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Solvothermal Synthesis of Four Polyoxometalate-Based Coordination Polymers Including Diverse Ag(I)···π Interactions

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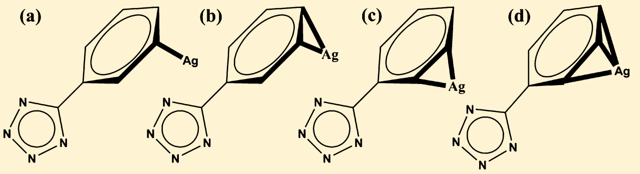
Supporting Information



ABSTRACT: Four 3D POM-based silver coordination polymers, namely, $[Ag_{17}(ptz)_{11}(PW_{12}O_{40})_2]_n$ (**1**), $[Ag_{17}(ptz)_{11}(PMo_{12}O_{40})_2]_n$ (**2**), $[Ag_{12}(ptz)_6(CN)_2(SiW_{12}O_{40})]_n$ (**3**), and $[Ag_{19}(ptz)_8(H_2ptz)(H_3ptz)(AgP_5W_{30}O_{110})\cdot 7H_2O]_n$ (**4**), have been obtained by solvothermal reaction of $AgNO_3$ and 5-phenyl-1*H*-tetrazole (Hptz) ligand in the presence of four types of polyoxometalates. Structural analysis shows that four types of Ag(I)···π interactions, m-η^1, m/p-η^2, o/m-η^2, and o/m/p-η^3, were observed in compounds **1**−**4**, depending on the polyoxometalates used. The *in situ* generated CN^- ion in compound **3** shows unprecedented mixed σ and π bonding modes, similar to the C_2^{2-} ion in well-studied silver acetylides. For **4**, the Na^+ ion in the Preyssler heteropolyoxoanion, $[NaP_5W_{30}O_{110}]^{14-}$, was exchanged by Ag(I) under solvothermal conditions, generating a novel $[AgP_5W_{30}O_{110}]^{14-}$ anion. In addition, the photoluminescence behavior of **1**−**4** was also investigated.

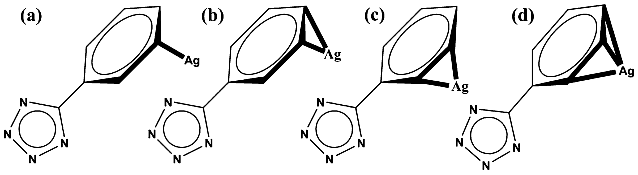
■ INTRODUCTION

Rational design and synthesis of molecular solid-state structures with desired properties via the manipulation of intermolecular interactions still remains a great challenge, because the relatively weak strength of intermolecular interactions is susceptible to external physical or chemical stimuli.[1−3] Among the different types of intermolecular forces, the relatively strong hydrogen bonding and metal−ligand complexation are most extensively studied, and a large number of coordination compounds have been reported on the basis of hydrogen bonding and metal−ligand complexation.[4−8] However, the coordination compounds that depend on relatively weak cation···π interactions have been seldomly observed, although the cation···π interactions play an important role in nature, particularly in protein structure, molecular recognition, and enzyme catalysis.[9−14]

Among cation···π interactions, Ag(I)···π interaction has been continuously investigated for nearly one century. Recent study of silver−aromatic complexes has moved from simple aromatic compounds to the highly conjugated arenes such as pyrene,[10a] perylene,[10a] coronene,[10b] benzo[*ghi*]perylene,[11] and naphtho-[2,3-*a*]pyrene.[12] However, the skillful use of multiazole ligands to construct complexes with Ag(I)···π interaction has been less investigated to date.[14]

Herein, on the basis of the 5-phenyl-1*H*-tetrazole (Hptz) ligand, four 3D POMs-based silver coordination polymers, namely, $[Ag_{17}(ptz)_{11}(PW_{12}O_{40})_2]_n$ (**1**), $[Ag_{17}(ptz)_{11}(PMo_{12}O_{40})_2]_n$ (**2**), $[Ag_{12}(ptz)_6(CN)_2(SiW_{12}O_{40})]_n$ (**3**), and $[Ag_{19}(ptz)_8(H_2ptz)(H_3ptz)(AgP_5W_{30}O_{110})\cdot 7H_2O]_n$ (**4**), have been obtained under solvothermal reaction of Hptz, $AgNO_3$, and four types of polyoxometalates. Structural analysis shows that four types of Ag(I)···π interactions were observed in **1**−**4** (Scheme 1). Notably, compounds **1**−**4** represent the seldom examples of POM-based silver coordination polymers with Ag(I)···π interactions.[14] The novel mixed σ and π bonding modes of the *in situ* generated CN^- ion in compound **3** and the Ag(I)-encapsulated Preyssler heteropolyoxoanion $[AgP_5W_{30}O_{110}]^{14-}$ in compound **4** were first observed.

