INTRODUCTION

Multifunctional open framework materials derived from the combination of components with inherent properties through self-assembly process have received much attention in recent years because of their fascinating structures and potential applications in many different areas, such as catalysis, size-selective uptake, and separation, storage, and conductivity. Of these, the chalcogenides, especially 3D chalcogenide frameworks, have received much attention in recent years because of their fascinating structures and potential applications. However, the preparation of such chalcogenide frameworks has been a challenge. Multifunctional open framework materials derived from the combination of components with inherent properties through self-assembly process have received much attention in recent years because of their fascinating structures and potential applications in many different areas, such as catalysis, size-selective uptake, and separation, storage, and conductivity. Of these, the chalcogenides, especially 3D chalcogenide frameworks, have received much attention in recent years because of their fascinating structures and potential applications. However, the preparation of such chalcogenide frameworks has been a challenge.

3d–4d–4f Heterotrimetallic 3D Chiral Frameworks Based on Octahedral \{Ni_6Ag_8S_{12}Cl\} or Trigonal Dipyramidal \{Co_2Ag_3S_6\} Clusters: Synthesis, Crystal Structures, and Characterization

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ABSTRACT: The self-assembly reactions of AgNO₃, Ln(NO₃)₃ (Ln = La, Eu, and Tb), n-penicillamine (n-pen, H₂L), and NiCl₂ (or CoCl₂) lead to the formation of six new compounds: (H₂O)₃[LnNi₆Ag₈L₁₂Cl(Ac)(H₂O)₄]·(H₂O)₂ (Ln = La (1); Eu (2); and Tb (3)) and (H₂O)₂[LnCo₂Ag₃L₆](H₂O)₃ (Ln = La (4); Eu (5); and Tb (6)). Single crystal X-ray analyses show that 1, 2, and 3 are isomorphous and have a 3D anionic framework in which the nodes are octahedral \{Ni₆Ag₈S₁₂Cl\} clusters, and Ln³⁺ ions and the connectors are the CCHCOO chains of the n-pen ligands. Moreover, 4, 5, and 6 are also isomorphous, possessing a 3D anionic framework with trigonal dipyramidal \{Co₂Ag₃S₆\} clusters, Ln³⁺ as nodes, and the CCHCOO chains of the n-pen ligands as connectors. Topology analyses indicate that the two series of 3d–4d–4f heterotrimetallic compounds have (3,3)-connected uig and (6,6)-connected pcau networks, respectively. The frameworks are rigid and stable. The porosity is retained after the guest molecules are removed and can take back guest molecules again. Solid-state UV–vis spectroscopy experiments show that compounds 1–6 are all medium gap semiconductors with band gaps of 1.82, 1.80, 1.83, 1.68, 1.71, and 1.72 eV, respectively.

Ln-doped open frameworks are uncommon, and the synthesis of this special framework still remains a great challenge. In marked contrast to the extensive studies of heterobimetallic compounds, relatively few papers are devoted to the studies of heterotrimetallic compounds, especially of d–d–f types, although interesting properties such as catalysis, photoactive materials, and molecular magnetism have been observed in many of them owing to the interactions among three types of metal ions locating in close proximity in one molecular system. Moreover, most of the heterotrimetallic compounds bear isolated structure and extended frameworks are rare. To our knowledge, only two reports focused on 3D d–d–f heterotrimetallic compounds have been published up to now.

