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Novel Silver-Containing Supramolecular Frameworks Constructed by Combination of Coordination Bonds and Supramolecular Interactions

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The hydrothermal reactions of $AgNO_3$, 4,4′-bipy, and carboxylate ligands gave rise to three supramolecular architectures, namely $[Ag(bipy)]\cdot H_2SIPA\cdot 1/2bipy\cdot H_2O$ (**1**), $[Ag(bipy)]\cdot 1/2H_2btec\cdot H_2O$ (**2**), and $[Ag(bipy)]_2\cdot H_2dpstc\cdot 2H_2O$ (**3**) (H_3SIPA = 5-sulfoisophthalic acid, bipy = 4,4′-bipyridine, H_4btec = 1,2,4,5-benzenetetracarboxylic acid, H_4dpstc = 3,3′,4,4′-tetracarboxydiphenyl sulfone). All complexes are extended from Ag–bipy linear chains by the combination of coordination bonds and supramolecular interactions in two different approaches. Complexes **1** and **3** comprise two-dimensional frameworks. In the two complexes, a one-dimensional ladderlike structure is first formed by the connection of a Ag–bipy chain through hydrogen bonding between a free carboxylate/bipy ligand and weak coordinative interactions between a free carboxylate ligand and silver ion. The ladderlike structure is then extended to a two-dimensional layer architecture by $\pi\cdots\pi$ interactions between bipy ligands of the Ag–bipy chains. Complex **2** possesses a three-dimensional framework. The free H_2btec^{2-} ligands form a two-dimensional layer network by hydrogen-bonding interactions between protonated and deprotonated carboxylate groups; meanwhile, $\pi\cdots\pi$ interactions between bipy ligands of Ag–bipy chains also result in a two-dimensional layer. The two layers are further connected by weak Ag–O interactions to generate a three-dimensional supramolecular structure.

Introduction

Supramolecular chemistry and crystal engineering are active fields of chemistry due to the novel structural topologies examined and potential applications in host–guest chemistry, catalysis, and electrical conductivity.[1] In the past decades, the development of supramolecular assembled chemistry allows the possibility to rationally design and prepare supramolecular architectures through noncovalent interactions, in which it is crucial to meet both geometric as well as energetic considerations.[2] Recently, a lot of supramolecular assemblies have been achieved by carefully selecting building blocks and organic ligands containing appropriate functional groups through supramolecular interactions (hydrogen bonding, $\pi\cdots\pi$ interactions etc.).[3] Three main lines of research have been followed, based on the basic building blocks as well as the supramolecular interactions. The first line is the extended supramolecular architecture derived from organic ligands, such as carboxylate, pyridine, or their derivatives, etc., through intermolecular hydrogen-bonding or $\pi\cdots\pi$ interactions. In this case, 1,3,5-benzenetricarboxylic acid is the most familiar research object and many supramolecular complexes via the self-assembly of 1,3,5-benzenetricarboxylic acid have been synthesized.[4−7] The second line is the high-dimensional supramolecular

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network extended from low-dimensional metal-containing molecules through hydrogen-bonding or weak coordinative interaction by free organic ligands in the molecules. The free organic ligands containing appropriate functional groups in the molecule play important roles in the formation of high-dimensional supramolecular architecture and in the stabilization of the whole structure.[8−10] The third line is the metal-containing hydrogen-bonded architecture. The existence of the hydrogen bond donor and acceptor in the metal-containing building block is the key in the construction of such supramolecular architectures.[11]

Doubtless, the hydrogen bond is the most familiar organizing force in supramolecular assembly due to its moderately directional intermolecular interaction that may control short-range packing,[5a] and many works have focused on the studies of hydrogen bond;[12] for example, the construction of a porous solid from hydrogen-bonded metal complexes of 1,3,5-benzenetricarboxylic acid with interesting properties has been achieved by Yaghi[13] and Munakata has described controlling the three-dimensional supramolecular channel-like copper compounds hosting a variety of anions by changing the hydrogen-bonding modes and distances.[14] However, other supramolecular interactions, such as $\pi\cdots\pi$ and weak coordinative interactions, etc., have been somewhat less documented, and only few examples generated by combination of multi supramolecular interactions have been reported.[15] Recently we began work on the construction of transition metal supramolecular complexes through combination of multi supramolecular interactions. Our 3-fold strategy was to select mixed ligands of benzoic carboxylates and multipyridines: (a) They are versatile ligands for coordination bonding. (b) They can provide hydrogen bond donors and acceptors. (c) Their aromatic rings may form $\pi\cdots\pi$ interactions. In this paper, we report three novel supramolecular silver(I) architectures, namely $[Ag(bipy)]\cdot H_2SIPA\cdot 1/2bipy\cdot H_2O$ (**1**), $[Ag(bipy)]\cdot 1/2H_2btec\cdot H_2O$ (**2**), $[Ag(bipy)]_2\cdot H_2dpstc\cdot 2H_2O$ (**3**) (H_3SIPA = 5-sulfoisophthalic acid, bipy = 4,4′-bipyridine, H_4btec = 1,2,4,5-benzenetetracarboxylic acid, H_4dpstc = 3,3′,4,4′-tetracarboxydiphenyl sulfone), constructed by combination of coordination bonds, hydrogen bonds, and $\pi\cdots\pi$ and weak coordinative interactions.