Scheme 1. Four Types of Ag−π Interaction in 1−4, m-η^1 (a), m/p-η^2 (b), o/m-η^2 (c), and o/m/p-η^3 (d)



■ EXPERIMENTAL SECTION

Materials and General Methods. $(NH_4)_{14}[NaP_5W_{30}O_{110}]\cdot nH_2O$ was synthesized according to the literature.[15] The other reagents and solvents employed were commercially available and used as received

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Table 1. Crystal Data for **1**−**4**

	1	**2**	**3**	**4**
formula	$Ag_{17}(ptz)_{11}(PW_{12}O_{40})_2$	$Ag_{17}(ptz)_{11}(PMo_{12}O_{40})_2$	$Ag_{12}(ptz)_6(CN)_2(SiW_{12}O_{40})$	$Ag_{19}(ptz)_8(H_2ptz)(H_3ptz)(AgP_5W_{30}O_{110})\cdot 7H_2O$
M_r	9184.78	7074.94	5091.67	11170.40
cryst color	yellow	orange	colorless	yellow
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	14.388(3)	14.138(4)	12.342(2)	23.927(5)
b/Å	14.732(3)	14.546(5)	12.447(2)	22.684(5)
c/Å	19.978(4)	19.922(6)	14.980(3)	33.277(7)
α/deg	70.97(3)	107.906(6)	97.787(3)	90
β/deg	89.92(3)	90.517(6)	107.293(3)	109.73(3)
γ/deg	72.09(3)	107.615(5)	108.721(3)	90
V/Å^3	3786.2(13)	3692(2)	2012.1(6)	17001(6)
D_c/g cm^{-3}	4.028	3.182	4.202	4.364
Z	1	1	1	4
T/K	173	298	173	173
F(000)	4070	3302	2262	19760
θ/deg	3.02−25.00	1.08−25.00	1.47−25.00	3.00−25.00
μ(Mo Kα)/mm^{-1}	20.404	4.283	20.027	22.602
data/params	13 065/1153	12 695/1141	6970/634	14 538/1277
obsd reflns	11 076	11 466	5819	12 002
GOF	1.019	1.178	1.022	1.046
R1, wR2[a,b] [$I > 2\sigma(I)$]	0.0747, 0.1953	0.0891, 0.2212	0.0749, 0.1942	0.0577, 0.1706
R1, wR2 (all data)	0.0839, 0. 2051	0.0977, 0.2274	0.0858, 0.2029	0.0692, 0.1865

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

without further purification. The C, H, and N microanalyses were carried out with a CE instruments EA 1110 elemental analyzer. The infrared spectrum was recorded on a Nicolet AVATAR FT-IR330 spectrophotometer with pressed KBr pellets. The fluorescence spectrum was obtained on a F-7000 FL spectrophotometer with solid pure sample.

Synthesis of $[Ag_{17}(ptz)_{11}(PW_{12}O_{40})_2]_n$ ***(1)***. $H_3PW_{12}O_{40}\cdot nH_2O$ (0.3 g, 0.1 mmol), Hptz (0.073 g, 0.5 mmol), and $AgNO_3$ (0.170 g, 1.0 mmol) were dissolved in 10 mL of distilled water with stirring at room temperature. The cloudy solution was put into a 25 mL Teflon-lined Parr, heated to 150 °C for 4000 min, and then cooled to room temperature at a rate of 3 °C h^{-1}. Yellow crystals (0.319g) were isolated (yield 57% based on $AgNO_3$). Anal. Calcd for $C_{77}H_{55}N_{44}O_{80}Ag_{17}P_2W_{24}$ (%): C, 10.07; H, 0.60; N, 6.71. Found: C, 10.44; H, 1.11; N, 6.99. IR for **1** (KBr, cm^{-1}): 3470 (s), 3053 (w), 2914 (w), 1610 (m), 1477(w), 1453 (m), 1366 (w), 1283 (w), 1239 (w), 1149 (w), 1072 (s), 1036 (w), 986 (s), 896(s), 813(s).

