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# Functional diversity in templated solid state reactions

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### FUNCTIONAL DIVERSITY IN TEMPLATED SOLID STATE REACTIONS

by Rebecca Christine Laird

A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemistry in the Graduate College of The University of Iowa

August 2014

Thesis Supervisor: Professor Leonard R. MacGillivray

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Graduate College The University of Iowa Iowa City, Iowa

## CERTIFICATE OF APPROVAL

## PH.D. THESIS

This is to certify that the Ph.D. thesis of

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has been approved by the Examining Committee for the thesis requirement for the Doctor of Philosophy degree in Chemistry at the August 2014 graduation.

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To my parents, Edward and Betty Grove for their endless love and encouragement, to my sister and my brother-in-law, Elizabeth and Matt Chupp for always listening and helping me to laugh, and, above all, to my husband Joseph Laird, who is my rock and foundation, my best friend, and the greatest supporter and partner in life that I could ever have. Thank you and I love you all. To laugh often and much; to win the respect of intelligent people and the affection of children, to leave the world a better place, to know even one life has breathed easier because you have lived, this is to have succeeded.

-Ralph Waldo Emerson

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#### **CHAPTER 1: INTRODUCTION**

#### 1.1. Supramolecular Chemistry

The field of supramolecular chemistry, as first defined by Jean-Marie Lehn, investigates "chemistry beyond the molecule."<sup>1-2</sup> While traditional organic chemistry focuses on the synthesis of molecules through the formation of covalent bonds such as carbon-carbon or carbon-oxygen bonds, supramolecular chemistry focuses on the non-covalent interactions (e.g. hydrogen bonding, van der Waals forces, pi-stacking, and metal coordinations) between a molecule and its surroundings. Each of these non-covalent interactions are reversible and often guide self-assembly of the molecules into larger, multi-component structures able to carry out specific processes.

Examples of supramolecular chemistry can be observed across nature with small molecules working together as larger units. A prominent example presents itself in the biomolecule deoxyribose nucleic acid (DNA) (Figure 1). As first demonstrated by Watson and Crick through X-ray studies, DNA consists of two single strands that are hydrogen bonded together and twisted into a double helix (Figure 1a).<sup>3</sup> The nucleotide bases within the DNA contain the initial "instructions" for proteins and other biomolecules.<sup>4</sup> To conserve the order of the bases, and therefore the genetic information contained within the DNA, the bases pair through hydrogen bonding of complementary shape and number (two hydrogen bonds between adenine and thymine, and three hydrogen bonds between cytosine and guanine) (Figure 1b). It is through this complementary hydrogen bonding that the DNA strands are able to self-assemble into the double helix.



Figure 1. DNA double helix: (a) single strands self-assemble to produce a double stranded helix and (b) complementary hydrogen bonding between DNA bases.

Inspired by these examples, supramolecular chemists have begun seeking to mimic nature through the development of host-guest assemblies that can carry out specific purposes. Recently, Leigh demonstrated the ability to synthesize small amino acid chains, mimicking the biomolecule ribosome (Figure 2).<sup>5-6</sup> Through the use of Leigh's molecular machine, small oligopeptides of specific amino acid sequence can be assembled. Furthermore, the desired oligopeptide is the sole product, with no other peptides detected. The assembly and performance of this molecular machine relies on supramolecular interactions both through self-assembly and reversibility, allowing the growing peptide to "walk" down the central motif.



Figure 2. Supramolecular machine synthesizing oligopeptides.

Atwood has also utilized supramolecular chemistry through host-guest assemblies to mimic transport processes often observed in biological cells. The macromolecules *C*alkylpyrogallol[4]arenes (PgCs) have shown great promise and versatility via their supramolecular interactions both through hydrogen bonding and metal coordinations with copper and zinc.<sup>7</sup> Metallo-PgC capsules have demonstrated functionality as carries for a variety of guest molecules. Through his studies, Atwood has discerned routes for the direct synthesis and assembly of Cu(II) pyrogallol[4]arenes capsules in both the dimeric and hexameric forms (Figure 3a), resulting in discrete hollow channels that can facilitate transport. Furthermore, Atwood has demonstrated the potential for ligand exchange to incorporate bridging ligands, creating linked capsules (Figure 3b).



Figure 3. Hollow PgC capsules: (a) discrete capsules and (b) linked capsules through bridging ligands.

Continuing this study, Atwood was able to use hydrogen bonding to self-assemble purely organic PgCs hexameric molecular capsules with a tailored interior, making the capsule selective for chlorine (Figure 4).<sup>8</sup>



Figure 4. Organic PgC capsules selective for chlorine.

#### 1.2. Solid-State Reactivity

While solution phase examples of supramolecular chemistry through host-guest systems have recently gained greater attention, our focus within the MacGillivray research laboratory has been on solid-state reactivity. Rather than assembling a machine to carry out a specific purpose, as has been demonstrated in the solution phase, our goal is to utilize supramolecular interactions to guide specific reactions in the crystalline state. In addition to often being a greener technique, conducting reactions in the solid state affords several benefits over solution phase reactivity.<sup>9-11</sup> Performing reactions in the solid state frequently allows for control over the selectivity and stereochemistry of the product. While molecules in the solution phase exhibit constant motion, molecules in the solid state display relatively little movement. This hindrance of movement often results in molecules interacting and reacting in the same way across the material, giving rise to

product selectivity. The constant movement observed in the solution phase may result in molecules interacting at several different faces and locations, giving multiple products and isomers. The selectivity of solid-state reactions gives rise to a second benefit, in the synthesis of products that may be otherwise difficult to obtain in the solution phase. Due to the potential for multiple products in the solution phase, the desired product may be unfavored or low yielding, whereas, if the product is selected for in the solid state, it will often be the sole product.

A key study exhibiting the many benefits of solid-state reactivity came from Schmidt and co-workers during work with cinnamic acid.<sup>12</sup> During these studies, it was observed that, in the presence of UV irradiation, the olefins of neighboring molecules would undergo the [2+2] photocycloaddition forming C-C covalent bonds, resulting in a cyclobutane ring (Figure 5). It was noted that, while the solution phase generated multiple products, the solid-state produced only one product, dependent on the polymorph.



Figure 5. Scheme of the [2+2] photocycloaddition reaction of cinnamic acid.

Three polymorphs of *trans*-cinnamic acid have been observed ( $\alpha$ ,  $\beta$ , and  $\gamma$ ).<sup>13</sup> While the  $\gamma$  polymorph is photostable, both the  $\alpha$  and the  $\beta$  forms are able to undergo the [2+2] photocycloaddition in the solid state. The crystal packing of the  $\alpha$  polymorph results in olefins aligned in a head-to-tail (ht) geometry, yielding the ht photoproduct  $\alpha$ -truxillic acid (Figure 6a). Conversely, the  $\beta$  polymorph packs with olefins aligned head-to-head (hh), giving rise to the hh photoproduct,  $\beta$ -truxinic acid (Figure 6b).



Figure 6. Comparison of the photoproducts from α and β polymorphs of *trans*-cinnamic acid: (a) α-truxillic acid and (b) β-truxinic acid.

Through studies of the three polymorphs, Schmidt derived a set of guidelines for the [2+2] photocycloaddition in the solid state, becoming known as the topochemical postulate.<sup>12</sup> The postulate states that, in order for a molecule to be photoactive in the solid state, olefins should be aligned parallel and separated by approximately 4.2 Å or less. The introduction of the [2+2] photocycloaddition in the solid state gave chemists a new method for the synthesis of covalent C-C bonds while also providing a means for selectivity for either the hh or ht product.

#### 1.3. Limitations of Solid-State Reactivity

While solid-state reactivity presents many benefits over solution phase reactivity, each benefit also bears a limitation. While performing reactions in the solid state can provide product selectivity, the unpredictability of crystal packing limits this benefit. Furthermore, though solid-state reactions can often yield products difficult to obtain in the solution phase, the lack of functional group diversity in the solid state limits the applications of this technique. In order to expand the applications of solid-state chemistry, these limitation must be overcome. Within the MacGillivray group, great efforts have been taken towards overcoming each of these limitations. The template method has been developed as a technique to guide crystal packing, giving a degree of predictability to molecule arrangement in the crystalline state. Through the template method, the MacGillivray group has also been able to integrate new functionalities into solid-state reactions, particularly the [2+2] photocycloaddition reaction.

#### 1.4. Template Method

stated previously, supramolecular chemistry relies on non-covalent As interactions including hydrogen bonding, van der Waals forces, pi-stacking, and metal coordinations. Each of these interactions plays a role in directing molecular arrangement and the overall packing within the crystal. With each interaction affecting the crystal packing with varying strengths, it is, to date, impossible to completely predict the crystal packing of a molecule. The unpredictability of crystal packing can result in crystalline material unable to undergo a desired reaction. In the case of the [2+2]photocycloaddition reaction, crystal packing, such as seen with the  $\gamma$  polymorph of *trans*cinnamic acid, may violate the topochemical postulate, rendering the molecule photostable. As a method to overcome photostability and guide olefin alignment in the crystalline state, MacGillivray and co-workers developed the template method.<sup>14</sup> As a form of crystal engineering, the template method relies on supramolecular interactions between the template and the olefinic molecule. The first example of the template method was the cocrystallization of the template resorcinol (res) with the photostable molecule 4,4' bispyridyl ethylene (4,4'BPE) (Figure 7). Since this first example, other templates have been demonstrated as both organic molecules and transition metal cations.



Figure 7. Scheme of the cocrystal (res)·(4,4'BPE), the first example of a templated [2+2] photocycloaddition in the solid state.

As a pure crystalline solid, 4,4'BPE is photostable. The photostability of 4,4'BPE is due to molecules canted nearly orthogonal within a plane with subsequent planes offset, preventing olefin alignment (Figure 8a).<sup>15</sup> When cocrystallized with res; however, the O-H…N hydrogen bonding directs the molecules into discrete assemblies in a 1:1 ratio (Figure 8b).<sup>14</sup> The template helps guide the 4,4'BPE molecules into a geometry where the C=C are aligned parallel and able to photoreact. Due to the reversibility of the hydrogen bonding, upon complete conversion to the cyclobutane product, the res template can be removed, allowing for isolation of the photoproduct. It is necessary to note, however, that while the templates can control local packing through assembly formation, they are unable to control overall packing of the assemblies within the crystal.



Figure 8. Olefin alignment guided through template method: (a) crystal packing of photostable 4,4'BPE and (b) crystal packing of (res)·(4,4'BPE) cocrystal exhibiting photoactive assemblies.

#### 1.4.1. Organic Templates

Much as organometallic chemists may screen for an appropriate ligand to give a desired molecular shape, or solution phase chemists may screen for a catalyst to optimize a reaction, solid-state chemists are able to screen for templates to optimize the [2+2]

photocycloaddition. Since the initial demonstration of res as a template, the MacGillivray group has developed a large library of organic templates bearing hydrogenbonding functional groups.<sup>16-17</sup> Many of these templates are synthesized as analogues of res, with additional functionality introduced on the benzene ring (Figure 9). While each res analogue consists of the 1,3-dihydroxy motif, the differences in functionality will affect not only the electronics of the molecule, and therefore the hydrogen bond strengths, but will also spatially affect the crystal packing of the assemblies.



Figure 9. Examples of res derived organic templates.

While res derived templates work well for olefins decorated with hydrogen bond acceptor groups, the MacGillivray group has also "reversed the code" and applied the template method to acid decorated olefins. The MacGillivray group has expanded the applications of the template method through successful demonstration of hydrogen bond accepting templates such as 1,8-bis(4-pyridyl)naphthalene (1,8 DPN) and 2,3-bis(4-methylenethiopyridyl)naphthalene (2,3-nap) (Figure 10), to template acids such as fumaric acid.<sup>18</sup>



Figure 10. Examples of hydrogen bond accepting templates: (a) 1,8 DPN and (b) 2,3-nap).

Further expansion of the template method has come quite recently through the recent use of the molecule indolocarbazole to serve as a hydrogen bond donor, resulting in double to quadruple aromatic stacks (Figure 11).<sup>19</sup>



Figure 11. Organic template indolocarbazole resulting in double to quadruple aromatic stacks.

#### 1.4.2. Transition Metal Templates

Additional development of the template method came through the integration of transition metal templates. The Ag(I) cation serves as the most commonly used transition metal template due to facile coordinatations to nitrogen atoms, making it an ideal template for pyridine decorated olefins. The Ag(I) cation coordinates with two N atoms in a linear fashion, giving rise to linear assemblies. These assemblies can be brought together through Ag(I)-Ag(I) argentophilic forces, producing self-assembled dinuclear assemblies that can align the C=C and facilitate the [2+2] photocycloaddition (Figure 12).<sup>20</sup>



Figure 12. Scheme of metal-organic assembly of [Ag<sub>2</sub>(stilbazole)<sub>2</sub>][(CO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] with Ag(I)-Ag(I) argentophilic forces facilitating olefin alignment.

Much as organic templates can be screened to optimize the rate and yield of the [2+2] photocycloaddition reaction in the solid state, the Ag(I) cation template can also be screened through tailoring of the counter anion. The anions selected are often oxoanions exhibiting weak coordinations to Ag(I), allowing for favorable coordination of the olefinic ligand molecule.<sup>20</sup> It was through such screening that the MacGillivray group was able to demonstrate the first [2+2] photocycloaddition reaction of a terminal olefin in the solid state (Figure 13).<sup>21</sup>



Figure 13. Scheme of [2+2] photocycloaddition of terminal olefins through the metalorganic assembly [Ag<sub>2</sub>(4-vinyl pyridine)<sub>4</sub>][(ClO<sub>3</sub>)<sub>2</sub>].

#### 1.5. Expanding Functional Group Diversity

While the use of templates has proven instrumental in overcoming unpredictable crystal packing and allowing for the photocycloaddition of otherwise photostable olefins, the drawback of limited functional group diversity in the solid state still remains. For the MacGillivray group, endeavors to expand functional group diversity in the solid state began with determining the tolerance of solid-state reactions, such as the [2+2] photocycloaddition, for modular changes in substitution and functionality. As previously demonstrated, templates often assemble at the termini of molecules. This observation lead to an investigation of varying the substitution pattern of the pyridine rings of BPE (Figure 14), and the eventual templating and photoreaction of each BPE molecule in the solid state.<sup>22-23</sup>



Figure 14. BPE series.

Other investigations have also demonstrated that the bispyridyl motif is not required for successful templating and, in fact, compounds bearing only one pyridine ring can be successfully templated (Figure 15), giving rise to prospects of incorporating new functional groups such as halogens and alkyl chains.<sup>24-25</sup>



Figure 15. Example of a monopyridine olefinic compound decorated with a halogen atom.

Expansion of functional group diversity has been achieved through integrating new spacers between pyridine termini. Two prominent studies from the MacGillivray group have produced cyclophane analogues and ladderanes. Cyclophanes (Figure 16), are a class of molecules bearing two aromatic rings bridged together and forced into co-facial alignment.<sup>26-29</sup>



Figure 16. Cyclophane molecule: (a) chem draw scheme of a cyclophane molecule and (b) crystal structure of a cyclophane molecule.

The alignment of the benzene rings gives these molecules interesting photophysical properties and applications in semiconductors, biosensors, organic dyes, and cellular diagnostics.<sup>30-31</sup> Work done in the MacGillivray group has shown that cyclophane analogues can be synthesized in the solid state through the [2+2] photocycloaddition of paradisubstitubed benzene rings decorated with vinyl pyridine moieties. (Figure 17).<sup>30-31</sup> Synthesis of these cyclophane molecules has allowed for the study of crystal packing motifs, as well as electronic properties in both the solution phase and solid state.



Figure 17. Synthesis of cyclophane analogues: (a) schematic for cyclophane synthesis through templated [2+2] photocycloaddition and (b) crystal structure of cyclophane photoproduct.

The synthesis of ladderanes in the solid state has also presented an opportunity to expand functional group diversity within our template systems. Initially discovered in 2002, ladderanes are found in the lipid membranes of ammonium-oxidizing bacteria and contain five linearly fused cyclobutane rings.<sup>32</sup> The total synthesis of ladderanes in the solution phase was elucidated in 2004 by E. J. Corey and generates of total yield of 0.2%.<sup>33</sup> The MacGillivray group has since shown that the ladderane motif can also be synthesized through the photocycloaddition of pyridine decorated trienes (Figure 18).<sup>34-35</sup> This templated reaction proceeds quantitatively in 72h of UV irradiation and gives an isolated yield of 85%. The generation of ladderanes in the solid state not only optimized the synthesis compared to Corey's solution phase procedure and introduced trienes into solid state reactivity, but further demonstrated the many benefits of solid state reactivity versus solution phase synthesis.





#### 1.6. Dissertation Overview

The research presented in this thesis aims to further overcome the limitations of solid-state reactivity in order to expand the applications of solid-state synthesis and materials design. In order to expand functional group diversity in the solid state, investigations towards the integration of new functionalities, post synthetic modification

(PSM) techniques, and the design of metal-organic assemblies will be discussed. In order to continue the use of templates and further their application, work surrounding crystal packing patterns and the design of new olefins will be discussed.

Chapter two focuses on the expansion of functional group diversity in solid-state reactivity through the integration of a terminal alkyne on a stilbazole derived molecule. The synthesis of the target molecule, as well as the crystal packing and photoreactivity will be discussed. Cocrystallization of the molecule with 4,6-diBr-res to facilitate the [2+2] photocycloaddition will also be described. The results of this chapter demonstrate the ability to incorporate new functionalities without disrupting the [2+2] photocycloaddition in the solid state. Furthermore, the introduction of the terminal alkyne presents the opportunity for PSM for continued expansion of functional group diversity.

Chapter three discusses the PSM of the terminal alkyne molecule through the Copper-Catalyzed Azide-Alkyne cycloaddition (click) reaction. Through the click reaction, the 1,2,3-triazole ring can be introduced into our systems as a synthetic and electronic linker within the molecule. Additionally, the click reaction provides for a reliable and straight forward method to introduce many new functionalities through the "R" group on the organic azide. The synthesis of two new click derived molecules (4,4'PTC and 4BPTC) will be discussed, as well as the electronic properties of the two molecules in both the solution phase and the solid state. The solid state electronic properties will be evaluated through investigation of crystal packing patterns and a series of computational studies. The results of this chapter demonstrate that the electronic properties of the click derived molecules exhibited in the solution phase are maintained in the solid state. Furthermore, while both molecules crystallize in the noncentrosymmetric space group Cc, 4BPTC exhibits traditional ht packing while 4,4'PTC exhibits rare hh packing.

Chapter four focuses on linking the click reaction with the [2+2]photocycloaddition reaction in the solid-state. The photoreactivity of 4,4'PTC will be discussed, as well as the preparation, crystal packing patterns, and photoreactivity of two 4,4'PTC cocrystals. The synthesis of two new click derived molecules (BTC and PTC) will also be discussed, as well as the crystal packing and photoreactivity of each molecule. The preparation and crystal packing data of silver complexes using BTC and PTC as ligands will be discussed with particular attention paid to the two photoactive complexes prepared from PTC. The  $[Ag_2(PTC)_2][(ClO_3)_2]$  complex photoreacts within discrete curved assemblies with the PTC ligands aligned ht within the assembly due to a J-shaped curvature of the ligand. The  $[Ag(PTC)_2][CF_3SO_2]$  complex assembles as discrete linear assemblies and photoreacts in a rare single-crystal to single-crystal (SCSC) photoreaction to produce 1D cross-linked polymers. The results of this chapter demonstrate the first known example of the coupling of the click reaction and the [2+2]photocycloaddition in either the solution phase or the solid state. Furthermore, the PTC ligand exhibits great versatility in the ability to photoreact within discrete assemblies and also in the SCSC reaction to yield cross-linked polymers.

Chapter five discusses the complementary hydrogen bonding of templates and the influences on crystal packing patterns within organic cocrystals. The preparation and crystal packing patterns of several cocrystals of 1,8 DPN and res derivatives will be described. Through the investigation of single crystal data, correlations between the properties of the functional groups on the res and the effects on crystal packing will be proposed. The results of this chapter demonstrate the complementary shape of the hydrogen bonding groups on both hydrogen bond donating and accepting organic templates and offers insight into forces driving crystal packing.

Chapter six focuses on expanding the applications of non-covalent templates to guide intramolecular [2+2] photocycloaddition reactions in the solid state. Design and synthesis of the target molecule, 1,8 DEPN, will be described. The crystal packing of 1,8

DEPN will be discussed as well as the photoreactivity of the molecule. Additionally, three metal-organic assemblies produced from 1,8 DEPN and Ag(I) templates will be discussed in regards to their crystal packing and photoreactivity. While 1,8 DEPN is photostable as a pure solid, all three metal-organic assemblies are photoactive. Isolation and recrystallization of the cyclobutane photoproduct will be demonstrated. Single crystal data will be examined to confirm the intramolecular [2+2] photocycloaddition. Both 1D and 2D NMR techniques will be used to validate the connectivity and stereochemistry of the photoproduct displayed in the single crystal data. The results of this chapter demonstrate the first known example of a non-covalent template facilitating an intramolecular [2+2] photocycloaddition reaction in the solid state. The displayed generality of this system to produce the same photoproduct through different templates supports a new avenue of cyclobutane synthesis and allows for the preparation of previously unobtainable products.

In all, the research described here will demonstrate our efforts at furthering the applications of supramolecular solid-state materials. It is my intent that the research presented in these chapters will serve as a continuation for the advancement of this emerging field.

## CHAPTER 2: INTEGRATION OF TERMINAL ALKYNES INTO OLEFINIC COMPOUNDS

#### 2.1. Introduction

Building from previous studies on expanding functional group diversity in the solid state, our focus turned towards integrating new functionalities that could undergo post-synthetic modifications (PSM). Though first suggested by Robson in 1990,<sup>36</sup> the term "post-synthetic modification" was coined in 2007 by Cohen, as an analogy to the post-translation modifications seen in proteins after polypeptide synthesis.<sup>37</sup> Prior to the development of PSM techniques, the introduction of new functionality into organic and metal-based materials was often hindered by incompatibility of the functionalities with the desired self-assembled product (e.g.- competition for hydrogen bonding and metal coordination).<sup>38-40</sup> The PSM technique has proven ideal as it allows for the incorporation of functionality after self-assembly of the precursor material, allowing for the systematic study of functional group relationships and tuning of materials' properties.<sup>41</sup> Integration of functionalities into our template systems that can undergo PSM would allow for the synthesis of a base compound, followed by several different PSM techniques to rapidly generate a library of analogous, yet diverse molecules that share a similar backbone but differ in key functionalities. The terminal alkyne functionality provides the opportunity for several different PSM techniques, including halogen addition, oxymercuration, hydroboration-oxidation, and catalytic reduction (Figure 19).<sup>42</sup>


Figure 19. Traditional PSM reactions of terminal alkynes: (a) halogen addition, (b) oxymercuration, (c) hydroboration-oxidation, and (d) catalytic reduction.

To this point, we propose the introduction of a terminal alkyne on a stilbazole derived molecule (Figure 20).



Figure 20. Proposed stilbazole molecule with terminal alkyne functional group.

While terminal alkynes have not previously been present in [2+2] photocycloadditions in the solid state, the alkyne functional group has been exploited in other solid state reactions. In particular, Lauher has demonstrated the ability to conduct alkyne polymerization reactions in the solid state (Figure 21a-b).<sup>43-44</sup> Much as the topochemical postulate dictates specific packing requirements for the [2+2] photocycloaddition in the solid state, Lauher has also been able to determine specific

requirements for alkyne solid-state polymerization. Furthermore, Lauher has demonstrated the use of host-guest systems analogous to out template method to align alkynes into proper geometries for polymerizations. Additionally, Desiraju has shown that, given proper molecular alignment, terminal alkyne decorated molecules, similar in structure to our proposed molecule, can undergo the Diels-Alder cyclization (Figure 21c).<sup>45-46</sup>



Figure 21. Examples of alkyne reactivity in the solid state: (a) polymerization of alkynes, (b) reactivity of alkynes within host-guest systems, and (c) Diels-Alder reaction of alkynes.

