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Asymmetric Catalysis

Homochiral Crystallization of Metal–Organic Silver Frameworks: Asymmetric [3+2] Cycloaddition of an Azomethine Ylide**

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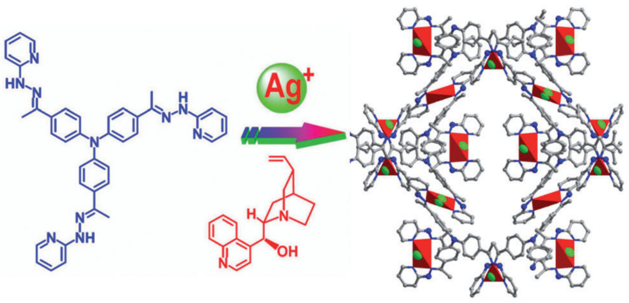
Metal–organic frameworks (MOFs) are hybrid solids with infinite network structures built from organic bridging ligands and inorganic connecting nodes. Besides the potential applications in many diverse areas,[1] MOFs are ideally suited for catalytic conversions, because they can impose size- and form-selective restriction through readily fine-tuned channels and pores, thus providing precise knowledge about the pore structure and the nature and distribution of catalytically active sites.[2,3] In particular, analogues of homogeneous asymmetric catalysts can be synthetically incorporated into MOFs, thus resulting in the incorporation of the selectivity of these single-site catalysts into micropores, and thereby enhancing the shape-, size-, and enantioselectivities of catalytic reactions in comparison to those performed in homogeneous solution.[4] While recent progress in MOF-based asymmetric catalysis has proved that these emerging catalysts provide a new exciting opportunity[5] for the synthesis of enantiopure compounds, including chiral drugs and fine chemicals, privileged asymmetric metal catalysts or organocatalysts that are incorporated into the nodes of frameworks are still quite limited.[6]

The 1,3-dipolar cycloaddition of azomethine ylides with electron-deficient olefins is an extremely versatile process to form highly substituted chiral pyrrolidines, which provide an important motif with widespread applications to the synthesis of biologically active compounds and natural products.[7] The cycloaddition reaction is also one of the most fascinating transformations and has inspired much research interest in the development of asymmetric catalytic variants. The configuration of the four new stereogenic centers of the product could be established in one step with complete atom economy.[8] Recently, elegant studies in this field have shown that chiral silver(I) and copper(I) bisdentate imine complexes are adequate homogeneous catalysts to afford the corresponding cycloadducts in good yields and high enantioselectivities.[9] Like for other precious-metal-catalyzed reactions, it is highly desirable to incorporate chiral metal complexes that are able to generate a metallodipole within the nodes of frameworks, thus resulting in efficient catalytic activity with the catalysts being recyclable and reusable to minimize the metal trace in the product.

By incorporating three pyridine–imine bidentate chelators into a triphenylamine fragment, we realized the homochiral crystallization of silver-based MOFs by using cinchonine or cinchonidine as chiral templates. We envisioned that the distorted tetrahedral silver(I) centers within the framework would not only act as chiral nodes to connect these ligands, but also be asymmetric catalytic sites for the 1,3-dipolar cycloaddition reactions. We also postulated that the twist configurations of the three phenyl rings attached to one nitrogen atom might exhibit atropisomeric chirality in the solid state,[10] thus facilitating the chiral transfer between the silver centers and finally leading to the formation of chiral MOFs. In the meantime, the coordination intermediate that corresponds to cinchonine moieties is expected to be useful for controlling the absolute chirality of the silver centers, such as those observed in the asymmetric catalytic reactions.[11]