Synthesis of $[Ag_{17}(ptz)_{11}(PMo_{12}O_{40})_2]_n$ ***(2)***. $H_3PMo_{12}O_{40}\cdot nH_2O$ (0.5 g, 0.27 mmol), Hptz (0.145 g, 1.0 mmol), and $AgNO_3$ (0.170 g, 1.0 mmol) were dissolved in 10 mL of distilled water with stirring at room temperature. The cloudy solution was put into a 25 mL Teflon-lined Parr, heated to 140 °C for 8000 min, and then cooled to room temperature at a rate of 3 °C h^{-1}. Red block crystals (0.450g) of **2** were obtained in 90% yield (based on $AgNO_3$). Anal. Calcd for $C_{77}H_{55}N_{44}O_{80}Ag_{17}P_2Mo_{24}$ (%): C, 13.07; H, 0.78; N, 8.71. Found: C, 13.32; H, 1.06; N, 8.80. IR for **2** (KBr, cm^{-1}): 3491 (s), 3047 (w), 2911 (w), 1603 (m), 1554 (w), 1453 (m), 1369 (m), 1280 (w), 1164 (w), 1152 (m), 1054 (s), 989 (s), 876 (w), 739(s).

Synthesis of $[Ag_{12}(ptz)_6(CN)_2(SiW_{12}O_{40})]_n$ ***(3)***. $H_4SiW_{12}O_{40}\cdot nH_2O$ (0.36 g, 0.125 mmol), Hptz (0.036 g, 0.246 mmol), and $AgNO_3$ (0.170 g, 1.0 mmol) were dissolved in 2 mL of acetonitrile and 8 mL of distilled water with stirring at room temperature. The cloudy solution was put into a 25 mL Teflon-lined Parr, heated to 160 °C for 3500 min, and then cooled to room temperature at a rate of 3 °C h^{-1}. Colorless crystals of **3** were obtained in 39% yield (based on Hptz). Anal. Calcd for $C_{44}H_{30}Ag_{12}N_{26}O_{40}SiW_{12}$ (%): C, 10.38; H, 0.59; N, 7.15. Found: C, 10.89; H, 0.67; N, 7.66. IR for **3** (KBr, cm^{-1}): 3440 (s), 3062 (w), 2107 (w, CN), 1610 (m), 1515 (w), 1444 (w), 1277 (w), 1244 (w), 1069 (w), 1012(s), 974 (w), 911 (s), 873 (w), 792 (s).

Synthesis of $[Ag_{19}(ptz)_8(H_2ptz)(H_3ptz)(AgP_5W_{30}O_{110})\cdot 7H_2O]_n$ ***(4)***. $(NH_4)_{14}[NaP_5W_{30}O_{110}]\cdot nH_2O$ (0.3 g, 0.036 mmol), Hptz (0.072 g, 0.5 mmol), and $AgNO_3$ (0.170 g, 1.0 mmol) were dissolved in 10 mL of distilled water with stirring at room temperature. The cloudy solution was put into a 25 mL Teflon-lined Parr, heated to 160 °C for 5000 min, and then cooled to room temperature at a rate of 3 °C h^{-1}. Yellow block crystals (0.256 g) of **4** were obtained in 47% yield (based on $AgNO_3$). Anal. Calcd for $C_{70}H_{69}Ag_{20}N_{40}O_{117}P_5W_{30}$ (%): C, 7.53; H, 0.62; N, 5.02. Found: C, 7.36; H, 0.79; N, 5.29. IR for **4** (KBr, cm^{-1}): 3438 (s), 3053 (w), 1603 (s), 1483(w), 1446 (m), 1383 (w), 1283 (w), 1247 (w), 1153 (w), 1072 (s), 1016 (w), 916(s), 785(s).

Crystal Structure Determination. Data of compounds **1** and **4** were collected on a Rigaku R-AXIS SPIDER IP CCD area detector with monochromatic Mo Kα radiation (λ = 0.710 73 Å) at 173 K. Data of compounds **2** and **3** were collected on a Bruker SMART Apex CCD diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.710 73 nm) at 298 and 173 K, respectively. Absorption corrections were applied by using the multiscan program SADABS.[16a] The structures were solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL-97 program.[16b,c] The hydrogen atoms of the organic ligands were generated geometrically (C−H, 0.96 Å; N−H, 0.90 Å). Crystal data as well as details of data collection and refinement for the compounds **1**−**4** are summarized in Table 1. Selected bond lengths and angles for **1**−**4** are listed in Supporting Information Table S1−S4. Crystallographic data in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. 957497 for **1**, 957498 for **2**, 957499 for **3**, and 957500 for **4**.

