H···N forces. The olefins reacted in a rare single-crystal-to-single-crystal (SCSC) transformation to give 4,4'-tpcb stereospecifically in 100% yield.

Monopyridines have also been assembled to undergo $[2 + 2]$ photodimerization in the solid state (Scheme 3). Cocrystallization of 4-chlorostilbazole (4-Cl stilbz) with either res or 4-ethyl-res afforded discrete three-component assemblies sustained by two O–H···N hydrogen bonds.

The olefin adopted head-to-head geometries and participated in Cl···Cl forces. The C=C bonds reacted to give the head-to-head cyclobutane $rctt$-1,2-bis(4-pyridyl)-3,4-bis(p-chlorophenyl)cyclobutane (4-Cl dpcb) in quantitative yield. Recently, Ramamurthy and coworkers have employed thiourea as a template to assemble substituted stilbazoles (e.g., 4-CN, 4-F, 4-Br stilbz) to undergo stereospecific photodimerizations in the solid state (Figure 4). Cocrystallization of 4-CN stilbz afforded infinite 1D tapes.

Figure 3 Cocrystals of photoactive (a) 2(nda)-2(2,2'-bpe) and (b) (tca)-2(4,4'-bpe).

Scheme 2 Synthesis of 4,4'-tpcb using Reb-im as a heteroditopic template.

Scheme 3 Synthesis of 4-Cl dpcb using res or 4-Et res as a template.
4.2 Reversing the code

The supramolecular “code” involving a template has been reversed such that the templates and olefins act as hydrogen-bond-acceptors and -donors, respectively. Code reversal was first demonstrated by MacGillivray and coworkers by using 2,3-bis(4-methylenethiopyridyl)naphthalene (2,3-nap) as a template and fumaric acid (fum) as the olefin (Figure 5).15 A four-component assembly sustained by O–H···N hydrogen bonds formed from cocrystallization of 2,3-nap and fum. The olefins were aligned and approximately parallel with a C=C separation of 3.84 Å. The solid reacted in a SCSC transformation to give ctba stereospecifically and in quantitative yield. A similar approach was later reported by Brunke and coworkers to direct the reactivity of a F-substituted diene in the form of p-di-[2-(4-pyridyl)ethenyl]-2-fluorobenzene (1,4-bpef).19 Cocrystallization of 1,4-bpef with 2,4-dihydroxybenzaldehyde produced a four-component assembly that reacted to give the corresponding F-substituted [2.2]paracyclophane in 60% yield.

In a related work, Santra and Birahda have shown that the diene 1,5-bis(4-pyridyl)-1,4-pentadiene-3-one (1,5-bppo) can be assembled to react in the solid state using tritopic phloroglucinol (pg) as a template (Scheme 5).20 The components generated a 1D ladderlike network sustained by O–H···N hydrogen bonds. Adjacent C=C bonds were parallel and separated by 3.60 and 3.85 Å. UV irradiation afforded the corresponding tricyclo[6.2.0.0]decane in quantitative yield.

4.4 Halogen bonds

In addition to hydrogen bonds, Metrangolo and coworkers have shown that the [2+2] photodimerization can be directed in the solid state using a template based on halogen bonds.21 Cocrystallization of 4,4′-bpe with a halogenated pentaerythritol (pery) afforded a 1D ribbon sustained by I···N halogen bonds (Figure 8). The olefins were
4.5 Coordination bonds

Transition-metal-ion complexes have been introduced as templates to direct [2+2] photodimerizations in the solid state. The photoreaction has been achieved in both discrete complexes and metal–organic frameworks (MOFs). MOFs are intriguing platforms to control the photodimerization owing to changes to bulk physical properties (e.g., porosity) that can occur in the porous frameworks.

4.6 Discrete assemblies

MacGillivray and coworkers reported the first metal complex to control a [2+2] photodimerization in a solid. A Schiff-base complex involving Zn(II) ions preorganized 4,4′-tpcb stereospecifically and in quantitative yield.