The ligand tris(4-(1-(2-pyridin-2-ylhydrazono)ethyl)-phenyl) amine (TPHA; Scheme 1), was readily prepared by reaction of tris(4-acetylphenyl)amine with 2-hydrazinylpyridine in a molar ratio of 1:3. Reaction of TPHA with $AgBF_4$ in methanol afforded new compound Ag-TPHA. Single-crystal structure analysis showed that Ag-TPHA crystallizes in the chiral space group $I2_13$ (Figure 1).[12] The silver(I) atom is positioned at a 2_1 fold axis and is coordinated by two identical bidentate chelators from two different ligands in a distorted tetrahedral geometry. The dihedral angle between the bidentate chelating rings is 49.4(6)°. The ligand is positioned at a three-fold axis to three bridged silver ions through its bidentate chelators. It adopts an atropisomeric chirality with a torsion angle of about 74.5(5)° between the pair of the phenyl rings. In this case, the Schiff base ligands could be viewed as three connecting nodes, the silver atoms worked as directional connectors. Accordingly, the homochiral frame-



Scheme 1. Homochiral crystallization of the ligand TPHA, which comprises three bidentate chelators, with silver(I) ions in the presence of chiral adduct in order to assembly the silver-based MOF.

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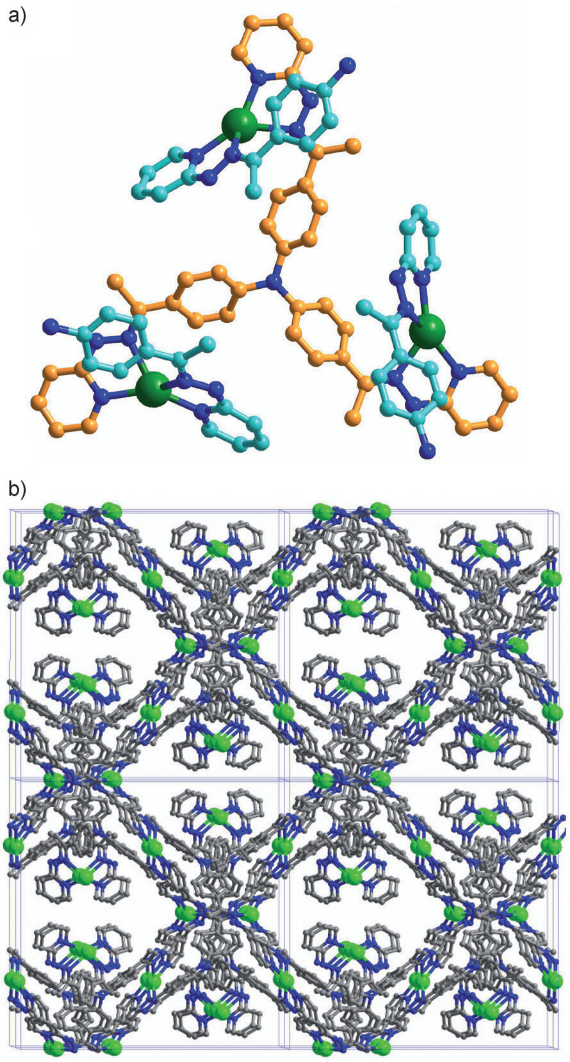


Figure 1. a) Crystal structure of Ag-TPHA showing the homochiral configuration of the silver centers and the atropisomeric chiralities of the triphenylamine fragments; b) Molecular packing pattern along the *c* axis showing the porous framework with the silver center well-positioned within the pores. The silver and nitrogen atoms are drawn in green and blue balls, respectively. Hydrogen atoms and solvent molecules are omitted for clarity.

work can be described as an intrinsic chiral (10,3)-*a* net, which is represented by the prototypal structures of SrSi$_2$ and α-Hg$_3$S$_2$Cl$_2$.[13] The three-dimensional MOF contains pores with a 7.5 × 8.0 Å^2 cross section. The distorted tetrahedral silver centers located within the pores were able to react with suitable substrates in order to reach a higher coordination number in an atropisomeric configuration.[14] The structural simplicity of the building blocks and the ability to control the assembly process by means of conformational chiral centers render this system promising for the development of a wide range of homochiral materials.