■ RESULTS AND DISCUSSION

Synthesis of Compounds 1−4. The study of polyoxometalate (POM)-based coordination polymers has been a field of rapid growth in coordination chemistry. A large number of POM-based coordination polymers have been reported.[17] However, POM-based silver coordination polymers including Ag(I)⋯π interactions are very rare.[14] Herein, four 3D POMs-based silver coordination polymers, including four types of Ag(I)⋯π interactions, have been obtained by the reaction of

$AgNO_3$, Hptz ligand, and four types of polyoxometalates ($PW_{12}O_{40}^{3-}$ for **1**, $PMo_{12}O_{40}^{3-}$ for **2**, $SiW_{12}O_{40}^{4-}$ for **3**, and $P_5W_{30}O_{110}^{15-}$ for **4**). The structural analyses reveal that the different POMs have a great influence on the type of Ag(I)···π interactions and the whole structures. Because $PW_{12}O_{40}^{3-}$ and $PMo_{12}O_{40}^{3-}$ have the same charge and the volume, compounds **1** and **2** are isomorphs. The distances of Ag(I)···π interactions in **1** and **2** are also similar. When using the $SiW_{12}O_{40}^{4-}$ in place of $PW_{12}O_{40}^{3-}$ and $PMo_{12}O_{40}^{3-}$ anion, the different structure of **3** was obtained, and the distances of Ag(I)···π interactions became obviously shorter than those of **1** and **2**. For compound **4**, the distinct structure and novel Ag(I)···π interactions in o/m/p-η^3 modes were observed in presence of the Preyssler-type $NaP_5W_{30}O_{110}^{14-}$ anion.

The nature of the solvent have a great influence on the relative strength of the cation···π interaction.[13a] Most Ag···π directed coordination compounds were prepared in low-polarity organic solvents.[13] Compounds **1**, **2** and **4** were synthesized in 10 mL of distilled water, while compound **3** was prepared in 2 mL acetonitrile and 8 mL distilled water. Notably, such Ag(I)···π interaction based coordination compounds formed in aqueous media have been seldomly observed.[14]

*Crystal Structure of $[Ag_{17}(ptz)_{11}(PW_{12}O_{40})_2]_n$ (**1**).* Crystal structural analysis shows that **1** consists of 11 ptz^- ligands, 17 Ag^+ ions, and 2 $PW_{12}O_{40}^{3-}$ anions. As shown in Figure 1a, Ag3, Ag6, Ag7, and Ag8 are linked by ptz^- ligands, forming a 1D chain of $[Ag(ptz)]_n$. Adjacent chains are connected by Ag1, Ag5, and ptz^- ligands through Ag−N bonds and Ag(I)···π interactions with o/m-η^2 mode (Ag5−C = 2.44(2)−2.49(2) Å), generating 2D silver-ptz networks (Figure 1b). The 3D frameworks $[Ag_{17}(ptz)_{11}]^{6+}$ of **1** can be viewed as a set of parallel 2D networks linked by Ag4 through Ag(I)···π interactions (Ag4−C = 2.52(3) Å) (Figure 1c) and Ag···Ag interaction (Ag1···Ag4 = 3.197(4) Å). The $PW_{12}O_{40}^{3-}$ anions locate on the voids of the 3D frameworks through Ag−O bond (Ag2−O = 2.464(17) Å; Ag4−O = 2.479(15) Å). The bond lengths of Ag−N are from 2.18(2) to 2.62(3) Å, comparable to those in the reported Ag-ptz-complexes.[18]

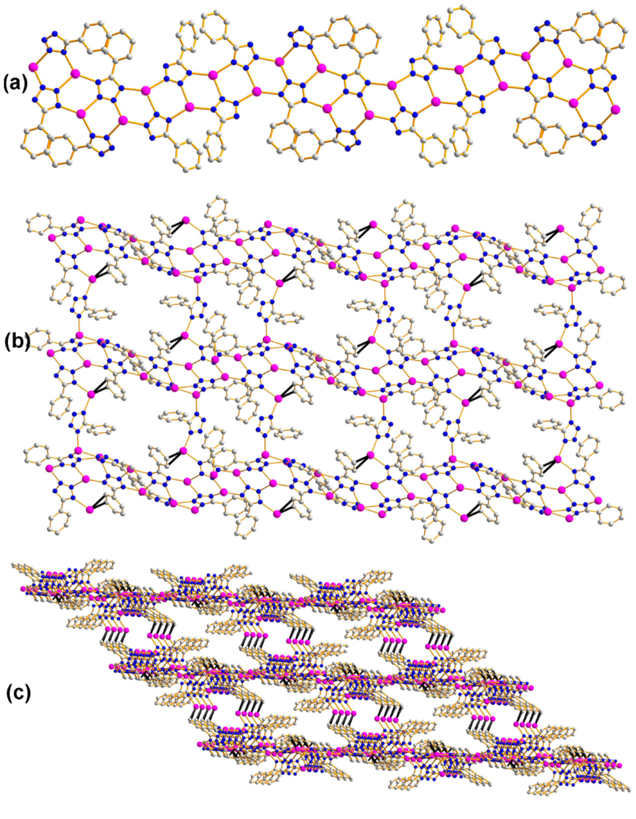


Figure 1. Ball and stick view of the 1D $[Ag(ptz)]_n$ chain (a), 2D network (b), and 3D $[Ag_{17}(ptz)_{11}]_n^{6n+}$ framework (c) of **1** (Ag, purple; C, gray; N, blue).

