

# Sunlight-Induced Covalent Marriage of Two Triply Interlocked Pd<sub>6</sub> Cages and Their Facile Thermal Separation

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**S** Supporting Information

**ABSTRACT:** A template-free triply interlocked Pd<sub>6</sub> cage (**2**) was synthesized by two-component self-assembly of *cis*-blocked 90° acceptor *cis*-(tmen)Pd(NO<sub>3</sub>)<sub>2</sub> (**M**) and 1,3,5-tris((*E*)-2-(pyridin-3-yl)vinyl)benzene (**L**). Assembly **2** was characterized by <sup>1</sup>H NMR and ESI-MS, and the structure was confirmed by X-ray crystallography, which revealed a parallel conformation of the olefin double bonds belonging to the adjacent cages in the solid state at a distance of 3.656 Å, thereby indicating the feasibility of [2+2] photochemical reaction. Two adjacent interlocked cages were covalently married together by intermolecular [2+2] cycloaddition in a single crystal-to-single crystal fashion upon exposure to sunlight/UV irradiation. Most surprisingly, the covalently married pair was easily separated thermally in aqueous medium under mild reaction conditions.

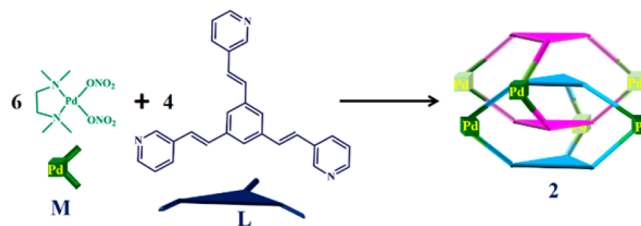
Mechanical interlocking is a crucial structural feature of proteins<sup>1</sup> and DNA<sup>2</sup> that significantly affects their stability and function and provides insight into protein folding mechanisms.<sup>1b</sup> Various attempts to mimic such molecular principles of interlocked systems employed by nature, template strategy,<sup>3</sup> and self-assembly<sup>4</sup> have become powerful protocols using hydrogen-bonding,<sup>5a</sup> hydrophobic interactions,<sup>5b</sup> anions,<sup>5c,d</sup> and  $\pi$ - $\pi$  interactions<sup>5e</sup> between subunits as driving forces. The interesting topological and physical properties of these interwoven systems make them attractive for a range of potential applications, such as biomaterials and molecular machines.<sup>6</sup> Sauvage, Fujita, Stoddart, and others have reported various interlocked systems such as rotaxanes,<sup>7a</sup> catenanes,<sup>7b-d</sup> Trefoil knots,<sup>8a,b</sup> Borromean rings,<sup>8c-e</sup> Solomon knots,<sup>8c</sup> etc. with highly sophisticated architectural complexity. Recently, a complex non-DNA pentafoil knot consisting of a closed-loop pentameric cyclic double helicate was prepared by combining the use of metal helicates, anion template, and reversible imine bond formation assisted by the gauche effect.<sup>9</sup> Nevertheless, most such systems are designed from monocyclic molecules. Linking crossover points of bicyclic or tricyclic species with appropriate connectivity to construct mechanically linked architectures is synthetically challenging and relatively rare.<sup>4c</sup>

Moreover, understanding the principles of crystal engineering<sup>10</sup> provides a map to design functional crystalline solids with remarkable stereocontrol. Intermolecular interactions in the solid state often play a crucial role by organizing the molecules with a precise geometry to produce regio- and stereoselective products that are inaccessible in solution. Subsequently,