To further investigate the absolute configuration of the crystals, solid-state CD spectra of bulk solids from different crystallizations were measured. The powder either exhibited a positive Cotton effect at 310 nm and a negative Cotton effect at about 254 nm, or the opposite signals, thus showing the formation of either excess *M* or *P* enantiomers in the crystallization, respectively. Based on the investigation of 20 independent crystallizations, the intensities showed a bimodal probability distribution, such as that observed in the 1,1′-binaphthyl melt and the crystallization of NaClO$_3$,[15] thus suggesting the statistical nature of spontaneous resolution crystallization. The occurrence of chiral bulk crystals chirality should be described as a chiral autocatalytic spontaneous symmetry breaking in which the secondary nucleation is cloned by the parent crystal: the crystal nuclei in the vicinity of an existing "parent" crystal has the same crystal structure as the parent crystal.[16]

Importantly, the addition of 10 mol% of (+)-cinchonine or (−)-cinchonidine results in a chiral catalytic effect that leads to the growth of homochiral crystals. Compound Ag-**1** (Figure 2), which was prepared by using (+)-cinchonine as additive, crystallized in the same space group as Ag-TPHA. The structural analysis of five randomly and consecutively selected crystals from one crystallization[17] suggested that the silver(I) centers had the same absolute configuration, *P*, with Flack parameters of nearly zero. Of the ten sets of randomly performed crystallizations, the CD spectra of the crystalline samples exhibited positive Cotton effects at 330 nm, which were assigned to the absorption of the triphenylamine moiety, and negative Cotton effects at 254 nm and around 470 nm, possibly assignable to the absorption of the n–π* and the MLCT transfer. Similarly, a chirality-inducing effect was observed in the presence of (−)-cinchonidine, resulting in the formation of another enantiomorph, Ag-**2**, which crystallized in the chiral space group I2$_1$3 with cell dimensions similar to those of Ag-TPHA and Ag-**1**. The CD spectrum of bulk crystals of Ag-**2** exhibits Cotton effects opposite to those of Ag-**1**, thus indicating that the homochiral crystallization is

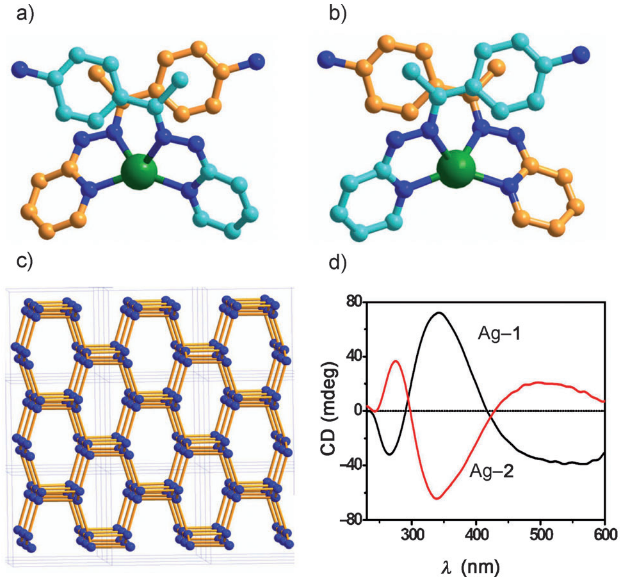


Figure 2. Molecule structures of a) Ag-**1** and b) Ag-**2** showing the chiral configuration of the silver centers in both cases; c) perspective view of the (10,3)a topology of Ag-TPHA with the blue balls representing the center nitrogen atoms of the trisphenylamine moiety; d) CD spectra of bulk crystalline solids of Ag-**1** and Ag-**2**, showing the opposite Cotton effects of the two compounds.

controllable through chiral induction.[18] From a mechanism point of view, the potential coordinating ability of the chiral cinchonidine moiety likely leads to the formation of a chiral intermediate that is comprised of a cinchonidine moiety and bidentate pyridine-imine chelators and in which the absolute configuration of the silver centers is fixed, as observed in several asymmetric catalytic reactions of silver–cinchonidine systems.[11] As the ligand adopts a conformational chirality (*M* for Ag-**1** or *P* for Ag-**2**) it potentially transfers the chirality from one silver center to another, the whole crystal is thus formed with controllable chirality.

