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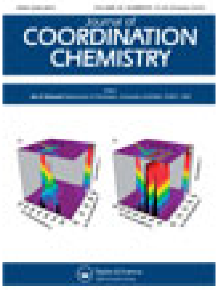

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Synthesis, characterization, and crystal structures of two Ag (I) coordination polymers based on biphenyl-2,2′,4,4′-tetracarboxylate

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Synthesis, characterization, and crystal structures of two Ag (I) coordination polymers based on biphenyl-2,2′,4,4′-tetracarboxylate

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In this article, $[Ag_8(btc)_2(2,2'\text{-bpy})_2]_n$ (**1**) and $[Ag_4(btc)(phen)_2]_n$ (**2**) (H_4btc = biphenyl-2,2′,4,4′-tetracarboxylic acid, 2,2′-bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline) have been synthesized under hydrothermal conditions and characterized by elemental analysis, IR spectra, thermogravimetric analyses, and single-crystal X-ray diffraction. Complex **1** shows a 3-D framework containing a 2-D bilayer network constructed from $(btc)^{4-}$ with Ag (I), whereas **2** features a 2-D supramolecular bilayer network. The differences of the two complexes demonstrate that nitrogen-containing chelating ligands have a significant effect on the formation and structure of the resulting complexes. Electrochemistry properties of **1** were also studied.

Keywords: Biphenyl-2,2′,4,4′-tetracarboxylate; Synthesis; Crystal structure

1. Introduction

The construction of inorganic–organic coordination polymers has attracted attention for potential as functional materials [1]. In construction of coordination polymers, polycarboxylate ligands, such as 1,4-benzenedicarboxylate [2], 1,3,5-benzenetricarboxylate [3], and 1,2,4,5-benzenetetracarboxylate [4], have been extensively employed in preparation of such complexes to generate multidimensional networks with interesting properties. Recently, biphenyltetracarboxylates, as an important subgroup of multicarboxylate ligands, have been investigated. Although many biphenyltetracarboxylate-bridged metal–organic frameworks (MOFs) of transition metals have been reported [5], those based on Ag (I) remain largely unexplored [6].

To extend our previous work [7] and fully understand the influence of the nitrogen-containing chelating ligands (2,2′-bpy and phen) on the assembly of biphenyltetracarboxylates and metal ions as well as the framework structures of their complexes, herein, we employed biphenyl-2,2′,4,4′-tetracarboxylic acid and Ag (I) incorporating 2,2′-bpy or phen as auxiliary ligand and obtained two complexes, $[Ag_8(btc)_2(2,2'\text{-bpy})_2]_n$ (**1**)

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and $[Ag_4(btc)(phen)_2]_n$ (**2**), which provide the first examples based on biphenyl2,2′,4,4′-tetracarboxylate-Ag (I).

2. Experimental

2.1. *Materials and methods*

All chemicals were commercially purchased and used as received. IR spectra were recorded as KBr pellets from 4000 to 400 cm^{-1} on a Bruker EQUINOX-55 spectrometer. Elemental analysis was determined with an Elementar Vario EL III elemental analyzer. Thermogravimetric analyses (TGA) were performed under nitrogen with a heating rate of 10°C min^{-1} using a NETZSCH STA 449F3 thermogravimetric analyzer. The X-ray powder diffraction (XRPD) pattern was recorded with a SHIMADZU XRD-7000 diffractometer.

2.2. *Syntheses*

2.2.1. Synthesis of $[Ag_8(btc)_2(2,2'\text{-bpy})_2]_n$ (1). A mixture of AgOAc (0.2 mmol), H_4btc (0.05 mmol), 2,2′-bpy (0.05 mmol), NaOH (0.2 mmol), and 10 mL H_2O was stirred for 30 min. The mixture was then placed in a 15 mL Teflon-lined stainless steel vessel and heated at 160°C for 3 days. Colorless block crystals were obtained when the mixture was cooled to room temperature. Yield: 36% based on Ag. Calcd for $C_{52}H_{28}Ag_8N_4O_{16}$ (%): C, 34.17; H, 1.54; N, 3.07. Found (%): C, 34.09; H, 1.57; N, 3.12. IR (KBr pellet, cm^{-1}): 3418 m, 1580 vs, 1472 w, 1409 m, 1358 s, 1243 w, 1154 w, 1002 m, 760 m, 690 m, 665 m, 423 w.

