Self-Assembly

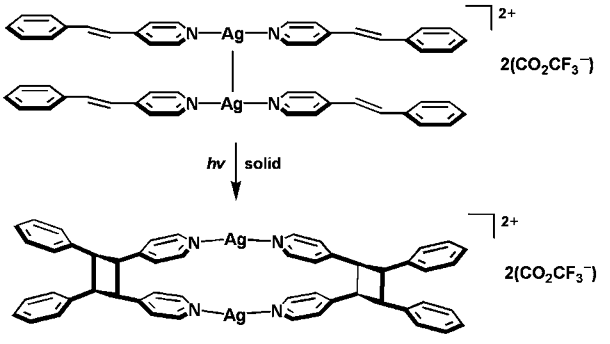
A Single-Crystal-to-Single-Crystal Transformation Mediated by Argentophilic Forces Converts a Finite Metal Complex into an Infinite Coordination Network**

*Qianli Chu, Dale C. Swenson, and Leonard R. MacGillivray**

Transition-metal ions play a prominent role in mediating chemical reactions, a central paradigm being catalysis.[1] The d orbitals of such ions are sources of directional bonding that organize substrates for stereocontrolled reactions that give molecular and polymeric products that cannot be obtained in the absence of the metal. Whereas a variety of transition-metal ions have been used to mediate chemical reactivity in the liquid phase,[1] such broad applicability to mediate reactivity in the organic solid state, particularly for the well-studied [2+2] photodimerization,[2] has not been realized.[3–8] In addition to forces that assemble molecules into strict geometries for stereocontrolled reactions, such ions can provide properties (e.g. color), and other components (e.g. counterions), that may be altered by the ensuing reaction that occurs within such solids.[4b,8]

Herein, we report the use of a transition-metal ion, in the form of Ag^I,[9] which mediates a [2+2] photodimerization in the solid state. Specifically, argentophilic forces, in the form of Ag$\cdots$Ag interactions,[10] are used to guide stacking[11] of olefins in the dinuclear complex $[Ag_2(\text{4-stilbz})_4][CO_2CF_3]_2$ (**1**; where 4-stilbz = *trans*-1-(4-pyridyl)-2-(phenyl)ethylene) for a regio-controlled head-to-head [2+2] photodimerization (Scheme 1). We show that the reaction occurs in 100 % yield by a rare single-crystal-to-single-crystal (SCSC) transformation that, in addition to carbon–carbon single-bond making, involves breaking and formation of Ag$\cdots$Ag and Ag$\cdots$C interactions, respectively. Remarkably, the formation and breakage of the covalent and noncovalent bonds are accompanied by long-range movement of the Ag^I ions and rotation of the carboxylate ions,[12] which result in the finite dinuclear complex being converted into an infinite, one-dimensional (1D) coordination network. This study represents the first case in which a closed-shell d^{10} metal cation has been used to direct a reaction in the crystalline state.

Interactions between closed-shell d^{10} metal ions have been used to construct supramolecular assemblies[13] that exhibit host–guest, photophysical, and electrical properties.[14] For Ag^I, such Ag$\cdots$Ag, or argentophilic, forces are evoked at separations < 3.4 Å, although separations up to 3.8 Å have been cited.[14] These separations fall within the distance criterion of Schmidt for a [2+2] a photodimerization in a solid.[2] Moreover, the ability of the Ag^I ion to engage in argentophilic forces, coupled with a tendency of the ion to exhibit linear coordination,[14] prompted us to investigate whether it would be possible to utilize Ag^I ions to guide the stacking of olefins in the solid state for a [2+2] photoreaction.[15]



Scheme 1.

Reaction of a solution of $AgCO_2CF_3$ in acetonitrile with 4-stilbz afforded large colorless plates of **1** upon slow evaporation. The formulation of **1** was confirmed by ^1H NMR spectroscopy, as well as powder and single-crystal X-ray diffraction data.