As was expected, the large pores of Ag-TPHA showed potential absorption ability toward methyl-2-(benzylideneamino) acetate (MBA), a possible substrate for common 1,3-dipolar cycloaddition reactions.[19] Crystalline Ag-TPHA (0.015 mmol) was soaked in a solution of MBA (1 mmol) in $CHCl_3$ (1.5 mL). ^1H NMR spectroscopy of the impregnated crystalline solid (Ag-**3**) showed characteristic peaks corresponding to the MBA molecule, and a molar ratio of 1:2 for Ag-TPHA (one mole of the catalyst has the molecular formula $C_{78}H_{72}N_2O_7Ag_3B_3F_{12}$) and the α-iminoester molecules. Interestingly, the quality of the impregnated crystals is sufficient for the following X-ray crystallographic analysis.[20] The same space group and the almost same cell dimensions between the impregnated crystal Ag-TPHA⊃MBA (Figure 3, Table 1) and the original Ag-TPHA crystals suggested that the framework of the catalyst was maintained during the absorbency process. Detailed structural analysis showed the co-existence of two molecules of 2-(benzylideneamino) acetate (MBA) with one molecule of Ag-TPHA. MBA molecules are positioned within the pores of the Ag-TPHA framework and have a nonplanar conformation. The shortest interatomic distance between the MBA molecule and the silver(I) center was about 3.68 Å and existed between the silver(I) center and the carbonyl oxygen atom. This interaction model is quite similar to that of the reaction intermediate of silver(I)-catalyzed [3+2] cycloaddition with MBA,[21] thus suggesting that Ag-TPHA is capable to activate an MBA molecule through an atropisomeric chiral silver(I) center. Further investigations also demonstrated the presence of π···π stacking interactions between the benzene rings of MBA molecules and the pyridine rings of the ligands in the framework. These interactions possibly provided additional chiral environments that benefitted the catalytic reaction by increasing its stereoselectivity.

The catalytic activity of the chiral solids with *P* configuration at the silver centers was assessed by asymmetric 1,3-dipolar cycloaddition reactions involving methyl-2-(benzylideneamino)acetate (MBA) and *N*-methylmaleimide (NMM, Scheme 2).[22] For five independent rounds, a catalyst loading of 3 mol% (9 mol% based on silver(I) ions) led to a decent yield of over 90% with an enantioselectivity of over 90% after 24 hours. The reaction gave almost exclusively the *endo* adduct in all cases. The high enantioselectivity in the case of the heterogeneous catalysts may originate from the restricted movement of the substrates within the confined microporous systems and/or potential multiple chiral inductions. Several control experiments were performed by using various compounds as catalysts. Under the same condition, no reaction took place either in the absence of a catalyst or in the presence of the ligand only. Noticeably, when Ag-**1** was removed by filtration of the reaction mixture after 12 hours, only 9% additional conversion was observed upon stirring for another 12 hours. This experiment suggests that Ag-**1** is a real heterogeneous asymmetric catalyst.[23] It is quite significant that solids of Ag-**1** can be easily isolated from the reaction suspension by a simple filtration, and reused at least three times with a slight decrease in the reactivity and enantioselectivity. This result is a key issue in the development of recyclable and reusable catalysts in the field of asymmetric catalysis.

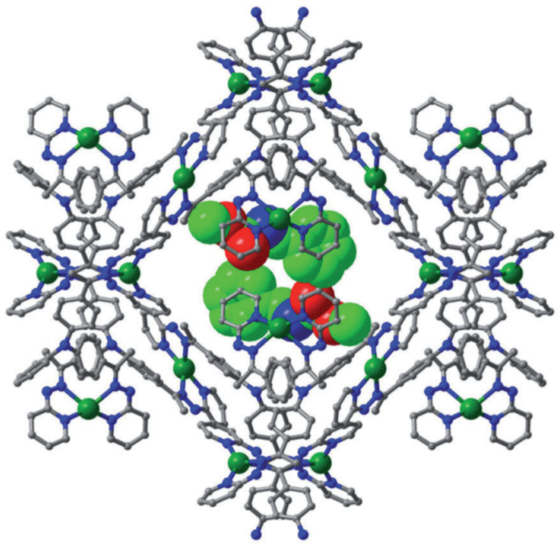
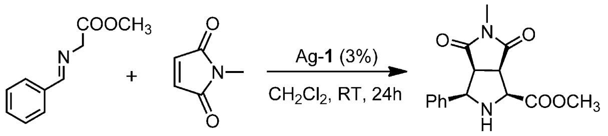