proximity between reaction centers of two substrates in the solid state may induce reactivity in otherwise unreactive molecules.<sup>11</sup> In this context, solid-state structural transformations by photochemical [2+2] reaction of C=C bonds in various coordination polymers (CPs) and organic compounds have been extensively investigated in recent times, but there are very few reports on single crystal-to-single crystal (SCSC) manner involving only simple linear olefins.<sup>12</sup> The directional property and strength of noncovalent interactions including halogen bonds, hydrogen bonds, and  $\pi$ - $\pi$  stacking have been carefully employed in organic systems to accomplish the prerequisite of [2+2] cycloaddition.<sup>13</sup> The role of the cation- $\pi$  interaction, for instance, in solid-state photodimerization has been extensively investigated by Yamada and co-workers.<sup>14</sup> MacGillivray et al. have successfully introduced several hydrogen-bonded templates such as resorcinol and its derivatives to synthesize a number of interesting cyclobutane derivatives.<sup>15a-c</sup> As observed in a recent report by Vittal et al., an organic polymer containing cyclobutane rings has been incorporated into a metal-organic framework (MOFs) by [2+2] cycloaddition.<sup>15d</sup> In contrast, photodimerization of discrete coordination cages in both solution and solid state is extremely rare.<sup>16</sup> Despite the success in CPs and organic compounds, the majority of the reported systems are essentially irreversible due to their low thermal stability.<sup>17</sup>

Herein we report the formation of a new triply interlocked Pd<sub>6</sub>-cage, [(tmen)Pd]<sub>6</sub>(L)<sub>3</sub>(NO<sub>3</sub>)<sub>12</sub> (**2**), by two-component self-assembly of *cis*-blocked 90° Pd(II) acceptor **M** and tritopic donor **L** [where tmen = *N,N,N',N'*-tetramethylethylenediamine, **L** = 1,3,5-tris((*E*)-2-(pyridin-3-yl)vinyl)benzene] (Scheme 1). Inspection of crystal packing shows that one pair of olefin double bonds of the adjacent cages is perfectly aligned parallel to each other in head-to-tail fashion, satisfying

**Scheme 1. Synthesis of (M<sub>3</sub>L<sub>2</sub>)<sub>2</sub> Interlocked Cage 2 by Two-Component Self-Assembly**

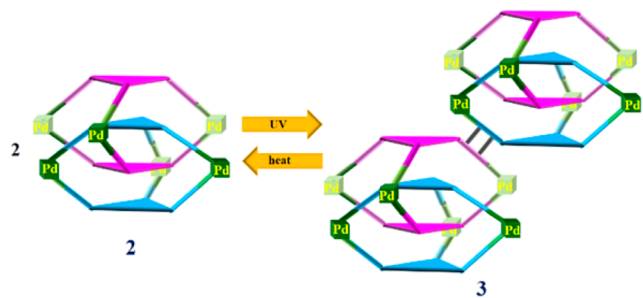


Received: November 4, 2014

Published: November 25, 2014

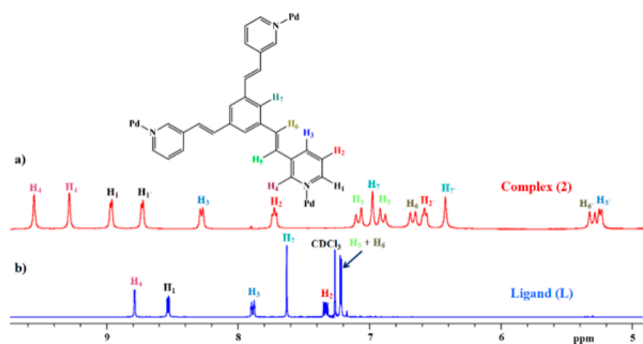
topochemical criteria established by Schmidt for photo-reactivity.<sup>18</sup> This inspired us to investigate [2+2] cycloaddition of this interlocked cage **2** in the solid state. In fact, the aforementioned olefin double bonds react under UV irradiation as well as upon exposure to sunlight, thereby yielding their intermolecular adduct accompanied by SCSC transformation (Scheme 2).

**Scheme 2. Schematic Representation of Reversible Intermolecular Photodimerization of Two Molecules of Interlocked Cage **2** and Thermal Separation of the Married Couple**



Furthermore, the cyclobutane ring appears to undergo selective cleavage in a reversible manner in aqueous medium at 90 °C (Scheme 2). While solid-state photodimerization in CPs or organic molecules is well known in the literature,<sup>12</sup> to the best of our knowledge, this is an unusual example of reversible intermolecular [2+2] cycloaddition in SCSC fashion and selective cleavage of cyclobutane ring into a discrete coordination cage.