Experimental Section

Materials and Analyses. All chemicals used are as purchased without further purification. IR spectra were recorded on a Magna 750 FT-IR spectrophotometer as KBr pallets. Elementary analyses were carried out in the elementary analysis group of this institute.

Preparation of the Complexes. $[Ag(bipy)]\cdot H_2SIPA\cdot 1/2bipy\cdot H_2O$ (1). $AgNO_3$ (0.02 g, 0.125 mmol) and NaH_2SIPA (0.033 g, 0.125 mmol) were dissolved in 16 mL of distilled water by vigorous stirring. 4,4′-bipy (0.020 g, 0.125 mmol) was added to the mixture and stirred for 15 min, and then the pH value was adjusted to 6 by NaOH. After being stirred for another 15 min, the resulting solution was sealed in a Teflon-lined stainless autoclave and heated at 170 °C for 8 days under autogenous pressure and then cooled to room temperature during 10 h. Yellow prismlike crystals of **1** suitable for X-ray analysis were obtained in 45% yield. Anal. Calcd for $C_{23}H_{19}AgN_3O_8S$: C, 45.64; H, 3.16; N, 6.94. Found: C, 44.23; H, 3.05; N, 6.86. IR (KBr, cm^{-1}): 3469 (s), 3359 (m), 1699 (vs), 1601 (s), 1406 (m), 1300 (s), 1230 (s), 1217 (s), 1190 (vs), 1173 (s), 1041 (vs), 814 (vs), 621 (vs).

$[Ag(bipy)]\cdot 1/2H_2btec\cdot H_2O$ (2). $AgNO_3$ (0.040 g, 0.25 mmol) and 1,2,4,5-benzentetracarboxylic dianhydride (0.027 g, 0.125 mmol) were dissolved in 16 mL of distilled water by vigorous stirring. 4,4′-bipy (0.020 g, 0.125 mmol) was added to the mixture and stirred for 15 min. The resulting solution was sealed in a Teflon-lined stainless autoclave and heated at 120 °C for 3 days under autogenous pressure and then cooled to room temperature during 8 h. Colorless prismlike crystals of **2** suitable for X-ray analysis were obtained in 42% yield. Anal. Calcd for $C_{15}H_{12}AgN_2O_5$: C, 44.14; H, 2.96; N, 6.86. Found: C, 43.65; H, 2.92; N, 7.15. IR (KBr, cm^{-1}): 3406 (vs), 3047 (m), 1691 (s), 1597 (vs), 1564 (vs), 1493 (s), 1412 (s), 1363 (vs), 1327 (s), 1174 (m), 1140 (m), 1101 (m), 806 (vs), 760 (s), 702 (m).

$[Ag(bipy)]_2\cdot H_2dpstc\cdot 2H_2O$ (3). A mixture of $AgNO_3$ (0.040 g, 0.25 mmol), 3,3′,4,4′-tetracarboxydiphenyl sulfone dianhydride (0.045 g, 0.125 mmol), and 4,4′-bipy (0.025 g, 0.125 mmol) in 16 mL distilled water was sealed in a Teflon-lined stainless autoclave and heated at 120 °C for 4 days under autogenous pressure and then cooled to room temperature during 8 h. Light-yellow prismlike crystals of **3** were isolated in 65% yield. Anal. Calcd for $C_{36}H_{28}Ag_2N_4O_{12}S$: C, 45.21; H, 2.95; N, 5.86. Found: C, 45.21; H, 2.70; N, 6.10. IR (KBr, cm^{-1}): 3406 (vs), 3080 (m), 1689 (w), 1601 (vs), 1489 (m), 1356 (s), 1321 (s), 1221 (m), 1167 (s), 1092 (m), 1068 (s), 810 (vs), 771 (s), 727 (s), 640 (m).

Crystallographic Analyses. The intensity data for **1**−**3** were collected on a Siemens SMART CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation at room temperature. All absorption corrections were performed using the SADABS program.[16] The structures were solved by direct methods[17] and refined on F^2 by full-matrix least squares using the SHELXTL-97 program package[18] on a Legend computer. All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms on carbon atoms were generated geometrically (C−H = 0.96 Å), and those on oxygen atoms were derived from the successive difference Fourier syntheses. The crystallographic data for complexes **1**−**3** are listed in Table 1, and selected bonds and angles, in Table 2. Crystallographic data (excluding structure factors) for the