The coordination mode Ag(I)···π interactions are diversified. Two types of Ag(I)···π interactions in η^2 modes (m/p-η^2 and o/m-η^2) were found in **1**, as shown in the Scheme 1b and 1c, respectively. Besides, Ag(I)···Ag(I) (Ag1···Ag4 = 3.197(4) Å) and Ag(I)···π interactions, π···π interactions with the center-to-center distance from 3.72 Å to 3.94 Å were also observed in 1.

*Crystal Structure of $[Ag_{17}(ptz)_{11}(PMo_{12}O_{40})_2]_n$ (**2**).* Compound **2** was prepared using the same procedure as described for **1**, but using $H_3PMo_{12}O_{40}\cdot nH_2O$ in place of $H_3PW_{12}O_{40}\cdot nH_2O$. Compound **2** is isomorphic with **1**, with the main differences being the linking mode between adjacent 1D chains (Figure 2a for **1** and Figure 2b for **2**). In compound **2**, the adjacent chains are connected by Ag5, Ag8, and ptz^- ligands through Ag−N bonds (Ag8−N = 2.215(10)−2.297(10) Å) and Ag(I)···π interactions with o/m-η^2 and m-η^1 modes (Ag8−C = 2.438(12)−2.477(11) Å; Ag5−C = 2.681(18) Å), generating 2D silver-ptz networks (Figure 2c).

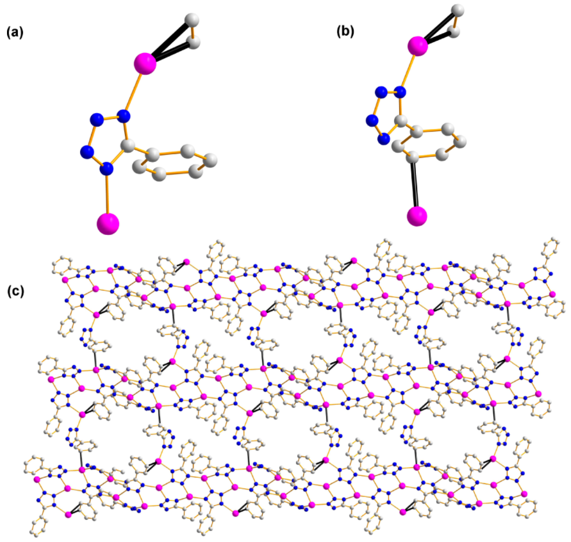


Figure 2. Ball and stick view of coordination mode of bridging ptz^- ligand linked the 1D chains (a) for **1** and (b) for **2**, and the 2D structure of **2** (c) (Ag, purple; C, gray; N, blue).

Three types of Ag(I)···π interactions modes (m-η^1, o/m-η^2 and m/p-η^2) were observed in **2**, as shown in the Scheme 1a-c. Besides, Ag(I)···Ag(I) (Ag6···Ag9 = 3.205(4) Å) and π···π weak interactions with center-to-center distance from 3.386 to 3.876 Å were found in **2**.

*Crystal Structure of $[Ag_{12}(ptz)_6(CN)_2(SiW_{12}O_{40})]_n$ (**3**).* Compound **3** contains 6 ptz^- ligands, 12 Ag^+ ions, 2 $SiW_{12}O_{40}^{4+}$ ions, and 2 CN^- ions, which generate from the *in situ* decomposition of acetonitrile. As shown in Figure 3a, Ag2, Ag5, Ag6, and Ag7 are linked by ptz^- ligands, forming a 1D chain of $[Ag(ptz)]_n$. Adjacent chains are connected by Ag8, Ag5, and ptz^- ligands through Ag−N bonds (Ag3−N = 2.20(2)−2.244(17) Å), generating 2D silver-ptz networks (Figure 3b). A set of parallel 2D networks further extend into a 3D frameworks