Figure 3. Crystal structure of Ag-TPHA⊃MBA showing the potential interactions between the framework and the molecules of MBA. The silver, nitrogen, and oxygen atoms are drawn in dark green, blue, and red balls, respectively. The carbon atoms in Ag-TPHA and MBA are drawn in grey and green, respectively. Hydrogen atoms, anions, and solvent molecules are omitted for clarity.

Table 1: Crystallographic data of the silver-based MOFs.[24]

	Space group	*a* [Å]	*R*(F)	wR_2	Flack parameter
Ag-TPHA	$I2_13$	25.381(4)	0.078	0.184	0.09(6)
	$I2_13$	25.369(5)	0.073	0.174	0.03(6)
Ag-**1**[a]	$I2_13$	25.689(1)	0.071	0.185	0.05(6)
Ag-**2**[a]	$I2_13$	25.866(2)	0.076	0.180	0.02(6)
Ag-**3**[b]	$I2_13$	25.582(1)	0.087	0.204	0.14(8)

[a] Materials were synthesized using chiral catalysis; [b] Crystals formed by capturing azomethine substrate in a $CHCl_3$ solution.



Scheme 2. 1,3-Dipolar cycloaddition of methyl-2(benzylidene amino)-acetate (MBA) with *N*-methylmaleimide (NMM).

Under identical experimental conditions, the presence of silver salt alone or with the co-existing ligands resulted in a reaction with high efficiency, but without enantioselectivity. In the presence of Ag-TPHA, the average conversion was 85% with the *ee* value varying from −20% to 60%. Additionally, the solids of the catalysts with opposite Cotton effect exhibited similar catalytic activities (yield about 88%) but gave products with opposite chirality (*ee* of −82%). We expect that our approach can be beneficial to the design and synthesis of efficient asymmetric catalysts for the synthesis of fine chemicals and pharmaceuticals, the enantiomorphs of which exhibit different optical properties and biological activities.

In summary, this work represents a new strategy for the creation of homochiral metal–organic frameworks for intrinsically asymmetric metal catalysis. The distorted tetrahedrally coordinated silver centers act as lattice nods to connect the ligand in a chiral (10,3)-*a* net, and locate within the chiral pores to interact with the active site of the substrate, thus ensuring the successful application in the asymmetric [3+2] cycloaddition. The structural simplicity of the building blocks and the ability to control the assembly process through conformational chiral adducts make this system a promising one for the development of a wide range of homochiral materials.

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0.1327]. Final R_1 [with $I > 2\sigma(I)] = 0.0710$, wR_2 (all data) = 0.1851. Crystal data for Ag-**2**: $C_{97}H_{117}N_{26}O_7Ag_3B_3F_{12}Cl_3$, $M = 2449.56$, Cubic, space group $I2_13$, yellow block, $a = 25.574(3)$ Å, $V = 16726(3)$ Å^3, $Z = 4$, $\rho_{\text{cald}} = 0.971\ \text{g cm}^{-3}$, μ(Mo-Kα) = 0.451 mm^{-1}, $T = 180(2)$ K. 4758 unique reflections [$R_{\text{int}} = 0.0947$]. Final R_1 [with $I > 2\sigma(I)] = 0.0783$, wR_2 (all data) = 0.1459.

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[22] The two dimensional sizes of the molecules of MBA and the product are calculated as 3.7×2.8 and 4.8×5.2 Å^2, respectively, possibly allowing the ingress or egress of the molecules of the substrates and the product through the cross section (7.5×8.0 Å^2) of the channels within the silver(I) containing MOFs.

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[24] CCDC 860787 (**1**), 860788 (**2**), 860785 (Ag-**1**), 860786 (Ag-**2**), and 885237 (Ag-**3**) contain 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.