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Table 1. Crystallographic Data for Complexes **1**−**3**

param	**1**	**2**	**3**
empirical formula	$C_{23}H_{19}AgN_3O_8S$	$C_{15}H_{12}AgN_2O_5$	$C_{36}H_{28}Ag_2N_4O_{12}S$
fw	605.34	408.14	956.42
space group	$C2/c$	$C2/c$	$P2_1/c$
T (°C)	293	293	293
a (Å)	22.9357(1)	18.8461(1)	14.8153(2)
b (Å)	11.3993(6)	11.4196(4)	11.3098(2)
c (Å)	17.7305(9)	14.1240(4)	20.5755(4)
α (deg)	90	90	90
β (deg)	94.744(2)	114.040(2)	96.501(1)
γ (deg)	90	90	90
V (Å^3)	4619.8(4)	2776.0(1)	3425.4(1)
Z	8	8	4
ρ_{calcd} (g cm^{-3})	1.741	1.953	1.855
λ (Å)	0.710 73	0.710 73	0.710 73
μ (mm^{-1})	1.019	1.482	1.279
R_1	0.0897	0.0511	0.0724
wR_2	0.1483	0.1000	0.1297

Table 2. Selected Bonds and Angles for **1**,[a] **2**,[a] and **3**[c]

	Compound **1**		
S−O(2)	1.428(8)	Ag−N(1)	2.145(7)
S−O(3)	1.435(7)	Ag−N(2)$^{\#1}$	2.151(7)
S−O(1)	1.444(8)	N(2)−Ag$^{\#2}$	2.151(7)
S−C(11)	1.780(1)		
O(2)−S−O(3)	113.3(5)	O(3)−S−C(11)	106.6(5)
O(2)−S−O(1)	113.5(6)	O(1)−S−C(11)	105.4(5)
O(3)−S−O(1)	111.0(5)	N(1)−Ag−N(2)$^{\#1}$	174.6(3)
O(2)−S−C(11)	106.3(5)		
	Compound **2**		
Ag−N(2)$^{\#1}$	2.149(4)	Ag−N(1)	2.157(4)
N(2)$^{\#1}$−Ag−N(1)	179.13(18)	C(16)−N(2)−Ag$^{\#2}$	119.7(4)
C(11)−N(1)−Ag	123.4(4)	C(17)−N(2)−Ag$^{\#2}$	123.2(4)
C(20)−N(1)−Ag	120.6(4)		
	Compound **3**		
Ag(1)−N(1)	2.156(6)	Ag(2)−N(3)	2.139(7)
Ag(1)−N(2)$^{\#1}$	2.158(6)	Ag(2)−N(4)$^{\#1}$	2.139(6)
Ag(1)−O(1)	2.599(7)	S−O(10)	1.421(9)
Ag(1)−Ag(2)	3.299(1)	S−O(9)	1.423(8)
N(1)−Ag(1)−N(2)$^{\#1}$	168.6(3)	N(3)−Ag(2)−Ag(1)	82.1(2)
N(1)−Ag(1)−O(1)	85.9(3)	N(4)$^{\#1}$−Ag(2)−Ag(1)	103.4(2)
N(2)$^{\#1}$−Ag(1)−O(1)	97.5(3)	O(10)−S−O(9)	120.0(5)
N(1)−Ag(1)−Ag(2)	107.9(2)	O(10)−S−C(39)	108.6(4)
N(2)$^{\#1}$−Ag(1)−Ag(2)	82.6(2)	O(9)−S−C(39)	107.3(5)
O(1)−Ag(1)−Ag(2)	95.8(2)	O(10)−S−C(31)	108.6(5)
N(3)−Ag(2)−N(4)$^{\#1}$	174.1(3)	O(9)−S−C(31)	107.4(4)

[a] Symmetry transformations used to generate equivalent atoms: #1, x, $y - 1$, z; #2, x, $y + 1$, z. [b] Symmetry transformations used to generate equivalent atoms: #1, x, $y - 1$, z; #2, x, $y + 1$, z. [c] Symmetry transformations used to generate equivalent atoms: #1, x, $y - 1$, z.

structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Nos. 197798 for **1**, 197799 for **2**, and 200465 for **3**.

Thermal Gravimetric Analysis. Thermogravimetric analyses (TGA) were performed on a Delta Series TGA7 instrument. Powder samples were loaded into alumina pans and heated from room temperature to 800 °C under argon at a heating rate of 10 °C/min.

Results and Discussions

Syntheses. Our aim is to construct transition metal-containing supramolecular complexes through the combination of multi supramolecular interactions. It has been documented that two strategies can be applied for the construction of extended arrays of transition metal-containing molecules linked via supramolecular interactions; one is combining hydrogen bonds or other interactions with coordination chemistry, and the other is with organometallic π-arene chemistry.[19] In this work, we focus on the former one. Benzoic carboxylates and 4,4′-bipy have versatile coordination ability, the ability for providing hydrogen-bond donors and acceptors, and the possibility for forming $\pi\cdots\pi$ interactions;[20−22] hence, they are employed in our studies. Our synthetic approach is to utilize the reaction of a Ag(I) salt and 4,4′-bipy to form a 1D linear Ag−bipy chain,[23] which then is extended to high dimensional supramolecular networks via coordination bonds or supramolecular interactions provided by benzoic carboxylates.