Difficulties with the integration of terminal alkynes into our template systems may come from the acidity of the terminal hydrogen. As shown by both Desiraju and Philp, the terminal hydrogen is acidic enough to participate in hydrogen bonding (Figure 22).<sup>47-48</sup> With our template method relying of non-covalent hydrogen bonding, the possibility of the terminal hydrogen also participating in hydrogen bonding may interrupt the formation of cocrystals with organic templates.



Figure 22. Hydrogen bonging of hydrogen atom on terminal alkyne.

Our goal, therefore, is to synthesize a stilbazole based molecule bearing a terminal alkyne functional group. Our key interest is to produce a photoreaction of this molecule through the use of the template method, thereby demonstrating the tolerance of the templated [2+2] photocycloaddition reaction in the solid state towards the introduction of new functionality. Future studies would involve the PSM of the alkyne both before and after the formation of the cyclobutane ring. In this chapter, our studies of the synthesis of the molecule and its crystal packing, as well as the templated photoreaction of the molecule will be discussed.

## 2.2. Experimental

## 2.2.1. Synthesis of 1-Bromo-4-[2-(4-pyridyl) ethenyl]

## benzene

4-picoline (12.1 g, 129 mmol), 4-bromobenzaldehyde (20 g, 108 mmol), and acetic anhydride (50 mL) were combined in a 100 mL round bottom flask. The reaction was refluxed for 24 hours. After refluxing for 24 hours, the reaction was cooled to room temperature. Once at room temperature, the reaction was poured into 400 mL of an ice/ deionized water mixture. While stirring, the solution was made alkaline through the addition of sodium hydroxide pellets. The brown precipitate that formed was collected

by vacuum filtration. The solid was triturated in 500 mL 4:1 hexanes: 2-propanol, to give the product (21.8 g, 77% yield). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm)  $\delta$ = 8.56 (2H, d, 5.6 Hz), 7.62 (4H, s), 7.56 (2H, d, 6.4 Hz), 7.54 (1H, d, 16.0 Hz), 7.31 (1H, d, 17.2 Hz).



Figure 23. Schematic for the synthesis of 1-Bromo-4-[2-(4-pyridyl) ethenyl] benzene.

#### 2.2.2. Synthesis of 1-Ethynyl-4-[2-(4-pyridyl) ethenyl]

#### benzene

1-Bromo-4-[2-(4-pyridyl) ethenyl] benzene (14.3 g, 55 mmol) was dissolved with 200 mL THF and 350 mL of triethylamine in a 1000 mL round bottom flask. To this was added both 2-methyl-3-butyl-2-ol (7.0 g, 83 mmol) and bis(triphenyl phosphine) palladium (II) dichloride (0.7 g, 1 mmol). The reaction was stirred at room temperature for 20 minutes. After 20 minutes, copper (I) iodide (0.3 g, 2.7 mmol) was added. The reaction was then refluxed for 24 hours. After 24 hours, the reaction was brought back to room temperature. The solution was vacuum filtered through a celite plug and washed with triethylamine. The filtrate was evaporated. The resulting solid was washed with ether and gravity filtered to collect 1-[2-(2-propanol)ethyne]-4-[2-(4-pyridyl) ethenyl] benzene (10.1 g, 70% yield).

1-[2-(2-propanol)ethyne]-4-[2-(4-pyridyl) ethenyl] benzene (4.7 g, 18 mmol) was placed in a 500 mL round bottom flask and dissolved with 250 mL toluene. Once dissolved, sodium hydroxide pellets (2.2 g, 55 mmol) were added to the reaction. The reaction was refluxed for 24 hours. After 24 hours, the reaction was gravity filtered while hot. The yellow filtrate evaporated to give a yellow solid. The solid was sublimed,

giving 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene as a white solid (1.37 g, 15% yield). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm)  $\delta$  = 8.56 (2H, d, 6.0 Hz), 7.67 (2H, d, 8.4 Hz), 7.57 (1H, d, 16.8 Hz), 7.56 (2H, d, 2.8 Hz), 7.52 (2H, d, 8.0 Hz), 7.32 (1H, d, 16.8 Hz), 4.32 (1H, s).



Figure 24. Schematic for the synthesis of 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene.

## 2.2.3. Synthesis of (4,6-diBr-res)·2(1-Ethynyl-4-[2-(4-

## pyridyl) ethenyl] benzene)

(1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene) (87.5 mg, 0.427 mmol) and 4,6diBr-res (57.0 mg, 0.213 mmol) were dissolved in 10 mL of acetonitrile upon heating. The solution was allowed to evaporate slowly at room temperature. Colorless prismatic crystals began to precipitate after 10 minutes. The crystals were separated from the mother liquor by vacuum filtrations and dried in air. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm)  $\delta$  = 10.22 (2H, s), 8.55 (4H, d, 6.8 Hz), 7.66 (4H, d, 9.2 Hz), 7.55 (4H, d, 5. 2Hz), 7.54 (1H, s), 7.49 (2H, d, 18.0 Hz), 7.48 (4H, d, 10.4 Hz), 7.29 (2H, d, 16.8 Hz), 6.64 (1H, s), 4.23 (2H, s).

## 2.2.4. Photoreactivity Experiments

Samples of 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene and (4,6-diBr-res)·2(1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene was monitored for photoreactivity. Each sample was prepared as a crystalline powder and spread between two Pyrex plates. The samples were exposed to broad spectrum UV-irradiation in a high-pressure broadband mercury photoreactor. The progress of the photoreactions was monitored by solution phase <sup>1</sup>H NMR spectroscopy in regular intervals of approximately 10 hours. Progression of the photoreactions could be confirmed by the disappearance of signals for the olefinic protons and the appearance of signals for the cyclobutane protons.

## 2.3. Results and Discussion

In this section, our efforts towards the integration of the terminal alkyne functional group into the [2+2] photocycloaddition in the solid state will be discussed. Specifically, the single crystal packing of 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene and the cocrystal (4,6-diBr-res) $\cdot 2(1$ -Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene) will be described, as well as correlations from the crystal data to the photoreactivity of both the single molecule and the cocrystal. The crystallographic data for the single molecule and the cocrystal can be found in the Appendix (Table A1).

Upon synthesis and purification of 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene, single crystals were grown from slow solvent evaporation in acetonitrile (10 mL). Thin colorless plates formed over a period of one day.

The asymmetric unit of 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene consists of a full molecule that crystallizes in the orthorhombic space group Pna2<sub>1</sub> (Figure 25a). Though fully conjugated, the molecule is not planar, with the plane of the benzene ring rotated 17.4° from the plane of the pyridine ring. Within the unit cell, molecules are arranged in head-to-tail (ht) dimers (Figure 25b). The molecules within the dimers are aligned nearly parallel, with the planes of the pyridine rings rotated 3.6° from parallel. The C=C are separated by 5.42 Å and 6.11 Å. Extended packing shows that the dimers are canted 77.1° from their nearest neighbor. As was demonstrated from previous studies with terminal alkynes, the terminal hydrogen takes part in hydrogen bonding with the

nitrogen atom on the pyridine ring of a neighboring molecule (Figure 25c). The hydrogen bonding propagates along the *b*-axis with a C-H $\cdots$ N bond distance of 2.2 Å, giving rise to chains of molecules aligned head-to-head (hh).



Figure 25. Single crystal data of 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene: (a) single molecule showing the rotation from planarity between the pyridine and benzene planes, (b) unit cell packing exhibiting ht dimers, and (c) C-H…N hydrogen bonding along the *b*-axis.

Upon exposure to UV irradiation, no photoreaction could be detected. The photostability of the molecule is supported by the single crystal data, which demonstrates violations of the topochemical postulate, including olefins not aligned parallel and C=C separations greater than 4.2 Å. In an effort to guide the crystal packing of 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene into a photoactive geometry, we proposed growing cocrystals with the template 4,6-diBr res (Figure 26).



Figure 26. Proposed cocrystallization of 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene with the template 4,6-diBr res to engineer photoactive assemblies.

Single crystals of the cocrystal (4,6-diBr-res)·2(1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene) were grown from 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene (87.5 mg) and 4,6-diBr-res (57.0 mg) through slow solvent evaporation in acetonitrile (10 mL). Colorless prismatic crystals began to precipitate after approximately 10 minutes.

The asymmetric unit of the cocrystal consists of a complete assembly with a 1:2 ratio of 4,6-diBr-res to 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene that crystallizes in the triclinic space group  $P\overline{1}$  (Figure 27a). Though single crystal data of 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene exhibited C-H…N hydrogen bonding, for the cocrystal, the hydroxyl groups of the 4,6-diBr res present as stronger hydrogen bond donors. The presence of stronger hydrogen bond donors prevents the C-H…N bonding and, instead, the two components crystallize in discrete assemblies maintained through O-H…N hydrogen bonds (1.9 Å). The O-H…N hydrogen bonding within the assemblies facilitates hh alignment of the 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene molecules, with the C=C separated by *ca.* 3.9 Å. Within the unit cell, the assemblies are aligned ht around an inversion center (Figure 27b). It is expected that this ht alignment would prevent the [2+2] photocycloaddition between assemblies, giving rise to only one photoproduct. Extended packing within the cocrystal demonstrates hh alignment of

assemblies. The hh assemblies are off-set due to Br-O halogen interactions giving C=C separation of 5.1 Å between assemblies (Figure 27c).



Figure 27. Crystal packing of (4,6-diBr-res)·2(1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene): (a) discrete assembly showing hh alignment of olefins, (b) unit cell packing exhibiting ht stacking of assemblies, and (c) extended packing showing assemblies stacking off-set and hh.

Upon exposing the cocrystal to UV irradiation, a photoreaction can be observed through solution phase <sup>1</sup>H NMR by the appearance of the signal at 4.7 ppm, indicating the formation of the cyclobutane ring (Figure 28). The cocrystal undergoes quantitative conversion to the cyclobutane product after 118h exposure to UV irradiation.



Figure 28. <sup>1</sup>H NMR data of [2+2] photocycloaddition: (a) <sup>1</sup>H NMR of cocrystal prior to exposure to UV irradiation and (b) <sup>1</sup>H NMR of cocrystal after quantitative conversion to cyclobutane project.

## 2.4. Conclusion

Through the Sonogashira coupling reaction, we have successfully synthesized an olefinic molecule bearing a terminal alkyne functional group. Crystal packing of the pure solid violates the topochemical postulate, rendering the molecule photostable. It is of interest to note; however, that the previous studies of terminal hydrogen acidity is supported by our molecule through the demonstration of C-H…N hydrogen bonded chains within the extended packing. Furthermore, the single crystal packing of the pure solid prevents other cycloaddition reactions such as the Diels-Alder cycloaddition. The [2+2] photocycloaddition of 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene can be achieved through the use of the template method. Cocrystallization with 4,6-diBr res gives rise to discrete assemblies in the crystalline state with hh olefin alignment. The cocrystal photoreacts quantitatively upon 118h exposure to UV irradiation. The demonstration of

the photocycloaddition within the cocrystal presents the first example of the [2+2] photocycloaddition of olefins with terminal alkynes present. The successful incorporation of terminal alkynes into our solid state reactions allows for opportunities towards the introduction of other new functional groups through PSM techniques, thereby helping to overcome limited functional group diversity in the solid state.

# CHAPTER 3: ELECTRONIC BEHAVIOR OF CLICK BASED PRODUCTS IN THE SOLID STATE

## 3.1. Introduction

While the integration of a terminal alkyne on an olefinic molecule gives rise to the possibility for traditional organic post-synthetic modifications (PSM) (as discussed in Chapter 2), the terminal alkyne functional group can also take part in the Copper-Catalyzed Azide-Alkyne Cycloaddition reaction (CuAAC). The CuAAC reaction belongs to a class of reactions first defined by Sharpless in 2001 known as "click" reactions.<sup>49</sup> Per Sharpless's definition, all click reactions adhere to a rigorous set of nine guidelines (Table 1).

Table 1. Guidelines for click reactions.

The synthesis must be modular.			
The reaction must be wide in scope.			
The synthesis must produce products in high yields.			
The reaction must have inoffensive byproducts.			
The synthesis must produce stereospecific products.			
The procedure requires simple reactions conditions.			
The synthesis must have readily available starting materials and reagents.			
The synthesis uses benign solvents.			
The reaction requires simple (nonchromatographic) product isolation.			

While many reactions can be classified as click reactions, the CuAAC is possibly the most well-known click reaction, and is often referred to as simply "the click reaction." (For the remainder of this thesis, the CuAAC will be referred to as the click reaction) The click reaction was published independently in 2002 by both the Sharpless and Meldal groups as a copper (I) catalyzed Huisgen 1,3-dipolar cycloaddition.<sup>50-51</sup> While the uncatalyzed cycloaddition of a terminal alkyne and an azide had been previously demonstrated, the thermal reaction produces both and a 1,4-disubstituted and a 1,5-disubstituted 1,2,3-triazole ring (Figure 29a).<sup>52</sup> Sharpless and Meldal revealed that, in the presence of a Cu(I) catalyst, the cycloaddition produces the 1,4-disubstituted 1,2,3-triazole ring exclusively (Figure 29b).<sup>50-51</sup>



Figure 29. Schematic of the Huisgen 1,3-dipolar cycloaddition between a terminal alkyne and an azide. (a) cycloaddition with heat, producing the 1,4-disubstituted and the 1,5-disubstituted 1,2,3-triazole rings and (b) Cu(I) catalyzed cycloaddition, producing the 1,4-disubstituted 1,2,3-trizole ring.

The use of the Cu(I) catalyst enables the cycloaddition reaction to meet many of the criteria for a click reaction, including high yielding, having inoffensive byproducts, and being regiospecific. Furthermore, because the reaction proceeds in a mixture of water and DMF at room temperature, the reaction also adheres to having simple reaction conditions, benign solvents, and simple product isolation. The final three criteria for a click reaction (modular, wide in scope, and readily available starting material and

reagents), are met through the nature of the catalytic cycle (Figure 30).<sup>53</sup> The coordination of the Cu(I) catalyst with the alkyne and azide functional groups allows for the synthesis of a wide range of diverse molecules that can be easily tailored through the variable R groups. Furthermore, the click reaction provides an avenue to generate a large library of analogous compounds to study the effects the subtle changes may have on properties and applications in both the solution phase and the solid state.



Figure 30. Schematic of the catalytic cycle of the click reaction.

The click derived 1,2,3-triazole ring presents many attractive features for integration into supramolecular chemistry. As described by Schubert in his recent review, the 1,2,3-triazole ring can participate in both anion and metal complexations (Figure 31).<sup>54</sup> Each of these interactions can be realized independently within a system, or can couple together with both anion complexation and metal complexation being present within the same system.



Figure 31. Potential anion and metal complexations of 1,2,3-triazole ring.

Whereas the click reaction has experienced great promise with widespread applications in organic synthesis and materials chemistry (e.g. supramolecular chemistry and fluorescence),<sup>55-61</sup> less is known with regard to how electronic information is propagated by the triazole ring itself. In this context, recent studies have reported the triazole ring to bridge electron-donor and -acceptor groups as part of charge-transfer conduits in solution.<sup>62-65</sup> Triazole rings have, thus, been incorporated into branched dendrimers to bridge donors and acceptors and enhance tunable photoluminescence (Figure 32a). Moreover, substitution patterns of donor and acceptor groups of triazoles are now being studied to discern modes of electronic bridging (Figure 32b). For example, triazole rings have been utilized to bridge an electron donor in the form of a fullerene to an acceptor in the form of a Zn(II) porphyrin (Figure 33c).<sup>64</sup>



Figure 32. Key molecules from studies utilizing 1,2,3-triazole rings to bridge electrondonor and –acceptor groups: (a) studies of 1,2,3-triazole ring linked branched dendrimers, (b) studies of substitution patterns on the 1,2,3-triazole ring, and (c) triazole bridging between a fullerene and a Zn-porphyrin.

Very recently, the triazole moiety has been revealed to support enhanced optical properties involving pyrimidine as an electron acceptor.<sup>65</sup> There has been only one report, however, that suggests a triazole to serve as an electronic bridge of small molecules in the crystalline state. In the report, the triazole acted as a bridge in starburst triphenylamines (Figure 33).<sup>66</sup> Without crystal packing information, however, correlations to electronic spectra can be difficult.



Figure 33. Key molecule in study of 1,2,3- triazole ring acting as a bridge in starburst triphenylamines in the crystalline state.

Our interests in triazoles lie in an ability of 1-[2-(4-pyridyl)ethenyl]-4-[3-(4-pyridyl)-1H-1,2,3-triazol-4-yl] benzene (4,4'PTC) and 1-[2-(4-pyridyl)ethenyl]-4-[3-(pyridin-2-yl-methyl)-1H-1,2,3-triazol-4-yl] benzene (4BPTC) (Figure 34) to function as building blocks for applications in self-assembly and supramolecular syntheses.<sup>67</sup> In this chapter, our studies in understanding the solid-state structures of 4,4'PTC and 4BPTC and the effects of crystal packing on the electronic properties of the compounds will be discussed.



Figure 34. Click-derived compounds for the study of crystalline-state electronic properties.

#### 3.2. Experimental

#### 3.2.1. Synthesis of 4-Azidopyridine

Sodium azide (2.46 g, 38 mmol) was dissolved with 40 mL deionized  $H_2O$  in a 100 mL round bottom flask. To the flask was added 4-chloropyridine hydrochloride (2.6 g, 18 mmol). The flask was wrapped in foil to protect the reaction from light. The reaction was refluxed for 24 hours behind a blast shield. After refluxing for 24 hours, the reaction was dark red in color. The reaction was brought back to room temperature. Once at room temperature, the product was extracted with 350 mL ethyl acetate. The aqueous layer was collected in an azide waste container. The organic layer was dried with magnesium sulfate and gravity filtered into a round bottom flask. The filtrate was

concentrated to give the product as a red oil (1.2 g, 56% yield). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm)  $\delta = 8.51$  (2H, d, 6.4 Hz), 7.14 (2H, d, 6.4 Hz).

$$NaN_3 + CI \longrightarrow N \cdot HCI \longrightarrow N \longrightarrow N_3$$

Figure 35. Schematic for the synthesis of 4-Azidopyridine.

#### 3.2.2. Synthesis of 1-[2-(4-pyridyl)ethenyl]-4-[1-(4-

#### pyridyl)-1H-1,2,3-triazol-4-yl] benzene (4,4'PTC)

4-azidopyridine (0.64 g, 5.3 mmol) was dissolved in 20 mL 4:1 DMF-deionized  $H_2O$  in a 250 mL round bottom flask. To the flask was added: copper (II) sulfate pentahydrate (0.61 g, 2.4 mmol), L-ascorbic acid (0.85 g, 4.9 mmol), and sodium carbonate (0.51 g, 4.9 mmol). The reaction was stirred for five minutes. After five minutes, 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene (1.0 g, 4.9 mmol) was added to the reaction. The flask was wrapped in foil to protect the reaction from light. The flask was capped with a septum and vented with two needles. The reaction was stirred at room temperature behind a blast shield for 24 hours. After 24 hours, the reaction was thick and The reaction was quenched through the addition of a solution of 4 mL orange. concentrated ammonium hydroxide, 3.7 g EDTA, and 96 mL deionized H<sub>2</sub>O. The reaction was stirred vigorously for 30 minutes. While stirring, a precipitate could be seen. The solid was collected through vacuum filtration. The filtrate was collected and the pH was measured to be basic. The filtrate was placed in an azide waste container. The precipitate was washed with chloroform. The solution was gravity filtered and the filtrate was evaporated. Evaporation gave a pale yellow solid. The solid was recrystallized in ethanol to give the product as a white solid (0.1 g, 6% yield). <sup>1</sup>H NMR  $(DMSO-d_6, 400 \text{ MHz}, \text{ppm}) \delta = 9.57 (1H, s), 8.84 (2H, d, 6.8 \text{ Hz}), 8.57 (2H, d, 6.0 \text{ Hz}),$  8.03 (2H, d, 6.8 Hz), 8.01 (2H, d, 8.4 Hz), 7.82 (2H, d, 8.4 Hz), 7.61 (1H, d, 16.8 Hz), 7.59 (2H, d, 5.6 Hz), 7.35 (1H, d, 16.8 Hz).



Figure 36. Schematic for the synthesis of 1-[2-(4-pyridyl)ethenyl]-4-[1-(4-pyridyl)-1H-1,2,3-triazol-4-yl] benzene.

## 3.2.3. Synthesis of 1-[2-(4-pyridyl)ethenyl]-4-[1-(pyridin-

#### 2-yl methyl)-1H-1,2,3-triazol-4-yl] benzene (4BPTC)

4-(Bromomethyl)pyridine hydrobromide (0.28 g, 1.6 mmol) was placed in a 250 mL round bottom flask and dissolved with 10 mL of 4:1 DMF: deionized H<sub>2</sub>O. Once dissolved, copper (II) sulfate pentahydrate (0.18 g, 0.7 mmol), sodium azide (0.11 g, 1.7 mmol), L-ascorbic acid (0.26 g, 1.5 mmol), and sodium carbonate (0.15 g, 1.5 mmol) were added to the reaction. The reaction was stirred at room temperature for five minutes. After five minutes, 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene (0.3 g, 1.5 mmol) was added to the reaction. The flask was wrapped in foil to protect the reaction from light, capped with a septum, and vented with two needles. The reaction was stirred at room temperature for 24 hours behind a blast shield. After stirring for 24 hours, the solution was thick and red. The reaction was quenched through the addition of a solution of 4 mL concentrated ammonium hydroxide, 3.7 g EDTA, and 96 mL deionized H<sub>2</sub>O. The reaction was stirred vigorously for 30 minutes. While stirring, a precipitate could be seen. The solid was collected through vacuum filtration. The filtrate was collected and the pH was measured to be basic. The filtrate was placed in an azide waste container.

filtrate was evaporated. Evaporation gave a pale white solid. The solid was sublimed to give the product as a white solid (0.075 g, 15% yield). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, ppm)  $\delta = 8.76$  (1H, s), 8.59 (2H, d, 6.6 Hz), 8.55 (2H, d, 5.1 Hz), 7.92 (2H, d, 7.5 Hz), 7.75 (2H, d, 8.7 Hz), 7.58 (1H, d, 17.8 Hz), 7.57 (2H, d, 6.3 Hz), 7.32 (1H, d, 16.8 Hz), 7.26 (2H, d, 6.3 Hz), 5.76 (2H, s).



Figure 37. Schematic for the synthesis of 1-[2-(4-pyridyl)ethenyl]-4-[1-(pyridin-2-yl methyl)-1H-1,2,3-triazol-4-yl] benzene.

#### 3.2.4. UV-Vis Absorbance Experiments

UV-Vis spectra were obtained using an Agilent UV-Visible Diode Array Spectrometer. UV-Vis spectra were recorded in dimethylformamide (DMF) (40  $\mu$ M and 20  $\mu$ M) and dichloromethane (DCM) (40  $\mu$ M and 20  $\mu$ M) at 1.0 nm intervals.

#### <u>3.2.5. Computational Studies</u>

Gas phase dimers were calculated using a computational method previously described by Piacenza and Grimme.<sup>68</sup> In particular, BLYP functional within RI approximation combined with def-TZVPP basis set and dispersion correction were used to optimize the geometry of the dimers, followed by a large aug-cc-pVTZ basis sets and BLYP functional single point energy calculation.<sup>69-74</sup> Three separate single point calculations were performed on the optimized dimer: one of the dimer itself and two of each component of the dimer in the optimized dimer geometry. The difference between three values the represents an interaction (binding) energy between the components in their corresponding optimized dimer positions. TURBOMOLE6.3 program suite was used in all gas phase calculations.<sup>75</sup> Geometries were optimized without any constraints

followed by the vibrational frequency analysis. The absence of negative frequencies confirmed that structures were on the potential energy surface minima.

