Invisible Silver Guests Boost Order in a Framework That Cyclizes and Deposits Ag₃Sb Nanodots

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the porous medium of metal–organic frameworks (MOFs) is a topical approach to wide-ranging functionalization purposes. We report the notable interactions of $AgSbF_6$ guests with the designer MOF host ZrL1 [$Zr_6O_4(OH)_7(L1)_{4.5}(H_2O)_4$]. (1) The heavy-atom guests of $AgSbF_6$ induce order in the MOF host to allow the movable alkyne side arm to be fully located by X-ray diffraction, but they themselves curiously remain highly disordered and absent in the strucutral model. The enhanced order of the framework can be generally ascribed to interaction of the silver guests with the host alkyne and thioether functions, while the invisible heavy-atom



guest represents a new phenomenon in the metalation of open framework materials. (2) The $AgSbF_6$ guests also participate in the thermocyclization of the vicinal alkyne units of the L1 linker (at 450 °C) and form the rare nanoparticle of Ag_3Sb supported on the concomitantly formed nanographene network. The resulted composite exhibits high electrical conductivity (1.0 S/cm) as well as useful, mitigated catalytic activity for selectively converting nitroarenes into the industrially important azo compounds, i.e., without overshooting to form the amine side products. The heterogeneous/cyclable catalysis entails only the cheap reducing reagents of NaBH₄, ethanol, and water, with yields being generally close to 90%.

■ INTRODUCTION

Metal-organic frameworks (MOFs)¹⁻⁶ of alkyne-equipped linkers have recently been found to enable versatile metalation and other postsynthetic modifications, e.g., thermally induced (200-600 °C) cascade cyclization of the alkyne units to generate π -rich nanographene surfaces in the porous MOF medium.⁷⁻¹⁰ The cyclization is a vigorous, complex process involving extensive bond reorganization of the linker backbone, which also offers opportunities to convert the metal guests into catalytically active species associated with the partially graphitized MOF solid. Along this line of exploring the interaction between metal guests and MOF hosts (e.g., as a topical area of MOF metalation $^{11-15}$), we have treated the newly synthesized MOF solid ZrL1 $[Zr_6O_4(OH)_7(L1)_{4.5}(H_2O)_4;$ see Figure 1 for linker molecule] with AgSbF₆ guests. Compared with the symmetrically backfolded analogues reported,⁹ the Zshaped L1 linker here is less bulky (with fewer side arms, e.g., to allow for more free space in the prospective MOF), and it is easier to make. Recounted below are two serendipitous and somewhat surprising findings from this study.

The first one is about the enhancement of the structural order of the MOF crystal by the $AgSbF_6$ guest. Because of the slender linker and its mobile side arms, as well as the variable carboxyl connections on the Zr–O joint, severe disorder prevails in the native crystals of ZrL1, with the linker molecule hardly resolved



Figure 1. Cyclizable alkyne linker H_2L1 and the bare-bones molecule bis(4-carboxylphenyl)butadiyne (H_2L2).

from the X-ray diffraction data. Similar, low-resolution diffraction from big crystals is no surprise to researchers on flexible open structures, as exemplified by proteins and a growing number of complex metal—organic frameworks.^{16,17} In other words, the long-range order underlying the shapely crystal

Received: January 4, 2021 Published: March 31, 2021



is beset with local atom swings that blur the positions. To facilitate structural study, heavy atom guests were occasionally inserted to serve as strong scattering centers (e.g., as a phasing method in protein crystallography) and to enhance the structural order.¹⁸ In the general practice of X-ray crystal analysis, the heavy atoms were the first to be located from the electron density map. In a formal sense, it would be unusual to have light atoms located instead of the heavy ones from the X-ray diffraction data of a crystal.