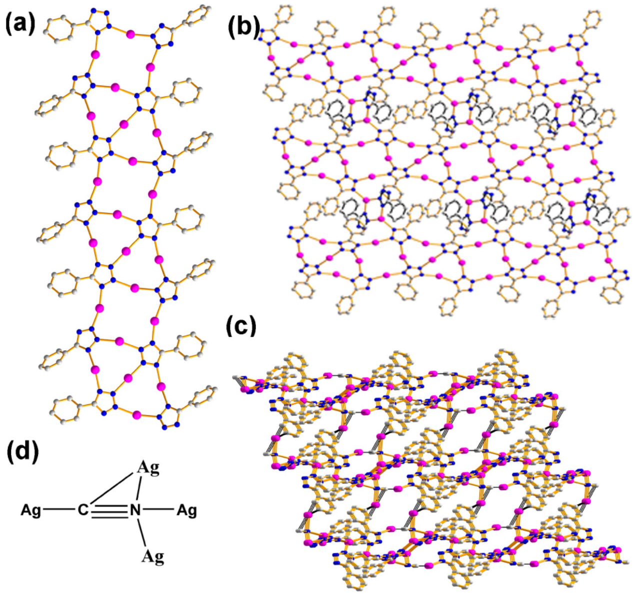


Figure 3. Ball and stick view of the 1D chain (a), 2D network (b), 3D framework (c) of **3**, and the coordination modes of CN^- in **3** (d) (Ag, purple; C, gray; N, blue).

$[Ag_{12}(ptz)_6(CN)_2]^{4+}$ through the connection of Ag(I)···π interactions in o/m-η^2 mode (Ag1−C = 2.16(5)−2.17(6) Å), Ag···Ag interaction (Ag6···Ag2=3.369(2) Å), and the Ag···CN^- interactions in $\mu_4(\eta^2{:}\eta^3)$ mode, as shown in Figure 3c. The $SiW_{12}O_{40}{}^{4-}$ anions locate on the voids of the 3D frameworks through Ag−O bond (Ag1−O = 2.545(19) Å; Ag5−O = 2.598(16) Å; Ag7−O = 2.461(16) Å).

The IR spectrum of **3** shows one band at 2107 cm^{-1}, which can be assigned to the $\nu_{(CN)}$ stretching vibration of the CN^- species. The $\nu_{(CN)}$ (2080 cm^{-1}) of free CN^- ion in water shifts to lower energy than that $\nu_{(CN)}$ stretching vibration for CN^- complexes, which was attributed to the weak σ donation of the strongly antibonding lone pair on CN^- to the metal.[19] The coordination behaviors of CN^- are shown in Figure 3d. It is noteworthy that CN^- ion acts as not only σ donor but also π donor, similar to $C_2{}^{2-}$ ion in well-studied silver acetylides.[20] We also searched the coordination mode of CN^- in CSD,[21] and no precedent of mixed σ and π bonding modes for CN^- was found. This novel coordination mode of CN^- ion is first reported here.

Crystal Structure of $[Ag_{19}(ptz)_8(H_2ptz)(H_3ptz)(AgP_5W_{30}O_{110})\cdot 7H_2O]_n$ (4). Compound **4** consists of 8 ptz^- ligands, 1 H_2ptz and 1 H_3ptz ligands, 19 Ag(I) ions, 1 Preyssler-type $AgP_5W_{30}O_{110}{}^{14-}$ anion, and 7 water molecules. As shown in Figure 4a, Ag3, Ag8, Ag11, and ptz^- form a Ag_3 building block, which is further connected by Ag5 and Ag7 through Ag−N bonds [Ag5−N = 2.094(10) Å; Ag7−N = 2.135(10)−2.156(10)], resulting in a 2D silver-ptz network (Figure 4b). The 2D structure can be simplified to a 6^3-hcb network based on the Ag_3 building block as three-connected node.

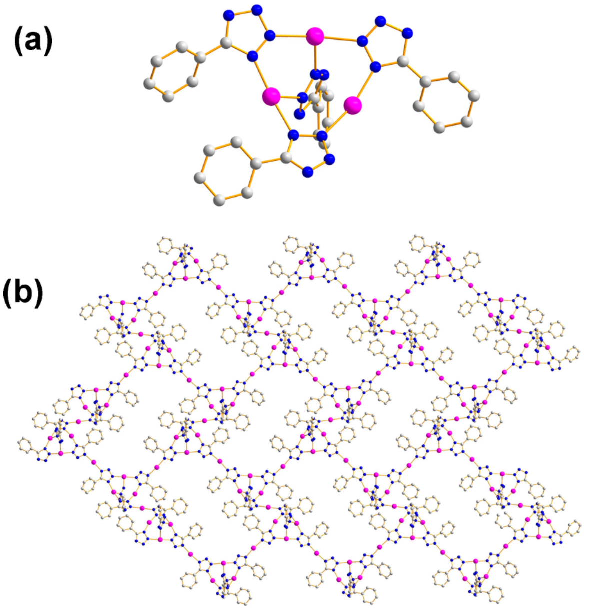


Figure 4. Ball and stick view of Ag_3 building block (a) and 2D 6^3-**hcb** network (b) of **4** (Ag, purple; C, gray; N, blue).