Gas phase HOMO and LUMO orbital plots were derived using M06-2X functional in combination with 6-31G(d,p) basis set. These calculations were performed using Gaussian 09 version B02.<sup>76</sup>

All periodic boundary calculations were performed using B3LYP functional with Grimme's dispersion correction used to account for weak intermolecular forces, as implemented in CRYSTAL'09.<sup>77-79</sup>

## 3.3. Results and Discussion

In this section, the electronic properties of the click-derived compounds 4,4'PTC and 4BPTC will be discussed. Specifically, the electronic properties of these compounds in the solution phase and the solid-state will be compared. Additionally, calculations based on the single crystal packing of each molecule, demonstrating correlations between the solution phase and the solid state, will be described. The crystallographic data for single crystals of 4,4'PTC and 4BPTC discussed in this chapter can be found in the Appendix (Table A2).

## 3.3.1. Electronic Behavior of Click Products in the Solution

## Phase

The electronic properties and bridging capabilities of 4,4'PTC and 4BPTC in the solution phase were evaluated through UV-Vis spectroscopy.<sup>80-83</sup> Spectra of both compounds were collected in the more polar dimethylformamide (DMF) and the less polar dichloromethane (DCM) at concentrations of 40  $\mu$ M and 20 $\mu$ M.

Spectra for each compound were measured at varying concentrations to ensure that aggregations were not forming. For 4,4'PTC, at both 40  $\mu$ M and 20 $\mu$ M DMF, the  $\lambda_{max}$  is measured at 323 nm (Figure 38a). When measured at 40  $\mu$ M and 20 $\mu$ M DCM, the  $\lambda_{max}$  for 4,4'PTC is measured at 317 nm (Figure 38b). The consistency of the  $\lambda_{max}$  as the concentration is decreased is indicative that the molecules are not aggregating in the solvent and that our measurements are of single molecules.



Figure 38. UV-Vis spectrum of 4,4'PTC in: (a) DMF (40  $\mu$ M on top and 20  $\mu$ M on bottom) and (b) DCM (40  $\mu$ M on top and 20  $\mu$ M on bottom).

For 4BPTC, at both 40  $\mu$ M and 20 $\mu$ M DMF, the  $\lambda_{max}$  is measured at 323 nm (Figure 39a). When measured at 40  $\mu$ M and 20 $\mu$ M DCM, the  $\lambda_{max}$  for 4BPTC is measured at 321 nm (Figure 39b). The consistency of the  $\lambda_{max}$  as the concentration is decreased is indicative that the molecules are not aggregating in the solvent and that our measurements are of single molecules.



Figure 39. UV-Vis spectrum of 4BPTC in: (a) DMF (40 μM on top and 20 μM on bottom) and (b) DCM (40 μM on top and 20 μM on bottom).

For each compound, the spectra collected at 40  $\mu$ M in the individual solvents were compared to measure the polarizability of the compounds. Electronically soft molecules are susceptible to the polarity of their surroundings.<sup>41</sup> Therefore, if either 4,4'PTC or 4BPTC are electronically soft (and therefore, able to facilitate electron distribution throughout the molecule), a shift in the  $\lambda_{max}$  should be observed as the polarity of the solvent changes.

For 4,4'PTC, significant changes in wavelength and intensity were observed for the peak at 323 nm (DMF) that underwent an increase in intensity and blue shift to 317 nm (DCM) (Figure 40a). In the case of 4BPTC, no significant change in the  $\lambda_{max}$  was observed. An increase in intensity of the peak at 323 nm for 4BPTC, however, was observed in less polar DCM (Figure 40b). The differences in the UV-Vis spectra of 4,4'PTC are consistent with solvochromatic behavior, which is typical for a molecule that is easily polarizable.<sup>84</sup>



Figure 40. Comparison of UV-Vis spectra measured in different solvents: (a) 4,4'PTC in 40µM DMF (red) and 40µM DCM (blue) and (b) 4BPTC in 40µM DMF (red) and 40µM DCM (blue).

#### <u>State</u>

Whereas evidence for the 1,4-disubstituted 1,2,3-triazole ring of 4,4'PTC to act as an electronic bridge was realized in the solution phase, that the electronic behavior is maintained in the solid state originates from crystal structures of both 4,4'PTC and 4BPTC.<sup>85</sup>

Single crystals of 4,4'PTC (8.5 mg) were grown from slow solvent evaporation in ethanol (9 mL). Thin colorless plates formed over a period of approximately 3 h.

The asymmetric unit of 4,4'PTC consists of a full molecule that crystallizes in the noncentrosymmetric space group Cc (Figure 41). The stilbazole moiety is planar with a 24.4° rotation from the triazole ring while the pyridyl "R" group exhibits a 23.6° rotation from the triazole. The overall twist of 4,4'PTC is 47.6° as measured with respect to the central benzene ring. Importantly, 4,4'PTC exhibits atypical head-to-head (hh) stacking in the solid, which is sustained by edge-to-face  $\pi$ -forces, with neighboring molecules canted at 48.2° as measured from the plane of the central benzene ring (Figure 41a). In the arrangement, the triazole rings of neighboring molecules are separated by 3.8 Å with the molecular dipoles being effectively aligned in the same direction. The hh alignment is further manifested through C-H<sup>...</sup>N forces (3.6 Å) between triazole rings of neighboring molecules (Figure 41b). Similar C-H<sup>...</sup>X<sup>-</sup> forces involving triazole rings to support anion binding have been reported.<sup>86</sup> Collectively, the hh packing of 4,4'PTC is propagated throughout the entire crystal, which accounts for the noncentrosymmetric packing.



Figure 41. Packing of 4,4'PTC: (a) hh stacking via edge-to-face forces and (b) CH…N interactions.

In contrast to 4,4'PTC, head-to-tail (ht) packing was realized for 4BPTC. Single crystals of 4BPTC (8.0 mg) were grown from slow solvent evaporation of toluene (5 mL). Colorless plates formed after approximately 5 days.

Similar to 4,4'PTC, 4BPTC also crystallizes in the noncentrosymmetric space group Cc (Figure 42). The asymmetric unit of 4BPTC, however, consists of two full molecules. Each molecule exhibits rotation from planarity between the central benzene ring and the triazole ring (molecule A: 9.6°, molecule B: 10.2°). The presence of the saturated linkage results in a dihedral twist between the triazole ring and the pyridyl "R" group (molecule A: 112.5°, molecule B: 110.4°). In contrast to 4,4'PTC, the two molecules are present as dimers that display a ht arrangement sustained by face-to-face  $\pi$ forces (*ca.* 3.7 Å). Adjacent triazole rings within the dimer are separated by 12.0 Å. C-H"N interactions are not present between neighboring triazole rings, as with 4,4'PTC. The dimers pack ht, with adjacent dimers being canted at approximately 37.6° with respect to the plane of the central benzene ring. The ht packing of non-conjugated 4BPTC is consistent with typical behavior of molecules to pack to cancel dipole moments. An origin of the noncentrosymmetric packing of 4BPTC, however, lies in the conformations of the alkene units. In particular, whereas the C=C bonds of stacked molecules of 4,4'PTC adopt *cisoid* conformations with respect to the N2/N3 N-atoms of each triazole ring, the two molecules present in the asymmetric unit of 4BPTC adopt either a *cisoid* or *transoid* conformation (Figure 42c).



Figure 42. Packing of 4BPTC: (a) ht packing *via* face-to-face  $\pi$ -forces, (b) extended packing, and (c) conformations of molecules of dimer.

Molecules in organic solids typically assemble ht, or antiparallel, so as to promote cancellation of molecular dipole moments.<sup>87-88</sup> For 4,4'PTC, we attribute the hh packing to the ability of the 1,4-disubstituted 1,2,3-triazole to serve as an electronic bridge between the two pendant stilbazole and pyridine groups. In effect, the bridge enables charge distribution to be spread throughout the molecule and, thus, support a hh  $\pi$ -stacked structure. The crystal packing is, thus, consistent with a bipyridine that is 'electronically soft', with the electron density being easily polarized by bridging behavior of the triazole.<sup>89</sup> Notably, in a survey of the Cambridge Structural Database (CSD) (version 5.34, update 3, November 2012) of structurally analogous triazoles, we

determined six of 32 molecules to exhibit noncentrosymmetric packing based on hh stacking geometries.<sup>90</sup>

Insight into the nature of the hh packing in 4,4'PTC was gained by periodic density-of-state (DOS) calculations derived directly from optimized crystal structures of 4,4'PTC and 4BPTC (Figure 43a-b). Specifically, for the LUCO of 4,4'PTC, contributions from the stilbazole, pyridine, and triazole involve crystalline band overlap in the 3.5 to 4.5 eV region, which supports the triazole ring to act as an electronic bridge. For 4BPTC, there are negligible contributions from triazole and pyridyl moieties to the LUCO. Gas-phase DFT calculations for single molecules of 4,4'PTC and 4BPTC are consistent with the triazole ring acting as a bridge between the stilbazole and the pyridine (Figure 43c). Electron density of the HOMO of 4,4'PTC is localized on the stilbazole and triazole while electron density of the LUMO is delocalized throughout the entire molecule. Similar to 4,4'PTC, the electron density for the HOMO of 4BPTC is localized on both the stilbazole and triazole. Unlike 4,4'PTC, however, electron density is not present on the pendant pyridyl "R" group in the LUMO of 4BPTC.



Figure 43. Density of states plots in crystalline environment: (a) 4,4'PTC and (b) 4BPTC. Highest crystalline (molecular) filled band (orbital) is aligned with 0 eV. Gasphase DFT calculations: (c) HOMO and LUMO of 4,4'PTC and 4BPTC. Note presence and absence of delocalized electron density in the LUMO of 4,4'PTC and 4BPTC, respectively. Isosurface density parameter was 0.03.

Gas-phase DFT calculations also demonstrate the hh face-to-face dimer of 4,4'PTC to exhibit a binding energy that is relatively stable and comparable to alternative ht geometries. The binding energy for the ht dimer of 4BPTC reflects a relatively stable geometry with hh orientations being consistently less stable in energy (Table 2). The calculations are also consistent with the relative planarities exhibited by the stilbazole and triazole moieties of 4,4'PTC and 4BPTC in the solids.

Molecule	Dimer Geometry	Orientation	Binding Energy (kcal/mol)
4,4'PTC	hh	cisoid-cisoid	-24.5
4,4'PTC	hh	cisoid-transoid	-25.1
4,4'PTC	hh	transoid-transoid	-21.3
4,4'PTC	ht	cisoid-cisoid	-24.4
4,4'PTC	ht	cisoid-transoid	-24.5
4,4'PTC	ht	transoid-transoid	-25.3
4BPTC	hh	cisoid-cisoid	-23.4
4BPTC	hh	cisoid-transoid	-23.2
4BPTC	hh	transoid-transoid	-22.5
4BPTC	ht	cisoid-cisoid	-23.9
4BPTC	ht	cisoid-transoid	-26.7
4BPTC	ht	transoid-transoid	-26.8

Table 2. Gas phase DFT calculations of binding energies with structures closest to experimental noted in bold.

To confirm that the single crystal data was representative of the bulk sample, powder X-ray diffraction (PXRD) data was collected on bulk samples of both 4,4'PTC (Figure 44) and 4BPTC (Figure 45). PXRD data of 4,4'PTC was collected on a Bruker D5000 q-q diffractometer using a Cu radiation source and a Kevex energy-sensitive detector. The scans were collected from 3° to 35° with a 0.02° step size and 4.5 seconds per step collection time. The PXRD data for 4BPTC was collected on a D8 Avance diffractometer using a Cu radiation source, Göbel mirrors, and a LYNXEYE detector. The scans were collected with a 2-theta range from 3° to 35° with a 0.005° step size and 0.3 second per step collection time. For both compounds, the data background was subtracted using the EVA program. The calculated PXRD patterns were calculated from the respective single crystal data using Mercury version 3.1.1.

The measured PXRD data of 4,4'PTC exhibits nice overlap with the calculated data, indicating that the single crystals are representative of the bulk sample. The

measured PXRD data of 4BPTC repeatedly exhibited peak intensities that differed greatly from the calculated pattern, indicating the presence of preferred orientation.<sup>91</sup> To better compare the measured data to the calculated data then, the simulated data for 4BPTC was also calculated with preferred orientation. Calculated data with preferred orientation was produced with Mercury 3.1.1 using an hkl plane of 011 with a March-Dollase parameter of 5. Upon comparison to the simulated data calculated with preferred orientation, it became evident that the single crystal data is representative of the bulk sample.



Figure 44. Calculated (top) and Measured (bottom) PXRD of 4,4'PTC.



Figure 45. Calculated (top), Calculated with 011 preferred orientation (middle), and Measured (bottom) PXRD of 4BPTC.

Shortly after the publication of our paper, a second paper was published investigating the nonlinear optics (NLO) of click-derived molecules in the crystalline state.<sup>92</sup> In order to exhibit NLO properties, the molecules must crystallize in a noncentrosymmetric space group, such as 4,4'PTC and 4BPTC which both crystallize in the Cc space group. The study focused on utilizing the triazole ring for electron delocalization within the molecules and the structure-property relationships of a family of novel click-derived molecules (Figure 46). This study by Lumpi provides further support for the need to evaluate crystal packing patterns of triazole bearing molecules as the functional group becomes further integrated into materials chemistry.



Figure 46. Family of click derived molecules for study of NLO properties.

#### 3.4. Conclusions

In summary, we have shown that the electronic bridging behavior of a 1,4disubstituted 1,2,3-triazole ring derived from a click reaction is maintained in the solid state. Both molecules, 4,4'PTC and 4BPTC, exhibit bridging patterns in the solution phase as demonstrated through UV-Vis spectroscopy. In the solid state, both molecules crystallize in the same noncentrosymmetric space group but involve different stacking geometries. For 4,4'PTC, unusual hh packing is supportive of electronic charge being distributed throughout the molecule *via* bridging while 4BPTC exhibits a more typical ht geometry. Density of state and DFT calculations based on the crystal packing patterns further support the electronic properties and offer insight into the electron distribution through the molecules. As we seek to expand functional group diversity in the crystalline state, we have gained a deeper understanding of the properties of the 1,2,3-triazole ring allowing for further applications of this functionality in the solid state.

## CHAPTER 4: PHOTODIMERIZATION OF CLICK-DERIVED PRODUCTS

### 4.1. Introduction

Through the integration of a terminal alkyne onto a stilbazole derivative, we have been able to utilize the click reaction as a post synthetic modification (PSM) technique, generating a library of new click-derived compounds with differing morphologies and properties in the crystalline state. Utilization of the click reaction as a facile synthetic tool offers many key benefits. As originally described by Sharpless and Meldal, the click reaction offers a green approach to synthetically link functional groups with regioselectivity.<sup>50-51</sup> Furthermore, a modular approach to the study of structure related properties can be readily achieved through tailoring of "R" groups on the azide and alkyne. Finally, while the click reaction has been documented extensively for synthetic purposes, it has more recently shown promise as a PSM technique of ligands within self-assembled metal-organic assemblies (Figure 47).<sup>93-96</sup> The versatility of the click reaction as a PSM technique has been demonstrated through ligands bearing alkynes, azides, and amine groups. Furthermore, these PSM reactions are often conducted on crystalline solids, thereby facilitating the isolation of the product.



Figure 47. Examples of click reaction PSM of MOFs: (a) PSM on an alkyne decorated ligand and (b) PSM of an amine decorated ligand.

In comparison to the click reaction, the solid-state [2+2] photocycloaddition also provides many synthetic benefits. As initially demonstrated by Schmidt, the solid-state [2+2] photocycloaddition provides a green, high yielding method to synthesize the cyclobutane ring.<sup>12</sup> The introduction of the template method to the solid-state [2+2] photocycloaddition furthered these benefits by allowing modular tailoring of the cycloaddition to synthesize a range of new products from previously photostable molecules.<sup>16-17</sup> Additionally, as was also seen from click reactions, the [2+2] photocycloaddition has also been readily used as a PSM technique of organic and metal-organic assemblies.<sup>97-100</sup>

When compared side-by-side, it becomes evident that the click reaction and the solid-state [2+2] photocycloaddition exhibit similar benefits for researchers (Figure 48). While the two reactions have each been well documented independently, it came as a

surprise that the reactions have not been combined within the same system in either the solution phase or the solid state.



Figure 48. Comparison of the benefits of the click reaction and the solid-state [2+2] photocycloaddition.

Given our new ease of synthesizing olefinic click-derived compounds, our goal then became to demonstrate the first example of a [2+2] photocycloaddition reaction on a click-derived molecule in the solid state. Given the recent documentation of click reactions as PSM techniques, we chose to reverse the role of the click reaction, utilizing it for synthesis, and then performing the [2+2] photocycloaddition as the PSM. In this chapter, we will discuss our efforts in expanding the library of olefinic click compounds, as well as comment on the photoreactivity of the pure compounds in the solid state. Additionally, the use of organic and transition metal templates to give rise to photoactive assemblies will be discussed. The crystal packing patterns of both the click molecules and the templated assemblies will be described in relation to the exhibited photoproperties. The crystal data can be found in the Appendix (Tables A3-A6).

# 4.2. Self-Assembly and Photoreactivity of Click Products

## with Organic Templates

As discussed in Chapter 3, the extended pi system of the click based molecule 4,4'PTC allows for the molecules to crystallize in a nearly planar geometry (Figure 40).<sup>85</sup> Despite the near planarity of the individual molecules and the head-to-head (hh) alignment, extended packing exhibits molecules that are canted 48.2° from their nearest neighbor, preventing C=C alignment, rendering the molecule photostable. Though the molecule is photostable, cocrystallization with templates may provide self-assembled photoacitve assemblies. The nearly planar nature of the molecule as well as the bis-(4-pyridyl) termini render 4,4'PTC isostructural to other compounds such as 4,4'BPE, 4,3' BPE, 4,2'BPE, the ladderane precursor, and the cyclophane precursor (Figure 49).<sup>22,23,30,31,34,35</sup> Photoreactions of each of these molecules have been successfully demonstrated in the solid state using resorcinol derived templates. With this in mind then, we proposed also cocrystallizing 4,4'PTC with organic templates to investigate the possible formation of photoactive assemblies.


Figure 49. Series of molecules isostructural to 4,4'PTC.

# 4.3. Experimental

# 4.3.1. Synthesis of (4,6-diI-res) · 4,4'PTC

4,4'PTC (0.4 mg,  $1.2x10^{-3}$  mmol) and 4,6-diI-res (1.3 mg,  $3.7x10^{-3}$  mmol) were dissolved in ~10 mL of acetonitrile upon heating. The solution was allowed to evaporate slowly at room temperature. Single crystal began to precipitate as colorless blades after 48 hours. The crystals were separated from the mother liquor by vacuum filtrations and dried in air. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm)  $\delta$  = 10.40 (2H, s), 9.60 (1H, s), 8.84 (2H, d, 6.0 Hz), 8.57 (2H, d, 6.4 Hz), 8.03 (2H, s), 8.01 (2H, d, 11.6 Hz), 7.83 (2H, d, 9.2 Hz), 7.76 (1H, s), 7.62 (1H, d, 16.8 Hz), 7.60 (2H, d, 12.0 Hz), 7.36 (1H, d, 16 Hz), 6.56 (1H, s).

# 4.3.2. Synthesis of (4,6-diBr-res) · 4,4'PTC

4,4'PTC (0.61 mg,  $1.8 \times 10^{-3}$  mmol) and 4,6-diBr-res (1.5 mg,  $5.6 \times 10^{-3}$  mmol) were dissolved in ~10 mL of acetonitrile upon heating. The solution was allowed to evaporate slowly at room temperature. Single crystal began to precipitate as colorless plates after

24 hours. The crystals were separated from the mother liquor by vacuum filtrations and dried in air. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, ppm)  $\delta$  = 10.35 (1H, s), 8.57 (2H, broad s), 8.33 (2H, broad s), 7.42 (6H, m), 6.65 (2H, broad s), 6.18 (2H, broad s), 4.58 (1H, s).

## 4.3.3. Photoreactivity Experiments

Samples of (4,6-diI-res)· 4,4'PTC and (4,6-diBr-res)· 4,4'PTC were each monitored for photoreactivity. Each sample was prepared as a crystalline powder and spread between two Pyrex plates. The samples were exposed to broad spectrum UVirradiation in a high-pressure broadband mercury photoreactor. Solution phase <sup>1</sup>H NMR spectroscopy was performed in regular intervals of approximately ten hours to detect and monitor progressions of photoreactions.

# 4.4. Results and Discussion

In an effort to facilitate a [2+2] photocycloaddition in the solid state, the 4,4'PTC was cocrystallized with the organic templates 4,6-diI res and 4,6-diBr res (Table 3). Here we will discuss the single crystal data of both cocrystals. The crystal packing will be analyzed with regard to olefin alignment both within and between assemblies as well as the degree of rotation within the 4,4'PTC molecule. This data will also be correlated to the photoreactive properties of the cocrystals as crystalline powders. Crystal data for  $(4,6-diI-res)\cdot(4,4'PTC)$  and  $(4,6-diBr-res)\cdot(4,4'PTC)$  can be found in the Appendix (Table A3).

Table 3. Overview of the cocrystals (4,6-diI-res)·(4,4'PTC) and (4,6-diBr-res)·(4,4'PTC).

Cocrystal	Space Group	Assembly	Photoreactivity
(4,6-diI-res)·(4,4'PTC)	PĪ	0D	Photostable
(4,6-diBr-res)·(4,4'PTC)	PĪ	0D	Photostable

Single crystals of the cocrystal (4,6-diI-res)·(4,4'PTC) were grown from slow solvent evaporation of 4,4'PTC (0.61 mg) and 4,6-dI-res (1.3 mg) in acetonitrile. Colorless blades were observed after approximately 48 h.

The cocrystal (4,6-diI-res)·(4,4'PTC) crystallizes in the space group PI, with the asymmetric unit consisting of a full assembly with two 4,6-diI res molecules and two 4,4'PTC molecules (Figure 50). The discrete assemblies are maintained through O-H…N hydrogen bonding between the template and the pyridine rings of 4,4'PTC (2.7 Å). In contrast to the hh packing of pure 4,4'PTC, within the assemblies of (4,6-diI-res)·(4,4'PTC), the 4,4'PTC molecules are aligned head-to-tail (ht), giving C=C separations of 8.9 Å, thereby violating the topochemical postulate (Figure 50a). Extended packing exhibits I-O interactions (3.4 Å), giving rise to assemblies off-set from one another (Figure 50b). T offset assemblies are also aligned ht with C=C separations of 6.2 Å between assemblies, again violating the topochemical postulate. Upon exposure to UV irradiation, no photoreaction could be observed, confirming the cocrystals to be photostable.



Figure 50. Crystal packing of cocrystal (4,6-diI-res)·(4,4'PTC): (a) discrete assembly exhibiting ht alignment of 4,4'PTC molecules and (b) extended packing of assemblies showing 4,4'PTC molecules alignment ht within and between assemblies (4,4'PTC shown in blue and green for clarity).

Though the packing both within the assemblies and between assemblies give rise to photostability, it was noted that the deviation from planarity for 4,4'PTC was decreased when compared to 4,4'PTC as a pure solid (Figure 51). As a pure solid, 4,4'PTC has a 47.6° rotation between the central benzene ring and the pyridine ring connected to the 1,2,3-triazole ring. Within the assemblies of the cocrystal (4,6-diIres)·(4,4'PTC), the 4,4'PTC molecule become more planar with rotation decreased to 19.4°. The decrease in rotation towards a more planar geometry lead us to pursue templating with an analogous resorcinol based template to investigate if we could engineer the olefins to be both aligned and parallel.



Figure 51. Crystal packing of 4,4'PTC (a) as a pure solid and (b) as part of the cocrystal (4,6-diI-res)·(4,4'PTC), demonstrating the decrease in twisting of the molecule when cocrystallized with a template.