Such an unusual case is found in the crystal of ZrL1 in which the uptake of AgSbF₆ guests led to stronger diffraction to resolve the backbone carbon atom positions, while the heavy guest atoms of Ag and Sb are not located; they are invisible to the Xray analysis. The abnormality, counterintuitive as it is, is easy to explain. Namely, the AgSbF₆ uptake restricts the motion (e.g., rotations along the alkynyl axes) of the linkers of the host net, and their increased order makes for stronger diffraction. The AgSbF₆ species, by comparison, is less tethered: sitting in the liquid-like open domain, the Ag⁺ can take various positions around the sulfur atom or the organic π clouds of the linker. In other words, the Ag(I)-linker interactions in this case do not fix the Ag/Sb positions for them to figure in the X-ray structure.

The second finding concerns the rarely observed intermetallic nanodots of Ag_3Sb^{197} generated in the process of themocylizing the alkynyl units of the MOF host. The resultant composite consists of the Ag₃Sb nanodeposit and the partially graphitized scaffold, and exhibits efficient cyclable/heterogeneous catalytic activities for making azo compounds from cheap nitro precursors, with yields being comparable to that of Pd-/Aucatalytic systems.^{20,21} It is worth noting that much efforts have been devoted to MOFs/MOFs derived catalysts for making aniline products from nitroarenes,²²⁻²⁴ but studies on modulating their catalytic activity for azo synthesis have been rare. Besides helping to solve the challenging structure of a porous framework, the AgSbF₆ guests in the present case take on some importance in the broader context of metalating MOFs for functionalization and application. For the metalation of metalseparation, 14,28,29 heavy metal removal, 30,31 and luminescence properties. $^{32-34}$

EXPERIMENTAL SECTION

The general procedures (including the single-crystal X-ray diffraction) are included in the SI.

Crystallization and Activation of ZrL1. Molecule H₂L1 (20 mg, 0.034 mmol) and a N,N-diethylformamide (DEF, 0.75 mL) solution of ZrCl₄ (8 mg, 0.034 mmol) and acetic acid (453 mg, 7.5 mmol) were added in a Pyrex glass tube (soda lime, 10 mm OD, 6 mm ID). The tube was flame-sealed and heated at 120 °C in an oven for 48 h, followed by programmed cooling to room temperature over 12 h to afford orange octahedron-shaped crystals (0.6-0.8 mm) with a yield of 52% based on H₂L1. For elemental analysis, the crystals were washed with N,Ndimethylformamide (DMF, 3×1.5 mL) and soaked in acetone (5×5 mL, replaced by fresh acetone every 4 h). The resulting crystals were then evacuated at 100 °C for 5 h. Elemental analyses (57.0% C, 3.30% H, 8.20% S) on the thus-activated sample indicates a formula of Zr₆O₄(OH)₇(L1)₄₅(H₂O)₄, (calculated: 56.9% C, 3.10% H, 8.10% S). FT-IR (KBr pellet, v/cm^{-1}): 3700–3000 (bb), 2919 (w), 2200 (m), 1708 (m), 1589 (s), 1535 (s), 1494 (s), 1423 (s), 1390 (s), 1253(m), 1182 (w) 1143 (m), 1083 (m), 1035 (m), 1014 (m), 956 (m),919 (w), 817 (s), 779 (s), 727 (w), 653 (s), 528 (w).

Entering AgSbF₆ into ZrL1 crystals. After opening the Pyrex glass tube containing the as-formed ZrL1 crystals, the mother liquor was carefully pipetted out and the crystals were rinsed with toluene (ca. 1 mL) 3 times (incidentally, crystals of ZrL1 soaked in toluene do not

diffract X-ray better than the as-formed, native sample, see Figure S15). A saturated toluene solution (0.5 mL) of $AgSbF_6$ was then added into the tube to immerse the crystals for 2 days, yielding the ZrL1- $AgSbF_6$ crystals for X-ray diffraction study. Using $AgBF_4$ or AgOTf (triflate: CF_3SO_3Ag) instead of $AgSbF_6$ and with this same procedure, crystals of ZrL1- $AgBF_4$ and ZrL1-AgOTf can be obtained, which also feature stronger X-ray diffraction to yield the same structure solution: with the linker molecule fully resolved in a disordered model but with no silver salt species located from the electron density map (similar to the X-ray structure solution of ZrL1- $AgSbF_6$).

