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Exploiting Aurophilic Interactions in a [2 + 2] Photocycloaddition: Single-Crystal Reactivity with Changes to Surface Morphology

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Supporting Information

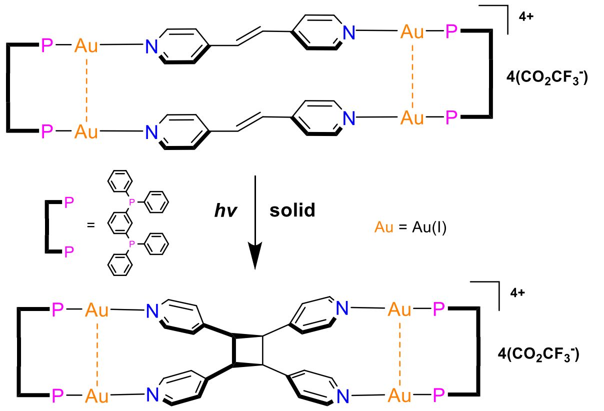
ABSTRACT: A single-crystal-to-single-crystal (SCSC) photodimerization is achieved using Au(I) coordination and aurophilic interactions. The rigid Au_2(dppbz)($CF_3COO)_2$ precursor (dppbz = 1,2-bis(diphenylphosphino)benzene) self-assembles with 1,2-*trans*-bis(4-pyridyl)ethylene (bpe) to afford a discrete $[Au_4(dppbz)_2(bpe)_2]^{4+}$ macrocycle in the solid state. The alkene undergoes a [2 + 2] photocycloaddition reaction. The photoreaction proceeds via a rare SCSC transformation in quantitative yield that generates $[Au_4(dppbz)_2(4,4'\text{-tpcb})]^{4+}$ (4,4′-tpcb = *rctt*-tetrakis(4-pyridyl)cyclobutane) stereoselectively. Mechanical strain induced by the photoreaction is evidenced by the formation of ramp features on single-crystal surfaces using scanning electron microscopy.

Noncovalent interactions (e.g., hydrogen bonding,[1] halogen bonding,[2] and metal/boron coordination[3]) have been exploited to direct the formation of covalent bonds in photoactive solids. The strategy relies on auxiliary molecules or "templates" to organize reactants (i.e., olefins) in a suitable geometry for a [2 + 2] photodimerization.[4] In this context, noncovalent interactions of gold continue to draw interest as a means to construct exceptionally diverse supramolecular architectures.[5] Gold(I) complexes involving aurophilic interactions have been shown to exhibit intriguing optical, electrical, magnetic, and catalytic properties for promising applications as advanced materials.[6] However, the use of aurophilic interactions to achieve photoreactivity in the solid state has rarely been investigated,[7] and single-crystal reactivity has still not been demonstrated.

Herein we report the use of gold coordination and aurophilic forces to achieve a quantitative [2 + 2] photocycloaddition via a rare single-crystal-to-single-crystal (SCSC) transformation.[8] We describe what is to our knowledge the first example of aurophilic forces directing a photodimerization in an SCSC transformation. Scanning electron microscope (SEM) images reveal submicron features in the form of ramps to appear on the surfaces of the single crystals, which is consistent with a mechanical strain being produced during the [2 + 2] photocycloaddition.

Our work is inspired by pioneering studies of Puddephatt, who has explored the applications of aurophilic interactions to design supramolecular networks such as macrocycles,[6c] catenanes,[9] oligomers,[10] and polymers.[11] Our approach is based on observations by Deák et al., who demonstrated the feasibility of using a rigid phosphine ligand (i.e., 1,2-bis(diphenylphosphino)benzene (dppbz)) to sustain aurophilic interactions and sustain the formation of a rectangular macrocycle involving 1,2-*trans*-bis(4-pyridyl)ethylene (bpe).[12] We expected the stacking of bpe in the macrocycle to be amenable for an intermolecular photocycloaddition according to Schmidt,[13] in particular, gold coordination and aurophilic interactions (i.e., Au(I)···Au(I)), direct stacking of bpe in the macrocycle $[Au_4(dppbz)_2(bpe)_2]^{4+}$ (**1**) (Scheme 1) wherein two bpe molecules react in the solid state to generate $[Au_4(dppbz)_2(rctt\text{-tpcb})]^{4+}$ (where: tpcb = *rctt*-tetrakis(4-pyridyl)cyclobutane) (**2**).