2.2.2. Synthesis of $[Ag_4(btc)(phen)_2]_n$ (2). The same synthetic method as that of **1** was used except that 2,2′-bpy was replaced by phen (0.1 mmol). Yield: 42% based on Ag. Calcd for $C_{40}H_{22}Ag_4N_4O_8$ (%): C, 42.97; H, 1.98; N, 5.01. Found (%): C, 42.65; H, 2.01; N, 5.09. IR (KBr pellet, cm^{-1}): 3424 m, 1574 vs, 1427 w, 1377 m, 1135 w, 1084 w, 995 m, 912 m, 830 m, 779 m, 734 m, 665 w, 633 w, 422 w.

2.3. *X-ray crystallography*

Intensity data were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K for **1** and 297(2) K for **2**. The structures were solved by direct methods and successive Fourier difference syntheses (SHELXS-97) and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHEXL-97) [8]. All hydrogen atoms were placed in calculated positions. The crystallography data and collected data for **1** and **2** are summarized in table 1. Selected bond lengths and angles are listed in table S1 and table S2.

Table 1. Crystal data and structure refinement for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{52}H_{28}Ag_8N_4O_{16}$	$C_{40}H_{22}Ag_4N_4O_8$
Formula weight	1827.74	1118.10
Wavelength (Mo-Kα) (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	11.3881(14)	15.4945(10)
b	13.8523(18)	15.3990(10)
c	15.613(2)	17.4359(9)
α	91.455(2)	90
β	91.979(2)	123.059(4)
γ	113.687(2)	90
Volume (Å^3), Z	2252.1(5), 2	3486.7(4), 4
Calculated density (Mg cm^{-3})	2.695	2.130
Absorption coefficient (mm^{-1})	3.489	2.277
F(000)	1744	2168
Reflections collected	11,771	17,317
Unique reflection	8101	6308
S on F^2	0.997	1.029
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.0553, 0.0994	0.0388, 0.0834
R_1, wR_2 (all data)	0.0847, 0.1120	0.0558, 0.0910

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

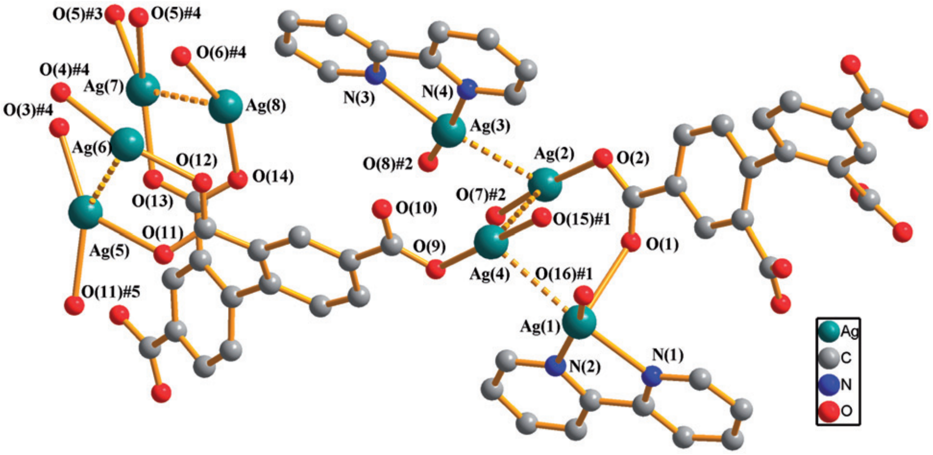

Figure 1. Coordination environment of Ag (I) in **1** (dotted lines indicate Ag···Ag interactions). All hydrogen atoms are omitted for clarity. Symmetry transformation codes: #1: x, y, $z-1$; #2: x, y, $z+1$; #3: $-x$, $-y$, $-z+1$; #4: $x-1$, y, $z+1$; #5: $-x$, $-y+1$, $-z+2$.