Compared to the case for first-row transition metals, Ag−multicarboxylates have less been documented, probably because they often appear as insoluble salts that make structural analyses difficult. Although some polymeric complexes have been successfully assembled from the reactions of benzoic multicarboxylic acids with silver(I) salts at room temperature,[24,25] unknown precipitates often formed when mixing the silver(I) salts and carboxylate ligands, even by slow diffusion. Our strategy to avoid of the formation of unknown precipitates formed by silver salts and carboxylate ligands as well as the isolation of Ag−bipy chainlike complexes without carboxylate ligands is to introduce hydrothermal synthetic method in our reactions, which is a well-known technique for the construction of extended structures, such as zolites,[26] organic−inorganic hybrid materials,[27] and metastable compounds,[28] in crystalline form. We first determined the hydrothermal reaction of NaH_2SIPA,

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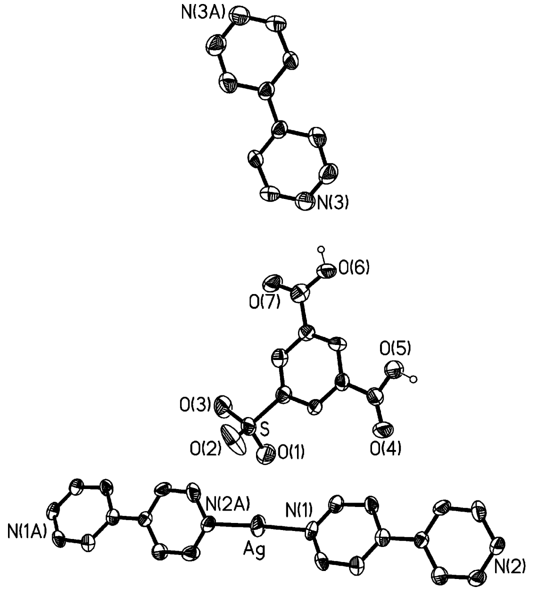
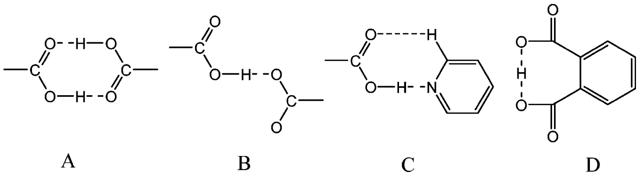


Figure 1. Coordination environment of the silver ion of **1** showing the free ligands with displacement ellipsoids at the 50% probability level.

Chart 1



4,4′-bipy, and $AgNO_3$. As expected, supramolecular complex **1**, extended from a linear Ag−4,4′-bipy chain and combination of supramolecular interactions provided by H_2SIPA^-, was successfully isolated in crystalline form in 45% yield. The successful isolation of **1** prompted us to extend our study to other carboxylates, and two similar complexes, **2** and **3**, also formed from Ag−bipy linear chains and supramolecular interactions were isolated in 42% and 65% yield, in the reactions of 1,2,4,5-benzentetracarboxylic dianhydride and 3,3′,4,4′-tetracarboxydiphenyl sulfone dianhydride systems, respectively. In the latter two reactions, the carboxylates comes from the hydrolysis of their dianhydrides followed by a deprotonation process. The hydrogen-bonding modes present in complexes **1**−**3** are listed in Chart 1.

Structural Description. [Ag(bipy)]·H_2SIPA·1/2bipy·H_2O (1). Complex **1** has a novel rectangular grid two-dimensional supramolecular network generated from combination of coordination bond, hydrogen bond, and $\pi\cdots\pi$ and weak coordinative interactions. The IR spectrum of **1** show four intense bands attributable to the $-SO_3$ group at 1230−1173 cm^{-1}, and the strong absorption peak around 1699 cm^{-1} is attributed to the −COOH group. As shown in Figure 1, there are two kinds of bipy that have different roles in the structure. One kind of bipy bridges silver(I) atoms directly to form a one-dimensional chain with the Ag−N distance being 2.145(7) Å and the dihedral angle of the two pyridine rings of bipy being 27.1°, while the other kind, with two pyridine rings being coplanar, does not take part in coordination and affords the hydrogen bond acceptor. Meanwhile, there also exists an uncoordinated carboxylate molecule, H_2SIPA^-, in which the sulfonate group is deprotonated and the two carboxylate groups are protonated (C−O distances of the two carboxylate groups being 1.217(11), 1.313(11) Å and 1.196(12), 1.321(11) Å, respectively), affording the hydrogen bond donor. As illustrated in Figure 2, the sulfonate oxygen atom (O(1)) makes a T-type linkage to the silver atom of the Ag−bipy chain at a weak bonding distance of 2.661 Å. One protonated carboxylate groups forms a strong hydrogen bond with the free bipy in a C fashion (Chart 1C) (N···O, H···N, N−H···O, C···O, H···O, C−H···O: 2.667 Å, 1.909 Å, 153.2°, 3.461 Å, 2.833 Å, 125.9°), and the other protonated carboxylate group fixes the free water molecule through strong hydrogen bonding (O···O distance: 2.637 Å), resulting in difficult removal of the water molecule from the molecule (see TGA part). Thus, the 1D Ag−bipy chain and the free bipy and H_2SIPA^- are engaged by hydrogen bonding as well as weak coordinative interactions to result in a one-dimensional ladderlike chain, in which the side pieces are formed by Ag−bipy chains and the rungs by bipy and H_2SIPA^- (Figure 2). It should be noted that the supramolecular synthon, pyridine-carboxylic acid motif, C (Chart 1C), is rare in the reported supramolecular architectures.[6] The C−H···O interactions may afford additional stability and rigidity for motif C, and this motif was previously used to design and prepare liquid-crystalline materials and 2D β networks.[29]