α-Amino acids (AAs) are essential molecules to form peptides and proteins that serve important biological functions. Because of their various coordination modes and chiral nature, AAs can be used as ligands for the construction of a wide range of 3d–4f heterotrimetallic clusters with interesting magnetic properties and chiral metal–organic frameworks (MOFs) with enantioselective recognition, separation, and catalytic proper-

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ties.14 However, among them, 3D frameworks based on heterometallic clusters are quite rare.15 Cysteine and penicillamine contain both hard (O and N) and soft (S) donors, which makes them good ligands for many heterometallic transition metal chalcogenide clusters (such as {Ni₆Ag₈S₁₂}^{16} and {Ni₆S₆H₂O}, extended chalcogenide frameworks based on single metal node18 and even several 1D or 2D polymeric clusters.8 Our continued investigations of 3d–4f heterometallic clusters based on amino acids have resulted in the discovery of six new 3d–4d–4f heterooctetrametallic 3D chiral frameworks: (H₂O)₃[Tb₂Ni₆Ag₈S₁₂Cl₂Li₆(Ac)(H₂O)₄](H₂O)₆, (H₂O)₃[TbNi₆Ag₈S₁₂Cl₂Li₆(H₂O)₄](H₂O)₄, (H₂O)₃[Tb₂Ni₆Ag₈S₁₂Cl₂Li₆(H₂O)₄](H₂O)₄, (H₂O)₃[Tb₂Ni₆Ag₈S₁₂Cl₂Li₆(H₂O)₄](H₂O)₄, (H₂O)₃[Tb₂Ni₆Ag₈S₁₂Cl₂Li₆(H₂O)₄](H₂O)₄, and (H₂O)₃[Tb₂Ni₆Ag₈S₁₂Cl₂Li₆(H₂O)₄](H₂O)₄. In an H tube with deionized water as a reactant layer between them.

Table 1. Crystal Data and Structure Refinement for 1, 4, and 5

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<tr>
<th></th>
<th>1</th>
<th>2</th>
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<tr>
<td>formula</td>
<td>C₆₂H₁₈₄Ag₈Cl₆La₁₂Ni₆O₆₁₁S₁₂</td>
<td>C₆₂H₁₈₄Ag₈Co₆La₁₂Ni₆O₆₁₁S₁₂</td>
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<td>trigonal</td>
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<tr>
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<td>10.1695(9)</td>
<td>10.1532(8)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>24.3687(14)</td>
<td>10.1695(9)</td>
<td>10.1532(8)</td>
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<tr>
<td>c (Å)</td>
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<td>90</td>
<td>90</td>
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<tr>
<td>b (deg)</td>
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<td>90</td>
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</tr>
<tr>
<td>g (deg)</td>
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<td>120</td>
<td>120</td>
</tr>
<tr>
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<td>37335(5)/3</td>
<td>37083(7)/3</td>
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<tr>
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<td>2.076</td>
<td>2.107</td>
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<td>18436/4359</td>
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<td>1.039</td>
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<td>R₁(</td>
<td>R</td>
<td>&gt; 2σ(</td>
<td>F</td>
</tr>
<tr>
<td>wR² (all data)</td>
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<td>0.002/0.000</td>
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<td>absolute structure parameter</td>
<td>0.021(13)</td>
<td>0.01(3)</td>
<td>0.02(3)</td>
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</table>

*1, a = 0.0642, b = 0.0000; 4, a = 0.0488, b = 3.2922; 5, a = 0.0812, b = 2.3256. *2 Rₘ = Σ]|F₉,s| − |F₉,l|)/Σ|F₉,l|, ∑|w(F₉,s − F₉,l)²)/Σ|w(F₉,l)²|, and w = σ²(F₉,l) + (aP)² + bP², where P = (P₀ + 2FE)/3.

Microscope equipped with OXRFD EDAX. Metal analyses were carried out by inductive coupled plasma emission spectrometer (ICP) Optima 2000DV. Magnetic measurement was carried out on a Quantum Design MPMS XL-7. The data was corrected for the sample holder and the diamagnetic contributions.