Perspective views of **1** are shown in Figure 1. The metal and organic components have assembled to form a dinuclear complex sustained by an Ag$\cdots$Ag force (Ag$\cdots$Ag distance: 3.41 Å; Figure 1 a).[16] The primary coordination sphere of the Ag^I ion is based on a T-shaped geometry that involves two *transoid* nitrogen atoms of two 4-pyridyl groups of two olefins and a single oxygen atom of a carboxylate ion (Figure 1 a, inset). The olefins that span the Ag$\cdots$Ag interaction lie approximately parallel, the pyridine units participating in offset, face-to-face π–π interactions (pyridine centroid–centroid distances 3.62 Å). The carboxylate group is twisted orthogonal to the stacked olefins such that each $-CF_3$ group points away from the metal complex. As a consequence of the assembly process, the C=C bonds, which are disordered (occupancies: site A 0.89(1); site B 0.11(1)) and adopt a criss-cross arrangement,[17] are separated by 3.82 Å. This distance satisfies the distance criterion for [2+2] photoreaction in a solid.[2] The complex self-assembles to form 1D quadruple π-stacked arrays (Figure 1 b), which are canted at 60° (Figure 1 c), with neighboring olefins offset and separated by 4.22 Å (C$\cdots$C distances [Å]: C(21)$\cdots$C(22)a 4.22, C(22)$\cdots$C(21)a 4.22, C(21)$\cdots$C(21)a 3.91, C(22)$\cdots$C(22)a 4.87; a: $1.5-x$, $0.5-y$, $-z$).

To test whether the olefins are photoactive, either single crystals or a powdered crystalline sample of **1** was exposed to UV radiation (broadband Hg lamp) for 18 h. As shown in Figure 2, a ^1H NMR spectrum (solvent: $[D_6]DMSO$) of photoreacted **1** reveals that the olefins reacted to give *rctt*-

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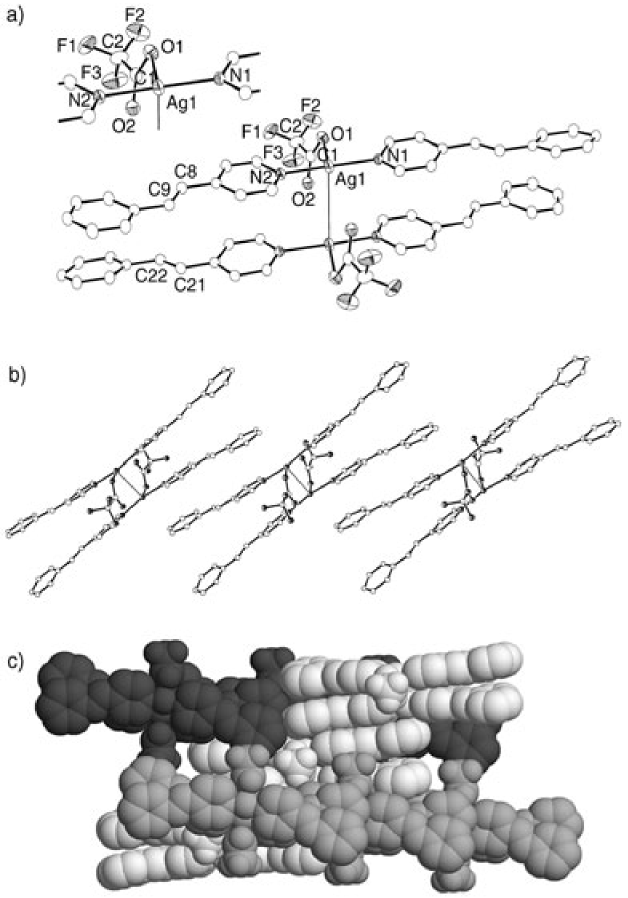

Figure 1. X-ray crystal structure of **1**: a) ORTEP view of the dinuclear assembly. Thermal ellipsoids set at 30 % probability. Inset: coordination environment of the Ag^I ion, b) 1D quadruple π-stacked arrays, c) space-filling view of adjacent 1D arrays (each strand is highlighted in different shade of gray). Selected interatomic distances [Å] and angles [°]: Ag1-N1 2.161(3), Ag1-N2 2.149(3), Ag1-O1 2.583(4), C8···C21 3.82, C8···C22 3.79, C9···C21 4.11, C9···C22 4.23; O1-Ag1-N1 94.7(1), N1-Ag1-N2 165.3(1), O1-Ag1-N2 98.1(1).

