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Intramolecular [2 + 2] Photodimerization Achieved in the Solid State via Coordination-Driven Self-Assembly

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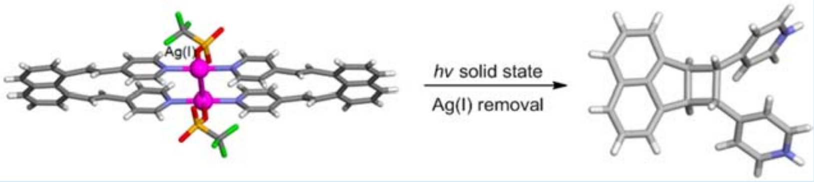
Supporting Information



ABSTRACT: An intramolecular [2 + 2] photocycloaddition is achieved in the organic solid state via self-assembly of Ag(I) ions and an *endo*-ditopic bipyridine. The cations aide to organize carbon−carbon double (C═C) bonds attached to the bipyridine for the cycloaddition reaction. The C═C bonds react regioselectively and quantitatively to afford a photoproduct with edge-sharing four-, five-, and six-membered rings. Our study demonstrates the first use of a metal−organic template to direct an intramolecular [2 + 2] photodimerization in the organic solid state.

For a [2 + 2] photocycloaddition to occur in the organic solid state, carbon−carbon double (C═C) bonds are expected to adhere to Schmidt's topochemical postulate, being aligned parallel and separated by <4.2 Å.[1] To overcome the effects of packing that hinder olefins from assembling into geometries to react in solids, small-molecule and metal-based templates have been reported.[2,3] The operation of a template relies on noncovalent forces to assemble and position olefins into multicomponent self-assembled structures for photoreaction. To date, templates have been applied exclusively to *inter*molecular photocycloadditions, enabling access to architecturally rich molecules difficult to obtain in solution.

In this study, we sought to determine whether the 1,8-naphthalene diene 1,8-bis[(*E*)-2-(4-pyridyl)ethenyl] naphthalene (**1**) undergoes an *intra*molecular [2 + 2] photodimerization[4] in the solid state (i.e., in absence of a template) to give *cis*-di(4-pyridyl)naphthocyclobutane (**2**) (Figure 1). The 1,8-substitution pattern[5,6] was expected to place the C═C bonds of the 4-vinylpyridine groups in close enough proximity to support an intramolecular reaction to generate **2**. A successful reaction would proceed via *endo*-ditpoic **1** in a *syn* conformation wherein the C═C bonds adopt a parallel orientation. From semiempirical PM3 calculations, the *syn*- and *anti*-conformations differed by only ~0.30 kJ/mol, which would allow **1** to crystallize in the *syn* conformation and react in a solid.[7]

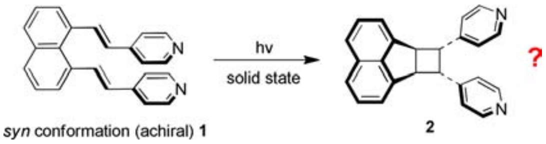


Figure 1. Crystallization of **1** in *syn* conformation for an intramolecular [2 + 2] photocycloaddition.

The bis(4-pyridine) **1** was, thus, synthesized using a modified procedure based on a Heck reaction. To determine the photoreactivity of pure **1**, single crystals (5 mg) of the diene were grown by slow evaporation in MeCN (10 mL). Colorless blade-like crystals grew within a period of *ca.* 1 h.

The asymmetric unit consists of two full molecules (A and B) of **1** that crystallize in the centrosymmetric space group $P\bar{1}$. The 4-pyridyl groups are splayed by 16.3° and 25.3° in A and B, with the pyridine rings rotated by 16.8° and 20.7° and the ring centroid-to-centroid distances separated by 5.2 and 4.9 Å, respectively (Figure 2). Each pair of C═C bonds in A and B, however, adopts 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).[8] The *anti*-relationship means that **1** adopts a unique[9] axially chiral conformation with the C═C bonds being related by an idealized C_2 rotation axis (Figure 2a). The C═C bonds of the diene **1**, thus, do not conform to the topochemical postulate of Schmidt[1] for a [2 + 2] photodimerization in a solid.

Molecules A and B of **1** are of the same handedness in the solid state. The dienes form chiral columns along the *a*-axis with adjacent molecules organized head-to-tail (Figure 2b). Dienes of neighboring columns lie head-to-head, being sustained by C−H···N forces (2.7 Å). Chiral layers, thus, form within the *ab*-plane with the stacked layers related by a center of inversion. The closest C═C bond separation of adjacent dienes is 4.5 Å, which is beyond the limit of Schmidt. When a crystalline powder of **1** was exposed to broad-band UV-