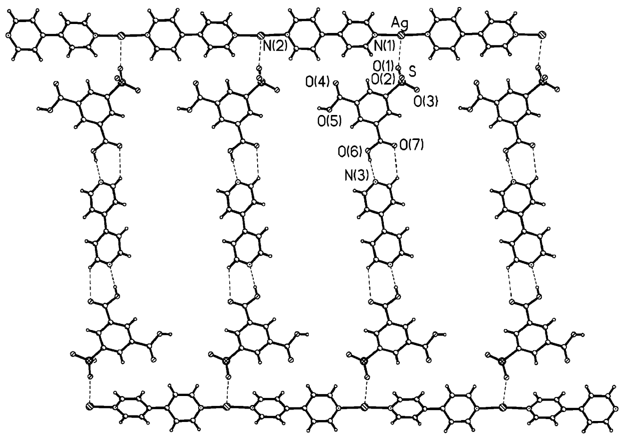


Figure 2. 1D ladderlike chain in **1**.

Aside from hydrogen bonds, the $\pi\cdots\pi$ interaction is another useful organizing force in supramolecular assembly.[30] In **1**, the $\pi\cdots\pi$ interactions (3.420 Å) between the pyridine rings of the Ag−bipy chain make the 1D ladderlike chain extend to a two-dimensional rectangular grid supramolecular architecture with the internal dimensions of the distorted quadrangle being 9.204 × 28.572 Å (Figure 3), much larger than that in [Cu(μ-4,4′-bipy)$(H_2O)_2(FBF_3)_2$]·4,4′-bipy generated only through hydrogen bonding of 4,4′-bipy (11.08 × 14.95 Å).[8]

[Ag(bipy)]·1/2H_2btec·H_2O (2). The replacement of H_2SIPA^- in **1** by H_2btec^{2-} results in the quite different structure of **2**. **2** has a three-dimensional supramolecular network connected by the combination of coordination bond,

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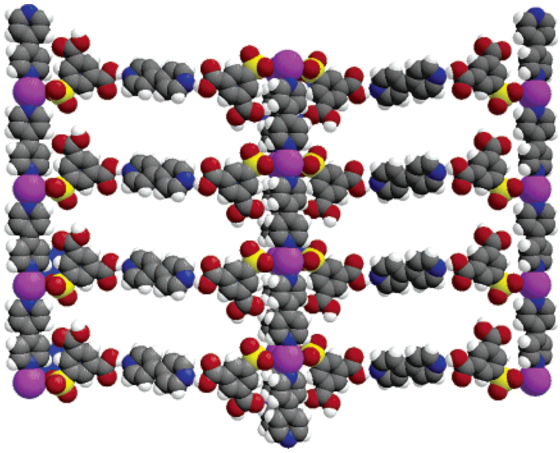

Figure 3. Space-filling representation of the 2D rectangular grid supramolecular architecture connected by $\pi\cdots\pi$ interactions in **1**.

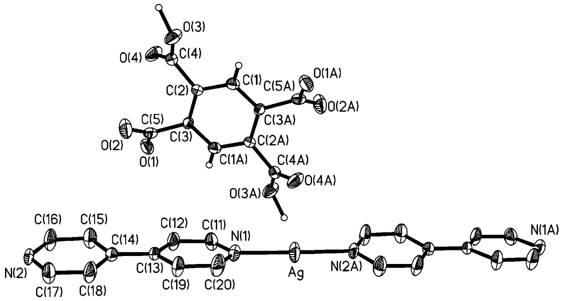

Figure 4. Coordination environment of the silver ion of **2** showing the free ligand with displacement ellipsoids at the 50% probability level.

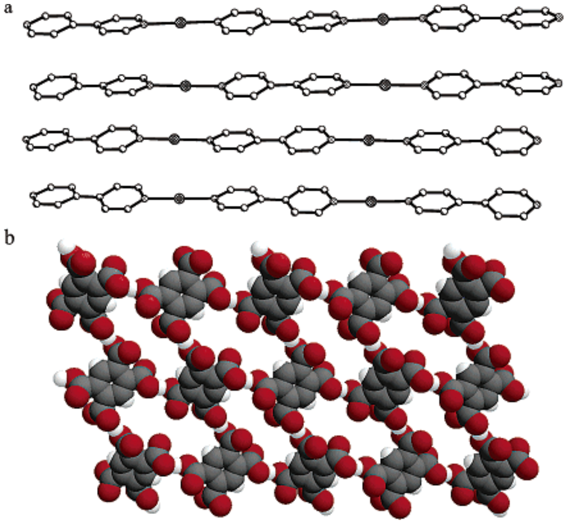

Figure 5. (a) 2D layer formed by $\pi\cdots\pi$ interactions of Ag−bipy chains in **2**. (b) Layer formed by hydrogen bonding of 1,2,4,5-benzentetracarboxylic acid in **2**.