Single crystals of the cocrystal (4,6-diBr-res)·(4,4'PTC) were grown from slow solvent evaporation of 4,4'PTC (0.61 mg) and 4,6-diBr-res (1.5 mg) in acetonitrile. Colorless plates were observed after approximately 24 h.

The cocrystal (4,6-diBr-res)·(4,4'PTC) crystallizes in the space group  $P\overline{1}$ , with the asymmetric unit consisting of a full assembly with two 4,6-diBr res molecules and two 4,4'PTC molecules (Figure 52). The discrete assemblies are maintained through O-

H…N hydrogen bonding between the template and the pyridine rings on 4,4'PTC (2.7 Å). Like the cocrystal (4,6-diI-res)·(4,4'PTC), the discrete assemblies of (4,6-diBr-res)·(4,4'PTC) violate the topochemical postulate with the 4,4'PTC molecules aligned ht, preventing olefin alignment and resulting in C=C separations of 9.3 Å (Figure 52a). Extended packing again exhibits halogen-oxygen interactions in the form of Br-O interactions (3.1 Å), giving rise to assemblies being off-set from one another (Figure 52b). Again, as seen with (4,6-diI-res)·(4,4'PTC), the 4,4'PTC of neighboring assemblies of (4,6-diBr-res)·(4,4'PTC) are aligned ht with C=C separations of 4.9 Å. Upon exposure to UV irradiation, no observable cyclobutane formation could be observed, confirming the photostability of the cocrystal.



Figure 52. Crystal packing of the cocrystal (4,6-diBr-res)·(4,4'PTC): (a) discrete assembly with ht alignment of 4,4'PTC molecules and (b) extended packing of assemblies showing ht alignment of 4,4'PTC molecules within and between assemblies (4,4'PTC molecules colored in blue and green for clarity).

Our initial proposal was that a template analogous to 4,6-diI res may facilitate the [2+2] photocycloaddition due to the increased planarity of 4,4'PTC. Though the cocrystal (4,6-diBr-res)·(4,4'PTC) is photostable, it is interesting to note that 4,4'PTC exhibits a deviation of only 16.3° from planar, making it more planar that either the pure solid (47.6°) or the (4,6-diI-res)·(4,4'PTC) cocrystal (19.4°) (Figure 53).



Figure 53. Crystal packing of 4,4'PTC (a) as a pure solid, (b) as part of the cocrystal (4,6-diI-res)·(4,4'PTC), and (c) as part of the cocrystal (4,6-diBr-res)·(4,4'PTC), demonstrating the decrease in twisting of the molecule when cocrystallized with a template, with the cocrystal (4,6-diBr-res)·(4,4'PTC) exhibiting the smallest twist.

## 4.5. Expanding the Click Library

Due to the photostability of 4,4'PTC, we sought to explore other click derived compounds for photostudies. As was discussed in Chapter 3, the click reaction presents a facile method to generate a library of analogous, yet diverse, molecules through the readily tailored "R" groups on the azide and alkyne.<sup>50-51</sup> To this end, we proposed the synthesis of two molecules, 1-[2-(4-pyridyl)ethenyl]-4-[1-(benzyl)-1H-1,2,3-triazol-4-yl]

benzene (BTC) and 1-[2-(4-pyridyl)ethenyl]-4-[1-(2-pyridyl)-1H-1,2,3-triazol-4-yl] benzene (PTC), following the same one-pot procedure used to synthesize 4BPTC (Figure 54). This one-pot synthesis proves ideal due to the ability to easily exchange one reagent for another and generate a new compound. Furthermore, per the definition of click reactions,<sup>49</sup> the synthesis proceeds with minimal purification and high yields. In order to generate the azide *in situ*, however, the brominated "R" group must have a –CH<sub>2</sub>-Br functionality.<sup>101</sup> The presence of a saturated carbon in the final product will prevent planarity of the molecule in the solid state, possibly preventing proper geometry for photoreactivity, however, gives a site of flexibility when packing.



Figure 54. Reaction scheme for one-pot synthesis of new click products BTC and PTC.

## 4.6. Experimental

# 4.6.1. Synthesis of 1-[2-(4-pyridyl)ethenyl]-4-[1-(benzyl)-

# 1H-1,2,3-triazol-4-yl] benzene (BTC)

Benzyl bromide (0.50 g, 29 mmol) was placed in a 250 mL round bottom flask and dissolved with 10 mL of 4:1 DMF: deionized  $H_2O$ . Once dissolved, copper (II) sulfate pentahydrate (0.33 g, 1.3 mmol), sodium azide (0.21 g, 3.2 mmol), L-ascorbic acid (0.47 g, 2.7 mmol), and sodium carbonate (0.28 g, 2.7 mmol) were added to the reaction. The reaction was stirred at room temperature for five minutes. After five minutes, 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene (0.50 g, 2.9 mmol) was added to the reaction. The flask was wrapped in foil to protect the reaction from light, capped with a septum, and vented with two needles. The reaction was stirred at room temperature for 24 hours behind a blast shield. After stirring for 24 hours, the solution was thick and red. The reaction was quenched through the addition of a solution of 4 mL concentrated ammonium hydroxide, 3.7 g EDTA, and 96 mL deionized H<sub>2</sub>O. The reaction was stirred vigorously for 30 minutes. While stirring, a precipitate could be observed. The precipitate was collected through vacuum filtration. The filtrate was collected and the pH measured to be basic. The filtrate was placed in an azide waste container. The precipitate was washed with chloroform. The solution was gravity filtered and the filtrate was evaporated. Evaporation gave a pale white solid. The solid was sublimed to give the product as a white solid (0.55 g, 61% yield) <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm)  $\delta$  = 8.74 (1H, s), 8.59 (2H, d, 6.4 Hz), 7.94 (2H, d, 8.4 Hz), 7.77 (2H, d, 8.4 Hz), 7.61 (1H, d, 16.4 Hz), 7.60 (2H, d, 6.4 Hz), 7.41 (5H, m), 7.43 (1H, d, 16.4 Hz), 5.7 (2H, s).



Figure 55. Schematic for the synthesis of 1-[2-(4-pyridyl)ethenyl]-4-[1-(benzyl)-1H-1,2,3-triazol-4-yl] benzene.

## pyridyl)-1H-1,2,3-triazol-4-yl] benzene (PTC)

2-Bromomethyl pyridine hydrobromide (1.36 g, 5.4 mmol) was placed in a 250 mL round bottom flask and dissolved with 10 mL of 4:1 DMF: deionized H<sub>2</sub>O. Once dissolved, copper (II) sulfate pentahydrate (0.61 g, 2.4 mmol), sodium azide (0.38 g, 5.8 mmol), L-ascorbic acid (0.86 g, 4.9 mmol), and sodium carbonate (0.52 g, 4.9 mmol) were added to the reaction. The reaction was stirred at room temperature for five minutes. After five minutes, 1-Ethynyl-4-[2-(4-pyridyl) ethenyl] benzene (1.0 g, 4.9 mmol) was added to the reaction. The flask was wrapped in foil to protect the reaction from light, capped with a septum, and vented with two needles. The reaction was stirred at room temperature for 24 hours behind a blast shield. After stirring for 24 hours, the solution was thick and red. The reaction was quenched through the addition of a solution of 4mL concentrated ammonium hydroxide, 3.7 g EDTA, and 96 mL deionized  $H_2O$ . The reaction was stirred vigorously for 30 minutes. While stirring, a precipitate was observed. The precipitate was collected through vacuum filtration. The filtrate was collected and the pH measured to be basic. The filtrate was placed in an azide waste The precipitate was washed with chloroform. The solution was gravity container. filtered and the filtrate was evaporated. Evaporation gave a pale white solid. The solid was sublimed to give the product as a white solid (0.91 g, 18% yield) <sup>1</sup>H NMR (DMSO $d_6$ , 400 MHz, ppm)  $\delta = 8.71$  (1H, s), 8.55 (3H, d, 6.0 Hz), 7.92, (2H, d, 8.0 Hz), 7.85 (1H, td, 8.3 Hz, 2.8 Hz), 7.74 (2H, d, 7.6 Hz), 7.57 (1H, d, 16.4 Hz), 7.56 (2H, d, 5.2 Hz), 7.37 (2H, m), 7.30 (1H, d, 17.6 Hz), 5.77 (2H, s).



Figure 56. Schematic for the synthesis of 1-[2-(4-pyridyl)ethenyl]-4-[1-(2-pyridyl)-1H-1,2,3-triazol-4-yl] benzene.

## 4.6.3. Photoreactivity Experiments

Samples of BTC and PTC were each monitored for photoreactivity. Each sample was prepared as a crystalline powder and spread between two Pyrex plates. The samples were exposed to broad spectrum UV-irradiation in a high-pressure broadband mercury photoreactor. Solution phase <sup>1</sup>H NMR spectroscopy was performed in regular intervals of approximately ten hours to detect and monitor progressions of photoreactions.

# 4.7. Results and Discussion

Upon synthesis and purification, the structures of both BTC and PTC were confirmed by solution phase <sup>1</sup>H NMR (Figure 57). The NMR spectra for each molecule confirmed the successful one-pot cycloaddition reaction of the *in situ* synthesized organic azide and the alkyne through the signals near 5.7 ppm indicating the  $-CH_2$ - of the "R" groups and the signal near 8.7 ppm indicating the proton on the triazole ring. Upon confirmation of successful synthesis and purification, each compound was recrystallized to produce single crystals. The single crystal data for BTC and PTC can be found in the Appendix (Table A4-A5).



Figure 57. <sup>1</sup>H NMR spectra of (a) BTC and (b) PTC confirming successful one-pot reactions.

Single crystals of BTC were grown from slow solvent evaporation in ethanol. Colorless plates were observed after approximately 24 h.

The asymmetric unit of BTC consist of a full molecule that crystallizes in the space group  $P2_1/c$  (Figure 58a). The stilbazole portion of BTC is nearly planar, with only a 6.8° rotation between the planes of the pyridine ring and central benzene ring. The break in planarity occurs, as predicted, at the saturation point linking the triazole ring to the terminal benzene ring. The rotation of the terminal benzene ring gives a dihedral angle of 95.9° between N1 of the triazole ring and C2 of the benzene ring. Extended packing shows the formation of ht dimers (Figure 58b). Though aligned parallel with respect to the central benzene rings, the ht nature results in C=C separations of 8.2 Å, violating the topochemical postulate.



Figure 58. Crystal packing of BTC: (a) geometry of the single molecule exhibiting a 95.9° dihedral angle and (b) ht dimers with C=C separation of 8.2 Å.

Along the *b*-axis, molecules align in ht chains in a nested J-shape motif with the molecules canted 52.7° from the nearest neighbor with respect to the plane of the central benzene rings (Figure 59). Upon exposure to UV irradiation, no photoreaction was observed, confirming the molecule to be photostable.



Figure 59. Extended packing of BTC with molecules aligned in a ht J-shape motif: (a) looking down the *b*-axis of the chains and (b) tilted view of the chains showing the molecules canted  $52.7^{\circ}$  from their nearest neighbor.

Single crystals of PTC were grown from slow solvent evaporation in acetonitrile. Colorless blades were observed after approximately 24 h.

The asymmetric unit of PTC consists of one full molecule that crystallizes in the  $P2_12_12_1$  space group (Figure 60a). Following the trend observed in the single crystal data of BTC, the stilbazole portion of PTC is also nearly planar, with a 5.6° rotation between the planes of the 4-pyridyl ring and central benzene ring. As was observed for BTC, and predicted for both molecules, the break in the planarity of PTC occurs at the saturation point between the triazole ring and 2-pyridyl ring. The rotation of the 2-pyridyl ring gives a dihedral angle of 35.6° between N1 of the triazole ring and N atom of the pyridine ring. Extended packing exhibits ht alignment of molecules canted nearly orthogonal (78.5°) to their nearest neighbor (Figure 60b). The molecules are offset from their neighbors giving C=C separations of 5.6 Å. The lack of olefin alignment as well as a

separation greater than 4.2 Å both violate the topochemical postulate and suggest that PTC will be photostable.



Figure 60. Crystal packing of PTC: (a) geometry of the single molecule exhibiting a 35.6° dihedral angle and (b) ht dimers with C=C separation of 5.6 Å.

The ht alignment of the PTC molecules (Figure 60b) propagates as chains along the *b*-axis (Figure 61). Upon exposure to UV irradiation, no photoreaction was observed, supporting the photostable conclusions derived from the single crystal data.



Figure 61. Extended packing of PTC showing ht chains along the *b c* plane.

## 4.8. Self-Assembly and Photoreactivity of Click Products

## with Silver Templates

Due to violations of the topochemical postulate, both BTC and PTC are photostable in the solid state. To circumvent crystal packing that prevents photoreactivity and guide the olefins into proper alignment, the template method was again employed. Unlike the organic templates used for 4,4'PTC, Ag(I) cation templates were used to guide the crystal packing of BTC and PTC.

The use of the Ag(I) cation as a template enables the synthesis of metal-organic Metal-organic assemblies such as metal-organic frameworks (MOFS), assemblies. metallocycles, and metallosupramolecular architectures have recently gained exposure as an ideal avenue towards directed materials design.<sup>102</sup> While the shapes of purely organic systems are dictated by the angles of the hybridized carbon atoms, the introduction of transition metals has allowed for new shapes and dimensions, giving rise to new architectures such as cages, bowls, and spheres.<sup>103</sup> The self-assembly of these metalorganic systems, as well as the wide array of transition metals and ligand spacers that can be utilized, makes directed synthesis of pre-determined shape and properties more attainable<sup>104-106</sup> and has given rise to applications in NLO materials (as described in Chapter 3), gas-storage, catalysis, luminescence, and biotechnologies.<sup>107-108</sup> Further expansion of the applications of metal-organic assemblies has come through postsynthetic modifications (PSM). As demonstrated in Figure 46, the click reaction has been effectively used as a PSM techniques for many different metal-organic assemblies.

Capitalizing on the functional group tolerance of the click reaction, the click reaction has also been used as a facile method to synthesize diverse ligands for metalorganic complexes.<sup>109</sup> As pyridine rings have often been integrated into ligands of metalorganic assemblies due to their ability to act as N donors, it has been proposed that 1,2,3triazole rings may act as an analogue to pyridine as N donors,<sup>110-112</sup> and even replace the pyridine ring in certain Ag(I) and Pd(II) assemblies.<sup>105</sup> Other studies have investigated ligands bearing both pyridine and 1,2,3-triazole rings and have shown that, while in some instances, the pyridine ring will favorable coordinate to the metal,<sup>110</sup> given the proper molecular geometry, both rings can coordinate to the metal center in a bidentate fashion (Figure 62).<sup>107</sup>



Figure 62. Examples of transition metal coordination to ligands bearing both pyridine and 1,2,3-triazole rings: (a) coordination to a Ag(I) cation by both N-donor types, (b) coordination to a Ag(I) cation by both N-donor types for the outer cations and exclusive 1,2,3-triazole ring for the interior cation, and (c) coordination of Pd(0) to pyridine rings exclusively.

Studying the self-assembly of metal-organic complexes using BTC and PTC proves intriguing not only due to the use of the click reaction to synthesize the ligands, but also due to the multimodality of the ligands. Both BTC and PTC bear several N-donor sites, with BTC containing a 4-pyridyl ring and a 1,2,3-triazole ring and PTC containing a 4-pyridyl ring, and a 1,2,3-triazole ring (Figure 63).



Figure 63. Scheme of PTC and PTC with N-donor sites circled.

The key focuses of this study will surround both the investigation of the self-assembly and crystal packing of the metal-organic complexes, as well as the generation of a photoreactive metal-organic assembly, utilizing the [2+2] photocycloaddition reaction as a PSM of the complex. Demonstration of the [2+2] photocycloaddition reaction would not only serve as a study of PSM within our complexes, but would also present the first example of a [2+2] photocycloaddition reaction on a click-derived molecule in either the solution phase or the solid state.

## 4.9. Experimental

## 4.9.1. Synthesis of [Ag(BTC)][ClO<sub>3</sub>]

BTC (8.0 mg, 0.024 mmol) and AgClO<sub>3</sub> (4.5 mg, 0.24 mmol) were dissolved in 1 mL of acetonitrile with heating. The solution was allowed to evaporate slowly at room temperature away from light. Colorless lath crystals began to precipitate after 1 hour. The crystals were separated from the mother liquor by vacuum filtrations and dried in air. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, ppm)  $\delta$  = 8.70 (1H, s), 8.60 (2H, broad), 7.90 (2H, d, 11.1 Hz), 7.74 (2H, d, 7.5 Hz), 7.57 (3H, overlapping doublet, 17.1 Hz), 7.373 (5H, m), 7.30 (1H, d, 16.2 Hz), 5.66 (2H, s).

# 4.9.2. Synthesis of [Ag<sub>2</sub>(BTC)<sub>4</sub>][(CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>)<sub>2</sub>]

BTC (8.0 mg, 0.024 mmol) and  $AgClO_3$  (6.6 mg, 0.24 mmol) were dissolved in 20 mL of acetonitrile with heating. The solution was allowed to evaporate slowly at

room temperature away from light. Colorless plate crystals began to precipitate after 48 hours. The crystals were separated from the mother liquor by vacuum filtrations and dried in air. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, ppm)  $\delta$  = 8.70 (1H, s), 8.55 (2H, d, 4.8 Hz), 7.90 (2H, d, 8.4 Hz), 7.74 (2H, d, 8.7 Hz), 7.59 (2H, d, 6.0 Hz), 7.52 (1H, d, 17.7 Hz), 7.48 (2H, d, 7.8 Hz), 7.38 (5H, m), 7.30 (1H, d, 17.1 Hz), 7.11 (2H, d, 8.4 Hz), 5.66 (2H, s), 2.29 (3H, s).

# 4.9.3. Synthesis of [Ag(PTC)<sub>2</sub>][(ClO<sub>4</sub>)]

PTC (8.0 mg, 0.024 mmol) and AgClO<sub>4</sub> (5.4 mg, 0.24 mmol) were dissolved in 1 mL of acetonitrile with heating. The solution was allowed to evaporate slowly at room temperature away from light. Yellow plate crystals began to precipitate after 24 hours. The crystals were separated from the mother liquor by vacuum filtrations and dried in air. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, ppm)  $\delta$  = 8.73 (1H, s), 8.57 (3H, m), 7.93 (2H, d, 8.1 Hz), 7.87 (1H, t, 8.0 Hz), 7.76 (2H, d, 8.1 Hz), 7.68 (2H, d, 5.7 Hz), 7.46 (1H, d, 19.2 Hz), 7.38 (2H, d, 7.2 Hz) (7.34 (1H, d, 17.1 Hz), 5.79 (2H, s).

# 4.9.4. Synthesis of [Ag<sub>2</sub>(PTC)<sub>2</sub>][(ClO<sub>3</sub>)<sub>2</sub>]

PTC (8.0 mg, 0.024 mmol) and AgClO<sub>3</sub> (4.5 mg, 0.24 mmol) were dissolved in 1 mL of acetonitrile with heating. The solution was allowed to evaporate slowly at room temperature away from light. Colorless prismatic crystals began to precipitate after 24 hours. The crystals were separated from the mother liquor by vacuum filtrations and dried in air. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, ppm)  $\delta$  = 8.72 (1H, s), 8.56 (3H, m), 7.93 (2H, d, 9.0 Hz), 7.85 (1H, dt, 1.2 Hz, 8.4 Hz), 7.75 (2H, d, 9.0 Hz), .63 (2H, d, 10.5 Hz), 7.60 (1H, d, 11.7 Hz), 7.37 (2H, d, 6.6 Hz), 7.32 (1H, d, 12.3 Hz), 5.78 (2H, s).

## 4.9.5. Synthesis of [Ag(PTC)<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub>]

PTC (8.0 mg, 0.024 mmol) and AgCF<sub>3</sub>SO<sub>3</sub> (6.6 mg, 0.24 mmol) were dissolved in 1 mL of acetonitrile with heating. The solution was allowed to evaporate slowly at room temperature away from light. Colorless rod crystals began to precipitate after 24 hours. The crystals were separated from the mother liquor by vacuum filtrations and dried in air. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, ppm)  $\delta$  = 8.72 (1H, s), 8.57 (3H, m), 7.93 (2H, d, 8.1 Hz), 7.85 (1H, dt, 18. Hz, 8.1 Hz), 7.78 (2H, d, 8.1 Hz), 7.64 (2H, broad), 7.61 (1H, d, 14.7 Hz), 7.37 (2H, d, 6.3 Hz), 7.33 (1H, d, 15.6 Hz), 5.78 (2H, s).

## 4.9.6. Photoreactivity Experiments

Samples of the BTC and PTC silver complexes were monitored for photoreactivity. Each sample was prepared as a crystalline powder and spread between two Pyrex plates. The samples were exposed to broad spectrum UV-irradiation in a highpressure broadband mercury photoreactor. The progress of the photoreactions were monitored by solution phase <sup>1</sup>H NMR spectroscopy in regular intervals of approximately 10 hours. Progression of the photoreactions were confirmed by the disappearance of signals for the olefinic protons and the appearance of signals for the cyclobutane protons.

## 4.10. Results and Discussion

Metal-organic complexes were self-assembled from AgX salts and either BTC or PTC, where X are oxoanions. The oxoanions were selected due to their weak coordinations to Ag(I) cations, facilitating the coordination between the Ag(I) cation and the click-derived ligand.<sup>20</sup> Firstly, two different metal-organic assemblies were prepared with BTC (Table 4). Each assembly will be discussed here with particular regard to N-donor coordination sites within the molecule, olefin geometry, and photoreactivity. The crystal data can be found in the Appendix (Table A4).

Organic Compound	Silver Template	N-donor site	Dimension	Photoreactivity
BTC	Ag Chlorate	4-pyridine, N3 of Triazole	1D	Photoactive
BTC	Ag p-Toluene Sulfonate	4-pyridine	0D	Photoactive

Table 4. Metal-organic assemblies of BTC.

Single crystals of [Ag(BTC)][ClO<sub>3</sub>] were grown from BTC (8.0 mg) and AgClO<sub>3</sub>

(4.5 mg) through slow solvent evaporation of acetonitrile. While crystallizing, the sample was protected from light. Colorless lath crystals began to precipitate after 1 hour.

The metal-organic assembly  $[Ag(BTC)][ClO_3]$  crystallizes in the space group C2/c. The Ag(I) cation coordinates to each available N-donor, with coordination to the pyridine ring and also to N3 of the triazole ring (Figure 64a). This coordination pattern gives rise to 1D polymeric chains. Argentophilic forces are not present, thus preventing the chains from aligning with their nearest neighbors. Rather, the chains pack crossing their neighbors above and below, giving C=C separations of 5.4 Å (Figure 64b), violating the topochemical postulate. Upon exposure to UV irradiation, a photoreaction could be detected, however, severe overlap of signals in the aromatic region prevents accurate calculation of the percent conversion. Furthermore, isolation of the photoproduct proved difficult and single crystals of the photoproduct could not be obtained. Due to the single crystal packing of the olefinic assembly violating the topochemical postulate, without single crystal data of the photoproduct, it is impossible to determine the location of the cycloaddition within the crystals.



Figure 64. Crystal packing of [Ag(BTC)][ClO<sub>3</sub>]: (a) liner 1D chains propagated through Ag(I) coordinations to both the pyridine and triazole rings and (b) extended packing showing crossed chains preventing olefin alignment.

Single crystals of  $[Ag_2(BTC)_4][(CH_3C_6H_4SO_3)_2]$  were grown from BTC (8.0 mg) and AgClO<sub>3</sub> (6.6 mg) through slow solvent evaporation of acetonitrile. While crystallizing, the sample was protected from light. Colorless plate crystals began to precipitate after 48 hours.