3. Results and discussion

3.1. *Crystal structures of 1 and 2*

X-ray analysis reveals that **1** crystallizes in the triclinic space group $P\bar{1}$ and is based on a 3-D framework containing a 2-D bilayer network constructed from $(btc)^{4-}$ with Ag (I). As shown in figure 1, the asymmetric unit of **1** contains eight Ag (I) ions, two $(btc)^{4-}$, and two 2,2′-bpy. In the asymmetric unit, eight unique Ag (I) ions display three types of coordination geometries. Ag (1) is coordinated by two oxygen atoms from two different $(btc)^{4-}$ ligands [Ag–O 2.588(7) and 2.188(6) Å] and two nitrogen atoms from one 2,2′-bpy ligand [Ag–N 2.371(8) and 2.216(7) Å] to furnish a distorted tetrahedral coordination. Different from those of Ag (1), Ag (2), Ag (4), Ag (6), and Ag (8) adopt angular coordination and are coordinated by two oxygen atoms from two different $(btc)^{4-}$ ligands [Ag–O 2.135(6)–2.167(6) Å], respectively. The remaining Ag (3), Ag (5), and Ag (7) exhibit a T-shaped coordination. Ag (3) is coordinated by one oxygen from one $(btc)^{4-}$ [Ag–O 2.152(6) Å] and two nitrogen atoms from one 2,2′-bpy ligand [Ag–N 2.382(8) and 2.200(7) Å]. Ag (5) and Ag (7) are coordinated by two oxygen atoms from two different $(btc)^{4-}$ ligands [Ag–O 2.275(7)–2.377(6) Å], respectively. All Ag–O and Ag–N bond lengths are in the normal ranges [9]. There are two kinds of Ag–Ag interactions in this unit: Ag–Ag distances [Ag (5)–Ag (6) = 2.8247(11) Å and Ag (7)–Ag (8) = 2.8051(12) Å] are significantly shorter than that (2.88 Å) in metallic silver [10], indicating strong Ag–Ag contact and Ag–Ag distances [Ag (1)–Ag (4) = 3.0073(11) Å, Ag (2)–Ag (3) = 2.9268(11) Å, and Ag (2)–Ag (4) = 3.1606(12) Å], below the sum of van der Waals radii (3.44 Å), which indicate a weak Ag–Ag interaction. The four Ag ions [Ag (1), Ag (2), Ag (3), and Ag (4)] are coplanar and form a tetranuclear $[Ag]_4$ chain [Ag (1)–Ag (4)–Ag (2)–Ag (3)].

Two independent $(btc)^{4-}$ ligands show different coordination modes, as shown in figure S1(a) and (b). One $(btc)^{4-}$ is an enneadentate ligand with one bridged-tridentate carboxylate and three bis-monodentate carboxylates. The other $(btc)^{4-}$ is a heptadentate ligand wherein one carboxylate is monodentate and the remaining three carboxylates have bis-monodentate coordination. The Ag (I) ions are linked by $(btc)^{4-}$ to form a 2-D bilayer network, which is further consolidated by tetranuclear $[Ag]_4$ chains (figure 2). Then these 2-D bilayer networks are linked by Ag–O bonds [Ag (5)–O (11) and Ag (7)–O (5) #3, or their symmetry related atoms] to generate a 3-D framework (figure 3).

When a larger aromatic ligand, phen, was employed instead of 2,2′-bpy, a 2-D supramolecular bilayer network **2** was obtained. The fundamental building unit of **2** consists of four Ag (I) ions, one $(btc)^{4-}$, and two phen. As shown in figure 4, four unique Ag (I) ions display three types of coordination geometries. Ag (1) and Ag (4) are coordinated by one oxygen from different $(btc)^{4-}$ ligands [Ag–O 2.238(3) Å and 2.218(3) Å] and two nitrogen atoms from two phen ligands [Ag–N 2.257(5)–2.393(5) Å] to result in T-shaped coordination. Ag (2) is coordinated by four oxygen atoms from three different $(btc)^{4-}$ ligands [Ag–O 2.283(3)–2.402(3) Å] to furnish a distorted tetrahedral coordination. The remaining Ag (3) is coordinated by two oxygen atoms from two different $(btc)^{4-}$ ligands [Ag–O 2.151(3) and 2.135(3) Å] to form a distorted tetrahedral coordination. The three Ag ions [Ag (2), Ag (3), and Ag (4)] are coplanar and form a trinuclear $[Ag]_3$ chain unit [Ag (2)–Ag (3)–Ag (4), Ag (2)–Ag (3) = 2.8348(5) Å, Ag (3)–Ag (4) = 3.0591(7) Å].