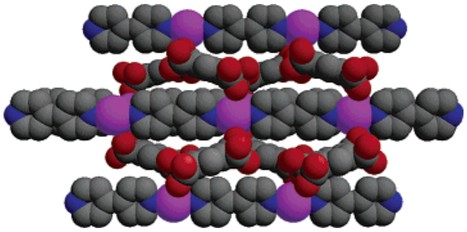

Figure 6. Space-filling representation of the 3D supramolecular architecture of **2** along the *c* axis.

hydrogen bond, and $\pi\cdots\pi$ and weak coordinative interactions. Figure 4 shows the coordination environment of the central silver ion and the free H_2btec^{2-}. Similar to **1**, bipy bridges silver(I) atoms directly to form a one-dimensional chain with the average Ag−N distance being 2.153(4) Å. The dihedral angle of the two pyridine rings of bipy is 8.0°, smaller than that in the Ag−bipy chain of **1**. There exist strong $\pi\cdots\pi$ interactions (from 3.310 to 3.670 Å) between the Ag−bipy chains, which result in a 2D layer structure (Figure 5a). The nearest distance of Ag−Ag is 3.577 Å, which is significantly longer than the van der Waals contact distance 3.40 Å, illustrating the lack of direct metal−metal contact between silver(I) ions. Each of two *para*-carboxylate groups is protonated, in agreement with the IR data in which a strong absorption peak around 1691 cm^{-1} for −COOH is observed. The H_2btec^{2-} ligand does not take part in coordination but balances the charge by its two deprotonated carboxylate groups and also provides a hydrogen bond acceptor and donor. Due to the steric hindrance, the four carboxylate groups may not lie in the phenyl ring plane;[21b,c] this results in the hydrogen-bonding motif B (Chart 1B) being quite different from that observed in 1,3,5-benzenetricarboxylic acid (Chart 1A),[7] in which the three carboxylate groups are almost coplanar. The strong hydrogen-bonding interactions between the carboxylate groups of H_2btec^{2-} (O····O distance: 2.531 Å) give rise to a two-dimensional layer with pores of dimensions 11.458 × 4.312 Å (Figure 5b). The free water molecule resides in the pores, and the hydrogen bonds between the deprotonated carboxylate oxygens and the free water molecules fall into longer distances from 2.925 to 2.957 Å, as compared to those observed in **1**. Interestingly, the oxygen atom of the protonated carboxylate group (C−O distances of the protonated carboxylate group are 1.211(6) and 1.312(7) Å, and those of the deprotonated carboxylate group are 1.240(7) and 1.257(7) Å) has a weak interaction with the silver ion in the Ag−bipy chain and a weak coordinative interaction at a longer range,[15] O····Ag (2.821 Å), engages the two layers to give rise to a 3D network, as shown in Figure 6.

$[Ag(bipy)]_2 \cdot H_2dpstc \cdot 2H_2O$ (3). X-ray diffraction shows **3** is a two-dimensional supramolecular framework connected by the combination of coordination bonds, hydrogen bonds, $\pi\cdots\pi$ interactions, and Ag−Ag weak interactions as well as weak coordinative interactions. As shown in Figure 7, two crystallographically independent silver(I) atoms are present: Ag1 and Ag2, which form two one-dimensional Ag−bipy chains by the connection of 4,4′-bipy, respectively. The dihedral angles of the two pyridine rings of bipy are 22.4 and 26.6° for the Ag1 and Ag2 chains, respectively. The two chains are engaged by the Ag−Ag weak interaction (Ag1−Ag2: 3.299 Å) as well as the $\pi\cdots\pi$ interactions (from 3.495 to 3.6038 Å) between the 4,4′-bipy in the two chains (Figure 8a). As found in **1** and **2**, the H_2dpstc^{2-} ligand does not take part in coordination but balances the charge by its two deprotonated carboxylate groups. Interestingly, there are two different hydrogen atoms existing per every two *ortho*-carboxylate groups. As shown in Figure 7, one of the two *ortho*-carboxylate groups, which are far apart from Ag−bipy

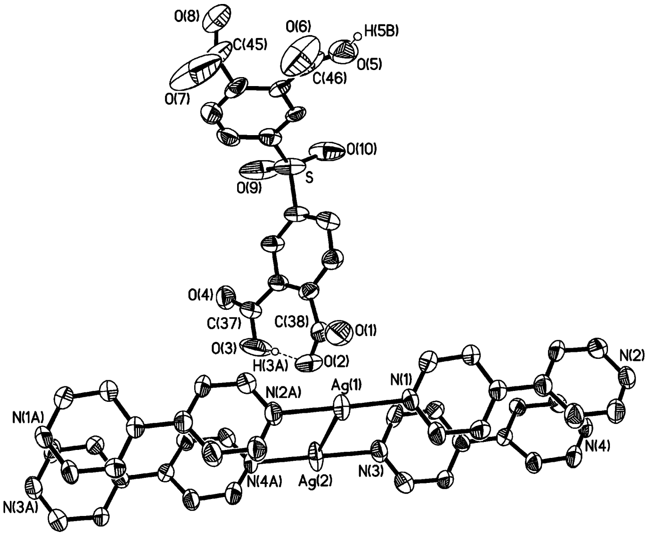

Figure 7. Coordination environment of the silver ion of **3** showing the free ligand with displacement ellipsoids at the 50% probability level.