Figure 6  Structures of (a) (5-OCH3-res)-(4-py-but) before photoreaction, (b) [3]-ladder product, (c) (5-OCH3)-(4-py-hex) before photoreaction, and (d) [5]-ladderane.

Figure 7  Templated synthesis of tpcp using 4-bn-res in 2(4-bn-res)-2(1,4-bpe).

Scheme 5  Photoactive ladderlike network of (1,5-bppo)-(pg).

Figure 8  Perspective representation of a single polymeric chain of (pery)(4,4′-bpe).
in up to quantitative yield. The \textit{rcct}-isomer was also generated in the Ir(II)-based solid. The tetranauclear assembly supported SCSC reactivity.

Ag(I) ions have been used to direct [2+2] photodimerizations in solids. Argentophilic forces (i.e., Ag⋯Ag interactions) were exploited by MacGillivray and coworkers to assemble and stack a stilbazole (4-stilbz) for reaction.\textsuperscript{25} Reaction of Ag(I) trifluoroacetate with 4-stilbz produced a disilver complex that organized two pairs of 4-stilbz. The Ag⋯Ag interaction displayed a metal–metal separation of 3.41 Å while the C=C bonds were crisscrossed and separated by 3.82 Å (Scheme 6a). The corresponding head-to-head cyclobutane was generated quantitatively in a SCSC reaction. The formation of the photoproduct was ascribed to pedal-like rotation of the C=C bonds in the solid. A similar complex was subsequently used to achieve the first photodimerization of terminal olefins in a solid. Reaction of Ag(I) chlorate with 4-vinylpyridine (4-vp) afforded a disilver complex (Scheme 6b)\textsuperscript{26} that generated \textit{cis}-1,2-bis(4-pyridyl)cyclobutane stereospecifically and in quantitative yield.

4.7 Metal–organic frameworks (MOFs)

The sizes and shapes of the cavities and pores of MOFs are defined by both the metals and organic bridges. Changes to the structures of the components have been shown to result in changes to properties and functions of the pores. Thus, it follows that a change in structure that accompanies a [2+2] photodimerization in the solid state can be considered a means to affect the properties of MOF materials.

In this context, Michaelides and coworkers were the first to describe a photoreaction integrated into a MOF. The framework was based on Cd(II) ions connected to fum ions that produced a rectangular grid network (Figure 11).\textsuperscript{27} The C=C bonds were parallel and separated by 3.37 Å between adjacent layers, which enabled the olefins to react to give cbta. Although the network did not possess cavities, the study established that reactive components can be incorporated into a MOF.

In a related work, Vittal and coworkers subsequently described the photoactive ladderlike coordination polymer [Zn(CF\textsubscript{3}CO\textsubscript{2})(μ-O\textsubscript{2}CCH\textsubscript{3})\textsubscript{2}(μ-4,4′-bpe)\textsubscript{2}]\textsubscript{n}.\textsuperscript{28} Each Zn(II)
center adopted a distorted octahedral geometry, with two acetate ions bridging a pair of Zn(II) ions in \([\text{Zn}_2(\mu\text{-bpe})_2\text{]}\)∞ with Zn···Zn distances of 3.85 Å. Each metal was chelated by a trifluoroacetate ion (Figure 12). The C=C bonds of parallel chains were separated by 3.75 Å. UV irradiation afforded 4,4′-tpcb quantitatively via a SCSC transformation.

Following the work of Vittal, MacGillivray and coworkers described the ability of the Schiff-base complex \([\text{Zn}_2\text{L(OH)}(4,4′\text{-bpe})_2\text{]}\text{[ClO}_4\text{]}_2\text{]}\) to support a linear photoreactive ladderlike coordination polymer (Figure 13). The metals were tetra-coordinated by \(\text{L} \) in the basal plane while the apical sites were coordinated by the bipyridines. Thus, the olefins were coordinated to neighboring dinuclear complexes, being stacked parallel and separated by 3.71 Å. UV irradiation generated 4,4′-tpcb stereospecifically in up to 95% yield.