**General Synthesis of (H₂O)₃[LnNi₆Ag₈L₁₂Cl₆(Ac)₆(H₂O)₄](H₂O)₂₈ (1–3).** To 20 mL of the 0.2 M sodium acetate buffer solution (pH = 5.2) containing 150 mg (1 mmol) of ligand (tetrapenicilamine), 1 mL of NiCl₂·6H₂O (119 mg, 0.5 mol/L) aqueous solution was added. After stirring for ten minutes, 113 mg (0.67 mmol) of AgNO₃ in 1 mL of water was added to the mixed solution. Red crystals were obtained by slow diffusion of 2 mL of the resulting solution and 2 mL of aqueous solution of AgNO₃ (0.25 M) in an H tube with deionized water as a buffer layer between them.

**Materials and Instrumentation.** All chemicals were obtained from commercial sources and used without further purification. X-ray powder diffraction (XRPD) measurements were carried out on a Rigaku D/MAX-2400 X-ray Diffractometer using Cu Kα (λ = 1.5418 Å) at room temperature. Elemental analyses were determined using a Vario EL III elemental analyzer. Thermogravimetric analyses were performed under a flow of nitrogen (40 mL/min) at a ramp rate of 10 °C/min, using a NETZSCH STA 449F3 instrument. FT-IR spectra were recorded in the range of 4000–400 cm⁻¹ on a JASCO FT/IR-430 spectrometer with KBr pellets. CD and UV–vis diffuse reflectance spectra were measured on a JASCO J-810 Spectropolarimeter and UV-550 spectrophotometer, respectively. Energy-dispersive X-ray spectroscopy (EDS) was performed by FEI Quanta 450 Scanning Electron Microscope equipped with OXRFD EDAX. Metal analyses were carried out by inductive coupled plasma emission spectrometer (ICP) Optima 2000DV. Magnetic measurement was carried out on a Quantum Design MPMS XL-7. The data was corrected for the sample holder and the diamagnetic contributions.
\((H_3O)_2[EuCo_2Ag_3L_6](H_2O)_3\) (5). Yield: 89%, based on Ag. Anal. Calcd. for \(C_{30}H_{66}Ag_3Co_2EuN_6O_{17}S_6\): C, 22.97; H, 4.24; N, 5.36%. Found: C, 23.18; H, 4.19; N, 5.27%. IR (KBr pellet, cm\(^{-1}\)): 3422 s, 3226 s, 2953 s, 1595 s, 1453 m, 1388 s, 1168 w, 1171 w, 1128 m, 1050 w, 942 w, 801 w, 705 w, 602 w.

\((H_3O)_2[TbCo_2Ag_3L_6](H_2O)_3\) (6). Yield: 93%, based on Ag. Anal. Calcd. for \(C_{30}H_{66}Ag_3Co_2TbN_6O_{17}S_6\): C, 22.87; H, 4.22; N, 5.33%. Found: C, 22.96; H, 4.21; N, 5.19%. IR (KBr pellet, cm\(^{-1}\)): 3422 s, 3227 s, 2954 s, 1586 s, 1452 m, 1388 s, 1172 w, 1128 m, 1050 w, 941 w, 803 w, 705 w, 601 w.

**X-ray Structure Determinations.** Intensity data were measured at 293(2) K on a Bruker SMART APEX II CCD area detector system. Data reduction and unit cell refinement were performed with Smart-CCD software. The structures were solved by direct methods using SHELXS-97 and were refined by full-matrix least-squares methods using SHELXL-97.

For 1, all nonhydrogen atoms were refined anisotropically except O25 (carboxylate oxygen atom from the coordinated Ac\(^-\) group). Hydrogen atoms on the coordinated water molecules could not be located. The hydrogen atoms were included in the structural model as fixed atoms (using idealized sp\(^2\)-hybridized geometry and C–H bond lengths of 0.95 Å) riding on their respective carbon atoms. Since the disordered water molecules and H\(_2\)O\(^+\) cations could not be unambiguously modeled, the Platon Squeeze option was utilized based on the model that included the coordinated H\(_2\)O only. Squeeze indicates 1 solvent regions in the cell corresponding to about 2484 electrons/cell or approximately three H\(_2\)O\(^+\) cations and 28 water molecules per formula, which is consistent with the results of EDS (no Na\(^+\) is detected), elemental analysis, and TGA. The maximum residual peak and hole on the final difference Fourier map corresponded to 1.299 e\(^-\)/Å\(^3\) (2.74 Å from O3) and −0.571 e\(^-\)/Å\(^3\) (0.76 Å from La1), respectively.