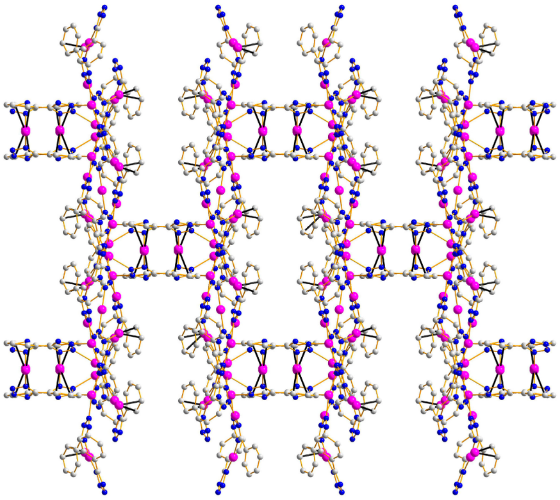


Figure 5. Three-dimensional framework constructed by Ag···π interactions in **4** (Ag, purple; C, gray; N, blue).

The 3D frameworks $[Ag_{19}(ptz)_8(H_{2.5}ptz)_2]^{14+}$ of **4** can be viewed as a set of parallel 2D networks linked by ptz ligand and Ag2 through Ag2···π interactions in o/m-η^2 mode and Ag10 through Ag10···π interactions in o/m/p-η^3 mode (Figure 5). The bond lengths of Ag2−C in o/m-η^2 mode are from 2.454(13) to 2.705(14) Å, while the bond lengths of Ag10−C in o/m/p-η^3 mode are from 2.374(14) to 2.7953(4) Å, which are shorter than the sum of van der Waals radii (3.11 Å) of Ag(I) ion and carbon atom.[22] Notably, the η^3 π-donor behavior of aryl ligands is uncommon. There are also Ag(I)···Ag(I) interactions with distances of 3.046(4)−3.3309(14) Å, which are shorter than twice the van der Waals radius of the silver of 3.44 Å.[23] The $AgP_5W_{30}O_{110}{}^{14-}$ anions locate on the voids of the 3D frameworks through Ag−O bond (Ag2−O = 2.444(9) Å; Ag7−O = 2.547(8) Å; Ag8−O = 2.593(8) Å; Ag9−O = 2.292(9)−2.541(8) Å; Ag10−O = 2.500(8) Å), as shown in Supporting Information Figure S3.

Notably, in compound **4**, one disordered Ag(I) replaced the encrypted Na^+ of the Preyssler-type $[NaP_5W_{30}O_{110}]^{14-}$ anion, forming an unprecedented $[AgP_5W_{30}O_{110}]^{14-}$ unit (Figure 6). As we have known, the Preyssler heteropolyoxoanion, $[NaP_5W_{30}O_{110}]^{14-}$, has attracted much attention since it was structurally resolved through X-ray diffraction by Pope and coworkers.[15] Its central Na^+ cation can be replaced by other ions with similar size, such as trivalent lanthanides and tetravalent actinides, under hydrothermal conditions.[24] However, encapsu-

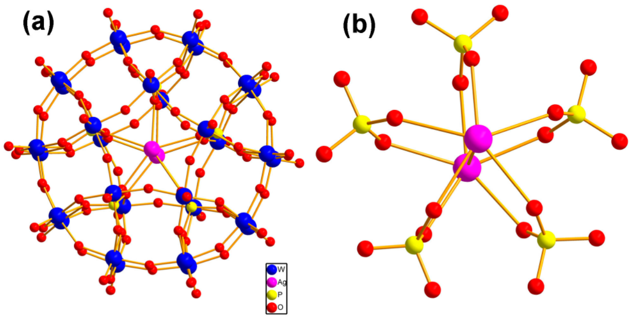


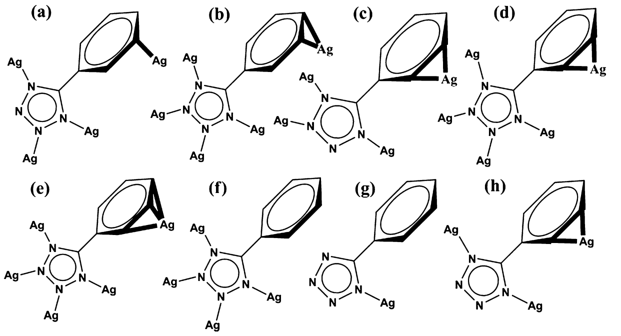
Figure 6. Ball and stick view of $AgP_5W_{30}O_{110}{}^{14-}$ (a) and the coordination mode of disordered Ag(I) in $AgP_5W_{30}O_{110}{}^{14-}$ of **4** (b).