Preparation of ZrL1-AgSbF₆-450. A solid sample of ZrL1 (20 mg), which was prewashed with toluene and then soaked in toluene overnight for further solvent exchange, was further soaked in a saturated toluene solution (1.0 mL) of AgSbF₆ for 24 h. Afterward, the solid was isolated by centrifugation and washed with toluene $(1.5 \text{ mL} \times 3 \text{ times})$ to remove the AgSbF₆ physically trapped on the surface; the resultant solid was then immersed in hexane for 4 h for solvent exchange. Afterward, the solid was isolated by centrifugation and dried under dynamic vacuum at 100 °C for 5 h. The loading of AgSbF₆ in thusobtained solids was determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) analysis, which indicates a silver content of 14.8 wt % corresponding to a Zr/Ag molar ratio of 1/1.5. Using AgBF₄ or AgOTf (triflate: CF₃SO₃Ag) instead of AgSbF₆, and following this same procedure, bulk samples of ZrL1-AgBF₄ and ZrL1-AgOTf can be also obtained, which feature silver contents of 17.3 wt % (Zr/Ag 1/1.7) and 11.5 wt % (Zr/Ag 1/1.2), respectively (ICP-OES results). To obtain ZrL1-AgSbF₆-450, the dried sample was heated to 450 °C at a rate of 5 °C/min and maintained at this temperature for 3 h followed by natural cooling down to room temperature under the protection of an argon flow. The silver content in the resultant sample was calculated according to the weight loss after heating, which is about 22.5 wt %. For comparison of catalytic activity, the sample of ZrL1-450 was made according to the identical procedures without presence of AgSbF₆.

Electrocatalysis. A ground catalyst solid of ZrL1-AgSbF₆-450 (5.0 mg) and a Nafion aqueous solution (50 μ L, 5 wt %, Dupont) were added to ethanol (450 μ L), and the resultant mixture was ultrasonicated for 30 min to afford a homogeneous suspension. The mixture (10 μ L) was then transferred onto a glassy carbon electrode (GCE, 0.19625 cm²), which was prewashed with distilled water and ethanol and dried in a high-purity nitrogen steam, with a catalyst loading of 510 μ g/cm². The glassy carbon electrode was prewashed adequately. The catalyst-coated glassy carbon electrode, Ag/AgCl, and Pt wire were used as the working, reference and counter electrode, respectively. Electrochemical measurements were conducted in an O₂ saturated 0.1 M KOH aqueous solution with an electrode rotation speed of 1600 rpm. The sweep rate of linear sweep voltammetry (LSV) curves was 10 mV/s for oxygen reduction reaction (ORR) and was 5 mV/s for oxygen evolution reaction (OER). The experimental potentials were later converted to the reversible hydrogen electrode (RHE) scale, for Ag/ AgCl reference in alkaline condition, $V_{RHE} = V_{Ag/AgCl} + V_{Ag/AgCl}^{\theta} + 0.059$ $pH = V_{Ag/AgCl} + 1.0095.$

Heterogeneous Catalysis of Nitroarenes Reduction toward Azo Compounds. A nitroarene substrate (0.10 mmol), NaBH₄ (0.40 mmol), ZrL1-AgSbF₆-450 (2.4 mg; the Ag/substrate molar ratio being 0.05:1), EtOH (0.9 mL), and H₂O (0.6 mL) were loaded into a 3 mL glass vial. The reaction mixture was stirred with a Teflon coated magnetic bar at 60 °C for several hours (specified in Table 1). After being cooled down to room temperature, the reaction mixture was bubbled with O₂ for around 10 min. Afterward, ZrL1-AgSbF₆-450 was removed by centrifugation, and the supernatant was extracted with DCM (0.5 mL × 3 times) and washed with H₂O (0.5 mL × 3 times). The organic layer was purged by a gentle nitrogen gas flow to remove solvent, and the residue was loaded onto a (microscale) pipet column (silica; eluted by 1:4 CH₂Cl₂/hexane, v/v) to isolate the pure product for yield calculation and NMR measurements.