For 4 and 5, the structural models incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. All the hydrogen atoms attached to carbon atoms were placed in calculated positions and refined using the riding model. Hydrogen atoms on the free water molecules could not be located. The maximum residual peak and hole on the final difference Fourier map, respectively, corresponded to 1.73 e\(^-\)/Å\(^3\) (1.04 Å from Co1) and −0.55 e\(^-\)/Å\(^3\) (0.73 Å from Co1) for 4, and 4.786 e\(^-\)/Å\(^3\) (1.09 Å from Co1) and −1.001 e\(^-\)/Å\(^3\) (0.55 Å from Co1) for 5.

Crystal data as well as details of data collection and refinement for 1, 4, and 5 are summarized in Table 1, and selected bond lengths and angles are given in Tables S1, S2, and S3, Supporting Information. Crystal data of compounds 2, 3, and 6 were also collected. Because of the weak intensities, only preliminary structures can be observed. Compounds 2 and 3 are isomorphous with 1, while 6 is isomorphous with 4 and 5, as also confirmed by powder XRD patterns and elemental analysis data. Their cell parameters are listed in Table S4, Supporting Information.
RESULTS AND DISCUSSION

Crystal Structures of 1–3. Compounds 1, 2, and 3 are isomorphous, and only the structure of 1 is described in detail. The structure of 1 can be described as a heterotrimetallic 3D framework based on 3-connected La$^{3+}$ and [Ni$_{6}$Ag$_{8}$S$_{12}$Cl] nodes, and the connectors are CCHCOO chains of the d-pen ligands (Figure 1). In the structure, each La$^{3+}$ ion has a {O$_{3}$} donor set. As shown in Figure 1b, the upper face is formed by two terminal water molecules and two carboxylate oxygen atoms from two d-pen ligands, while the lower face is occupied by one water molecule, two carboxylate oxygen atoms from the chelating acetate anion, and one carboxylate oxygen atom from the third d-pen ligand. A distorted monocapped square antiprism configuration around the La$^{3+}$ ion is completed by the additional binding of one water molecule from the cap position. The bond lengths of La–O are in the range of 2.471(6)–2.713(7) Å and the bond angles around La$^{3+}$ ion range from 51.0(3) to 153.1(3)$^\circ$.

The 14-nuclear [Ni$_{6}$Ag$_{8}$S$_{12}$Cl] cluster shows approximate $T_d$ symmetry with six Ni$^{2+}$ ions arranged to form a Ni$_{6}$ octahedron, eight Ag ions distributed at the centers of triangular faces, and one Cl$^{-}$ anion located at the center. The Ni–Ni and Ag–Ag separations are in the range of 6.90–7.26 and 3.96–4.20 Å, respectively. Each of the 12 thiolate atoms acts as a μ$_{3}$-bridge to coordinate to one Ni$^{2+}$ and two Ag$^{+}$ ions. The corresponding Ag–S–Ni are in the range of 116.32(11)–127.54(10)$^\circ$. Although many {M$_{6}$} or {L$_{n}$M$_{6}$} compounds bearing the Ni$^{2+}$ ion range from 87.5(2) to 176.9(2)

From another point of view, the framework can also be treated as the combination of La$^{3+}$ nodes and octahedral [Ni$_{6}$Ag$_{8}$L$_{12}$Cl] molecular building blocks (MBBs) (Figure 1e) whose surface is decorated by 12 carboxylate groups that point to six directions. However, only three of the carboxylate groups are used to coordinate to three La$^{3+}$ ions in meridional-mode.