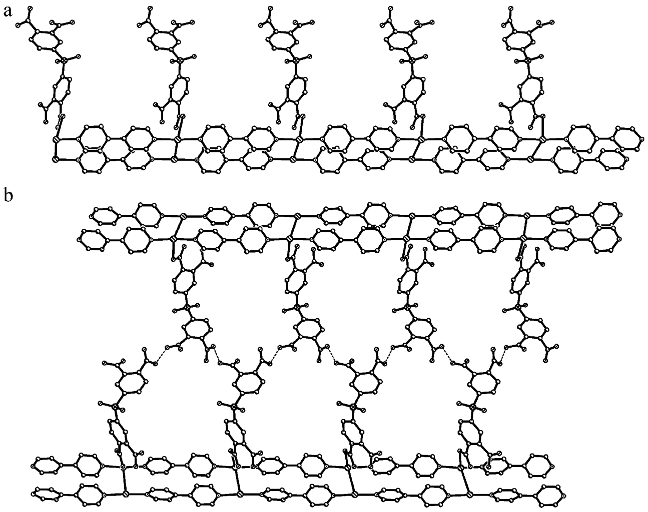

Figure 8. (a) One-dimensional Ag−bipy chain of **3** showing that the carboxylate ligand has weak coordination to the silver ion. (b) One-dimensional double-ladder structure in **3** generated from hydrogen-bonding and weak coordinative interactions.

chains, is protonated; however, an intramolecular hydrogen bond has been observed in the other *ortho*-carboxylate group (Chart 1D),[31] where the hydrogen atom is located toward the benzene ring and the distance of O(3)−O(2) is 2.337 Å, which is slightly shorter than those reported in other *ortho*-carboxylate groups.[32] The O(1) atom has a weak coordination to Ag1 with the Ag−O distance being 2.599 Å. The protonated and deprotonated carboxylate groups provide the hydrogen bond donor and acceptor, respectively, with the C−O distances of the deprotonated group being 1.208 and 1.219 Å and the C−O distances of the protonated group being 1.295 and 1.226 Å. Actually, the hydrogen-bonding interactions between the deprotonated (O(7)) and protonated (O(5)) carboxylate groups in B fashion (Chart 1B) link the 1D chain to generate a one-dimensional double-ladder structure with the O····O distance being 2.702 Å, as shown in Figure 8b.

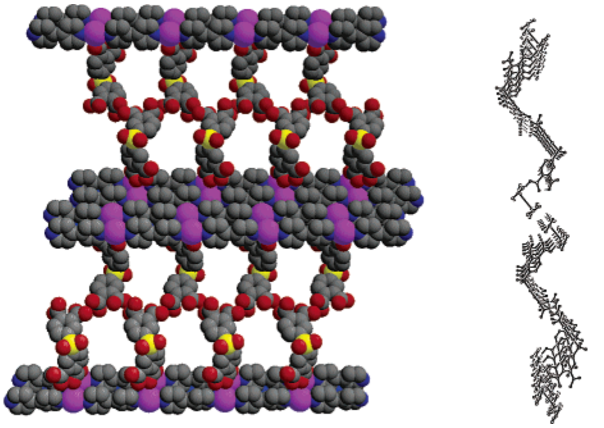

Figure 9. Two-dimensional layer generated from $\pi\cdots\pi$ interactions of bipy in Ag−bipy chains along the *c* axis (left) and the pucker structure along the *b* axis (right).

As in **1**, the weak $\pi\cdots\pi$ interactions (3.649 Å) between the 4,4′-bipy in the Ag2−bipy chains make **3** extend to a two-dimensional layer with pores of dimensions 9.624 × 8.577 Å (Figure 9). Actually, the layer is a pucker structure (Figure 9) due to the existence of the sulfoxide group in H_2dpstc^{2-}, which make the two benzene rings almost vertical to each other. The free water molecules are congregated near the carboxylate groups through hydrogen-bonding interactions with the O····O distances ranging from 2.684 to 2.975 Å.