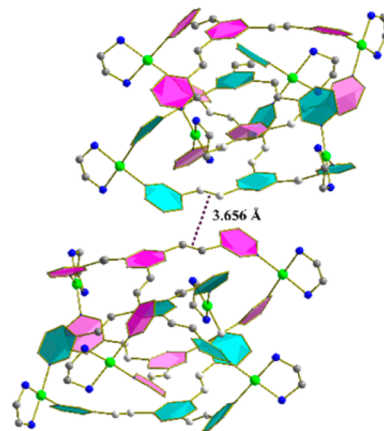
To functionalize the external surface of coordination cage with vinyl moiety, we prepared tritopic donor **L** in 81% yield following Wittig–Horner reaction between 1,3,5-tris-(diethoxyphosphomethyl)benzene (**1**) and nicotinaldehyde (Scheme S1).<sup>19</sup> When the donor **L** was treated with yellow aqueous solution of *cis*-(*tmen*)Pd(NO<sub>3</sub>)<sub>2</sub>(**M**) in a 2:3 molar ratio at room temperature for 24 h, a sharp visual color change with the consumption of suspended solid ligand indicated progress of the reaction. Product was isolated as an off-white precipitate by triturating the concentrated reaction mixture with excess cold acetone. Since all the proton signals split into two peaks with equal intensity in the <sup>1</sup>H NMR spectrum (Figure 1) instead of a single peak as expected for a simple trigonal pyramidal M<sub>3</sub>L<sub>2</sub> cage, our first impression was that the reaction had led to the formation of interpenetrated architecture.



**Figure 1.** Partial <sup>1</sup>H NMR spectra of **2** (a) recorded in D<sub>2</sub>O, and the <sup>1</sup>H NMR of the donor **L** (b) recorded in CDCl<sub>3</sub>.

Substantial downfield shifts observed in proton resonances of H<sub>1</sub> and H<sub>4</sub> of pyridine rings can be ascribed to metal–ligand coordination. Similarly, two sets of signals corresponding to all other internal protons assigned with noticeable upfield shift as compared to ligand **L** are also consistent with the interlocked structure (Figure 1). Furthermore, the appearance of several prominent peaks at *m/z* = 1146.9 [2 – 3NO<sub>3</sub><sup>−</sup>]<sup>3+</sup>, 844.7 [2 – 4NO<sub>3</sub><sup>−</sup>]<sup>4+</sup>, and 542.4 [2 – 6NO<sub>3</sub><sup>−</sup>]<sup>6+</sup> in ESI-MS spectra indicated a [6+4] combination of **M** and **L** in the product.

Finally, single-crystal X-ray diffraction study unambiguously concluded the formation of a Pd<sub>6</sub> triply interlocked structure consisting of two identical M<sub>3</sub>L<sub>2</sub> cages (Figure 2). Colorless



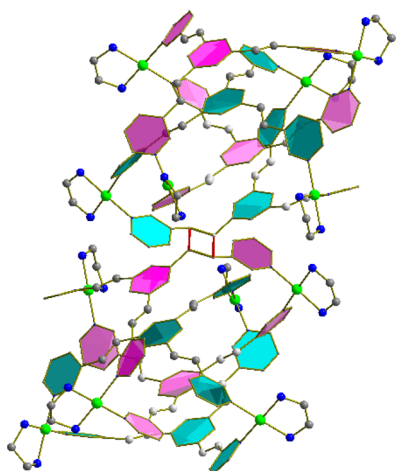
**Figure 2.** Crystal packing of **2** showing relative arrangement of olefin double bonds. Color code: Pd = green, N = blue, C = gray or light gray. Hydrogen atoms, counteranions, and methyl groups are omitted for clarity.

rectangular crystals were obtained by slow vapor diffusion of acetone into the concentrated aqueous solution of **2** over 2 weeks at room temperature. As a consequence of severely disordered nitrate ions and solvent molecules, the diffraction pattern of the crystal was poor.