Crystal Structures of 4–6. Compounds 4, 5, and 6 are also isomorphous. Only the structure of 4 is described in detail. Compound 4 crystallizes in chiral trigonal P3$_{2}$1 space group and possesses a 3D anion framework structure with trigonal dipyramidal {Co$_{2}$Ag$_{3}$S$_{6}$} clusters, La$^{3+}$ ion as nodes, and the

...
Figure 3. (a) Overall structure of 4. CH$_3$ groups and water molecules are omitted for clarity. (b) Coordination polyhedron of the La$^{3+}$ ion. Symmetry code: A, y, x, −z. (c) Structure of the \{Co$_2$Ag$_3$S$_6$\} cluster. (d) Coordination mode of the \{Co$_2$Ag$_3$L$_6$\} MBB.

Figure 4. Packing diagram of 4 viewed along the c direction. Free water molecules and hydronium ions are represented as a space filling mode, while atoms in the framework are represented as wires or sticks mode.
CCHCOO chains of the d-pen ligands as connectors (Figure 3). Each La\(^{3+}\) ion presents a distorted square antiprismatic geometry and coordinates to four carboxylate oxygen atoms from two monobidentate coordinated carboxylate groups (La–O bond distances are in the range of 2.538(7)–2.677(8) Å) and four carboxylate oxygen atoms from four mononodentate coordinated carboxylate groups (La–O bond distances are in the range of 2.398(8)–2.429(6) Å). The bond angles around La\(^{3+}\) metal ion ranges from 71.8(3) to 157.1(2)°, and the La–O bond distances are in the expected range for such complexes.\(^8\)

The structure of the \{Co\(_2\)Ag\(_3\)S\(_6\)\} cluster can be described as a trigonal dipyramid. Three Ag\(^{+}\) ions are arranged into a triangle with \(\angle\text{Ag}···\text{Ag}···\text{Ag}\) close to 60°. Compared with 1, the absence of a central Cl\(^−\) anion allows shorter Ag···Ag separations (2.949(1) and 2.909(2) Å). Two Co\(^{2+}\) ions act as apexes of the bipyramid. The Co\(^{2+}\) and Ag\(^{+}\) ions are bridged by a thiolate atom, and the corresponding \(\angle\text{Co}···\text{S}···\text{Ag}\) angles are in the range of 111.88(11)–113.27(11)°. The Co···Co and average Co···Ag separations are 6.94 and 3.86 Å, respectively. Each Ag\(^{+}\) ion adopts a 2-coordinated linear \(\{\text{S}_2\}\) donor set with two S atoms from two \(\text{d}-\text{pen}\) ligands. The average Ag···S bond distance is 2.376(8) Å, and the S···Ag–S angles are close to 180°. Each Co\(^{2+}\) ion has a \(\{\text{S}_2\text{N}_2\}\) donor set. Three N atoms and three S atoms from three \(\text{d}-\text{pen}\) ligands are used to coordinate to the metal ion and a slightly distorted octahedral polyhedron is formed. The average Co···N and Co···S bond distances are 1.99(2) and 2.265(4) Å, respectively. The bond angles around Co\(^{2+}\) ion range from 84.3(2) to 174.6(2)°. The D-pen ligands in \(\{\text{Co}_2\text{Ag}_3\text{L}_6\}\) MBBs (Figure 3d) bearing six carboxylate groups that point to four metal ions, and the di- 

\[\text{Co}_{12}\text{Ag}_{18} \left(\text{CH}_3\text{COO}\right)_{24} \left(\text{D}-\text{pen}\right)_{24} \text{Cl}_{15}\] 