1,2-bis(4-pyridyl)-3,4-bis(phenyl)cyclobutane (4-pyr-ph-cb) in 100 % yield. The formation of the photoproduct is shown by the disappearance of the signals of the olefinic protons ($\delta = 7.50$ ppm) and the emergence of signals for the cyclobutane protons ($\delta = 4.60$ ppm). Optical microscopy revealed that the transparency and shape of the single crystals remained intact during the photoreaction, which suggested that the reaction occurred by a SCSC transformation.

An X-ray diffraction analysis of photoreacted **1** confirms that the reaction occurred by a SCSC transformation. As shown in Figure 3, the olefins of **1** reacted to give head-to-head 4-pyr-ph-cb in $[Ag_2(\text{4-pyr-ph-cb})_2][(CO_2CF_3)_2]$ (**2**) in quantitative yield (Figure 3 a). The photoproduct adopts two orientations, with the cyclobutane ring of **2** exhibiting site occupancies different than that of the olefins of **1** (occupancies: site A 0.60; site B 0.40). These occupancies are consistent with the C=C bonds of the olefins undergoing a pedal-like motion in **1**[17] prior to the photoreaction.

The generation of 4-pyr-ph-cb is accompanied by major repositioning[12] of the Ag^I and carboxylate ions. Specifically, each Ag^I ion has moved approximately 1.16 Å (Ag···Ag distance in **2**: 5.73 Å) in a direction approximately parallel to the newly formed C–C bonds,[12a] while each carboxylate ion has undergone an approximate 90° rotation such that each $-CF_3$ group is oriented approximately perpendicular to the pyridyl groups (Figure 3 b). Despite such long-range movement and rotation, the Ag–N and Ag–O bonds remain intact. In particular, the nitrogen and oxygen atoms form a trigonal planar coordination geometry around each Ag^I ion, with each metal atom lying approximately 0.37 Å out of the plane of the donor atoms.

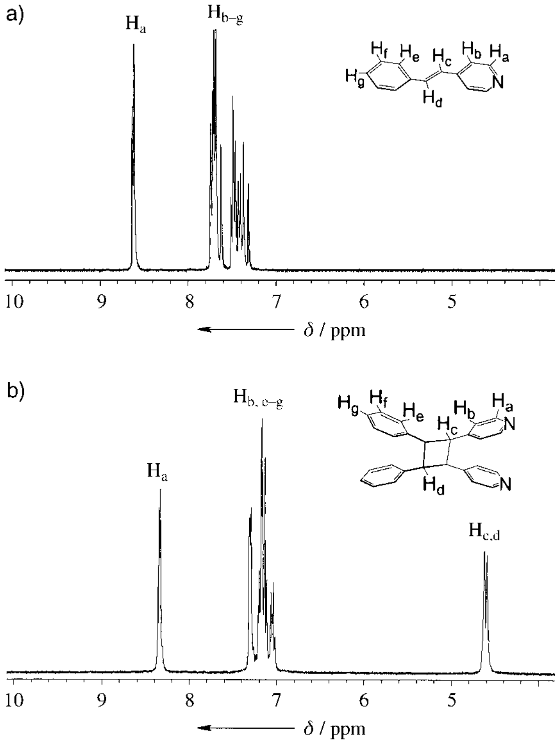

Figure 2. ^1H NMR spectra: a) **1** before photoreaction and b) **2** after photoreaction.