Scheme 1. Use of Au(I)···Au(I) to Direct Intra-macrocycle [2 + 2] Photocycloaddition in the Solid State



The preparation of **1** was adapted from Deák et al.[12] The preparation afforded single crystals as colorless irregular prisms by the slow diffusion of *n*-hexane into a CH_2Cl_2 solution (1:3) of Au_2(dppbz)($CF_3COO)_2$ and bpe over a period of 2 days. Powder X-ray diffraction revealed a diffractogram consistent with that reported.[12] Whereas the single crystals of Deák et al. readily decay, the crystals reported here were sufficiently stable to support full X-ray data collection. Repeated experiments also showed the crystals to be highly photoactive. Single-crystal X-ray diffraction confirmed a formula of $[Au_4(dppbz)_2(bpe)_2]_3(CF_3COO)_{12}\cdot 2CH_2Cl_2\cdot 2H_2O$.

The macrocycle crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit consists of one and one-half macrocycles (assemblies A and B), six $CF_3CO_2^-$ ions, and

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CH_2Cl_2/H_2O solvent molecules. The X-ray structure reveals the stacked pairs of bpe molecules to be parallel and separated by (A) 3.86 and (B) 3.28 Å (Figure 1).

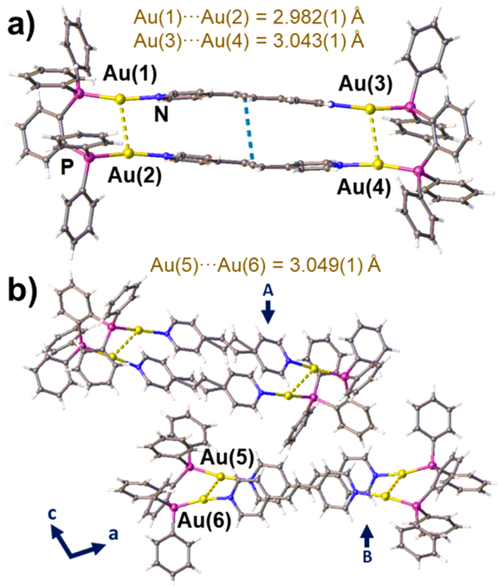

Figure 1. X-ray structure of **1**: (a) macrocycle (assembly A) and (b) extended view of discrete assembles. Counter ions and solvent atoms are omitted for clarity.

The self-assembly of the components of $[Au_4(dppbz)_2(bpe)_2]^{4+}$ give rise to $[Au_4(dppbz)_2]^{2+}$ as corners and bpe as edges (Figure 1a). The Au(I) centers are coordinated linearly (assembly A (deg): P(1)−Au(1)−N(1) 167.0(4), P(2)−Au(2)−N(2) 166.6(4), P(3)−Au(3)−N(3) 167.8(5), P(4)−Au(4)−N(4) 167.4(4); assembly B: P(5)−Au(5)−N(5) 169.9(4), P(6)−Au(6)−N(6) 166.3(4)) and are engaged in significant aurophilic forces (Au(1)···Au(2) 2.982(1) Å, Au(3)···Au(4) 3.043(1) Å, Au(5)···Au(6) 3.049(1) Å) (Figure 1b).[14] The C═C bonds of the alkene in assembly A are disordered over two sites, displaying a crisscross arrangement with a separation distance of 3.86 Å. The C═C bonds of assembly B, which sits on a center of inversion, are parallel and separated by 3.28 Å. We note that there is evidence of the C═C bonds of assembly B having undergone a photodimerization, as demonstrated by the peaks in the final difference electron density map consistent with a cyclobutane ring (Figure S2). The refinement of the peaks, however, was not possible owing to severe disorder. The distances of the stacked C═C bonds in both cases are within the range of Schmidt for a [2 + 2] photodimerization.[13] The assemblies pack end-to-end with C═C bonds of neighboring assemblies separated on the order of 10 Å. Both assemblies pack through combinations of edge-to-face π−π interactions as well as C−H···O and C−H···F contacts with surrounding $CF_3CO_2^-$ counterions.

The photoactivity of **1** was evaluated by exposing the single crystals to UV radiation (UV light gel nail dryer) for 17 h.[15] The formation of 4,4′-tpcb was evidenced by the emergence of a cyclobutane peak at 4.82 ppm on the ^1H NMR spectrum. Optical microscopy showed the transparency of the single crystals to be maintained during the photoreaction.