Whereas argentophilic forces supported reactive discrete complexes, Vittal and coworkers reported a \([2+2]\) photodimerization involving the solvated 1D coordination polymer \([\text{Ag}(4,4′\text{-bpe})(\text{H}_2\text{O})]\text{[CF}_3\text{CO}_2\text{-CH}_3\text{CN}}\text{]}\). Adjacent 1D polymers produced a 2D brick wall structure sustained by Ag···Ag forces and hydrogen bonds. Olefins of two consecutive layers were misaligned and separated at 5.15 Å. UV irradiation, however, resulted in an unusual solid-state reorganization that led to a photodimerization of the C=C bonds in up to quantitative yield. Similar observations involving the 1D double- and triple-stranded polymers \([\text{Cd}(4,4′\text{-bpe})(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})]\)∞ and \([\text{Pb}_3(4,4′\text{-bpe})_3(\text{O}_2\text{CCF}_3)_4(\text{O}_2\text{CCH}_3)_2]\)∞ (Figure 14), respectively, were made by the same group. For the former, adjacent polymers exhibited C=C bonds separated on the order of 4.33 Å. Dehydration of the solid, however, afforded a photoactive material that reacted to give 4,4′-tpcb on UV irradiation in 100% yield. For the latter, the reaction proceeded in a two-step pathway wherein UV irradiation followed by mortar-and-pestle grinding facilitated quantitative conversion of 4,4′-bpe to 4,4′-tpcb.

Miao and Zhu have described the integration of a \([2+2]\) photodimerization into a 2D MOF. The components of \([\text{Cd}_2(\text{CH}_3\text{COO})_2(3\text{-sulfobenzoato})(4,4′\text{-bpe})_2\text{]}\text{[H}_2\text{O}]\cdot4\text{H}_2\text{O}\)∞ generated a 2D MOF with one edge based on
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Figure 15 3D network [Cd$_2$(O$_2$CCH=CHCO$_2$)$_2$(bpe)$_2$] along the a-axis. The olefins are directed along the c-axis and act as pillars of rectangular grids. Hydrogens are omitted for clarity.

stacked 4,4'-bpe in a ladderlike chain and the other edge being a single 4,4'-bpe linker. The 2D structures assembled into 3D networks via interpenetration. UV irradiation generated 4,4'-tpcb in quantitative yield. An isostructural solid involving the photoproduct 4,4'-tpcb also formed on reaction of the individual components.

Michaelides et al. reported the first photodimerization in a 3D MOF. The solid was based on a reported 2D layered structure composed of Cd(II) dimers linked by fum. The 2D layers were pillared using 4,4'-bpe to give a 3D MOF with a structure that conforms to a quasi α-Po topology (Figure 15). Thus, the fum ions were bridging ligands in a 2D grid while double columns of 4,4'-bpe ligands acted as linkers. The close proximity between pairs of Cd(II) ions assemblyed 4,4'-bpe parallel and separated by 3.95 Å. UV irradiation afforded 4,4'-tpcb stereospecifically and in quantitative yield. Vittal later reported that reaction of Zn(II) ions and either fum, muconic acid (muco), or 1,4-benzene dicarboxylic acid (bdca) affords a series of interpenetrated 3D MOFs (Figure 16). The MOFs involving muco and bdca reacted to generate 4,4'-tpcb via SCSC transformations.

4.8 MOF with diene components

Dienes have been assembled to react in MOFs. In particular, Eddaoudi and coworkers employed Cu(II) ions to assemble the anion of the heterocyclic diolefin chelidonic acid (cdo) for a double [2+2] photodimerization (Figure 17). The dicarboxylate reacted in a 1D polymer via a SCSC transformation to give an unusual catenelike photodimer.