Table 1. Formation of Azo Compounds from Reduction of Nitrobenzenes Catalyzed by ZrL1-AgSbF₆-450



^{*e*}Reaction conditions: substrate (0.1 mmol), NaBH₄ (0.4 mmol) and ZrL1-AgSbF₆-450 (2.4 mg, Ag/substrate molar ratio: 0.05/1), EtOH (0.9 mL) and H₂O (0.6 mL); after being stirred at 60 °C, the reaction mixture was bubbled with O₂ for 10 min at room temperature. a: All molar yields are isolation yield based on nitrobenzenes; b: the solvent is pure EtOH (1.5 mL); c: EtOH/H₂O = 0.3/1.2, v/v; d: the fifth round.

RESULTS AND DISCUSSION

A solvothermal reaction of H₂L1 and ZrCl₄ in DEF (*N*,*N*-diethylformamide) yielded yellow octahedral ZrL1 crystals (Figure 2A). Powder X-ray diffraction (PXRD) reveals a lattice similar to the UiO-type PCN-111 (see Figure 1 for its linker),^{35,36} featuring an fcc (face-centered cubic) array of Zr₆O₄(OH)₄ clusters (Figure S2) and linear linkers. Elemental analyses (57.0% C, 3.30% H, 8.20% S) and solution ¹H NMR (Figure S3) on the activated sample indicates a formula of Zr₆O₄(OH)₇(L1)_{4.5}(H₂O)₄, (calcd: 56.9% C, 3.10% H, 8.10% S). The ligand deficiency (i.e., 4.5 L1 linkers instead of 6 for full occupancy) indicates the Zr₆O₄(OH)₄ node to average 9 connections, with the remaining coordination sites filled in by OH⁻/H₂O (or capping species such as HCOO⁻). Open metal sites as such are common in Zr(IV)-MOF structures and can be exploited for topical catalysis applications.^{37,38}

With the big (0.6–0.8 mm), octahedral crystals at hand, we proceeded with X-ray data collection. The diffraction data, however, only revealed the Zr–O cluster in the cubic cell (a = 33.8 Å), with the backbone atoms of the linker molecule all



Figure 2. (A) Photographs of single crystals of ZrL1 and the AgSbF₆loaded ZrL1-AgSbF₆ and (B) X-ray single crystal structure of ZrL1-AgSbF₆ as represented by an octahedral unit featuring $Zr_6O_4(OH)_4$ clusters at the corners. Atom colors: cyan, Zr; red, O; yellow, S; gray, C. Disorders are omitted for clarity.

smeared out. Long exposure times (even 5 min per degree) did not help even with the already sizable crystals, which points to intrinsic low resolution due to severe disorder.

We then took a page from previous work in which insertion of heavy metal guests led to a full X-ray structure including even the floppy thioether side chains.¹⁸ We soaked the native ZrL1 crystals in a saturated toluene solution of AgSbF₆. The X-ray diffraction from the AgSbF₆-loaded crystal (ZrL1-AgSbF₆) offered higher resolution and located the entire framework (Fm $\overline{3}$ m; no. 225). The side arm is disordered over both sides of the backbone (by crystal symmetry), and it also splits on each side into two slightly splaying parts. The side arms are confined within the octahedral cavities of the fcu net (Figure 2B). The structure is porous and contains about 51% solvent accessible void space, not counting void space that overlaps with partially occupied ligand side arms. The residual electron density peaks in the void space are weak and not arranged in an interpretable pattern, less than 1.5 $e^{-}/Å^{3}$, indicating AgSbF₆ and other guests are too disordered to be modeled from the diffraction data.