A single-crystal structure analysis of **1** exposed to UV radiation revealed all stacked C═C bonds to react to generate 4,4′-tpcb in quantitative yield (Figure 2). The X-ray analysis showed the generation of the cyclobutane ring to result in a slight weakening of the aurophilic forces (Au(1)···Au(2) 3.159(2), Au(3)···Au(4) 3.110(2), Au(5)···Au(6) 3.142(2) Å). The results contrast previous observations using argentophilic (i.e., Ag···Ag) forces, where the formation of the cyclobutane is accompanied by the complete breaking of the supramolecular force.[16] Free movement of the Au(I) atoms is likely restricted by the rigid dppbz ligand. The photodimerization also resulted in the lengthening of the *b* axis and the expansion of the cell volume by ca. 2% (i.e., 13493(2) to 13760(4) Å^3). The expansion contrasts with previous studies of coordination complexes in which the unit-cell volume decreases following the photocycloaddition.[8,16,17]

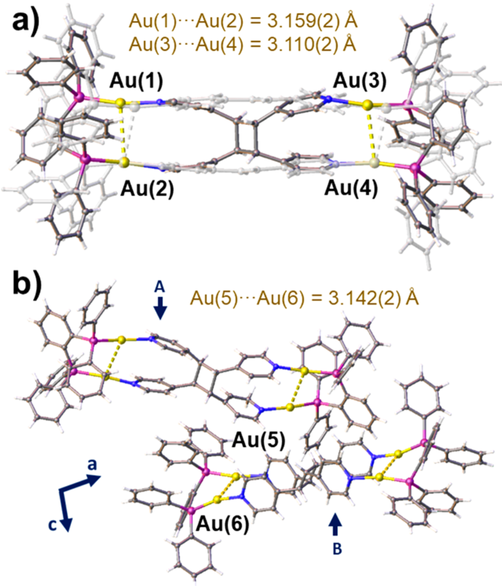

Figure 2. X-ray structure of **2**: (a) Overlay views of **1** (light gray) and **2** (gray) and (b) extended view of assemblies A and B. Counter ions and solvent atoms are omitted for clarity.

Unusual features appeared on the surfaces of the single crystals during the course of the photoreaction. SEM revealed the unreacted and reacted single crystals to display smooth surfaces and ramps with arrowheads on uneven surfaces, respectively (Figure 3). Ramp-like features are commonly

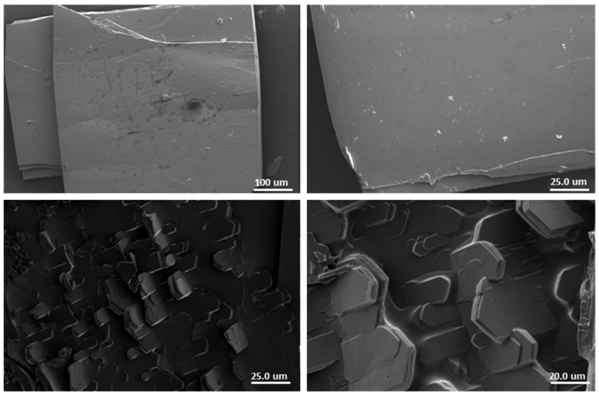

Figure 3. SEM images of the crystal surface before photocycloaddition (top) and after photocycloaddition (bottom).

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observed in single crystals of ZSM-5 crystals.[18] The observation is consistent with the formation of intergrown sections with well-developed crystal faces.[19] Irie et al. have also reported steps to appear on surfaces of single crystals in reversible photocyclizations of 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene. In the study, the distance between the edges of two pyridine rings shortened to allow molecules to pack closely to each other, which coincided with a decrease in the *c* axis.[20] From our SEM images, we demonstrate that the expansion of the unit cell volume likely results in mechanical tension that adversely affects the surface crystallinity to generate the ramp features.

In conclusion, we have demonstrated that aurophilic interactions based on Au(I)···Au(I) assist the stacking of olefins in the solid state for a [2 + 2] photocycloaddition via an SCSC transformation. We have also shown that the photocycloaddition generates ramps on the surfaces of the single crystals, which is accompanied by the expansion of the unit cell. We are currently investigating the fluorescence and conductivity properties of the Au(I) complexes. Our study may provide new avenues for the synthesis of functional materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b01306.

> Details of syntheses, NMR studies, and X-ray structure solutions (PDF)

Accession Codes

CCDC 1906774−1906775 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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