Lang and coworkers have reported an extension of the MOF to the diene 1,4-bpdp. Hydrothermal treatment of 1,4-bpdp with Zn(II) ions with 5-sulfoisophthalic acid or 1,4-bpdp with Cd(II) ions and 1,3-phenylenediacetic acid afforded the photactive 2D and 3D MOFs [Zn$_4$(µ$_3$-OH)$_2$(5-sufoisophthalate)$_2$(1,4-bpdp)$_2$]$_n$ and [Cd$_2$(1,3-pda)$_2$(1,4-bpdp)$_2$]$_n$, respectively. For the former, the stacked olefins were aligned offset or “out of phase.” UV irradiation of the solid produced the corresponding offset cyclobutane dimer in 100% yield. For the latter, the olefins were eclipsed or “in phase,” with the photoreaction generating the paracyclophane tpcbb (Figure 18). Both solids reacted via a SCSC transformation.

4.9 Mixed coordination and hydrogen bonds

The self-assembly process to direct [2+2] photodimerizations in the solid state has been extended to
combinations of coordination and hydrogen bonds. More specifically, Hill and Briceño reported that both crystalline [Mn(2,4-bpe)2(OH2)4](ClO4)2·2(2,4-bpe)·2H2O and [Mn(2,4-bpe)2(NCS)2(OH2)2] possess olefins organized by Mn–N coordination and O–H···N hydrogen bonds that involve coordinated H2O molecules that conform to geometries for photoreaction (Figure 19).38,39 UV irradiation of both solids resulted in the regioselective formation of the head-to-tail photodimer rctt-2,4-tpcb. In a related work, Vittal has described the ability of stacked olefins in [Zn(4,4′-bpe)2(H2O)4](NO3)2·8/3(H2O)·2/3(4,4′-bpe) to undergo photodimerization to afford 4,4′-tpcb in 100% yield.40 The components formed a 1D hydrogen-bonded complex wherein the reactive olefins participated in a combination of Zn–N coordination and O–H···N hydrogen bonds that involved coordinated H2O molecules.

4.10 Charge-controlled

Whereas the auxiliary approach to direct [2+2] photodimerizations in the solid state has involved the self-assembly of neutral components, related studies to direct the photoreaction using charged species, or salts, have been reported. Hydrogen bonds between cations and anions, as well as cation–π interactions, have been used to direct the assembly and packing41 of olefins into the appropriate geometry for photoreaction.

In a pioneering work, Ito and coworkers demonstrated that cinnamic acids undergo [2+2] photodimerizations in the solid state, which are mediated by salt formation.42 Diammonium cinnamates, as well as ammonium fum, displayed photoreactivity owing to hydrogen bonds between the cations and anions (Scheme 7). Head-to-head dimers formed in reasonable yields with moderate to high stereoselectivities. Vittal and coworkers also demonstrated that (E)-4,4′-stilbenedicarboxylic acid, when ground with 1,3-diaminopropane, forms a diammonium salt that undergoes [2+2] photodimerization to afford the corresponding rctt-photodimer in quantitative yield.43 In a related work, Vittal and coworkers reported on salts with cations, as opposed to anions, that undergo photodimerizations wherein the stereochemistry was anion controlled.44 Specifically, formation of the trifluoroacetate and sulfate salts of (E)-3-(4-pyridyl)acrylic acid (4-pa) and subsequent photodimerization generated head-to-tail and head-to-head dimers, respectively (Figure 20a and b). The C=C bonds were separated on the order of 3.7 Å. Head-to-tail and head-to-head geometries were dictated by N–H···O, O–H···O, and C–H···O hydrogen forces.

Briceño and coworkers have employed charge-assisted hydrogen bonds to form reactive ionic assemblies of protonated unsymmetrical olefins (e.g., stilbz, 4-Cl-stilbz) using the dicarboxylate salt of 1,2,4,5-benzenetetracarboxylic acid (bdta) (Scheme 8).45 In each case, 1D ribbons sustained by pyridinium-carboxylate forces formed. The interactions resulted in head-to-tail stacking of the olefins and, on UV irradiation, afforded the head-to-tail dimers of stilbz and 4-Cl stilbz in quantitative yield.