The metal-organic assembly  $[Ag_2(BTC)_4][(CH_3C_6H_4SO_3)_2]$  crystallizes in the space group P1. The Ag(I) cation coordinates linearly to the pyridine ring of the BTC molecules only and does not interact with the N2 or N3 atoms or the triazole rings (Figure 65a). Argentophilic forces bring two Ag(I) cations together with a Ag(I)-Ag(I) distance of 4.4 Å. The Ag(I) anions are further tethered through bridging coordination of the p-toluene sulfonate anion. The argentophilic forces and the bridging anion give rise to discrete assemblies with BTC molecule aligned head-to-head (hh). The hh molecules are tilted approximately 82° from one another with respect to the central benzene ring, with the C=C separated by 5.0 Å, preventing photodimerization within the assembly.

The nearest neighbor assemblies are packed off-set but parallel, preventing photodimerizations between assemblies (Figure 65b). Upon exposure to UV irradiation, a photoreaction could be detected, however, severe overlap of signals in the aromatic region prevents accurate calculation of the percent conversion. Furthermore, isolation of the photoproduct proved difficult and single crystals of the photoproduct could not be obtained. Due to the single crystal packing of the olefinic assembly violating the topochemical postulate, without single crystal data of the photoproduct, it is impossible to determine the location of the cycloaddition within the crystals.



Figure 65. Crystal packing of  $[Ag_2(BTC)_4][(CH_3C_6H_4SO_3)_2]$ : (a) discrete assemblies with olefins aligned but canted and (b) extended packing showing neighboring assemblies not properly aligned for the [2+2] photocycloaddition.

Three different metal-organic assemblies were prepared with PTC (Table 5). Each assembly will be discussed here with particular regard to N-donor coordination sites within the molecule, olefin geometry, and photoreactivity. The crystal data can be found in the Appendix (Table A6).

Organic Molecule	Silver Template	N donor site	Dimension	Photoreactivity
PTC	Ag Perchlorate	4-pyridyl ring	0D	photostable
РТС	Ag Chlorate	4-pyridyl and 2- pyridyl ring	0D	photoactive
PTC	Ag Trifluoromethane sulfonate	4-pyridyl ring	0D	photoactive

Table 5. Metal-organic assemblies of PTC.

Single crystals of  $[Ag(PTC)_2][(ClO_4)]$  were grown from PTC (8.0 mg) and  $AgClO_4$  (5.4 mg) through slow solvent evaporation of acetonitrile. While crystallizing, the sample was protected from light. Yellow plate crystals began to precipitate after 24 hours.

The metal-organic assembly  $[Ag(PTC)_2][(ClO_4)]$  crystallizes in the space group P1. Though PTC has three rings with N-donor atoms, the Ag(I) cation coordinates only the 4-pyridyl ring of the PTC molecule. The Ag(I) cation coordinates with two PTC molecules in a linear fashion, forming 0D discrete assemblies (Figure 66). Argentophilic forces are not present, with nearest neighbor assemblies aligned nearly parallel with 5.0° rotation between the PTC molecules with respect to the plane of the central benzene rings but off-set with Ag(I)-Ag(I) and C=C distances of 5.1 Å each, violating the topochemical postulate. Upon exposure to UV irradiation, no photoreaction could be measured, confirming the photostability of the assembly.



Figure 66. Crystal packing of [Ag(PTC)<sub>2</sub>][(ClO<sub>4</sub>)] that exhibits off-set assemblies, thus preventing photodimerization.

Single crystals of  $[Ag_2(PTC)_2][(ClO_3)_2]$  were grown from PTC (8.0 mg) and AgClO<sub>3</sub> (4.5 mg) through slow solvent evaporation of acetonitrile. While crystallizing, the sample was protected from light. Colorless prismatic crystals began to precipitate after 24 hours.

The metal-organic assembly  $[Ag_2(PTC)_2][(ClO_3)_2]$  crystallizes in the space group P1. Unlike the complex  $[Ag(PTC)_2][(ClO_4)]$  which exhibits Ag(I) coordination to only the 4-pyridyl ring of the PTC molecule, the  $[Ag_2(PTC)_2][(ClO_3)_2]$  complex exhibits Ag(I) coordinations to both the 4-pyridyl and the 2-pyridyl rings of the PTC molecules. The PTC molecules and Ag(I) cations self-assemble in a 1:1 ratio with a total of four components making up a discrete assembly (Figure 67a). Within the assembly, the PTC ligand exhibits a J-shaped motif, facilitated by the triazole ring and CH<sub>2</sub>- linkage (Figure 67b). This J-shape, or "fish hook," geometry aligns the PTC ligands in a ht fashion, giving a center of inversion within the assembly and aligning the olefins with C=C separations of 3.8 Å, thus adhering to the topochemical postulate. Extended packing demonstrates the assemblies are off-set, thereby preventing dimerizations between assemblies (Figure 67c).



Figure 67. Single crystal packing of [Ag<sub>2</sub>(PTC)<sub>2</sub>][(ClO<sub>3</sub>)<sub>2</sub>]: (a) discrete J-shape assemblies with C=C aligned ht, (b) coloration of discrete assembly highlighting J-shaped motif of PTC allowed due to triazole ring and CH<sub>2</sub>linkage, and (c) extended packing exhibiting assemblies off-set, preventing photoreactions between assemblies.

Upon exposure to UV irradiation, the [2+2] photocycloaddition is observed. The progress of the photodimerization was monitored by solution phase <sup>1</sup>H NMR (Figure 68). While the formation of the cyclobutane ring can be confirmed, the reaction is not quantitative, proceeding to *ca*. 50% conversion. The cyclobutane product has proven difficult to purify, and, to date, we have been unable to obtain the photoproduct as a single crystal. Though we are unable to isolate the photoproduct as a single crystal. Though we are unable to isolate the photoproduct as a single crystal packing of the  $[Ag_2(PTC)_2][(ClO_3)_2]$  assemblies strongly supports photodimerization exclusively within the assemblies.



Figure 68. <sup>1</sup>H NMR spectrum of [2+2] photocycloaddition of [Ag<sub>2</sub>(PTC)<sub>2</sub>][(ClO<sub>3</sub>)<sub>2</sub>].

Additional for the intra-assembly photodimerization of support  $[Ag_2(PTC)_2][(ClO_3)_2]$  comes from previous examples of the [2+2] photocycloaddition reaction. Photoactive J-shaped assemblies have been previously realized in purely organic systems (Figure 69).<sup>113-115</sup> These J-shape of "fish hook" molecules self-assemble in the solid state through hydrogen bonding between acid groups, aligning the olefins for the [2+2] photocycloaddition reaction. The earliest example of a J-shaped assembly was demonstrated by Feldman through his rigid naphthalene derived molecules (Figure More recently, Wheeler has demonstrated J-shaped molecules with greater 69a).<sup>113</sup> flexibility through his sulfonamidecinnamic acid molecules (Figure 69b).<sup>114,115</sup> Our  $[Ag_2(PTC)_2][(ClO_3)_2]$  assembly demonstrates the first known example of a metal-organic assembly exhibiting discrete assemblies derived from a J-shape motif (Figure 69c). The J-shape of PTC is facilitated through the flexibility of the "R" group on the triazole ring. The angle of connectivity through the five-membered triazole coupled with the flexibility of the CH<sub>2</sub> group allows for the necessary curve of the molecule to achieve the J-shape.



Figure 69. Analogous organic J-shape assemblies: (a) naphthalene derived J-shaped assembly from Feldman, (b) sulfonamide cinnamic acid derived J-shape from Wheeler, and (c) our metal-organic J-shaped assembly derived from the click reaction.

In order to evaluate the tolerance of the photodimerization of PTC in the presence of other templates, single crystals of  $[Ag(PTC)_2][CF_3SO_3]$  were grown from PTC (8.0 mg) and AgCF\_3SO\_3 (6.6 mg) through slow solvent evaporation of acetonitrile. While crystallizing, the sample was protected from light. Colorless rod crystals began to precipitate after 24 hours.

The metal-organic assembly  $[Ag(PTC)_2][CF_3SO_3]$  crystallizes in the space group C2/c. As was seen with the  $[Ag(PTC)_2][(CIO_4)]$  assembly, the Ag(I) cation of the  $[Ag(PTC)_2][CF_3SO_3]$  assembly only coordinates to the 4-pyridyl ring of the PTC molecule. The self-assembly gives rise to discrete assemblies in 1:2 ratio of Ag(I):PTC with a single Ag(I) cation coordinating in a linear fashion to two PTC molecules (Figure 70a). Extended packing shows argentophilic forces are not present, preventing hh alignment of the assemblies. Instead, the assemblies are off-set in such a manner that the olefins are aligned ht with C=C separations of 4.0 Å (Figure 70b).



Figure 70. Single crystal packing of [Ag(PTC)<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub>]: (a) discrete linear complexes self-assemble through Ag(I) coordination to the 4-pyridyl rings, and (b) extended packing demonstrating off-set assemblies with C=C aligned ht and separated by 4.0 Å.

Disorder within the X-ray data of the olefinic assembly reveals the presence of the photodimerized coordination polymer product. Cross linking of metal-organic assemblies through the solid-state [2+2] photocycloaddition has been realized for other assemblies as well.<sup>95-98</sup> These examples demonstrate cross-linking both to form discrete assemblies (Figure 71a) and also to generate coordination polymers (Figure 71b).



Figure 71. Examples of [2+2] photodimerization cross-linking in metal organic frameworks: (a) scheme of cross-linking within discrete assemblies and (c) scheme of cross-linking to form coordination polymers.

For the  $[Ag(PTC)_2][CF_3SO_3]$  assembly, the [2+2] photocycloaddition reaction occurs prior to exposure to UV irradiation in a rare single-crystal to single-crystal (SCSC) reaction with 65% conversion (Figure 72). The extended packing of the discrete olefinic assemblies gives rise to the formation of a 1D coordination polymer that propagates through the crystal upon formation of the cyclobutane ring.



Figure 72. SCSC photodimerization of [Ag(PTC)<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub>] generating a 1D coordination polymer.

## 4.11. Conclusion

Both the click reaction and the [2+2] photocycloaddition reaction offer many similar benefits that complement each other well. It was noted, however, that the two reactions have never been performed in tandem on a molecule. While <sup>1</sup>H NMR data of the BTC metal-organic complexes indicate the occurrence of photodimerization, difficulty in crystallization has inhibited further investigation of the BTC ligand. The successful dimerization of PTC ligands through the [2+2] photocycloaddition reaction within our metal-organic complexes  $[Ag_2(PTC)_2][(ClO_3)_2]$  and  $[Ag(PTC)_2][CF_3SO_3]$ , however, demonstrates the first coupling of the click reaction with the [2+2] photocycloaddition reaction that can be supported through both <sup>1</sup>H NMR and single The reaction of  $[Ag_2(PTC)_2][(ClO_3)_2]$  is achieved in a crystal X-ray diffraction data. discrete J-shaped, or "fish-hook," assembly that, to date, has only been realized in purely organic assemblies. In this way, the triazole ring is used as a synthetic bridge to aid in the alignment of the C=C bonds. For  $[Ag(PTC)_2][CF_3SO_3]$ , a lack of coordination to the 2-pyridyl group affords a linear discrete complex that we show undergoes a SCSC photoreaction that generates a 1D coordination polymer. That PTC sustains both discrete and infinite assemblies in PSM processes demonstrates the versatility of the click-derived ligand in self-assembly. The [2+2] photocycloaddition of these two assemblies represents the first examples of a [2+2] photocycloaddition reaction performed on a product of a click reaction in either the solution phase or the solid state, and opens new avenues for the use of both reactions as combinations for synthesis of ligands and PSM of metal-organic assemblies.

# CHAPTER 5: EXPANSION OF THE TEMPLATE LIBRARY THROUGH COMPLEMENTARY SHAPE AND BONDING GEOMETRY

## 5.1. Introduction

As discussed in Chapter 1, the template method relies on supramolecular interactions such as hydrogen bonding and metal coordinations to guide photostable olefins into photoactive geometries. The template method centers on the self-assembly of the template and olefin as a technique to circumvent unpredictable crystal packing.<sup>16, 17</sup> Much as DNA base pairing is conserved through hydrogen bonding patterns of complementary shape, the organic template resorcinol (res) serves as an ideal template for the [2+2] photocycloaddition due to the 1,3 disubstituted pattern of the hydroxyl groups on the benzene ring (Figure 73a). The 4.8 Å spacing between the hydrogen bond donating hydroxyl groups often facilitates hydrogen bond accepting olefins to be favorably spaced aligned for the [2+2] photocycloaddition reaction in the solid state (Figure 73b).



Figure 73. Hydrogen bond donating template resorcinol: (a) 1,3 disubstitution pattern provides 4.8 Å distance between hydroxyl groups and (b) discrete assembly of (res)·(4,4'BPE) cocrystal providing proper olefin geometry for the [2+2] photocycloaddition.

Building from the success of res, complementary hydrogen bond shape has been applied to other organic templates within the MacGillivray lab. The organic template 1,8-bis(4-pyridyl) naphthalene (1,8 DPN) reverses the template code, serving as a hydrogen bond acceptinh template. The naphthalene ring of 1,8 DPN is decorated with two 4-pyridyl rings in a 1,8 disubstituted patterns. The 1,8 disubstituted pattern results in the pyridine rings exhibiting a 3.5 Å centroid to centroid distance, and the nitrogen atoms separated by 4.0 Å (Figure 74a). The favorable 4.0 Å spacing between the nitrogen atoms can facilitate the templated [2+2] photocycloaddition reaction of acid decorated olefins such as fumaric acid<sup>116</sup> (Figure 74b) and (*E*,*E*)- 2,5- dimethylmuconic acid<sup>18</sup>.



Figure 74. Hydrogen bonding template 1,8 DPN: (a) 1,8 disubstitution pattern provides 4.0 Å distance between nitrogen atoms on the pyridine rings and (b) discrete assembly of (1,8 DPN) · (fumaric acid) cocrystal providing proper olefin geometry for the [2+2] photocycloaddition.

In contrast to these templates, the organic template catechol (cat) is not able to successfully template olefinic compounds into pure, discrete 1:1 photoactive assemblies. The 1,2 disubstituted pattern of cat gives a 2.7 Å spatial separation between the alcohol groups, preventing the assemblies that provide ideal alignment of olefins for the [2+2] photocycloaddition in the solid state (Figure 75a). Indeed, when crystallized in a 1:1 ratio with 4,4'BPE, photostable linear chains result rather than discrete assemblies (Figure

75b).<sup>117</sup> When cocrystallized with 2,4'BPE, however, discrete three-component 1:1:1 assemblies form through the aid of water molecules, producing photoactive cocrystals (Figure 75c).<sup>118</sup>



Figure 75. Hydrogen bonding template catechol: (a) 1,2 disubstitution pattern provides 2.7 Å distance between alcohol groups, (b) 1D chains of the photostable (cat) (4,4'BPE) cocrystal, and (c)assemblies of the photoactive (cat) (2,4'BPE) cocrystals exhibiting three component assemblies of cat, 2,4'BPE, and water.

While the spatial arrangement of the hydrogen bonding groups are important for successful templating, research in the MacGillivray group has demonstrated that functional group substitution on the backbone of templates also affects the success of this method.<sup>16, 17</sup> Variation of functional group substitution, and as a result electronic properties, of a template gives rise to cocrystals with different degrees of reactivity, despite the fact that the spatial arrangement of the hydrogen bonding remains unchanged. Indeed, the [2+2] photocycloaddition reaction of an olefin can often be optimized for both yield and rate through the screening of various templates. Furthermore, the

differences in functional groups also gives rise to different crystal packing motifs due to both electronic properties and spatial requirements from the size of the substituents.<sup>16, 17</sup>

In order to further expand the applications of the template method, a deeper insight into the effects of functional group substitutions towards crystal packing is required. For this chapter, we have investigated the crystal packing of several cocrystals synthesized from res-derived templates and the template 1,8 DPN (Figure 76). Like the DNA base pairs, res and 1,8 DPN are complementary in their hydrogen bonding shape and are predicted to self-assemble as 1:1 discrete assemblies. By studying cocrystals consisting of only templates and excluding olefinic compounds, we are able to focus on the effects of the functional groups towards crystal packing regardless of photoreactivity. The crystal packing patterns of each cocrystal will be discussed and compared to evaluate the effects of the substitutions. The crystal data can be found in the Appendix (Tables A7-A8).



Figure 76. Resorcinol derived templates cocrystallized with 1,8 DPN for the cocrystal series.

## 5.2.Experimental

## 5.2.1. Synthesis of 1,8 bis(4-pyridyl) naphthalene (1,8

## DPN)

1,8-bis(4-pyridyl) naphthalene was prepared in three steps.

Step 1: Purification of 1,8 diaminonaphthalene

1,8 diaminonaphthalene (12.1 g, 76.5 mmol) was placed in a 1 L beaker. Hexanes (600 mL) was added to the beaker. The solution was heated vigorously and stirred until concentrated to 400 mL. The solution was gravity filtered while boiling. The filtrate yielded the purified product as pink needle like crystals which were collected by vacuum filtration (5.4 g, 45% yield).

#### **Step 2:** Synthesis of diiodonaphthalene

Deionized water (80 mL) and sulphuric acid (50 mL) were poured into a 2 L beaker. The beaker was placed into a salt/ice bath and the acid solution was stirred. The purified 1,8 diaminonaphthalene (7.8 g, 50.6 mmol) was added to the beaker, immediately forming a white precipitate. The solution was stirred for approximately five minutes with ice added to the flask to keep the reaction cool. While continuing to stir, a solution of sodium nitrite (7.53 g, 11.1 mmol) in deionized water (100 mL) was prepared and added to the reaction drop wise through an addition funnel. During the addition, the solution turned brown. A solution of potassium iodide (18.5 g, 11.1 mmol) in deionized water (50 mL) was added drop wise through an addition funnel. During the addition, the solution foamed and formed aggregates. Ice was added to the reaction to prevent this. After the addition, the solution was heated to 70°C. During this time, a black precipitate formed. Upon reaching 70°, the temperature was held constant for 15 minutes. After 15 minutes, the solution was made basic through the addition of sodium hydroxide pellets. Once basic, the solution was brought back to room temperature. The black precipitate was collected by vacuum filtration. The precipitate was washed thoroughly with 600 mL

of ethyl ether. The solution was gravity filtered. The filtrate was then transferred to a separatory funnel and washed three times with 10% HCl (150 mL per wash), three times with a solution of saturated sodium thiosulfate (100 mL per wash), and three times with deionized water (100 mL per wash). The organic layer was dried with magnesium sulfate and gravity filtered. The solvent was removed leaving dark brown needles. The crystals were recrystallized in hot hexanes to give the product diiodonaphthalene as red needles (4.8 g, 25% yield).

## Step 3: Synthesis of 1,8 bis(4-pyridyl) naphthalene

Diiodonaphthalene (4.8 g, 0.0126 mol) was placed in a 1 L round bottom flask and dissolved with 400 mL THF. A freshly-prepared solution of potassium carbonate (23.6 g, 0.171 mol) in 250 mL deionized water was added to the solution. Then, bis(triphenyl phosphine) palladium (II) dichloride (2.6 g, 0.00378 mol) was added to the reaction. The reaction was stirred for 15 minutes. After 15 minutes, 4-pyridine boronic acid (4.7 g, 0.0379 mol) was added to the reaction. The reaction was then refluxed for seven days. After seven days, the reaction was brought back to room temperature. Using a separatory funnel, the THF was extracted from the water. The THF was removed to leave a dark brown solid. The solid recrystallized with ethyl acetate to give a light tan crystalline solid. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, ppm)  $\delta$  = 8.18 (2H, s), 8.15 (4H, d, 4.5 Hz), 7.70 (2H, t, 7.8 Hz), 7.48 (2H, d, 7.8 Hz), 7.00 (4H, d, 6.6 Hz).


Figure 77. Schematic for the synthesis of 1,8-bis(4-pyridyl) naphthalene.

#### 5.2.2. Synthesis of (res) $\cdot$ (1,8 DPN)

1,8 DPN (10.0 mg, 0.035 mmol) and res (4.0 mg, 0.036 mmol) were dissolved in ~10 mL of acetonitrile upon heating. The solution was allowed to evaporate slowly at room temperature. Single crystal began to precipitate as colorless blades after 24 hours. The crystals were separated from the mother liquor by vacuum filtrations and dried in air. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, ppm)  $\delta$  = 9.17 (2H, s), 8.18 (2H, s), 8.15 (4H, d, 4.5 Hz), 7.70 (2H, t, 7.5 Hz), 7.48 (2H, d, 8.7 Hz), 7.01 (4H, d, 5.7 Hz), 6.90 (1H, t, 7.9 Hz), 6.17 (2H, d, 6.6 Hz).

# 5.2.3. Synthesis of (4 Cl-res) (1,8 DPN)

1,8 DPN (10.0 mg, 0.035 mmol) and 4 Cl-res (5.0 mg, 0.035 mmol) were dissolved in ~10 mL of acetonitrile upon heating. The solution was allowed to evaporate slowly at room temperature. Single crystal began to precipitate as colorless blades after 24 hours. The crystals were separated from the mother liquor by vacuum filtrations and dried in air. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, ppm)  $\delta$  = 8.19 (1H, s), 8.15 (4H, d, 5.7 Hz), 7.70 (2H, t, 7.2 Hz), 7.48 (2H, d, 6.9 Hz), 7.05 (2H, s), 7.01 (4H, d, 6.3 Hz), 6.41 (1H, d, 2.4 Hz), 6.20 (2H, dd, 9.0 Hz 2.7 Hz).

## 5.2.4. Synthesis of (4 Br-res) $\cdot$ (1,8 DPN)

1,8 DPN (10.0 mg, 0.035 mmol) and 4 Br-res (6.0 mg, 0.035 mmol) were dissolved in ~10 mL of acetonitrile upon heating. The solution was allowed to evaporate slowly at room temperature. Single crystal began to precipitate as colorless blades after 24 hours. The crystals were separated from the mother liquor by vacuum filtrations and dried in air. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, ppm)  $\delta$  = 8.19 (1H, s), 8.15 (2H, d, 6Hz), 7.70 (2H, t, 8.1 Hz), 7.48 (2H, d, 7.2 Hz), 7.176 (2H, d, 9.0 Hz), 7.01 (4H, d, 6.3 Hz), 6.41 (1H, d, 3.3 Hz), 6.17 (1H, dd, 3.9 Hz, 8.4 Hz).

#### 5.2.5. Synthesis of $(4, 6 \text{ diBr-res}) \cdot (1, 8 \text{ DPN})$

1,8 DPN (10.0 mg, 0.035 mmol) and 4,6 diBr-res (9.5 mg, 0.035 mmol) were dissolved in ~10 mL of acetonitrile upon heating. The solution was allowed to evaporate slowly at room temperature. Single crystal began to precipitate as colorless blades after 24 hours. The crystals were separated from the mother liquor by vacuum filtrations and dried in air. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm)  $\delta$  = 10.32 (1H, s), 8.17 (4H, broad s), 7.60 (4H, s), 7.0 (6H, s), 6.63 (1H, s).

## 5.2.6. Synthesis of $(1,8 \text{ naphthalene diacid}) \cdot (1,8 \text{ DPN})$

1,8 DPN (10.0 mg, 0.035 mmol) and 1,8 naphthalene diacid (7.7 mg, 0.035 mmol) were dissolved in ~10 mL of acetonitrile upon heating. The solution was allowed to evaporate slowly at room temperature. Single crystal began to precipitate as colorless blades after 24 hours. The crystals were separated from the mother liquor by vacuum filtrations and dried in air. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, ppm)  $\delta$  = 8.15 (4H, q, 8.4 Hz), 7.92 (4H, d, 7.2 Hz), 7.70 (2H, t, 8.0 Hz), 7.61 (2H, t, 7.8 Hz), 7.48 (4H, d, 6.6 Hz), 7.01 (4H, d, 6.0 Hz).