Thermogravimetric Analyses (TGA). Thermogravimetric analysis (TGA) has determined the thermal stability of complexes **1**−**3**. For **1**, the weight loss of 3.06% from 101 to 234 °C is equivalent to the loss of one uncoordinated water molecule (H_2O/[Ag(bipy)]·H_2SIPA·1/2bipy·H_2O, calcd: 2.98%). A total weight loss of 12.67% is achieved from 241 to 310 °C, which corresponds to the loss of 0.5 uncoordinated 4,4′-bipy molecule/formula unit (0.5 bipy/[Ag(bipy)]·H_2SIPA·1/2bipy·H_2O, calcd: 12.98%). After 310 °C, the free H_2SIPA^- and the 1D Ag−bipy chain start to decompose and the decomposition ends above 800 °C. For **2**, the first weight loss of 3.98% from 98 to 174 °C is equivalent to the loss of the free water molecule (H_2O/[Ag(bipy)]·1/2H_2btec·H_2O, calcd: 4.40%) and the second weight loss of 29.77% from 189 to 280 °C corresponds to the loss of 0.5 uncoordinated H_2btec^{2-} molecule (0.5 H_2btec^{2-}/[Ag(bipy)]·1/2H_2btec·H_2O, calcd: 30.63%). After 270 °C, the 1D Ag−bipy chain starts to decompose and the decomposition ends above 800 °C. For **3**, the weight loss of 3.46% from 73 to 210 °C is equivalent to the loss of two uncoordinated water molecule (2 H_2O/$[Ag(bipy)]_2$·H_2dpstc·2H_2O, calcd: 3.76%); after 220 °C, the free H_2bpstc^{2-} starts to be released from the structure and ends about 280 °C, where the decomposition of the one-dimensional Ag−bipy chain starts.

In general, the free water molecules are fixed by organic ligands through hydrogen-bonding interactions and the strength of the hydrogen bond determines the temperature of the free water molecules releasing from the structure.[21b] TGA can provide an indication of the strength of the

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Table 3. Comparison of Stabilities of Supramolecular Interactions for **1**−**3**

compd	hydrogen-bonding dists (Å)	weak coordinative interactns (Å)	temp for lost free water (°C)	temp for lost free ligands (°C)
1	2.637, 2.724	2.661	234	241−310
2	2.531, 2.925−2.958	2.821	174	189−270
3	2.684−2.975, 2.702	2.599	210	220−280

hydrogen bond and other supramolecular interactions. On the basis of the thermal decomposition behavior of **1**−**3**, the stability of the supramolecular architectures constructed by the coordination bond and supramolecular interactions is obvious. First, as shown in Table 3, the temperatures for the loss of free water molecules are gradual increasing in the order **2**, **3**, and **1** (174, 210, and 234 °C, respectively). This is in agreement with the structural data. From **2**, to **3**, and then to **1**, the distances of hydrogen bond change from 2.925−2.957, to 2.684−2.975, and then to 2.637 Å, indicating the gradual increasing of the strength of hydrogen-bonding interactions, which increase the difficulty for removal of the water molecules from the structures (**2** < **3** < **1**).

Second, the temperatures for the loss of free organic ligands are also gradually increasing in the order **2**, **3,** and **1**. In **1**, as mentioned above, the C−H···O interactions may afford additional stability and rigidity to the supramolecular synthon (Chart 1C) and make the whole supramolecular network more stable than for **2** and **3**. Although the hydrogen-bonding interaction between carboxylate ligands in **2** (2.531 Å) is stronger than that in **3** (2.702 Å), **3** loses carboxylate ligand at a higher temperature than that for **2**. This may arise from the carboxylate oxygen atom in **3** having a stronger coordination to silver ion (2.599 Å) than that in **2** (2.821 Å). Hence, the release of H_2dpstc^{2-} in **3** from the molecule is more difficult than that of H_2btec^{2-} in **2**. Meanwhile, the strength of hydrogen bonds in **2** and **3** can also be reflected from the C−O distances of deprotonated carboxylate groups. In **2**, the hydrogen-bonding interaction is much stronger than that in **3**, which make the C−O distance elongated extremely and results in the C−O distances of the deprotonated carboxylate group in **2** (1.257 and 1.240 Å) being much longer than those in **3** (1.208 and 1.219 Å).

Conclusions

In conclusion, a new family of Ag-containing supramolecular architectures, **1**−**3**, has been successfully designed and synthesized from the extension of a Ag−bipy linear chain by the combination of coordination bonds, hydrogen bonds, $\pi \cdots \pi$ interactions, and Ag−Ag weak interactions as well as weak coordinative interactions in the reaction systems of benzoic carboxylate/4,4′-bipy/$Ag(NO_3)$. In **1**−**3**, the linear 1D Ag−bipy chains may be first formed through coordination bonds and the supramolecular interactions allow them to extend to higher dimensional architectures. To the best of our knowledge, **1** is the first two-dimensional supramolecular architecture that possesses large rectangular pores, constructed from two kinds of free organic ligands and 1D Ag−bipy chains through the linkage of coordination bonds and multi supramolecular interactions. The hydrogen-bonding supramolecular synthon C in **1** may play an important role to stabilize the two free molecules (H_2SIPA^- and bipy). TGA analyses prove well the stability of the three complexes. Although many coordination polymers have been widely studied on the basis of coordination bonds, a smaller number of examples focus on the combination of coordination bond and multi supramolecular interactions. In this work, the introduction of mixed ligands provides the probability of generating multiple binding forces,[33] such as coordination bonds, hydrogen bonding, and other supramolecular interactions. It may be believed that low-dimensional coordination polymers, such as the Ag−bipy chain described here, are good choices for the construction of novel porous materials through supramolecular interactions.[2b]

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Supporting Information Available: Three X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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