The impregnation by the $AgSbF_6$ guests, however, is evidenced otherwise. The yellow, fluorescent (with dim yellow emission, Figure S4) ZrL1 crystals, after being soaked in $AgSbF_6$ /toluene, become brown and nonemissive (e.g., due to heavy atom quenching of fluorescence from $AgSbF_6$). Moreover, the resulted ZrL1- $AgSbF_6$ crystal sample contains 14.8 wt % Ag (1.5:1 Ag/Zr atom ratio) as per inductively coupled plasmaoptical emission spectrometry (ICP-OES) analysis. The $AgSbF_6$ uptake also changed the PXRD intensity profile: e.g., it makes the (200) peak stronger than the (111) peak (cf. patterns b and c, Figure 3), consistent with increased electron density around



Figure 3. X-ray powder patterns (Cu K α , $\lambda = 1.5418$ Å): (a) calculated from the single-crystal structure of PCN-111 (ZrL2); (b) as-made ZrL1; (c) as-made ZrL1-AgSbF₆; (d) activated ZrL1; (e) activated ZrL1-AgSbF₆; (f) sample of (e) heated at 450 °C for 3 h (ZrL1-AgSbF₆-450): the indices are for Ag₃Sb; g) sample of e) heated at 250 °C for 3 h (ZrL1-AgSbF₆-250).

the face center (center of the octahedral cage) of the fcc cell. As it were, the face centers sit *midway* between the (111) planes of the heavy (strongly diffracting) Zr clusters and *in* the (200) planes of the Zr clusters; electron density around the face center therefore weakens (111) and strengthens (200) peak. For further illustration, the PCN-111 (based on H₂L2, Figure 1) structure,³⁵ having no side arms to occupy the octahedral voids, features a strongest (111) peak relative to the (200) peak (pattern a, Figure 3).

After solvent exchange (with acetone) and solvent removal, both ZrL1 and ZrL1-AgSbF₆ showed broader PXRD features (patterns d and e, Figure 3) indicative of framework degradation. In particular, the peaks of the AgSbF₆-loaded sample appear to be slightly sharper and they are shifted to higher angles (i.e., indexable onto a cubic lattice with a = 28.2Å), indicating some lattice contraction which was also observed in a framework based on the same strut units but with twice the side arms to occupy the voids.9 In spite of their enhanced chemical stability (e.g., in water), degradation of crystalline order upon activation is common in Zr(IV)-carboxyl networks, ^{39–41} which is in line with the lability arising from the ionic coordination links. The framework degradation/collapse reduces the surface area and compromises their application as porous materials. For example, the activated ZrL1 sample, being partially collapsed, exhibits little N2 uptake (77 K; Figure S5), while its CO₂ sorption (195 K; Figure 4 and Figure S6a) reveals a modest Langmuir surface area of 109 m^2/g .

To improve stability, thermal treatment to cascade-cyclize the alkynyl units (as featured in L1) is helpful.⁹ Unlike the high-temperature (e.g., 800 $^{\circ}$ C), all-breaking carbonization of MOF



Figure 4. CO₂ (195 K) adsorption and desorption isotherms for the samples of activated ZrL1 and ZrL1-AgSbF $_{6}$ -450.

solids,^{42–44} alkyne cyclization can be initiated more mildly (ca. 250 °C, without the need of $AgSbF_{6}$; see spectrum c of Figure S7 for the IR), so as to preserve the chemical functions of the MOF precursor. The extensive cascade annulations can also result in covalent bridging of the linker molecules, thereby enhancing stability. Recent studies also indicated that the porosity and surface area can be largely improved by thermocyclization, even if the crystallinity may be lost.⁷