## 5.3. Results and Discussion

In order to better understand the effects of functional group substitution towards crystal packing, the packing of each cocrystal was investigated and compared. Here we will discuss the crystal packing of each cocrystal with particular regard to space group, symmetry, and hydrogen bond lengths (Table 6). Crystal data for the cocrystals can be found in the Appendix (Tables A7-A8).

Cocrystal	Space Group	Assembly formation	H-Bond Distance
(res)·(1,8 DPN)	P21/c	1:1 discrete assembly	~2.75 Å
(4 Cl-res)·(1,8 DPN)	C2/c	1:1 discrete assembly	2.68 Å, 2.76 Å
(4 Br-res)·(1,8 DPN)	P21/c	1:1 discrete assembly	2.72 Å, 2.73 Å
(4,6 diBr-res)∙ (1,8 DPN)	Pna2 <sub>1</sub>	1:1 discrete assembly	2.68 Å, 2.70 Å
(1,8 naphthalene diacid)·(1,8 DPN)	P2 <sub>1</sub> /n	1:1 discrete assembly	2.59 Å, 2.69 Å

Table 6. Crystal data for cocrystal series.

To serve as the foundation for our study on the effects of functional group substitution towards crystal packing, cocrystals of res and 1,8 DPN were grown and evaluated. Single crystals of the cocrystal (res) $\cdot$ (1,8 DPN) were grown from slow solvent evaporation of res (4.0 mg) and 1,8 DPN (10.0 mg) in acetonitrile. Colorless blades were observed after 24 hours.

The cocrystal (res)·(1,8 DPN) crystallizes in the monoclinic space group P2<sub>1</sub>/c. As predicted, discrete 1:1 assemblies form through the complementary hydrogen bonding motif between res and 1,8 DPN (Figure 78a). The hydrogen bond distances within the assemblies are ~2.75 Å. Extended packing reveals columns of assemblies along the *b*-axis that are maintained through C-H··· $\pi$  interactions between neighboring assemblies (Figure 78b). The columns are repeated along the *c*-axis to form 2D sheets maintained through further C-H··· $\pi$  interactions between columns. The C-H··· $\pi$  interactions both within and between the columns result in assemblies aligned nearly parallel (~3.0° rotation from parallel) within a column and neighboring columns canted nearly orthogonal (~78.0°).



Figure 78. Crystal packing of the cocrystal (res)  $\cdot$  (1,8 DPN): (a) discrete 1:1 assembly and (b) extended packing in the *b c* plane.

To begin our functional group series, we investigated only a single substitution on the res molecule, in the form of the template 4 Cl-res. The substitution of the chlorine atom on the 4 position of the benzene ring arranges the new functionality ortho to the hydroxyl group in the 3 position and para to the hydroxyl group in the 1 position. It is predicted that the electronegativity of the chlorine atom should strengthen the hydrogen bonds between the molecules, which may be detected as a shortening of the O-H…N distances.

Single crystals of (4 Cl-res)·(1,8 DPN) were grown from slow solvent evaporation of 4 Cl-res (5.0 mg) and 1,8 DPN (10.0 mg) in acetonitrile. Colorless blades were observed after 24 hours.

The cocrystal (4 Cl-res)·(1,8 DPN) crystallizes in the monoclinic space group C2/c. As was also observed with the (res)·(1,8 DPN) cocrystal, the (4 Cl-res)·(1,8 DPN) cocrystal self-assembles into 1:1 discrete assemblies (Figure 79a). Unlike the (res)·(1,8 DPN) cocrystal however, the hydrogen bond distance at the 1 and 3 position are not of equal length. The O-H···N distance at the 1 position is 2.76 Å [similar to the (res)·(1,8 DPN) cocrystal], while the O-H···N distance at the 3 position, ortho to the electronegative chlorine atom, is shorter at 2.68 Å. This suggests that the chloro substitution indeed is affecting the bonding strength within the assembly when compared to the (res)·(1,8 DPN) cocrystal.

Extended packing reveals assemblies aligned head-to-head (hh) with the chloro substitutions pointed in the same direction, forming 1D columns along the *b*-axis (Figure 79b). The assemblies are not aligned, but rather off set with 7.50 Å centroid-centroid distances between the res molecules, thereby distancing the chloro groups. The columns repeat down the *a*-axis forming 2D sheets, with the neighboring columns aligning in opposite directions, giving a head-to-tail (ht) arrangement. The columns are parallel, and related through  $\pi$ - $\pi$  interactions between the pyridine rings of neighboring 1,8 DPN molecules (4.33 Å). The 2D sheets are repeated along the *c*-axis through C-H- $\pi$  interactions (~3.6 Å) between the naphthalene rings and the res rings of neighboring sheets, canting the sheets 77. 2° (Figure 79c).



Figure 79. Crystal packing of the cocrystal (4 Cl-res)  $\cdot$  (1,8 DPN): (a) discrete 1:1 assembly, (b) extended packing of 2D sheet of assemblies in the *a b* plane, and (c) view of repeating 2D sheets along the *c*-axis.

To continue our investigation, we again grew cocrystals from a singly substitution res-derived template, 4 Br-res. As a slightly less electronegative atom, it was expected that the bromo substitution would affect the hydrogen bonding strength to a lesser extent than the chloro substitution within the (4 Cl-res) $\cdot$ (1,8 DPN) cocrystal.

Single crystals of (4 Br-res)·(1,8 DPN) were produced from slow solvent evaporation of 4 Br-res (6.0 mg) and 1,8 DPN (10.0 mg) in acetonitrile. Colorless blades were observed after 24 hours.

The cocrystal (4 Br-res)·(1,8 DPN) crystallizes in the monoclinic space group  $P2_1/c$ . Following the observed trends, this cocrystal also self-assembles into 1:1 discrete assemblies (Figure 80a). Unlike the (4 Cl-res)·(1,8 DPN) cocrystal where two different hydrogen bond lengths were measured, the hydrogen bond lengths in the (4 Br-res)·(1,8 DPN) cocrystal are nearly the same, with an O-H…N distance of 2.72 Å at the 1 position and an O-H…N distance of 2.73 Å at the 3 position. These lengths are comparable to the hydrogen bond lengths measured in the (res)·(1,8 DPN) cocrystal, indicating that the strength of the hydrogen bond is not drastically affected. Much as the (4 Cl-res)·(1,8

DPN) cocrystal exhibited sheets of assemblies in the extended packing, the cocrystal (4 Br-res)·(1,8 DPN) also exhibits extended sheets, though in a different packing motif. Extended packing of (4 Br-res)·(1,8 DPN) displays assemblies aligned in a ht fashion forming a 1D sheet with the planes of the pyridine rings of neighboring 1,8 DPN molecules aligned parallel (Figure 80b). Adjacent 1D sheets pack ht in the opposite direction forming a 2D column. Neighboring 2D columns are packed nearly orthogonal at 76.8°.



Figure 80. Crystal packing of the cocrystal (4 Br-res)·(1,8 DPN): (a) discrete 1:1 assembly and (b) extended packing exhibiting layers of ht aligned assemblies.

After investigating two singly substituted templates, we chose to investigate the template 4,6 diBr-res, as a representative of the effects of two substitutions. The template 4,6 diBr-res now has electronegative groups ortho and para to each hydroxyl group, and is predicted to have a greater effect on the strength of the hydrogen bonds than either the  $(4 \text{ Br-res}) \cdot (1,8 \text{ DPN})$  or the  $(4 \text{ Cl-res}) \cdot (1,8 \text{ DPN})$  cocrystals. Though the electronics of 4,6 diBr-res may be different from the other templates presented thus far in this series, the shape of the hydrogen bonding motif remains the same as our previous three hydrogen bond donors. The consistent spatial arrangement of the 1,3 disubstituted

pattern on the benzene ring is expected to produce self-assembled 1:1 discrete assemblies.

Single crystals of (4,6 diBr-res)·(1,8 DPN) were grown from slow solvent evaporations of 4,6 diBr-res (9.5 mg) and 1,8 DPN (10.0 mg) in acetonitrile. Colorless blades were observed after 24 hours.

The cocrystal (4,6 diBr-res) (1,8 DPN) crystallizes in the orthorhombic space group Pna<sub>21</sub>. As predicted, the cocrystal self-assembles into 1:1 discrete assemblies through complementary hydrogen bonding (Figure 81a). The O-H…N distances (2.68 Å and 2.70 Å) are shorter than any of the other hydrogen bond distances measured within the series, [except for the 3 position of the (4 Cl-res) (1,8 DPN) cocrystal (2.68 Å) which is equal], indicating that, indeed, the hydrogen bonds are stronger within the (4,6 diBrres)·(1,8 DPN) assemblies due to the presence of two electronegative functional groups in the 4 and 6 position. Extended packing displays columns of assemblies aligned hh and off-set, with centroids of neighboring res molecules separated by 7.37 Å, thereby distancing the bromo functional groups (Figure 81b). The planes of the pyridine rings between neighboring 1,8 DPN molecules are nearly planar with 3.90° rotation. Neighboring columns packing in a similar fashion, aligning hh in the opposite direction. Similar to the extended packing of the (4 Br-res) (1,8 DPN) cocrystal, the pairs of ht aligned sheets pack nearly orthogonal  $(82.5^{\circ})$  to the nearest neighbor pair of ht aligned sheets (Figure 81c). This motif of pairs of sheets is maintained through O-Br halogen interactions.



Figure 81. Crystal packing of the cocrystal (4,6 diBr-res)·(1,8 DPN): (a) discrete 1:1 assembly, (b) extended packing exhibiting off-set columns of hh aligned assemblies, and (c) orthogonal packing of sheets.

In addition to the res-derivatives, we sought to complete our study with a template that was complementary in both in the hydrogen bonding pattern and backbone with 1,8 DPN. For this cocrystal, we used 1,8 DPN and 1,8 naphthalene diacid.

Single crystals of (1,8 naphthalene diacid)·(1,8 DPN) were grown from 1,8 naphthalene diacid (7.7 mg) and 1,8 DPN (10.0 mg) in acetonitrile. Colorless blades were observed after 24 hours.

The cocrystal (1,8 naphthalene diacid)·(1,8 DPN) crystallizes in the monoclinic space group P2<sub>1</sub>/n. Though the oxygen atoms of the alcohol group are closer together (3.3 Å) than in res (4.8 Å), the two components still self-assemble in 1:1 discrete assemblies maintained through hydrogen bonding (Figure 82a). The O-H····N distances (2.59 Å and 2.69 Å) are shorter than the O-H····N distances measured in the (res)·(1,8 DPN) cocrystal, indicating stronger hydrogen bonds. The two molecules within the assembly do not lie in the same plane, with the planes of the naphthalene rings rotated 22.57° from planarity. The assemblies pack in ht dimers with a center of inversion between the assemblies sustained by near face-to-face  $\pi$  stacking between the naphthalene rings. The naphthalene rings of the same molecules are planar in relation to the neighboring dimer, while the nearest naphthalene ring is rotated 22.57° from planarity (Figure 82b). The ht dimers are packed nearly orthogonally at 89.0° to one adjacent dimer and parallel to another (Figure 82c). This arrangement is propagated through C-H… $\pi$  interactions.



Figure 82. Crystal packing of the cocrystal (1,8 naphthalene diacid) (1,8 DPN): (a) discrete 1:1 assembly, (b) ht aligned planar dimers, and (c) extended packing of dimers.

## 5.4. Olefinic Templates

Our goal has been to expand the applications of the template method through the development of a better understanding of the effects of functional group substitution on crystal packing patterns. Additionally, we have sought to expand the applications of the template method through the incorporation of olefins within the templates themselves. It was our anticipation that an olefinic template may be photoactive while guiding another olefin into proper alignment for the [2+2] photocycloaddition, thereby giving rise to two

different [2+2] photocycloadditions within the same cocrystal. To investigate this, we employed the commercially available natural product resveratrol (Figure 83).



Figure 83. The olefin decorated template resveratrol.

Resveratrol can be extracted from the skins and seeds of grapes, cranberries, and peanuts, and is also found in red wine.<sup>119</sup> This compound has demonstrated beneficial effects for combating Alzheimer's disease and potential as a chemo-prevention of breast cancer through inhibiting tumor cell growth.<sup>120</sup> While these health benefits certainly make this a molecule of interest to many scientists, our interest in the molecule lies in its hydrogen bonding capabilities. One terminus of the resveratrol bears a 1,3-disubstitued benzene ring with two hydroxyl groups giving the molecule a "resorcinol terminus," while the other terminus of the molecule bears only one hydroxyl group on the 4 position of the benzene ring. This third hydrogen bond donating group gives the molecule a degree of unpredictability in view of the crystal packing. It was our goal however, that cocrystallization with the template 1,8 DPN would provide insight into the hydrogen bonding patterns of resveratrol and also insight into the ability to guide the olefins of resveratrol into a photoactive geometry.

## 5.5. Experimental

#### 5.5.1. Synthesis of (resveratrol) (1,8 DPN)

1,8 DPN (10.0 mg, 0.035 mmol) and resveratrol (8.1 mg, 0.035 mmol) were dissolved in ~10 mL of acetonitrile upon heating. The solution was allowed to evaporate slowly at room temperature. Single crystals began to precipitate as colorless blades after 24 hours. The crystals were separated from the mother liquor by vacuum filtrations and dried in air. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm)  $\delta$  = 8.8 (2H, d, 8.18 Hz), 8.15 (4H, d, 4 Hz), 8.0 (2H, t, 7.70 Hz), 6.8 (2H, d, 7.48 Hz), 7.39 (2H, d, 8.4 Hz), 7.01 (4H, d, 4.0 Hz), 6.92 (1H, d, 16.4 Hz), 6.86 (1H, d, 16.4 Hz), 6.74 (2H, d, 8.4 Hz), 6.37 (2H, s), 6.10 (1H, s).

## 5.5.2. Photoreactivity Experiments

Samples of the cocrystal were prepared as crystalline powders and spread between two Pyrex plates. The samples were exposed to broad spectrum UV-irradiation in a high-pressure broadband mercury photoreactor. Detection and progression of the photoreactions was monitored by solution phase <sup>1</sup>H NMR spectroscopy in regular intervals of approximately 10 hours.

## 5.6. Results and Discussion

The crystal packing of (resveratrol)·(1,8 DPN) will be discussed in this section with particular regard to the geometry of the resveratrol and the effects of the third hydrogen bond donating group. Crystal data for this cocrystal can be found in the Appendix (Table A9).

Single crystals of the cocrystal (resveratrol)·(1,8 DPN) were grown from slow solvent evaporation of resveratrol (8.1 mg) and 1,8 DPN (10.0 mg) in acetonitrile. Colorless blades were observed after 24 hours.

The cocrystal (resveratrol)·(1,8 DPN) crystallizes in the triclinic space group  $P\overline{1}$ . Though there are three hydrogen bond donating groups, the cocrystal still assembles in 1:1 discrete assemblies with only two O-H···N hydrogen bonds (2.70 Å) (Figure 84a). The resveratrol molecule within each assembly is non-planar, with a 35.14° twist between the planes of the two benzene rings. The third alcohol group on the 4 position of the benzene ring is hydrogen bonded to water that was present in the acetonitrile. The water molecule is further hydrogen bonded to a molecule of acetonitrile, giving a total of two solvent molecules per assembly. Extended packing exhibits hh rows of assemblies separated by solvent molecules (Figure 84b). These hh rows propagate in opposite directions resulting in a 2D sheet with partial overlap of the naphthalene rings, allowing for face-to-face  $\pi$  interactions (3.77 Å and 4.14 Å). The 2D sheets repeat throughout the crystal in opposite directions, giving columns of ht aligned assemblies (Figure 84c). Examination of the crystal packing suggests that the cocrystal will be photostable due to improper alignment of the olefins. Upon exposure to UV irradiation, the photostability of the cocrystals was confirmed.



Figure 84. Crystal packing of the cocrystal (resveratrol)·(1,8 DPN): (a) discrete 1:1 assembly with hydrogen bonding to water and acetonitrile, (b) extended packing of rows of assemblies aligned hh (solvent omitted for clarity), and (c) columns of ht aligned assemblies (solvent omitted for clarity).

## 5.7. Conclusion

The unpredictability of crystal packing limits the application of solid-state The template method has been developed as a way to circumvent this reactivity. limitation, allowing for the self-assembly of molecules to guide crystal packing. Even through the template method however, crystal packing can still be unpredictable, with template screening a common practice to optimize photoreactions in the solid state. It has been our goal then to study a series of cocrystals functionalized with varying groups and substitution patterns to evaluate crystal packing motifs. From this, we have been able to observe the reliability of the self-assembly of discrete assemblies, monitor the length, and therefore relative strengths, of the hydrogen bonds as influenced by the substitutions on the res, and also observe patterns in packing motifs. Furthermore, we have sought to expand the applications of templates by integrating olefins into the template itself, anticipating dual photocycloaddition reactions. Though we have been unable to produce a cocrystal with a photoactive template, the crystal packing of the cocrystal has given us insight into the necessary requirements for a photoactive template, which will be discussed in depth in chapter 6.

# CHAPTER 6: TEMPLATED INTRAMOLECULAR [2+2] PHOTOCYCLOADDITION IN THE SOLID STATE

# 6.1. Introduction

As described in chapter 1, for molecules to undergo a [2+2] photocycloaddition in the solid state, carbon-carbon double (C=C) bonds are expected to adhere to Schmidt's topochemical postulate by being aligned parallel and separated  $\leq 4.2$  Å.<sup>12,121,122</sup> To overcome effects of crystal packing that typically hinder an olefin from adopting a geometry to react, small-molecule and metal-based templates have been developed.<sup>23</sup> The use of templates relies on noncovalent forces (e.g. hydrogen bonds, metal coordination) to deliberately assemble and position alkenes into self-assembled structures for photoreaction. To date, the template method has been applied exclusively to intermolecular photocycloadditions, which have provided access to architecturally-rich molecules (e.g. ladderanes) difficult to obtain in solution.

In this chapter, the use of a template to direct an intramolecular [2+2] photodimerization in the solid state will be presented. Argentophilic forces based on Ag(I) ions are used to direct an intramolecular photocycloaddition of 1,8-bis[(*E*)-2-(4-pyridyl)ethenyl]naphthalene (1) to give *cis*-di(4-pyridyl)naphthocyclobutane (2). The resulting photoproduct 2 possesses a hydrocarbon framework composed of an array of edge-fused four-, five-, and six- membered rings.<sup>29</sup> Specifically, we expected the bis(pyridine) 1 to assemble with two Ag(I) ions to form a dinuclear molecular rectangle<sup>123</sup> wherein the C=C bonds are positioned for a [2+2] photodimerization (Figure 85a). We show that intramolecular photodimerizations occur in Ag<sub>2</sub>(1)<sub>2</sub>[(X)<sub>2</sub>] (where X<sup>-</sup> = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> (1a), CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup> (1b), and ClO<sub>3</sub><sup>-</sup> (1c)) wherein 1 reacts to give the cyclobutane photoproduct 2 regioselectively and in quantitative yield. We also show that 1 reacts via a heretofore not reported axially-chiral conformation involving a criss-cross arrangement of C=C bonds that is reminiscent of chiral conformations adopted by

unsymmetrically substituted and sterically-congested 1,8-diarylnaphthalenes (Figure 85b).<sup>124-126</sup> To our knowledge, our work provides the first example of an intramolecular [2+2] photodimerization mediated by a template in the solid state.



Figure 85. Scheme of assembly formation of diolefin 1: (a) Self-assembly of expected achiral conformer of 1 and AgX template and (b) intramolecular Ag(I)-mediated [2+2] photocycloaddition of the chiral conformer of 1 in the solid state to give 2.

# 6.2. Experimental

6.2.1. Synthesis of 1,8-bis[(E)-2-(4-

pyridyl)ethenyl]naphthalene (1,8 DEPN)

1,8-bis[(E)-2-(4-pyridyl)ethenyl]naphthalene was prepared in three steps following a modified Heck reaction.<sup>127</sup>

Step 1: Purification of 1,8 diaminonaphthalene

1,8 diaminonaphthalene (12.1 g, 76.5 mmol) was placed in a 1 L beaker. Hexanes (600 mL) was added to the beaker. The solution was heated vigorously and stirred until concentrated to 400 mL. The solution was gravity filtered while boiling. The filtrate

yielded the purified product as pink needles which were collected by vacuum filtration (5.4 g, 45% yield).

Step 2: Synthesis of diiodonaphthalene

Deionized water (80 mL) and sulphuric acid (50 mL) were poured into a 2 L beaker. The beaker was placed into a salt/ice bath and the acid solution was stirred. The purified 1,8 diaminonaphthalene (7.8 g, 50.6 mmol) was added to the beaker, immediately forming a white precipitate. The solution was stirred for approximately five minutes with ice added directly to the flask to keep the reaction cool. While continuing to stir, a solution of sodium nitrite (7.53 g, 11.1 mmol) in deionized water (100 mL) was prepared and added to the reaction drop wise through an addition funnel. During the addition, the solution turned brown. A solution of potassium iodide (18.5 g, 11.1 mmol) in deionized water (50 mL) was added drop wise through an addition funnel. During the addition, the solution foamed and formed aggregates. Ice was added to the reaction to prevent this. After the addition, the solution was heated to 70°C. During this time, a black precipitate formed. Upon reaching 70°C, the temperature was held constant for 15 minutes. After 15 minutes, the solution was made basic through the addition of sodium hydroxide pellets. Once basic, the solution was brought back to room temperature. The black precipitate was collected by vacuum filtration. The precipitate was washed thoroughly with 600 mL of ethyl ether. The solution was gravity filtered. The filtrate was then transferred to a separatory funnel and washed three times with 10% HCl (150 mL per wash), three times with a solution of saturated sodium thiosulfate (100 mL per wash), and three times with deionized water (100 mL per wash). The organic layer was dried with magnesium sulfate and gravity filtered. The solvent was removed leaving dark brown needles. The needles were recrystallized in hot hexanes to give the product diiodonaphthalene as red needles (4.8 g, 25% yield).

Step 3: Synthesis of 1,8-bis[(E)-2-(4-pyridyl)ethenyl]naphthalene

Diiodonaphthalene (1.0 g, 2.6 mmol), 4-vinylpyridine (0.69 g, 6.6 mmol), bis(triphenyl phosphine) palladium (II) dichloride (0.19 g, 0.26mmol), and triethylamine (5 mL) were placed in a 100 mL round bottom flask. The flask was wrapped in foil to protect from light and the reaction was refluxed for five days. After five days, the reaction was brought back to room temperature and dissolved with 200 mL dichloromethane. The reaction was washed three times with deionized water (100 mL per wash). The solvent from the organic layer was removed to give a dark brown solid. The solid was washed with ether by sonicating for 20 minutes. After 20 minutes, the solution was gravity filtered to collect the solid. The solid was recrystallized in ethyl acetate. The resulting solid was purified through column chromatography on a silica column using 3:1 THF: Petroleum Ether (0.45 g, 51.5% yield) <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 600 MHz, ppm)  $\delta$  = 8.35 (4H, d, 6.8 Hz), 8.17 (2H, d, 14.8 Hz), 7.98 (2H, d, 9.2 Hz), 7.72 (2H, d, 6.8 Hz), 7.58 (2H, t, 7.0 Hz), 7.38 (4H, d, 6.0 Hz), 7.00 (2H, d, 15.2 Hz). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 600 MHz, ppm)  $\delta$  = 149.8, 144.2, 136.1, 135.3, 134.3, 129.6, 129.5, 127.4, 126.8, 126.0, 120.8.



Figure 86. Schematic for the synthesis of 1,8-bis[(*E*)-2-(4-pyridyl)ethenyl]naphthalene.