is featured by six deprotonated carboxylate groups pointing along the center-thiolate direction. The preparation of a similar \(\text{Ni}_{12}\text{Ag}_{18} \left(\text{CH}_3\text{COO}\right)_{24} \left(\text{D}-\text{pen}\right)_{24} \text{Cl}_{15}\) cluster has been reported, but it has never been used as building blocks to build extended structure.\(^\text{17}\) So, 4, 5, and 6 are the first 3D polymeric compounds based on the \(\text{M}_6\text{M'}_8\text{L}_{12}\text{Cl}_{4}\) building blocks. In the structure of 1, among the 12 active sites (deprotonated carboxylate groups) of the \(\{\text{Ni}_{12}\text{Ag}_{18}\text{Cl}_{6}\}\) MBB, only three were used to coordinate to the lanthanide ions. EDS, ICP, and CHN analysis are in agreement with the crystal structure formula. Similar synthesis reaction but using CoCl\(_2\) led to the formation of brownish black crystals of compounds 4, 5, and 6. The increase of the metallic coordination number from 4 (Ni\(^{2+}\), for 1, 2, and 3) to 6 (Co\(^{2+}\), for 4, 5, and 6) leads to an entirely different MBB, \(\{\text{Co}_{12}\text{Ag}_{6}\}\), featured by six deprotonated carboxylate groups pointing along the center-thiolate direction. The preparation of a \(\{\text{Ni}_{12}\text{Au}_{18}\text{Cl}_{6}\}\) cluster has been reported, but it has never been used as building blocks to build extended structure.\(^\text{17}\) So, 4, 5, and 6 are the first 3D polymeric compounds based on the \(\text{M}_6\text{M'}_8\text{L}_{12}\text{Cl}_{4}\) building blocks. In the six active sites (deprotonated carboxylate groups) of the \(\{\text{Co}_{12}\text{Ag}_{6}\}\) MBB were all used to coordinate to the lanthanide ions. Both EDS and ICP experiments indicated that the ratio of Co/Ag/La is 2.3:1, which is consistent with the formula. The magnetic susceptibility measurement was performed on microcrystalline samples of 4 at 300 K. The effective magnetic moment is 5.48\(\mu_\text{B}\) close to the value 5.36\(\mu_\text{B}\) expected for two independent Co\(^{2+}\) ions, which confirms that the Co ions remain at +2 state during the reaction.

The solid-state luminescent spectra of the six compounds were measured at room temperature; unfortunately, no emission peaks were observed, which can be explained as the quenching effect due to the presence of transition-metal ion (Ni\(^{2+}\) or Co\(^{2+}\)) with unpaired electrons.\(^\text{26}\)

To analyze their chirality, solid-state circular dichroism (CD) spectra for 1 and 4 were recorded on bulk samples with a KBr pellet between 200 and 550 nm at room temperature (Figure S2, Supporting Information). The CD spectrum of 1 displays positive cotton effects at about 312 and 463 nm and negative cotton effects at about 256 and 392 nm. The CD spectrum of 4 shows clear cotton effects with positive signals at about 314 and 389 nm and negative signals at about 257 and 450 nm. These results suggest that the bulk samples (1 and 4) are the same.
handed conformation, which is consistent with the single crystal structural analyses.

To examine the thermal stabilities of 1 and 4, thermogravimetric analysis (TGA) experiments were performed by heating the crystalline sample under nitrogen atmosphere in the temperature range of 20–800 °C (Figure S3, Supporting Information). The TGA curve of 1 reveals that the first weight loss of 16.38% in the temperature region of 20–250 °C corresponds to the loss of all the water molecules (ca. 16.46%) and might be accompanied by a process of proton transfer to the framework.13a After 250 °C, the material shows a striking weight loss, indicating complete decomposition of the framework. Compound 4 exhibits two distinct weight losses. The first step (5.88%) involves loss of noncoordinating water molecules at temperature below 230 °C (ca. 5.92%) and is also accompanied by a process of proton transfer to the framework. Then, 4 continues to lose its weight until 800 °C.