lation of Ag(I) into Preyssler anion has not been reported up to now, maybe due to the ionic radii of Ag(I) being mismatched with the size of the interior cavity.

Ag(I)···π Interactions in ***1−4***. The versatile coordination behavior of ptz^- ligands makes the formation of diverse structures possible. As shown in Scheme 1, the ptz^- ligands display four types of Ag(I)···π interactions coordination modes: type I, the ptz^- coordinate one Ag(I) only with *m*-position of phenyl group (η^1); type II, one ptz^- connects one Ag(I) upon *m*- and *p*-position of phenyl group (η^2); type III, ptz^- ligand links one Ag(I) with *o*- and *m*-position of phenyl group (η^2); type IV, one ptz^- combines one Ag(I) upon *m*-, *p*-, and *o*-position of phenyl group (η^3). Besides the Ag(I)···π interactions of ligands, the coordination bonds and π···π interactions also contribute to the stability of the resulting 3D supramolecular framework.

The coordination modes of ptz^- ligands for compounds **1−4** are summarized in Scheme 2. Four types of coordination modes (b, d, f and h) were found in compound **1**, while five types of coordination modes (a, b, d, f and h) were exit in compound **2**. The ptz^- ligands in **3** adopt coordination modes c and f. For **4**, there are four types of coordination modes (d, e, f and g) for ptz^- ligands.

Scheme 2. Eight Types of Coordination Modes of ptz^- Ligand in Compounds 1−4



Photoluminescent Properties. The emission spectra of compounds **1**, **2**, **4**, and the free Hptz ligand in solid state at room temperature are shown Figure 7. It can be observed that the free Hptz ligand exhibits intense photoluminescence with an emission maximum at ca. 319 and 413 nm upon excitation at 270 nm. The emission of compounds **1** and **2** can be observed at ca. 491 and 500 nm, respectively, with the excitation at 320 and 330 nm. When excited at 365 nm in the solid state at room temperature, compound **4** displays a wide luminescence spectrum with two emission maximum at ca. 417 and 498 nm.

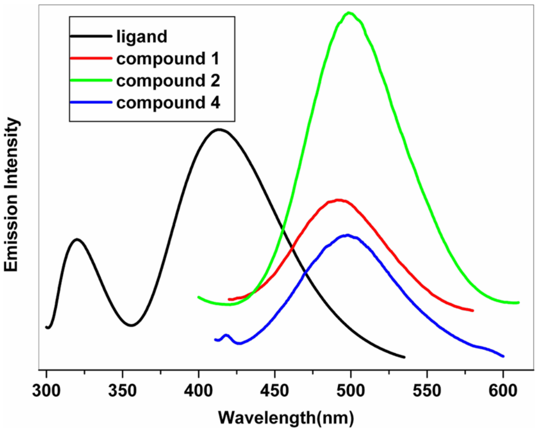


Figure 7. Emission spectra of Hptz ligand, **1**, **2**, and **4** in the solid state.

They would originate from intraligand πL → πL* transition emission (LLCT).[18,25] Compared with the emission of the free ligand, the strong red shift in compounds **1**, **2**, and **4** may be ascribed to the increase of the ligand conformational rigidity, which is due to the coordination to Ag(I) ions and deprotonation of the ptz^- ligand resulting in a decrease of the nonradiative decay of intraligand excited states.

■ CONCLUSION

In summary, four 3D POM-based silver coordination polymers have been synthesized under hydrothermal conditions. Four types of Ag(I)···π interactions, m-η^1, m/p-η^2, o/m-η^2, and o/m/p-η^3, were observed in compounds **1−4**, depending on the polyoxometalates used. The different POMs have a great influence on the type of the Ag(I)···π interaction. The *in situ* generated CN^- ion in compound **3** shows unprecedented mixed σ and π bonding modes, similar to $C_2{}^{2-}$ ion in well-studied silver acetylides. An unprecedented Preyssler-type $[AgP_5W_{30}O_{110}]^{14-}$ anion was observed first in compound **4**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format, Tables S1−S9, additional figures of the structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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