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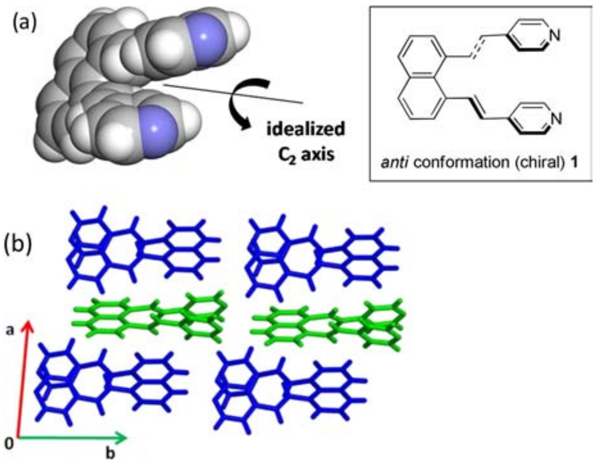

Figure 2. X-ray structure of **1**: (a) C_2 rotation axis of chiral *anti* conformer (right: schematic of *anti*-conformation) and (b) 2D chiral layer in *ab*-plane.

radiation (500 W medium-pressure Hg lamp) for a period of *ca.* 40 h, **1** was determined to be photostable.

To address the photostability of **1** as a pure form, we turned to Ag(I) ions. Whereas Ag(I) has been utilized by us,[10] and others,[11] to assemble $C{=}C$ bonds within acyclic complexes for *inter*molecular cycloadditions, we reasoned that a self-assembly process involving **1** and Ag(I) could generate a discrete self-assembled macrocycle in the form of a dinuclear Ag(I)-based rectangle[12] with $C{=}C$ bonds positioned to react (Figure 3). Self-assembled coordination complexes involving *endo*-ditopic building blocks are of an ongoing interest in supramolecular chemistry,[12b] yet have not been exploited to direct an intramolecular [2 + 2] photodimerization in a solid.

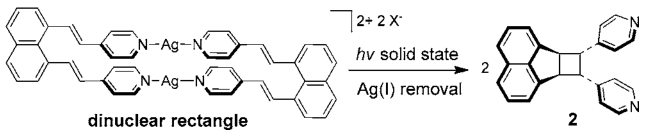

Figure 3. Use of dinuclear Ag(I) rectangle to direct intramolecular [2 + 2] photodimerization in solid state.

Crystalline powders of $[Ag_2(\mathbf{1})_2][(X)_2]$ (where $X^- = CF_3SO_3^-$ (**1a**), $CH_3C_6H_4SO_3^-$ (**1b**), and ClO_3^- (**1c**)) were, thus, grown by slow solvent evaporations of solutions of **1** (0.024 mmol) and the appropriate Ag(I) salt (0.048 mmol) in MeCN (15 mL). Single crystals of **1a** and **1b** were obtained as colorless rods and laths, respectively, from slow evaporations from MeCN. While numerous conditions were employed for **1c**, single crystals suitable for X-ray diffraction could not be obtained.

Single-crystal X-ray diffraction confirmed the formation of Ag(I)-based rectangles.[12] The asymmetric unit of **1a** consists of two Ag(I) ions, two coordinated molecules of **1**, and corresponding anions that form dinuclear rectangles[12] in the centrosymmetric space group $P\bar{1}$ (Figure 4). The assembly is sustained by argentophilic forces (Ag$\cdots$Ag 3.45 Å), with each Ag(I) ion being coordinated to two dienes of opposite handedness (Figure 4a). The vinylpyridine groups lie less splayed (11.6°) and rotated (6.4°) compared to free **1** while the $C{=}C$ bonds lie in closer proximity, displaying inner/outer C-to-C separations of 2.8 Å/4.4 Å and a centroid-to-centroid distance of 4.0 Å. As with pure **1**, however, the $C{=}C$ bonds adopt an antiparallel conformation. We note that both sets of $C{=}C$ bonds of **1a**, however, are disordered at room temperature (C11/C12 95% antiparallel/5% parallel; C18/C24 91% antiparallel/9% parallel), with no disorder present at a lower temperature (210 K). These observations are consistent with the $C{=}C$ bonds of the dinuclear rectangles being dynamically disordered in the solid. Metrics associated with the X-ray structure of **1b** are comparable to **1a**, with the Ag$\cdots$Ag separation being 3.80 Å. A higher *R* value for **1b** prohibits observations of disorder.

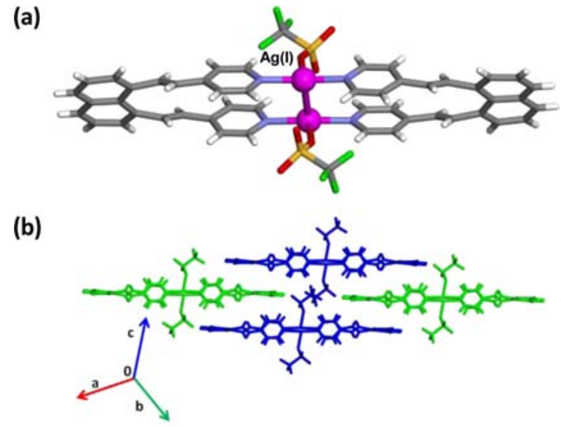

Figure 4. X-ray structure of **1a** (210 K): (a) discrete dinuclear assembly and (b) extended packing.