An important consequence of the movement and rotation of the ions is that Ag···C interactions[18] (Ag···C(phenyl) distances: Ag(1)···C9C 2.63 Å) have formed between each repositioned Ag^I ion and a *para*-carbon atom of a phenyl group of a neighboring photoproduct (Figure 3 c and inset). These forces link adjacent complexes of **2** to give a linear coordination polymer.[8] The Ag···C forces of the newly formed coordination polymer compare favorably to those networks with aromatics (e.g. cyclophanes) as donor ligands.[18] In the case of **2**, the photodimerization has, in effect, forced the Ag···Ag interactions[10] to break and the Ag···C interactions to form,[18] which, in turn, has resulted in the 1D geometry of the olefins of **1** being captured,[19] through coordination bonds, within the 1D polymer of **2**. To our knowledge, the photoconversion **1** into **2** represents the first case in which a finite metal complex has been transformed into an infinite coordination network in the solid state by a [2+2] photoreaction.[20,21]

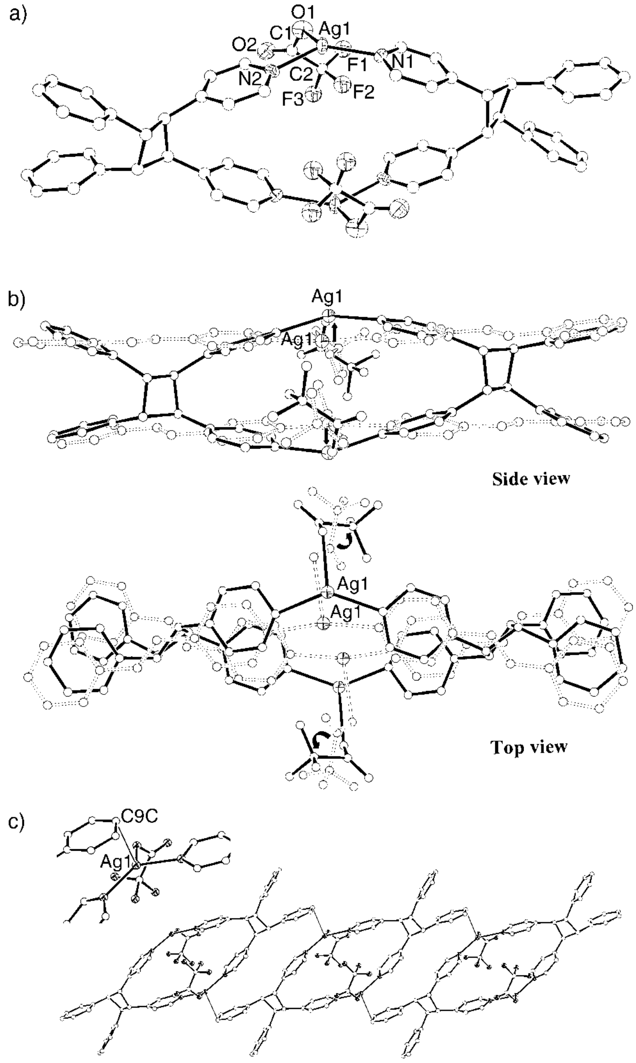

Figure 3. X-ray crystal structure of **2**: a) ORTEP view of the dinuclear assembly, thermal ellipsoids set at 30 % probability. b) overlay views of **2** (solid) and **1** (dashed) (arrows indicate movement of Ag^I atoms and carboxylate ions), c) newly formed 1D coordination polymer (inset: coordination environment of the Ag^I ion). Selected interatomic distances [Å] and angles [°]: Ag1-N1 2.22(1), Ag1-N2 2.27(1), Ag1-O1 2.44(2); N1-Ag1-N2 136(1), N1-Ag1-O1 112(2), N2-Ag1-O1 104(2).

Herein, we have revealed that argentophilic forces involving Ag^I ions can guide the stacking of olefins in the solid state for a regiospecific [2+2] photodimerization. The olefins assembled in a geometry that converts a finite metal complex into an 1D coordination network by a SCSC transformation.[8] Based these observations, we are now determining the reliability of using Ag···Ag interactions to direct reactivity in the solid state and plan to expand the reactants to olefins of increasing structural complexity.[11] That a finite complex can be converted into an infinite network by using a photodimerization and pyridyl units—chemical reactivity and ligands common to organic solid-state chemistry[2,22]—suggests this approach may also provide an entry to solids with properties that may be deliberately modified using photoresponsive building units.[25]

Experimental Section

Preparation of **1**: 4-stilbz was prepared according to a published procedure.[23] $AgCO_2CF_3$ was commercially available. Compound **1** was obtained by evaporation of a solution of 4-stilbz (0.100 g, 0.55 mmol) and $AgCO_2CF_3$ (0.061 g, 0.28 mmol) in acetonitrile (2.0 mL).