Complex **2** was crystallized in triclinic system with space group *P* $\bar{1}$ . It has idealized *D*<sub>3</sub> symmetry and the asymmetric unit consists of six crystallographic independent Pd<sup>II</sup> and four ligands. The coordination environment of each Pd center is almost square-planar with the average Pd–N bond distance in the range of 1.99–2.13 Å. The efficient quadruple stacking of the central aromatic rings presumably makes the interlocked structure more stable as compared to the discrete M<sub>3</sub>L<sub>2</sub> cage or other possible structures that can be formed by self-assembly of **M** and **L**. In addition, central aromatic rings of the two cages are slightly twisted by ~30° to attain favorable  $\pi$ – $\pi$  stacking, and the distance between the two centroids of the adjacent aromatic rings is measured to be about 3.5 Å (Figure 2). The olefinic groups of each monomer of interlocked system are aligned in a criss-cross manner relative to each other.

Interestingly, for efficient crystal packing through  $\pi$ – $\pi$  interaction, one pair of the C=C bonds in two adjacent interlocked cages is perfectly positioned parallel to each other, keeping a center-to-center distance of 3.656 Å (Figure 2). This type of crystal packing is congenial for [2+2] cycloaddition in the solid state, since reactivity of the molecules is strongly associated with the packing in the crystal lattice. Such cyclobutane ring formation would lead to the photochemical marriage between two interlocked cages.

Exposure of the single crystals of **2** to sunlight for a period of 48 h showed no visual change initially. However, routine  $^1\text{H}$  NMR analysis of the exposed material (**3**) was found to be very much complicated, which gave a preliminary indication of cyclobutane ring formation, as it was associated with the symmetry loss (see Figures 4 and S7). DOSY NMR spectroscopy confirmed the presence of a single species, with a clear single band at  $\log D = -9.82$  ( $D = 1.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) (Figure S8), which further supported the complete conversion into a dimerized adduct. As expected from the double bond alignment in **2**, only 25% of the total donors were photoreactive, as estimated from the integration of  $^1\text{H}$  NMR signals (Figure 4). Solubility of the exposed material decreased significantly in aqueous medium. Optical microscopy showed that both transparency and single-crystal nature remained intact during the reaction, suggesting SCSC transformation. Finally, reliable evidence for the photochemical marriage was obtained from X-ray analysis which confirmed that indeed an intermolecular [2+2] cycloaddition reaction took place in one of the donors in head-to-tail orientation, thus giving rise to the corresponding cationic cyclobutane derivative accompanied by SCSC transformation in a quantitative yield with the formation of new bonds across the adjacent cages (Figure 3).



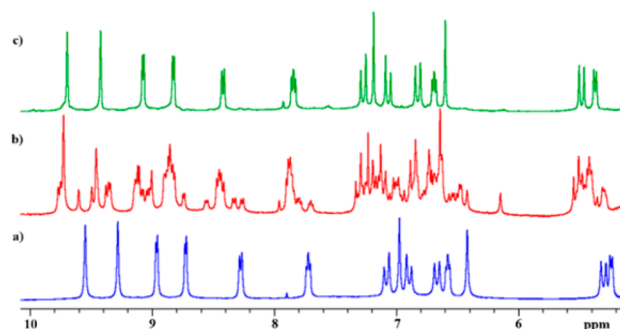
**Figure 3.** Crystal structure of the complex **3**. Color code: Pd = green, N = blue, C = gray or light gray. All the hydrogen atoms, counterions, methyl groups, and solvent molecules are removed for the sake of clarity.

The pyridyl and central aromatic rings of the dimerized donors are bent toward each other (Figure 3). There is a slight change in cell parameters during this process, but the space group ( $P\bar{1}$ ) of the system is retained. Similarly, it has  $S_2$  point group symmetry. Six  $\text{Pd}^{\text{II}}$ , three ligands (L), and one-half dimerized ligand are present in the asymmetric unit. Moreover, a similar result was obtained when the single crystals of **2** were subjected to UV irradiation at  $0^\circ\text{C}$  for 12 h.