# 6.2.2. Synthesis of $[Ag_2(1,8 \text{ DEPN})_2][CF_3SO_3]_2$ (1a)

1,8 DEPN (8 mg, 0.024 mmol) and silver trifluoromethane sulfonate (13 mg, 0.048 mmol) were combined in a vial and dissolved with 15 mL acetonitrile and heat. Single crystals were grown from slow solvent evaporation. The vial was wrapped in foil to protect the complex from light. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, ppm)  $\delta$  = 8.36 (4H, d, 5.4 Hz), 8.20 (2H, d, 17.1 Hz), 7.99 (2H, d, 8.7 Hz), 7.74 (2H, d, 5.4 Hz), 7.60 (2H, t, 7.4 Hz), 7.41 (4H, d, 5.4 Hz), 7.02 (d, 2H, 15.9 Hz).

# 6.2.3. Synthesis of [Ag<sub>2</sub>(1,8 DEPN)<sub>2</sub>][CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>]<sub>2</sub> (1b)

1,8 DEPN (8 mg, 0.024 mmol) and silver p-toluene sulfonate (13 mg, 0.048 mmol) were combined in a vial and dissolved with 15 mL acetonitrile and heat. Single crystals were grown from slow solvent evaporation. The vial was wrapped in foil to protect the complex from light. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, ppm)  $\delta$  = 8.37 (4H, d, 6.6 Hz), 8.21 (2H, d, 16.5 Hz), 8.00 (2H, d, 7.8 Hz), 7.73 (2H, d, 7.2 Hz), 7.60 (2H, t, 7.2 Hz), 7.47 (2H, d, 8.4 Hz), 7.43 (4H, d, 5.1 Hz), 7.11 (2H, d, 8.7 Hz), 7.02 (2H, d, 15.0 Hz), 2.28 (3H, s).

# 6.2.4. Synthesis of [Ag<sub>2</sub>(1,8 DEPN)<sub>2</sub>][ClO<sub>3</sub>]<sub>2</sub> (1c)

1,8 DEPN (8 mg, 0.024 mmol) and silver chlorate (9 mg, 0.048 mmol) were combined in a vial and dissolved with 15 mL acetonitrile and heat. Crystalline powder was grown from slow solvent evaporation. The vial was wrapped in foil to protect the complex from light. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz, ppm)  $\delta$  = 8.37 (4H, d, 6.3 Hz), 8.21 (2H, d, 16.8 Hz), 8.00 (2H, d, 8.4 Hz), 7.73 (2H, d. 7.5 Hz), 7.60 (2H, t, 8.0 Hz), 7.43 (4H, d, 5.7 Hz), 7.02 (2H, d, 15.9 Hz).

## pyridyl-cyclobut[a]acenaphthylene (2)

Upon completion of the photoreaction of **1c** (10 hours of irradiation), the sample was removed from the photoreactor. The photoproduct **2** was isolated from the silver template through basic extraction using 1M NaOH and CHCl<sub>3</sub>. Evaporation of the CHCl<sub>3</sub> gave the desired product. The product (5 mg) was recrystallized by slow solvent evaporation from acetonitrile (10 mL) and HBr (added drop wise). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 600 MHz, ppm)  $\delta$  = 8.38 (4H, d, 5.6 Hz), 7.79 (2H, d, 8.0 Hz), 7.58 (2H, dd, 6.6 Hz, 8 Hz), 7.46 (2H, d, 6.8 Hz), 7.35 (4H, d, 5.2 Hz), 4.74 (2H, d, 3.6 Hz), 3.97 (2H, d, 3.6 Hz). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 600 MHz, ppm)  $\delta$  = 149.9, 147.0, 139.4, 131.9, 128.3, 123.9, 123.3, 119.5, 49.9, 45.5.

# 6.2.6. Photoreactivity Experiments

Samples of 1,8 DEPN and the silver complexes were monitored for photoreactivity. Each sample was prepared as a crystalline powder and spread between two Pyrex plates. The samples were exposed to broad spectrum UV-irradiation in a high-pressure broadband mercury photoreactor. The progress of the photoreactions was monitored by solution phase <sup>1</sup>H NMR spectroscopy in regular intervals of approximately 10 hours. Progression of the photoreactions were confirmed by the disappearance of the signals for the olefinic protons and the appearance of signals for the cyclobutane protons.

# 6.2.7. NMR Experiments

Samples of 1,8 DEPN and the silver complexes were characterized using Avance-300, Avance-400, and Avance-600 Bruker NMR spectrometers operating at 300, 400, and 600 MHz, respectively. <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced from the <sup>1</sup>H and <sup>13</sup>C chemical shifts of DMSO-D<sub>6</sub> (<sup>1</sup>H, 2.50 ppm; <sup>13</sup>C, 39.5 pm). The compounds **1** and **2** were characterized by a battery of one- and two-dimensional (1D and 2D) homonuclear and <sup>1</sup>H-<sup>13</sup>C heteronuclear experiments [<sup>1</sup>H, <sup>13</sup>C, 2D correlated spectroscopy (COSY),

nuclear Overhauser effect spectroscopy (NOESY), heteronuclear single quantum coherence (HSQC), and heteronuclear multiple bond correlation (HMBC)]. Gradientassisted versions of the pulse sequences and inverse detection were used for these 2D experiments. <sup>1</sup>H spectral widths and 90° pulse widths are optimized for each sample. A recycle delay (D1) of 4.0s was used in all the 2D experiments. An optimal range of mixing times for NOESY experiments was determined using the one dimensional version of spin-lattice relaxation measurements. Typical parameters for the NMR experiments were as follows: <sup>1</sup>H [time domain data points (TD), 32k; NS, 32], <sup>13</sup>C (TD, 64k; NS, 10k), 2D COSY (TD, 2k; TD1, 150; NS, 16; DS, 32), NOESY [TD, 2k; TD1, 150; NS, 16; DS, 64; mixing times, 0.2, 0.6, 1.2 and 2.0s], <sup>13</sup>C-<sup>1</sup>H HSOC (TD, 2k; TD1, 256; NS, 16; DS, 128) and <sup>13</sup>C-<sup>1</sup>H HMBC (TD, 4k; TD1, 256; NS, 32; DS, 64). TD, NS, and DS refer to time domain data points, number of scans, and dummy scans, respectively. All NMR data were processed with TOPSPIN 1.3 suite of software programs. The 1D  $^{1}$ H data were processed with zero-filling to 64k data points and 0.2 Hz exponential line broadening, whereas <sup>13</sup>C spectra were processed with zero-filling to 128k data points and 1.0 Hz of exponential line broadening. The 2D NMR data were processed with the zerofilling to 2,048 points and 1,024 points in acquisition and second dimension, respectively.

## 6.3. Results and Discussion

Pioneering work of Hopf has reported the ability of [2.2]paracyclophane to act as a covalent scaffold that directs an intramolecular [2+2] photodimerization of two stacked and well positioned acryloyl groups in the solid state.<sup>128-130</sup> Crystallization of a pseudo*gem* 'cinnamophane' as a pure form generated a lattice wherein the two pendant C=C bonds were preorganized to react. UV-irradiation of the solid smoothly transformed the diene to the corresponding *rctt*-cyclobutane according to the postulate of Schmidt (Figure 87).



Figure 87. Scheme of Hopf's cinnamophane covalent scaffold which can undergo the [2+2] photocycloaddition.

In our work, we have sought to determine whether the 1,8-naphthalene diene **1** may undergo an intramolecular [2+2] photodimerization in the solid state to give **2**. From reports by us, and others, the 1,8-substitution pattern was expected to place the C=C bonds of the 4-vinyl pyridine groups in sufficiently close proximity that supports an intramolecular cycloaddition that forms **2**. A successful reaction would proceed via **1** in a *syn* conformation wherein the C=C bonds adopt a parallel orientation. According to semi-empirical PM3 calculations, the *syn* and *anti* conformations differ by only ~0.29 kJ/mol in energy, which would allow **1** to crystallize in the *syn* conformation to react in a solid.<sup>131</sup>

Upon synthesis and purification of the novel olefinic template 1,8 DEPN, the structure was confirmed through 1D and 2D solution phase NMR (Figure 88). Upon successful confirmation of the structure, the compound was recrystallized to produce single crystals. The single crystal data for 1,8 DEPN can be found in the Appendix (Table A10).



Figure 88. Solution phase NMR data of 1,8 DEPN: (a) <sup>1</sup>H NMR spectra showing the spin-spin coupling patterns. The resonance assignments were derived from a set of standard one and two-dimensional homonuclear and heteronuclear experiments and (b) COSY, <sup>13</sup>C-<sup>1</sup>H HSQC and <sup>13</sup>C-<sup>1</sup>H HMBC spectra of 1. The resonance assignment pathways indicated here from COSY to HMBC and HSQC to HMBC cross-sections reveal the unique through-bond interactions characteristic of 1. H<sub>b</sub> and H<sub>c</sub> are correlated to a common carbon C<sub>c</sub> by 3-bond HMBC and 1-bond HSQC interactions respectively, whereas H<sub>e</sub> and H<sub>d</sub> are correlated to C<sub>d</sub> (common carbon) by 3-bond HMBC and 1-bond HSQC interactions respectively.

Single crystals of 1,8 DEPN (5 mg) were readily grown from slow evaporation of acetonitrile (10 mL). Colorless blade-like crystals grew within a period of *ca* 1 hour.

The asymmetric unit consists of two full molecules of 1,8 DEPN (A and B) that crystallize in the centrosymmetric space group  $P\overline{1}$ . Consistent with reported 1,8-diarylnaphthalenes, the pyridyl groups lie splayed by 16.3° and 25.3° in A and B, with the pyridine rings being rotated by 16.8° and 20.7° and ring centroid-to-centroid distances being 5.2 and 4.9 Å, respectively. Each pair of C=C bonds in A and B, however - and in contrast to the cinnamophane of Hopf - adopt an *anti* conformation with inner/outer C-to-C separations of 2.8 Å/4.6 Å (A) and 2.8 Å/4.5 Å (B). The *anti* geometry means that 1,8 DEPN adopts an axially-chiral conformation in the solid with the C=C bonds being related by an idealized C<sub>2</sub> rotation axis (Figure 89a). To our knowledge, 1,8 DEPN provides the first example of a 1,8-divinylnaphthalene characterized in the crystalline state. Moreover, the chiral conformation means that the C=C bonds within 1,8 DEPN do not conform to the topochemical postulate of Schmidt for a [2+2] photodimerization in a solid.

Molecules A and B present in the asymmetric unit are of the same handedness. The dienes pack to form chiral columns along the *a*-axis with adjacent molecules being organized head-to-tail (ht) (Figure 89b). Dienes of neighboring columns lie head-to-head (hh), being sustained by C-H…N forces (2.7 Å). As a consequence of the assembly process, 2D chiral layers form within the *ab*-plane with adjacent layers being related by a center of inversion (Figure 89c). The closest C=C bond separation of adjacent dienes is 4.5 Å, which is also beyond the limit of Schmidt for a photoreaction. When a crystalline powder of 1,8 DEPN was exposed to broadband UV-radiation (500 W medium-pressure Hg lamp) for a period of *ca* 40 h, 1,8 DEPN was determined to be photostable.<sup>132</sup> Given the photostable crystal packing of 1,8 DEPN, it became evident that templates would be needed to facilitate the [2+2] photocycloaddition reaction in the solid state.



Figure 89. Single crystal data of 1,8 DEPN: (a) approximate C<sub>2</sub> rotation axis of chiral *anti* conformer, (b) 2D chiral layer in *ab*-plane, and (c) 2D layers alternating in chirality down the *c*-axis.

Whereas 1,8 DEPN is photostable as a pure compound, the diene reacts regioselectively and up to quantitative yield using Ag(I) ions as templates. Thus, [Ag<sub>2</sub>(1,8 crystalline powders of  $DEPN_2$ ][CF<sub>3</sub>SO<sub>3</sub>]<sub>2</sub> (1a), $[Ag_2(1, 8)]$  $DEPN_{2}[CH_{3}C_{6}H_{4}SO_{3}]_{2}$  (1b), and  $[Ag_{2}(1,8 DEPN)_{2}][ClO_{3}]_{2}$  (1c) were grown by slow solvent evaporation of a solution of 1,8 DEPN (0.024 mmol) and the appropriate Ag(I) salt (0.048 mmol) (despite preparing the complexes in a 1:2 ratio, a 1:1 ratio within the assemblies was observed in the single crystal data for both complexes 1a and 1b) in acetonitrile (15 mL). When each solid was exposed to UV-radiation (500 W mediumpressure Hg lamp) for a period of ca 40 h, <sup>1</sup>H NMR spectroscopy (DMSO- $d_6$ ) revealed 1,8 DEPN to undergo a [2+2] photodimerization to give 2 in up to quantitative yield (conversions: **1a**: 47%; **1b**: 59%; **1c**: 100%). The photoreactions were evidenced by up to near complete disappearances of the olefinic peaks at 8.2 and 7.0 ppm and the emergence of peaks at 4.7 and 4.0 ppm in the cyclobutane region (Figure 90a). The generation of the cyclobutane photoproduct was also substantiated using <sup>1</sup>H-<sup>1</sup>H COSY, <sup>1</sup>H-<sup>13</sup>C HSQC, and <sup>1</sup>H-<sup>13</sup>C HMBC correlations, with NOE cross peaks and relative intensities confirming the stereochemistry of the photoproduct (Figure 90b).<sup>133</sup> Salient features in the <sup>1</sup>H-<sup>13</sup>C HMBC spectra were correlations of the H<sub>c</sub> and H<sub>d</sub> cyclobutane protons with aromatic carbons C<sub>b</sub> and C<sub>e</sub>, respectively.



Figure 90. Solution phase NMR data of photoproduct **2**: (a) <sup>1</sup>H NMR spectra showing the spin-spin coupling patterns. The resonance assignments were derived from a set of standard one and two-dimensional homonuclear and heteronuclear experiments and (b) COSY, <sup>13</sup>C-<sup>1</sup>H HSQC and <sup>13</sup>C-<sup>1</sup>H HMBC spectra of **2**. The resonance assignment pathways indicated here from COSY to HMBC and HSQC to HMBC cross-sections reveal the unique through-bond interactions characteristic of **2**.

Single-crystal X-ray diffraction data confirmed the formation of dinuclear rectangles that direct the photodimerization of 1,8 DEPN to form the cyclobutane photoproduct. Single crystals of **1a** and **1b** were each obtained as colorless rods and

laths, respectively, from slow evaporations from acetonitrile. Several different crystallization parameters were tested for complex **1c**, however, adequate single crystals could not be obtained. The single crystal data for **1a** and **1b** can be found in the Appendix (Table A11).

The asymmetric unit of **1a** and **1b** each consist of two Ag(I) ions, two coordinated molecules of 1,8 DEPN, and corresponding anions that self-assemble to form dinuclear rectangles in the centrosymmetric space groups  $P\overline{1}$  and  $P2_1/c$ , respectively (Figure 91).



Figure 91. Discrete dinuclear rectangles of (a) 1a and (b) 1b.

Both assemblies are sustained by argentophilic forces (Ag····Ag (Å): (3.45 **1a**; 3.80 **1b**)), with each Ag(I) ion being coordinated to two dienes of opposite handedness. Within the assemblies, the vinyl pyridine groups lie less splayed (**1a**: 11.6°, 11.6°; **1b**: 12.9°, 12.8°) than the pure form, while the pyridine rings also lie rotated from each other (**1a**: 6.4°, 6.4°; **1b**: 24.0°, 24.0°). The C=C bonds of coordinated **1** are also in close proximity, displaying inner/outer C-to-C separations of 2.8 Å/4.4 Å and 2.8 Å/4.4 Å and ring centroid-to-centroid distances of 4.0 and 4.3 Å for **1a** and **1b**, respectively. As in the case of pure **1**, the C=C bonds of each diene adopt an antiparallel geometry. Notably, both sets of C=C bonds in **1a** display disorder at room temperature (C11/C12 95.1%)

antiparallel, C18/C24 91.4% antiparallel). We note that an appreciably high R value for **1b** at room temperature likely prohibits an observation of disorder.

The lack of observable disorder at the lower temperature is consistent with the C=C bonds being dynamically disordered in the solid. The organization of the components in the solids are, thus, consistent with the C=C bonds having a capacity to undergo pedal motions to support the photoreactions in the solids.<sup>134-136</sup>

Extended packing of each assembly further supports the intramolecular photodimerization determined through the NMR studies of the photoproduct. Extended packing of **1a** exhibits assemblies off-set and sustained through edge-to-face C-H $\cdots \pi$  interactions (Figure 92a). In contrast, the extended packing of **1b** exhibits off-set, face-to-face aligned assemblies along the *a*-axis, with adjacent assemblies aligned orthogonally along the *c*-axis (Figure 92b). For both complexes however, it is expected that olefin separations between assemblies will prevent inter-assembly photoreactions, supporting the idea of pedal motion within the assembly to give rise to the intramolecular photoproduct **2**.



Figure 92. Extended packing of dinuclear assemblies of: (a) 1a and (b) 1b.

## 6.4. Isolation and Characterization of 2

To confirm the stereochemistry of 2 that was determined from solution phase NMR studies, the cyclobutane photoproduct was recrystallized for single crystal X-ray analysis. The photoproduct 2 was isolated via a liquid phase extraction using  $CHCl_3$  and NaOH. Extraction afforded 2 as a cream-colored powder.

Single crystals of **2** (8 mg) were grown from slow evaporation of an acetonitrile solution (10 mL) with HBr added drop wise to give **2** as a salt. Pale yellow laths grew within a period of approximately 2 days.

The asymmetric unit of **2** consists of the dication of **2** and two bromine anions that crystallize in the centrosymmetric space group C2/c (Figure 93a). The single cyclobutane ring in the molecule supports the intramolecular [2+2] photocycloaddition. Individual molecules are oriented in a pseudo-chair geometry with the pyridine rings opposite of the naphthalene moiety (Figure 93b). The molecules align in hh columns along the *b*-axis (Figure 93c). The hh columns are repeated hh and off set along the *a*-axis and ht along the *c*-axis.



Figure 93. Single crystal data of **2**: (a) Dication of **2** (b) Space filling model of **2** with bromine anions removed for clarity (c) Packing of dication **2** showing head-to-head alignment along the *b*-axis and head-to-tail alignment down the *c*-axis.

# 6.5 Conclusion

In conclusion, we have shown the first non-covalent template directed intramolecular [2+2] photocycloaddition in the solid state. Molecule **1** was specifically designed for the [2+2] photocycloaddition, through 1,8 disubstitution of the naphthalene ring. Argentophilic forces between the Ag(I) cations facilitated the intramolecular cycloaddition. Varying the template demonstrated the generality of the photoreaction, with the photocycloaddition of each complex proceeding intramolecularly. It is our goal to expand the supramolecular applications of the non-covalent template directed intramolecular [2+2] reaction scheme to photoreact novel compounds to generate photoproducts such as ladderanes and cyclophanes. As seen with **2**, these photoproducts will be inherently hh and therefore unsymmetrical, giving the potential for postsynthetic

modifications. Furthermore, the isostructural nature if **1** to the template 1,8 DPN gives promise of future applications of **1** as an olefinic template.

#### **CHAPTER 7: CONCLUSION**

Both supramolecular solid-state chemistry and solid-state synthesis offer substantial benefits over solution phase chemistry. Due to the limited movement in the solid state, selectivity for a stereospecific product can often be attained. Through this selectivity, products that may otherwise be difficult to synthesize in the solution phase can be easily generated in the solid state. Furthermore, the use of specific functional groups within a solid-state system can facilitate discrete self-assembly through supramolecular interactions, allowing for the execution of controlled processes.

While solid-state chemistry indeed provides many benefits over solution phase chemistry, the growth of this field and expansion of applications has been hindered due to limitations including a lack of functional group diversity and the inherent unpredictability of crystal packing. In order to continue the development of the field of solid-state chemistry, work must be done to overcome these limitations. The research presented in this thesis demonstrates our efforts to overcome the limitations of low functional group diversity and unpredictability of crystal packing in solid-state reactivity and thus further expand the applications of solid-state chemistry.

Through carefully selected functional groups, we have demonstrated the ability to synthesize novel olefinic compounds able to undergo post-synthetic modifications (PSM) to effectively produce a series of analogous olefinic compounds bearing different functional groups in a single position. As was presented in chapter 2, initial coupling of a terminal alkyne onto a stilbazole derived molecule provided an opportunity for PSM of the alkyne. Prior to PSM of the alkyne, the photoreactivity of the molecule was evaluated to determine the tolerance of the photoreaction in the presence of another pibonded functional group. The pure, crystalline solid packs in a manner that violates the topochemical postulate, exhibiting linear chains sustained through C-H…N interactions. The lack of appropriate olefin geometry renders the molecule photostable. The introduction of the organic template, 4,6-diBr res, however, provided stronger hydrogen

bond donors in the form of hydroxyl groups on the res, overcoming the C-H···N hydrogen bonds and guiding the alkyne bearing molecule into discrete 2:1 assemblies through O-H···N hydrogen bonds. These assemblies adhere to the topochemical postulate are able to photodimerize in the solid state to yield the cyclobutane product.

Confirmation of the tolerance of the [2+2] photocycloaddition in the solid state to the newly introduced terminal alkyne provided motivation to continue to investigate other functional groups through PSM of the alkyne. The copper-catalyzed azide-alkyne cycloaddition (click) reaction, as first demonstrated by Sharpless and Meldal, proved to be an ideal PSM technique, requiring both a terminal alkyne and an organic azide. As described in chapter 3, the click reaction provides a facile method to systematically introduce both a 1,4-disubstituted-1,2,3-triazole ring and a multitude of new functionality through the "R" group of the organic azide. While varying the "R" group provides the most immediate avenue for expansion of functional group diversity, the 1,2,3-triazole ring also provided intriguing new studies due to the potential for many supramolecular interactions at both the N2 and N3 positions as well as through the C-H bond. Before measuring the photoreactivity of the novel click-derived olefinic molecules, we first sought a better understanding of the behavior and packing patterns of the 1,4disubstituted-1,2,3-triazole ring in the solid state. For this study, the electronic bridging properties in both the solution phase and the solid state were measured. The electronic properties in the solid state were determined through single crystal X-ray diffraction data and further supported through computational studies. The single crystal packing of 4,4'PTC and 4BPTC provide ideal comparisons of a molecule able to bridge to both termini (4,4'PTC) and a molecule where bridging to one termini is prevented due to a saturated carbon (4BPTC). Though both molecules pack in noncentrosymmetric space groups, the crystal packing of 4,4'PTC exhibits rare head-to-head (hh) packing, supporting an electronically soft molecule, while 4BPTC exhibits the more common head-to-tail (ht) packing supporting an electronically hard molecule. Furthermore, these

results demonstrated that the solution phase properties exhibited by these click-derived molecules are maintained in the crystalline state.

With a better understanding of the properties of the 1,4-disubstituted-1,2,3triazole ring in the crystalline state, we moved forward to study to photoreactivity of the click-derived molecules. It was surprising to note that, while the click reaction and the [2+2] photocycloaddition reaction share many common benefits, the two reaction had not been combined to be performed in tandem in either the solid state or the solution phase. The photoreactivity of three different click-derived molecules (4,4'PTC, BTC, and PTC) were evaluated. All three molecules proved photostable as pure solids when exposed to UV irradiation. The nearly planar 4,4'PTC was cocrystallized with organic templates yielding photostable cocrystals comprised of ht discrete assemblies. Building from recent studies incorporating click-derived molecules into metal-organic assemblies, both BTC and PTC were templated with Ag(I) cations. While each BTC metal complex exhibited signs of photoreactivity, the photoproducts could not be isolated, nor could the progress of the photoreactions be accurately measure. The PTC metal complexes demonstrated both photostable and photoactive complexes. The metal complex  $[Ag_2(PTC)_2][(ClO_3)_2]$ exhibits discrete macrocyclic J-shaped assemblies off-set from one another. Within each assembly the olefins are aligned and parallel giving rise to an intra-assembly photodimerizations producing the ht photoproduct. This complex represents the first example of a J-shaped metal-organic assembly, with the J-shape previously seen exclusively in pure organic systems. Furthermore, it presents the first known example of the [2+2] photocycloaddition reaction performed on the product of a click reaction. The metal complex [Ag(PTC)<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub>] exhibits linear discrete assemblies resulting from different coordination patterns. Though no longer a macrocycle able to direct intraassembly dimerization, the linear assemblies are off-set in such a manner as to align olefins according to the topochemical postulate. Indeed, this complex demonstrates rare single-crystal to single-crystal (SCSC) photodimerization prior to exposure to UV

irradiation. These two complexes demonstrate not only the ability to combine the click reaction with the [2+2] photocycloaddition reaction, but also the versatility of the PTC ligand as it exhibits different crystal packing motifs with different Ag(I) templates while maintaining the [2+2] photodimerization reaction.