Solid-state photoreactions: UV irradiation of either single crystals or powdered crystalline **1** (500 W Hg lamp) over 18 h resulted in 100 % conversion of 4-stilbz to 4-pyr-ph-cb. The irradiation experiments were performed by placing either single crystals or finely ground samples of **1** between two pyrex plates and turning the sample in 9 h intervals to ensure uniform irradiation. ^{1}H NMR for **1** (300 MHz, [D$_6$]DMSO): $\delta = 8.62$ (dd, 4H), 7.50 (m, 18H); ^{1}H NMR for **2** (300 MHz, [D$_6$]DMSO): $\delta = 8.44$ (dd, 4H), 7.30 (m, 14H), 4.60 ppm (m, 4H).

X-ray crystallography: Crystal data for **1**: monoclinic, C2/c, $a = 22.048(2)$, $b = 13.156(2)$, $c = 17.9566(2)$ Å, $\beta = 98.44(1)°$, $V = 5152(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.50\,g\,cm^{-3}$, $R_1 = 0.051$ for 3965 reflections with $I > 2\sigma(I)$. Crystal data for **2**: monoclinic, $C2/c$, $a = 21.544(2)$, $b = 13.548(1)$, $c = 17.694(2)$ Å, $\beta = 99.00(1)°$, $V = 5101(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.52\,g\,cm^{-3}$, $R_1 = 0.096$ for 1977 reflections with $I > 2\sigma(I)$. All crystal data were measured on a Nonius KappaCCD single-crystal X-ray diffractometer. All non-hydrogen atoms of **1** were refined with anisotropic thermal parameters except the atoms of the low-occupancy site of the disordered olefin. These atoms were given isotropic thermal parameters that were restrained to be similar to the U_{iso} of the corresponding atom on the high-occupancy site of the disordered ligand. The conformation of the low-occupancy site was restrained to be the same as that of the high-occupancy site. The occupancies refined to 0.89(1) (A) and 0.11(1) (B). The carboxylate ion displayed highly anisotropic thermal motion and was modeled as disordered for the final cycles of refinement. The disordered sites were restrained to have the same conformation and corresponding atoms were given the same anisotropic thermal parameters (i.e. U(O1) = U(O1′), U(C1) = U(C1′)…). The occupancies refined to 0.59(1) (A) and 0.41(1) (B). Upon reaction, the single crystal of **2** fractured into several highly mosaic single-crystal domains. The data from one of these single-crystal domains were successfully indexed and integrated. An examination of zonal precession syntheses indicated minimal interference from other single-crystal domains. Owing to the high degree of mosaicity, data above 37.5° 2θ were excluded from the refinement as there were essentially no data above background levels in this shell. The reaction product was disordered (the cyclobutane can form in one of two orientations yielding two chemically equivalent complexes with partial occupancy) and the occupancies converged to and were fixed at 0.60 (A) to 0.40 (B). The limited data set limited the refinement model. The Ag and O atoms, as well as the N atoms, were refined with anisotropic thermal parameters while all other atoms were refined with isotropic thermal parameters. The pyridyl rings of the photoproduct were treated as rigid groups. The equivalent N atoms (N1A, N1B…) from each disordered site were found in close proximity and were given the same anisotropic thermal parameters. For the remaining atoms, chemically equivalent disorder atom sites (C1A, C1B; C2A, C2B…) were given the same isotropic thermal parameter. The carboxylate groups were disordered and were restrained to exhibit the same conformation. The thermal parameters for O1 were restrained by the rigid bond restraint to the thermal parameters of the Ag atom for the final cycles of refinement. The bond lengths and angles described above refer to the major occupied sites. All crystallographic calculations were conducted using SHELXL-97.[24] CCDC-261658 (**1**) and CCDC-261660 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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