The reversible water adsorption studies of 1 and 4 were also carried out before 150 °C (Figures S4 and S5, Supporting Information). Compound 1 loses its weight of 16.86%, 11.56%, 11.27%, and 11.03% in the first, second, third, and fourth cycles, respectively, suggesting that 1 can reversibly absorb 24 water molecules back from air (ca. 11.24%) after the loss of original solvent molecules. Compound 4 loses its weight of 6.08% in the first cycle, corresponding to the loss of three water molecules and two hydronium ions (ca. 5.92%). However, a little larger weight loss was observed in the second, third, and fourth cycles (6.61%, 6.48%, and 6.55%, respectively), indicating that 4 can reversibly absorb 5.6 water molecules back from air (ca. 6.49%) after the loss of original solvent molecules. Moreover, the PXRD patterns (Figures S6 and S7, Supporting Information) of 1 and 4 heated at 150 °C for 30 min are almost the same as those of the original phases. All the results indicate, the guest-free frameworks of 1 and 4 are rigid and stable. The porosity is retained for both compounds and can take back guest molecules again.

The optical properties of the six compounds were investigated with solid-state UV−vis spectroscopy at room temperature, and the results are plotted in Figures 6, S10, and S11, Supporting Information, respectively. The band gap energies ($E_g$) were calculated from formula $E_g = 1240/\lambda_g$ (eV), where $\lambda_g$ stands for the wavelength in the minima of the second derivatives of the optical absorption curve. As a result, the band gaps for 1–6 are 1.82, 1.80, 1.83, 1.68, 1.71, and 1.72 eV, respectively, indicating all the compounds are medium gap semiconductors. Besides, all the $E_g$ are in the energy range suitable for visible-light photocatalytic applications.27 Compared with the bulk Ag$_2$S (1 eV),28 there is a noticeable blue shift of the absorption edges, which is consistent with other M−Ag heterometallic chalcogenides.29

Previously, two 3D compounds [Cd(1-cysteinate)] and [Zn(1-cysteinate)] bearing 1D Cd−S ladder chain or zigzag Zn−S skeleton were reported.18b Solid-state optical experiments show huge blue shifts of the band gap up to 2.59 and 1.37 eV with respect to the bulk MS structures for the two compounds, respectively. Compared with the two compounds, less blue shift of the band gaps in 1–6 might be partially ascribed to the presence of polynuclear MS clusters in the frameworks.

### CONCLUSIONS

With the help of an S-, N-, and O-donor amino acid derivative (N-penicillamine), the simultaneous incorporation of 3d−4d transition metal chalcogenide clusters (either octahedral [Ni$_2$Ag$_3$S$_3$Cl$_2$] or trigonal dipyramidal {Co$_2$Ag$_3$S$_6$}) and 4f metal ions into a 3D framework has been achieved successfully, and two series of chiral heterotrimetallic framework with utg or pcu topology were obtained. Optical measurements show that the six compounds are all medium gap semiconductors. Consequently, this work proves that the S-containing amino acid is a good candidate for the construction of transition metal chalcogenide clusters, which can be further connected into 3D frameworks with the help of 4f metal ions. However, the active sites of the molecular building blocks ([Ni$_2$Ag$_3$S$_3$Cl$_2$] and {Co$_2$Ag$_3$S$_6$}) in the six compounds were only partly (for 1–3) or fully (for 4–6) used when being coordinated by 4f metal ions. This suggests that new compounds with structural diversity may be obtained by reasonable utilization of the active sites of the molecular building blocks. Furthermore, the quenching of luminescence due to the use of Ni$^{2+}$ or Co$^{2+}$ ions also suggest that other 3d transition-metal ions without unpaired electrons need to be tried. Further studies on the ideas are in progress.

### ASSOCIATED CONTENT

* Supporting Information
Crystallographic data (CIF format) and crystallographic tables for 1–6; Figure S1–S12. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**
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