Although [2+2] cycloaddition reactions have largely reached maturity, reversible cleavage of the cyclobutane ring into olefins remains elusive owing to the thermal instability of many such systems at high temperature.<sup>17</sup> Such reversible reaction is essential for potential applications in photoswitches, sensor techniques, optical recording, etc.<sup>20</sup> However, the challenge still remains to cleave the ring with stereospecificity, as a mixture of *cis*- and *trans*-olefins may not be suitable for recycling. Typical CPs and MOFs are the most promising candidates for this

study due to their high thermal stability. Very recently, Vittal and co-workers observed such selective cleavage in a metal-organic salt and Zn(II)-based CPs by heating at  $250^\circ\text{C}$  in the solid state.<sup>17</sup>

However, thermogravimetric analysis (Figure S11) showed that complex **2** is stable only up to  $230^\circ\text{C}$ . Since the solubility of the dimerized adduct in water is significantly less as compared to its monomeric interlocked form (**2**), our strategy of heating the cyclobutane derivative in aqueous medium should, in principle, promote the cleavage of the cyclobutane ring, as per Le Chatelier's principle. With this idea in mind,  $\text{D}_2\text{O}$  solution of dimerized adduct was stirred at  $90^\circ\text{C}$ , and the reaction was monitored by  $^1\text{H}$  NMR spectroscopy (Figure S10). During the course of the reaction, cyclobutane adduct **3** gradually disappeared; alternatively, another set of signals attributable to **2** appeared. The nature of the peaks in the  $^1\text{H}$  NMR spectrum, including their integration ratios, indicated a selective cleavage of the cyclobutane ring (Scheme S2) to form complex **2**. ESI-MS analysis further supported the conversion of the married couple into interlocked monomer **2**. After a period of 2 h, the dimerized product completely transformed into **2**, as depicted in Figure 4. This facile conversion into the monomeric



**Figure 4.** Partial  $^1\text{H}$  NMR spectra recorded in  $\text{D}_2\text{O}$  showing reversible photodimerization and selective thermal cleavage of cyclobutane ring: (a) complex **2**, (b) photodimerized complex **3**, and (c) after heating aqueous solution of **3** at  $90^\circ\text{C}$ , showing quantitative transformation to **2**.

interlocked form under mild conditions is quite remarkable. To the best of our knowledge, this is a unique example of selective cleavage of cyclobutane ring in married cages in solution by heating under such mild reaction conditions.

In summary, a unique  $\text{Pd}_6$  triply interlocked cage was synthesized by two-component self-assembly of *cis*-(*tmen*) $\text{Pd}(\text{NO}_3)_2$  and a tritopic donor (L). The strong  $\pi$ - $\pi$  stacking interaction among the central aromatic rings assisted exclusive formation of the interlocked cage despite other possible structures. Moreover, explicit manipulation of intermolecular interactions directed the interlocked cages to be aligned in such a fashion in the crystal lattice that a pair of olefin double bonds in the adjacent cages is juxtaposed parallel to each other with a distance of  $3.656 \text{ \AA}$ . This led to the photochemical marriage between the adjacent cages by [2+2] cycloaddition in a SCSC manner upon UV irradiation or exposure to sunlight. In addition, the poor solubility of photodimerized adduct in water has further been utilized for thermal divorce through selective cleavage of the cyclobutane ring at  $90^\circ\text{C}$ . In principle, such reversible photoreactive systems could potentially be extended to develop materials for photoswitches and optical data storage devices.<sup>20</sup> The scope of employing a template strategy to direct

reactivity by controlling crystal packing is currently under study in our laboratory for the fabrication of new metal–organic polymeric complexes by photopolymerization.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Materials, experimental details, synthetic and characterization data (NMR, FTIR, ESI-MS), and crystallographic table including single-crystal X-ray data for **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

P.S.M. is grateful to the DST-New Delhi for Swarnajayanti fellowship research grant. P.S.M. also thanks the Johnson Matthey Ltd. UK, for supplying PdCl<sub>2</sub> as a loan.

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