The ZrL1-AgSbF₆ solid was heated at 450 °C for 3 h in an argon atmosphere to forge extensive conjugation/ring fusion throughout the solid state. The resultant black solid (ZrL1- $AgSbF_{6}$ -450) retains 70% of the original mass, with the loss attributable to the departure of H₂O and carboxyl/sulfur groups, and AgSbF₆ decomposition (see Figure S8 for more details). The alkyne stretching at 2204 cm⁻¹ (IR, Figure S7) disappeared after heating, consistent with extensive cyclization (see Figure S9 for a possible reaction scenario). PXRD (pattern f, Figure 3) reveals no peaks at $2\theta < 20^\circ$, indicating the thermocyclized matrix to be amorphous; in the higher angle region, however, appeared peaks of the Ag₃Sb phase (derived from the AgSbF₆ guest; no such peaks were seen at 245 °C, as shown in Figure 3g). Scanning electron microscopy (SEM) reveals the Ag₃Sb to exist as smooth nanodots (30–80 nm in diameter, Figure 5a; 3:1 Ag/Sb atom ratio as per analysis by local energy dispersive X-ray, EDX, Figure S10) evenly dispersed on the organic matrix (this latter retains the octahedral form of the parent MOF crystals, Figure 5b). The corresponding EDX elemental map of Ag and Sb atoms (Figure 5c,d) indicated Ag₃Sb to be evenly distributed. The average EDX results indicate a 4:3 Ag/Sb atom ratio (Figure S11); the higher Sb content (relative to Ag₃Sb) here suggests that Sb also exist in some amorphous, unidentified form.

In spite of the amorphous nature of the thermocylized matrix, ZrL1-AgSbF₆-450 exhibits enhanced CO₂ sorption and a larger Langmuir surface area of 388 m²/g (Figure 4): over 3.5 times that of activated ZrL1 (109 m²/g). ZrL1-AgSbF₆-450 also shows good electrical conductivity (ca. 1.0 S/cm in a two-probe setup on a compressed powder at room temperature). The combination of porosity and conductivity (the Ag₃Sb nanodots being also possibly useful) prompted us to explore electrocatalysis properties. Unfortunately, the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) results



Figure 5. SEM image of ZrL1-AgSbF₆-450 with (a) showing Ag₃Sb nanoparticles on the surface and (b) octahedral shape inherited from MOF precursors; EDX elemental maps of (c) Ag (Inset: image of the selected mapping area) and (d) Sb (green refers to Ag and blue Sb).

are unimpressive, with onset potentials around 0.8 V for ORR and 1.6 V for OER and small current densities for both (Figure S12 and S13), indicating weak electrocatalytic activity of the $AgSbF_6$ -derived species. More active metal (e.g., Pd or Co) guests can be tested in the future.

We then turned to the selective reduction of nitro compounds into value-added, technologically important azo products.^{45,46} One challenge is to specifically target the intermediate azo product,⁴⁷ as many metal catalysts tend to overshoot and form amines instead. Other methods for azo syntheses include amine oxidation but can involve toxic oxidants (e.g., Hg²⁺).^{48,49} To mitigate the catalytic activity for selective reduction, precious metals (e.g., Au) have been confined in meticulously crafted organic cages;^{50,51} and Ag species loaded into a zeolite exhibited some selectivity but with low conversion and entailing 25 atm H₂ pressure at 115 °C.⁵² In this context, the Ag₃Sb-strewn ZrL1-AgSbF₆-450 composite was examined for potentially moderated activity (as compared with the overactive Ag nanoparticles⁵³) for azo production, as a convenient and reusable heterogeneous catalyst.^{54,55}

The reaction involved the addition of nitroarenes (0.1 mmol), NaBH₄ (0.4 mmol), ZrL1-AgSbF₆-450 (2.4 mg; Ag⁺ is 0.05 equiv to substrate), and 1.5 mL of a solvent mixture of H₂O and EtOH into a 4 mL vial, and the mixture was heated at 60 °C for several hours followed by bubbling with O₂ for 10 min. Water affects the reaction: nitrobenzene was completely converted within 4 h with $H_2O(0.6 \text{ mL})$ and EtOH (0.9 mL), while over 8 h was needed in pure EtOH (1.5 mL). But higher water content (e.g., 1.2 mL) stops the reaction. Under optimized conditions $(EtOH/H_2O = 0.9/0.6, v/v; 4 h)$ the reaction selectively generated the azo and hydrazo compounds, while the latter can be easily oxidized to the azo product by bubbling O_2 for 10 min. If NaBH₄ is increased to 8 equiv to substrate or if the reaction time is extended to 9 h, the hydrazo compound dominates. As a control, no reaction was detected without ZrL1-AgSbF₆-450 or with using ZrL1 or ZrL1-450 instead; and very low yield was obtained when the reaction was catalyzed by ZrL1-AgSbF₆ or ZrL1-AgSbF₆-250 (see Table S2), highlighting the indispensability of silver loading and higher-temperature (e.g., at 450 $^{\circ}$ C) treatment for improving catalytic activity.