When **1a**–**c** was exposed to UV-radiation (500 W medium-pressure Hg lamp) for a period of *ca.* 40 h, ^{1}H NMR spectroscopy (DMSO-d_6) revealed the bipyridine **1** to undergo an intramolecular [2 + 2] photodimerization to generate a cyclobutane photoproduct in up to quantitative yield (conversions: **1a**, 47%; **1b**, 59%; **1c**, 100%). For **1a** and **1b**, the photoreaction was incomplete with no side products having been formed. In contrast to pure **1**, photoreactions were clearly evidenced by up to the complete disappearance of olefinic peaks at 8.2 and 7.0 ppm and emergence of peaks at 4.7 and 4.0 ppm in the cyclobutane region (see Supporting Information (SI), Figure S5). We attribute the generation of **2** in the solid state to the $C{=}C$ bonds undergoing pedal motions to form the cyclobutane rings,[14] with the auxiliary template components supporting an environment that accommodates the disorder.

To confirm the structure of the photoproduct, the cyclobutane was isolated via extraction from reacted **1c** using $CHCl_3$ and NaOH. The extraction afforded **2** as a cream-colored powder, which was characterized by NMR spectroscopy. Single crystals of a salt of **2** (8 mg) were synthesized from slow evaporation of a MeCN solution (10 mL) in the presence of HBr added dropwise. Pale yellow laths of [2H-**2**][2Br] grew within a period of *ca.* 2 d.

The asymmetric unit consists of one-half of a 2H-dication of **2** and one Br^- ion that crystallize in the space group $C2/c$ (Figure 5). Adjacent ions participate in $N^+{-}H\cdots Br^-$ hydrogen bonds [N$\cdots$Br separations (Å): N(14)$\cdots$Br(1) 3.20(1) and N(14′)$\cdots$Br(1) 3.21(1)] (Figure 5a). The dication, which is disordered over two sites (occupancies: 50/50), assumes a pseudochair geometry with the pyridine rings oriented opposite to the naphthalene ring through the cyclobutane ring [C–C bond distances (Å) C17–C17′ 1.57(1), C17–C18 1.57(1), C18–C18′ 1.58(1), C18′–C17′ 1.58(1)] (Figure 5b). The ions assemble head-to-tail within the *bc*-plane (Figure 5c). The structure of the cyclobutane ring supports the intramolecular [2

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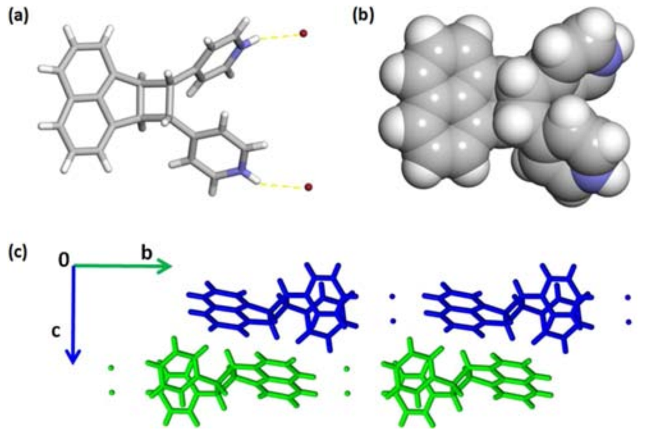

Figure 5. X-ray structure of [2H-**2**][2Br]: (a) dication of [2H-**2**][2Br], (b) space-filling model, and (c) packing of dication and bromides showing head-to-tail columns.

+ 2] photocycloaddition of **1** being directed by the Ag(I) ions. The generation of **2** in [2H-**2**][2Br] was also substantiated using a suite of ^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC, and ^{1}H−^{13}C HMBC correlations, with NOE cross peaks and relative intensities confirming the stereochemistry of the photoproduct (see SI, Figure S5).[13]

In conclusion, we have reported an intramolecular [2 + 2] photodimerization in the solid state via self-assembly of a Ag(I) metal−organic template. The photodimerization involves a 1,8-naphthalene ring that is mediated by argentophilic forces within self-assembled rectangles. The diene **1** is photostable as a pure solid. Given that intramolecular reactions are important in organic synthetic chemistry,[15] our results now enable the organic solid state to be viewed as a more attractive medium to control intramolecular reactivity. We are working to expand applications of principles of supramolecular chemistry to achieve intramolecular cycloadditions to form photoproducts of increasingly novel frameworks. The geometries of the resulting cyclobutanes may allow the intramolecular reaction to act as a reliable covalent synthon to generate unsymmetrical molecular architectures in organic solids.

■ ASSOCIATED CONTENT

Supporting Information

Details of syntheses, NMR studies, and X-ray structure solutions.[16] The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b00527.

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Notes

The authors declare no competing financial interest.

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