In addition to expanding functional group diversity through PSM of the terminal alkyne, we have sought to further develop the use of the template method through studies of crystal packing patterns of the templates. As discussed in chapter 5, several cocrystals were synthesized from a res derivative and the hydrogen bond accepting template, 1,8 DPN. The single crystal packing of each cocrystal was investigated with attention towards assembly formation and hydrogen bond lengths. These studies confirmed the reliability of discrete assembly formation and also that substitutions on the res backbone can affect the hydrogen bonding strength. Building from this study we also sought to develop a photoactive template that could produce a double photoreaction with both components of the cocrystal photodimerizing. While our current attempts with resveratrol have been unsuccessful, inspiration towards a photoactive template through an intramolecular [2+2] photocycloaddition was cultivated.

As described in chapter 6, further developments of the template method were made through the newly synthesized molecule 1,8 DEPN. Isostructural to the template 1,8 DPN, it was our intention to synthesize a new olefinic template that could both template the [2+2] photocycloaddition reaction of other olefins, as well as photoreact itself while serving as a template. Before a study of this nature can be accomplished however, a full understanding of the photoreactivity of 1,8 DEPN as an olefinic molecule must be obtained. As a pure solid, 1,8 DEPN is photostable due to olefins crossed in the *anti*-conformation. When complexed with Ag(I) cations, however, discrete assemblies of varying photoreactivity result. Though crystal packing of the metal-organic complexes shows the olefins are in the *anti*-conformation at low temperature, data collected at room temperature displays disorder around the double bonds, suggesting pedal motion within
the assemblies to give rise to the intramolecular [2+2] photocycloaddition. Photoproduct isolated from quantitatively photoreacted [Ag<sub>2</sub>(1,8 DEPN)<sub>2</sub>][ClO<sub>3</sub>]<sub>2</sub> demonstrates a highly strained, multi-ring confirming the intramolecular system, [2+2]This study represents the first templated intramolecular [2+2] photocycloaddition. photocycloaddition reaction in the solid state. Furthermore, the generality of the photoreactivity of 1,8 DEPN has been demonstrated through isolation of the same photoproduct through the use of three different templates. The reliable photoreactivity of 1,8 DEPN gives promise for future use as a photoreactive template with other olefinic molecules.

Supramolecular solid-state chemistry and solid-state synthesis represent an important and rapidly emerging field in chemistry and materials science. In order to continue the development of these fields however, steps must be taken to overcome limitations such as limited functional group diversity and unpredictable crystal packing. The research described here has demonstrated our recent efforts to overcome both limitations and continue the advancement of solid-state chemistry.

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## APPENDIX: TABLES OF CRYSTALLOGRAPHIC DATA

Table A-1	. Relevant crystallographic parameters for the crystals of 1-Ethynyl-4-[2-(4-
	pyridyl) ethenyl] benzene and (4,6-diBr-res)·2(1-Ethynyl-4-[2-(4-pyridyl)
	ethenyl] benzene).

Compound	Alkyne	(4,6-diBr-res)·2(Alkyne)
Chemical Formula	(C <sub>15</sub> H <sub>11</sub> N)	$(C_6H_4O_2Br_2)\cdot 2(C_{15}H_{11}N)$
Formula Mass	205.25	678.41
Crystal System	Orthorhombic	Triclinic
Space Group	Pna2 <sub>1</sub>	P1
a/ Å	9.5628(11)	8.804(2)
b/ Å	15.264(2)	9.679(3)
c/ Å	7.6766(12)	18.845(5)
α/°	90.000	94.689(13)
$eta/^{\circ}$	90.000	93.382(12)
γ/°	90.000	108.079(13)
V/ Å <sup>3</sup>	1120.5(3)	1515.4(7)
T/K	200(2)	293(2)
Z	4	2
Crystal dimensions	0.32x0.26x0.03	0.24x0.05x0.005
Calculated density	1.217	1.487
Radiation type	Μο Κα	Μο Κα
Wavelength	0.7107	0.7107
$\theta_{max}$	25.35	25.35
$\mu / \text{mm}^{-1}$	0.071	2.710
No. of reflections measured	15233	18747
No. of independent reflections	1451	5173
Parameters	147	379
$R_1 (I > 2\sigma(I))$	0.1344	0.1091
$w\mathbf{R}(F^2) (I > 2\sigma(I))$	0.3502	0.2228
R <sub>1</sub> (all data)	0.1872	0.3172
$w \mathbf{R}(F^2)$ (all data)	0.3759	0.2819

Table A-1 continued

Goodness of fit on $F^2$	2.141	0.899

Compound	4,4'PTC	4BPTC
Chemical Formula	$C_{20}H_{15}N_5$	$C_{21}H_{17}N_5$
Formula Mass	325.37	339.40
Crystal System	monoclinic	monoclinic
Space Group	C c	C c
<i>a</i> ∕ Å	37.700(4)	42.009(5)
b/ Å	5.7148(6)	5.9508(6)
c/ Å	7.2827(8)	13.5541(14)
a/°	90.00	90.00
$\beta/^{\circ}$	96.164(5)	92.817(5)
γ/°	90.00	90.00
<i>V</i> / Å <sup>3</sup>	1560.0(3)	3384.3(6)
T/K	293(2)	293(2)
Z	4	8
Crystal dimensions	0.36x0.19x0.01	0.42x0.34x0.03
Calculated density	1.39	1.33
Radiation type	Μο Κα	Μο Κα
Wavelength	0.7107	0.7107
$\theta_{max}$	27.88	25.35
μ / mm <sup>-1</sup>	0.086	0.083
No. of reflections measured	4357	31087
No. of independent reflections	1375	2967
Parameters	226	469
$\mathbf{R}_1 (I > 2\sigma(I))$	0.0454	0.0377
$w \mathbf{R}(F^2) \ (I > 2\sigma(I))$	0.1027	0.0879
R <sub>1</sub> (all data)	0.0797	0.0506
$w\mathbf{R}(F^2)$ (all data)	0.1178	0.0958
Goodness of fit on $F^2$	0.977	1.05
CCDC number	934959	934960
	1	

Table A-2. Relevant crystallographic parameters for the crystals of 4,4'PTC and 4BPTC.

Compound	(4,6-diBr-res)·(4,4'PTC)	(4,6-diI- res)·(4,4'PTC)
Chemical Formula	$(C_6H_4Br_2) \cdot (C_{20}H_{15}N_5)$	$(C_6H_4I_2) \cdot (C_{20}H_{15}N_5)$
Formula Mass	1186.56	1374.52
Crystal System	Triclinic	Triclinic
Space Group	PĪ	ΡĪ
<i>a</i> / Å	8.8693(9)	9.3137(10)
<i>b</i> / Å	11.1874(12)	9.3845(10)
<i>c</i> / Å	14.1606(15)	14.6019(17)
$\alpha/^{\circ}$	100.905(5)	77.367(5)
$eta/^{\circ}$	104.865(5)	87.044(5)
γ/°	110.295(5)	84.532(6)
$V/ Å^3$	1212.3(2)	1239.1(2)
T/K	293(2)	293(2)
Z	1	1
Crystal dimensions	0.16x0.16x0.025	0.16x0.05x0.01
Calculated density	1.625	1.842
Radiation type	Μο Κα	Μο Κα
Wavelength	0.7107	0.7107
$\theta_{\max}$	25.35	25.35
$\mu / mm^{-1}$	3.378	2.572
No. of reflections measured	17588	17921
No. of independent reflections	4180	4336
Parameters	316	316
$\mathbf{R}_1 (I > 2\sigma(I))$	0.0672	0.656
$w\mathbf{R}(F^2) \ (I > 2\sigma(I))$	0.2168	0.2058
R <sub>1</sub> (all data)	0.1140	0.1488
$w\mathbf{R}(F^2)$ (all data)	0.2576	0.2586
Goodness of fit on $F^2$	0.938	0.813

Table A-3. Relevant crystallographic parameters for the crystals of (4,6-diBr-res)·(4,4'PTC) and (4,6-diI-res)·(4,4'PTC).

Compound BTC [Ag(E		[Ag(BTC)][ClO <sub>3</sub> ]	$\begin{matrix} [Ag_{2}(BTC)_{4}][(CH_{3}C_{6}\\H_{4}SO_{3})_{2}] \end{matrix}$
Chemical Formula	$C_{22}H_{18}N_4$	[Ag(C <sub>22</sub> H <sub>18</sub> N <sub>4</sub> )][ClO <sub>3</sub> ]	$\begin{matrix} [Ag_2(C_{22}H_{18}N_4)_4][(CH_3\\C_6H_4SO_3)_2] \end{matrix}$
Formula Mass	338.40	868.13	955.86
Crystal System	monoclinic	monoclinic	triclinic
Space Group	$P2_1/c$	C2/c	ΡĪ
<i>a</i> / Å	16.2825(8)	20.418(2)	9.3197(9)
b/ Å	5.6181(3)	11.1642(11)	18.4542(18)
c/ Å	19.5951(10)	18.4923(18)	26.904(3)
α/°	90.000	90.000	99.683(5)
$eta/^{\circ}$	102.361(3)	92.316(5)	90.151(5)
$\gamma/^{\circ}$	90.000	90.000	93.642(5)
$V/ \text{\AA}^3$	1750.94(16)	4211.9(7)	4551.6(8)
T/K	293(2)	293(2)	293(2)
Z	4	4	4
Crystal dimensions	0.335x0.19x0.01	0.24x0.10x0.075	0.21x0.15x0.05
Calculated density	1.284	1.369	1.395
Radiation type	Μο Κα	Μο Κα	Μο Κα
Wavelength	0.7107	0.7107	0.7107
$\theta_{max}$	25.35	25.35	25.35
$\mu / mm^{-1}$	0.078	0.591	0.541
No. of reflections measured	16383	19242	65569
No. of independent reflections	3073	3701	15978
Parameters	235	280	1153
$\mathbf{R}_1 (I \ge 2\sigma(I))$	0.0577	0.0544	0.0483
$w\mathbf{R}(F^2) \ (I \ge 2\sigma(I))$	0.1718	0.1912	0.1526
R <sub>1</sub> (all data)	0.1272	0.0746	0.0976
$w \mathbf{R}(F^2)$ (all data)	0.2293	0.2228	0.2003
Goodness of fit on $F^2$	0.771	0.925	0.793

Table A-4. Relevant crystallographic parameters for the crystals of BTC,  $[Ag(BTC)][ClO_3], [Ag_2(BTC)_4][(CH_3C_6H_4SO_3)_2].$ 

Compound	РТС
Chemical Formula	$C_{21}H_{17}N_5$
Formula Mass	339.40
Crystal System	orthorhombic
Space Group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> / Å	4.7892(6)
b∕ Å	9.4634(10)
<i>c</i> / Å	37.911(4)
α/°	90.00
$eta /^{\circ}$	90.00
$\gamma/^{\circ}$	90.00
$V/ Å^3$	1718.2(3)
T/K	293(2)
Z	4
Crystal dimensions	0.33x0.08x0.03
Calculated density	1.312
Radiation type	Μο Κα
Wavelength	0.7107
$\theta_{max}$	25.35
$\mu / mm^{-1}$	0.082
No. of reflections measured	23067
No. of independent reflections	2990
Parameters	235
$\mathbf{R}_1 (I \geq 2\sigma(I))$	0.0753
$w\mathbf{R}(F^2) \ (I \ge 2\sigma(I))$	0.2262
R <sub>1</sub> (all data)	0.1684
$w\mathbf{R}(F^2)$ (all data)	0.2920
Goodness of fit on $F^2$	0.943

Table A-5. Relevant crystallographic parameters for the crystals of PTC.

Compound	$[Ag(PTC)_2][(ClO_4)]$	$[Ag(PTC)_2][(ClO_3)]$	[Ag(PTC) <sub>2</sub> ][CF <sub>3</sub> SO <sub>3</sub> ]
Chemical Formula	$[Ag(C_{21}H_{17}N_5)_2][(ClO_4)]$	$[Ag(C_{21}H_{17}N_5)_2][(ClO_3)]$	$[Ag(C_{21}H_{17}N_5)_2][CF_3SO_3]$
Formula Mass	904.13	544.70	935.73
Crystal System	Triclinic	Triclinic	Monoclinic
Space Group	ΡĪ	PĪ	C2/c
<i>a</i> / Å	11.0241(2)	8.3780(9)	26.251(3)
b/ Å	14.6056(15)	9.3305(10)	10.5149(11)
<i>c</i> / Å	15.0858(16)	13.8765(15)	14.6367(15)
$\alpha/^{\circ}$	68.404(5)	83.970(5)	90.00
$eta /^{\circ}$	74.635(5)	89.230(5)	93.301(5)
$\gamma/^{\circ}$	69.530(5)	703224(5)	90.00
V/Å <sup>3</sup>	2089.9(4)	1014.83(19)	4033.4(7)
$T/\mathrm{K}$	293(2)	293(2)	293(2)
Z	2	2	4
Crystal dimensions	0.36x0.20x0.07	0.24x0.23x0.08	0.19x0.09x0.025
Calculated density	1.437	1.783	1.541
Radiation type	Μο Κα	Μο Κα	Μο Κα
Wavelength	0.7107	0.7107	0.7107
$\theta_{\max}$	27.88	27.88	27.88
$\mu / mm^{-1}$	0.603	1.166	0.620
No. of reflections measured	40941	16147	30959
No. of independent reflections	7339	3554	3556
Parameters	523	280	127
$\mathbf{R}_1 (I \geq 2\sigma(I))$	0.1087	0.0513	0.1824
$w\mathbf{R}(F^2) \ (I \ge 2\sigma(I))$	0.3478	0.1576	0.4731
R <sub>1</sub> (all data)	0.1232	0.0650	0.2238
$w\mathbf{R}(F^2)$ (all data)	0.3639	0.1804	0.4981
Goodness of fit on $F^2$	1.633	0.993	1.900

Table A-6. Relevant crystallographic parameters for the crystals of  $[Ag(PTC)_2][(ClO_4)]$ ,  $[Ag(PTC)_2][(ClO_3)]$ , and  $[Ag(PTC)_2][CF_3SO_3]$ .

Compound	(res) · (1,8 DPN)	(4,6-diBr-res)·(1,8 DPN)
Chemical Formula	$(C_6H_6O_2) \cdot (C_{20}H_{14}N_2)$	$(C_6H_4Br_2) \cdot (C_{20}H_{14}N_2)$
Formula Mass	392.44	550.24
Crystal System	Monoclinic	Orthorhombic
Space Group	$P2_1/c$	Pna2 <sub>1</sub>
<i>a</i> / Å	15.2236(16)	19.3364(19)
b/ Å	22.973(3)	22.142(3)
<i>c/</i> Å	18.3625(19)	15.3933(16)
α/°	90.00	90.00
$eta /^{\circ}$	104.777(5)	90.00
$\gamma/^{\circ}$	90.00	90.00
$V/ \text{\AA}^3$	6115.3(12)	6590.6(13)
T/K	293(2)	293(2)
Z	12	11
Crystal dimensions	0.25x0.12x0.015	0.39x0.12x0.04
Calculated density	1.279	1.525
Radiation type	Μο Κα	Μο Κα
Wavelength	0.7107	0.7107
$\theta_{max}$	25.35	25.35
$\mu / mm^{-1}$	0.082	3.407
No. of reflections measured	84760	104591
No. of independent reflections	10633	12014
Parameters	811	866
$\mathbf{R}_1 (I \ge 2\sigma(I))$	0.1264	0.0412
$w\mathbf{R}(F^2) \ (I \ge 2\sigma(I))$	0.2920	0.0887
R <sub>1</sub> (all data)	0.3725	0.0815
$w \mathbf{R}(F^2)$ (all data)	0.3985	0.1009
Goodness of fit on $F^2$	0.862	0.899

Table A-7. Relevant crystallographic parameters for the crystals of (res)·(1,8 DPN) and (4,6-diBr-res)·(1,8 DPN).

Compound	(4-Cl-res)·(1,8 DPN)	(4-Br-res)·(1,8 DPN)	(1,8 naphthalene diacid) · (1,8 DPN)
Chemical Formula	$(C_6H_5Cl) \cdot (C_{20}H_{14}N_2)$	$(C_6H_5Br) \cdot (C_{20}H_{14}N_2)$	$(C_{12}H_8O_4) \cdot (C_{20}H_{14}N_2)$
Formula Mass	426.88	471.34	298.52
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	C2/c	P2 <sub>1</sub> /c	$P2_1/n$
<i>a</i> / Å	30.643(4)	9.5342(10)	8.5435(9)
b∕ Å	7.4974(8)	17.2905(18)	23.056(3)
<i>c</i> / Å	18.8543(19)	12.9716(14)	12.3273(12)
$lpha/^{\circ}$	90.00	90.00	90.00
$eta/^{\circ}$	105.227795)	90.570(5)	96.411(5)
γ/°	90.00	90.00	90.00
$V/ \text{\AA}^3$	4179.6(8)	2138.3(4)	2413.0(5)
T/K	293(2)	293(2)	293(2)
Z	8	4	4
Crystal dimensions	0.29x0.15x0.06	0.31x0.26x0.21	0.17x0.13x0.09
Calculated density	1.357	1.464	1.372
Radiation type	Μο Κα	Μο Κα	Μο Κα
Wavelength	0.7107	0.7107	0.7107
$\theta_{max}$	27.88	27.88	25.35
$\mu / mm^{-1}$	0.209	1.948	0.091
No. of reflections measured	34694	36591	27622
No. of independent reflections	3673	3768	4242
Parameters	280	280	343
$\mathbf{R}_1 (I > 2\sigma(I))$	0.0496	0.0347	0.0543
$w\mathbf{R}(F^2) \ (I \ge 2\sigma(I))$	0.1586	0.1049	0.1182
R <sub>1</sub> (all data)	0.0768	0.0477	0.1451
$w\mathbf{R}(F^2)$ (all data)	0.1990	0.1329	0.1474
Goodness of fit on $F^2$	0.791	0.712	0.847
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Table A-8. Relevant crystallographic parameters for the crystals of (4-Cl-res)·(1,8 DPN), (4-Br-res)·(1,8 DPN), and (1,8 naphthalene diacid) · (1,8 DPN).

Compound	(Resveratrol) · (1,8 DPN)
Chemical Formula	$(C_{14}H_{12}O_3) \cdot (C_{20}H_{14}N_2)$
Formula Mass	510.57
Crystal System	Triclinic
Space Group	PĪ
a/ Å	10.1520(11)
b/ Å	11.1757(12)
c/ Å	14.4878(15)
a/°	75.398(5)
β/°	83.612(5)
γ/°	70.708(5)
<i>V</i> / Å <sup>3</sup>	1500.6(3)
T/K	293(2)
Z	2
Crystal dimensions	0.28x0.10x0.095
Calculated density	1.130
Radiation type	Μο Κα
Wavelength	0.7107
$\theta_{max}$	25.35
μ / mm <sup>-1</sup>	0.072
No. of reflections measured	26059
No. of independent reflections	5254
Parameters	408
$R_1 (I > 2\sigma(I))$	0.0453
$w\mathbf{R}(F^2) \ (I > 2\sigma(I))$	0.1351
R <sub>1</sub> (all data)	0.0711
$w\mathbf{R}(F^2)$ (all data)	0.1651
Goodness of fit on $F^2$	1.022

Table A-9. Relevant crystallographic parameters for the crystals of (Resveratrol)·(1,8 DPN).

Compound	1,8 DEPN	1,8 DEPNcb
Chemical Formula	$C_{24}H_{18}N_2$	$C_{24}H_{20}Br_2N_2$
Formula Mass	334.40	496.24
Crystal System	Triclinic	Monoclinic
Space Group	PĪ	C2/c
<i>a</i> / Å	9.4274(9)	16.3504(16)
b∕ Å	12.3411(12)	14.9527(15)
<i>c</i> / Å	15.5934(16)	9.2389(9)
$\alpha/^{\circ}$	83.302(5)	90.00
$eta /^{\circ}$	82.714(5)	92.387(5)
$\gamma/^{\circ}$	79.240(5)	90.00
$V/ \text{\AA}^3$	1759.85	2256.8(4)
<i>T</i> /K	150(2)	150(2)
Z	4	4
Crystal dimensions	0.48x0.13x0.03	0.35x0.14x0.06
Calculated density	1.262	1.567
Radiation type	Μο Κα	Μο Κα
Wavelength	0.7107	0.7107
$\theta_{max}$	25.35	25.35
$\mu / mm^{-1}$	0.074	3.603
No. of reflections measured	15127	16505
No. of independent reflections	6371	1981
Parameters	469	245
$\mathbf{R}_1 (I \ge 2\sigma(I))$	0.1283	0.0606
$w\mathbf{R}(F^2) \ (I \ge 2\sigma(I))$	0.3784	0.1346
R <sub>1</sub> (all data)	0.2015	0.0698
$w$ R( $F^2$ )(all data)	0.4149	0.1375
Goodness of fit on $F^2$	1.105	1.220
CCDC number	977456	977455

Table A-10. Relevant crystallographic parameters for the crystals of 1,8 DEPN and 1,8 DEPNcb.

Compound	[Ag <sub>2</sub> (1,8 DEPN) <sub>2</sub> ][CF <sub>3</sub> SO <sub>3</sub> ] <sub>2</sub>	$[Ag_2(C_{24}H_{18}N_2)_2][CH_3C_6H_4SO_3]_2$
Chemical Formula	$[Ag_2(C_{24}H_{18}N_2)_2][CF_3SO_3]_2$	$[Ag_2(C_{24}H_{18}N_2)_2][CH_3C_6H_4SO_3]_2$
Formula Mass	1182.68	1226.92
Crystal System	Triclinic	Monoclinic
Space Group	PĪ	$P2_1/c$
<i>a/</i> Å	10.3809(11)	14.3300(15)
b/ Å	10.9748(11)	10.8862(11)
<i>c/</i> Å	11.0438(12)	17.8919(18)
$\alpha/^{\circ}$	109.430(5)	90.00
$eta/^{\circ}$	98.185(5)	110.048(5)
$\gamma/^{\circ}$	97.328(5)	90.00
$V/~{ m \AA}^3$	1153.7(2)	2622.0(5)
$T/\mathrm{K}$	210(2)	190
Z	1	2
Crystal dimensions	0.23x0.07x0.07	0.22x0.06x0.01
Calculated density	1.702	1.554
Radiation type	Μο Κα	Μο Κα
Wavelength	0.7107	0.7107
$\theta_{\rm max}$	27.88	25.35
$\mu / mm^{-1}$	1.020	0.885
No. of reflections measured	38166	35601
No. of independent reflections	4053	4595
Parameters	316	344
$\mathbf{R}_1 (I \geq 2\sigma(I))$	0.0296	0.044
$w\mathbf{R}(F^2) \ (I \ge 2\sigma(I))$	0.0818	0.0898
R <sub>1</sub> (all data)	0.0377	0.0803
$w\mathbf{R}(F^2)$ (all data)	0.0884	0.1085
Goodness of fit on $F^2$	0.988	0.930
CCDC number	977458	977457

Table A-11. Relevant crystallographic parameters for the crystals of  $[Ag_2(1,8 DEPN)_2][CF_3SO_3]_2$  and  $[Ag_2(1,8 DEPN)_2][CH_3C_6H_4SO_3]_2$ .