Substituted nitrobenzenes were also tested. All three methylnitrobenzene isomers afford azo products in good yields (entries 4–6, Table 1). Fluoro substitution does not affect the reaction (entry 7, Table 1). The conversion is also compatible with alkene groups, which were unaffected (entries 8–9, Table 1). After five catalytic cycles, no significant decrease in silver loading (Figure S14) and catalytic activity were observed, showcasing ZrL1-AgSbF₆-450 as a reusable heterogeneous catalyst with efficiency comparable to precious metal (e.g., Pd, Au) systems.^{20,21,50}

SUMMARY

To conclude, two major instances of serendipity have been observed from the alkyne-rich framework ZrL1. (1) The first instance included an unusual, inverted order in the X-ray structure with regard to the heavy $AgSbF_6$ (or $AgBF_4/AgOTf$) guests and lighter side arms: the impregnation with the Ag(I)salts was found to enhance the diffraction intensity as well as the structural order of the host framework of ZrL1 to allow full resolution of the linker molecule but not the Ag(I) salt species (i.e., these heavy atom centers remain curiously invisible to the X-ray diffraction analysis, unlike the common observation of heavy metal ions being the first to come out in the electron density map). (2) The AgSbF₆ guests were converted into the rarely reported Ag₃Sb nanoparticles under the energetic (450 °C) condition of linker thermocylization/partial graphitization, with the resultant Ag₃Sb/nanographene composite enabling a reusable heterogeneous catalyst for selectively reducing nitro compounds into azo products. The reactive, carbon/alkyne-rich backbone of the linker molecules apparently acted as a reducing agent as well as a promoter in forging the intermetallic nanophase of Ag₃Sb. One can also imagine the alkyne-decked pores of the MOF host as some working nano foundry in which various other metal salts can be incorporated, so as to be thermally converted into functional metal/alloy species closely composited and synergized with the concomitantly formed nanographene grid. Such molecular metallurgy, as is coupled and integrated with the thermal/chemical reactivity of the porous host, opens new avenues to novel metal-based nano species (e.g., the Ag₃Sb particles discovered herein) otherwise difficult to access.

The luck, on the other hand, is rooted in the broad design exercise on cyclizable alkyne building blocks and in the rich and under-explored interactions between metal guests and the dynamic medium of open frameworks. Such interactions, however, can be challenging to study: for example, it remains unclear how the "invisible" AgSbF₆, AgBF₄, and AgOTf guests bond with the host net, while guests like Co₂(CO)₈ and HgBr₂ (Figures S16 and S17) were found not to enhance the structural resolution of the native crystals. Perhaps, the heavy, thermally sedate Ag⁺ ion and the counterions electrostatically aggregate together to better restrict the side chain motions, relative to the nonionic, molecular species of Co₂(CO)₈ and HgBr₂.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at ACS Publications Web site at DOI: xxxx. . The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00012.

Single crystal structure determination, TGA, BET plots, EDX results and NMR data (PDF)

Accession Codes

CCDC 2012402 2069047 2069048 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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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by a GRF grant from the Research Grants Council of HKSAR (CityU 11306018) and the National Natural Science Foundation of China (21871061). The singlecrystal X-ray diffractometer was funded by the US National Science Foundation through the Major Research Instrumentation Program under grant no. CHE 1625543.

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