Photodimerizations with charged compounds have been studied in several styryl dyes wherein alkylation of an N-heterocycle (e.g., pyridine, benzothiazole) generates a salt.46 Gromov and coworkers have also shown that when a styryl dye and a crown ether (e.g., 18-C-6; Scheme 9) are covalently connected, stereospecific [2+2] reactions are facilitated by inclusion of the cation within the ethereal host.47 In addition, Gromov also showed that counteranion
4.11 Fish-hook assemblies

Hydrogen bonding has been utilized to organize U-shaped olefinic diacids into “fish-hook” assemblies that preorganize C=C bonds in the solid state for photoreaction. Initially, work by Feldman and coworkers reported a “U”-shaped naphthalene dicarboxylic acid to self-assemble via carboxylic acids to form a dimer sustained by O–H···O hydrogen bonds (Scheme 10). The naphthalene unit preorganized the C=C bonds parallel and separated by 3.62 Å. UV irradiation produced the corresponding cyclobutane in quantitative yield.

Later, Wheeler and coworkers demonstrated that chiral sulfonamidecinnamic acids self-assemble into hydrogen-bonded dimers wherein the olefins lie parallel, with the C=C bonds separated by 3.68 Å. The approach was expanded to cross-photoreactions that generate heterodimers. On UV irradiation, the quasiracemate cocrystals underwent asymmetric photodimerizations to afford an enantiomerically pure α-truxillic acid photoproduct (Figure 21).

Scheme 10 Photoactive assembly of a U-shaped naphthalene dicarboxylic acid.
5 OTHER CYCLOADDITIONS

Other cycloadditions are, in principle, amenable to control using templates in the solid state. Both [4+4] and [4+2] cycloadditions are, for example, known to proceed in solids.

Ito and coworkers, for example, have demonstrated that 1,2-diamines (e.g., cyclohexane-1,2-diamine) can be reacted with anthracene-9-propionic acid (9-ap) in a double salt formation to afford a solid that reacts to give a head-to-head photodimer in 55% yield. Ito and coworkers have also demonstrated that the salt formed from 9-(N,N-dimethylamino)anthracene (dmaa) and furan-2-carboxylic acid reacts to give the head-to-tail dimer in near quantitative yield. An unsymmetrical [4+4] cycloaddition has also been reported via salt formation involving dmaa and the diacid muco. The salt assembled with anthracene pairs arranged in a head-to-tail fashion with C=C bonds separated by 3.58 and 3.65 Å (Figure 22). On UV irradiation, the head-to-tail photoadduct formed in quantitative yield.

Examples of [4+2] cycloadditions in the solid state remain relatively rare, owing to an inherent difficulty in arranging two different molecules in a suitable geometry for reaction. Desiraju and Radha Kishan reported the first solid-state [4+2] cycloaddition, which involved a propiolic acid derivative (Figure 23a and b). Kochi and coworkers employed charge transfer and donor–acceptor interactions to achieve photoreactive two-component crystals of anthracene and a 1,4-dithiin derivative (Figure 23c and d).

6 CONCLUSION

In this chapter, we have focused on methods to direct [2+2] photodimerizations in the solid state using templates. The templates exploit principles of supramolecular chemistry to overcome problems of close packing so as to afford a reliable means to generate covalent bonds in solids. Hydrogen bonding and/or coordination bonds have been primary forces to direct reactivity. We expect the template

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**Figure 21** [2+2] Photoreaction of a quasiracemic supramolecular assembly of two sulfonamidecinnamic acids.

**Figure 22** Crystal structure of 2(dmna)-(muco).

**Figure 23** (a) Schematic and (b) capped-stick model of two propiolic acids and (c) schematic and (d) capped-stick model of anthracene and a 1,4-dithiin derivative undergoing [4+2] cycloaddition.

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approach to be applicable for the design of more complex molecules and direct additional cycloaddition reactions.

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