The $(btc)^{4-}$ shows two different coordination modes (bis-monodentate coordination for 4(4′)-carboxylate groups, monodentate and bis-monodentate coordination for 2(2′)-carboxylates, figure S1c). Ag (I) ions are linked by $(btc)^{4-}$ to form a 1-D double-chain structure. The phen ligands are alternate at the two sides of the double chain. The chains are further interconnected to form a 2-D supramolecular bilayer network by π–π contacts of phen ligands between adjacent chains (the centroid–centroid distance of phen rings is 3.632 Å) (figure 5).

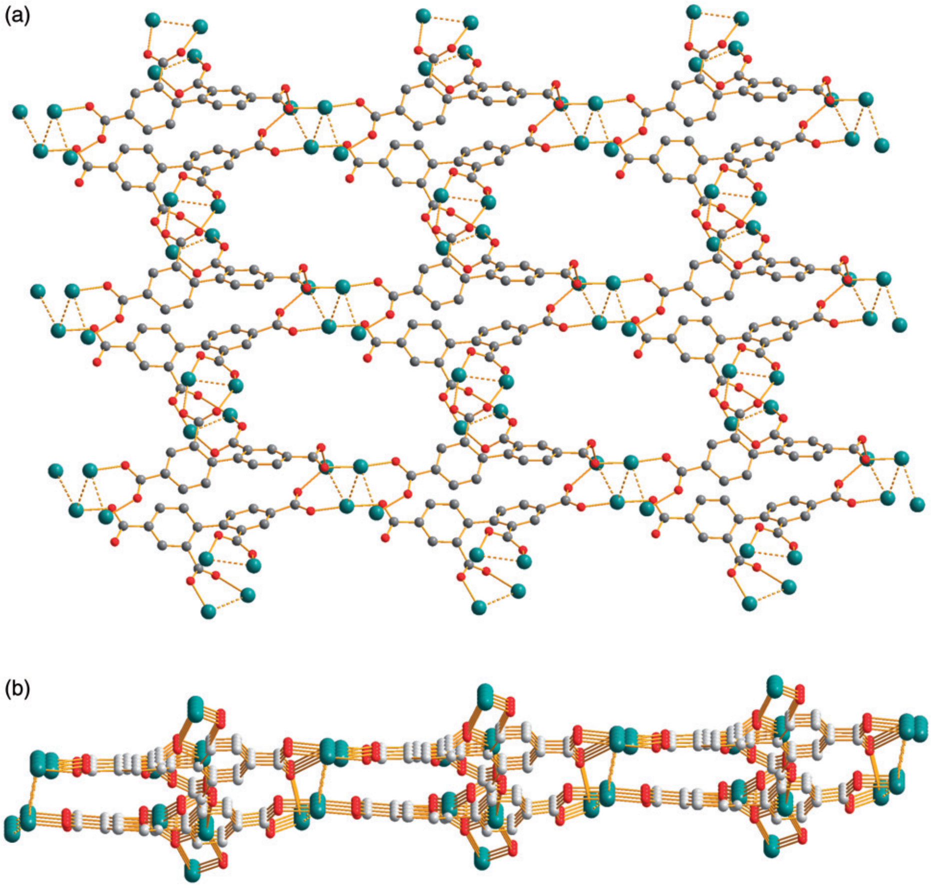

Figure 2. (a) The 2-D bilayer network of **1** and (b) side view along the *a*-axis showing the bilayer 2-D network of **1**. The 2,2′-bpy molecules and all hydrogen atoms are omitted for clarity.

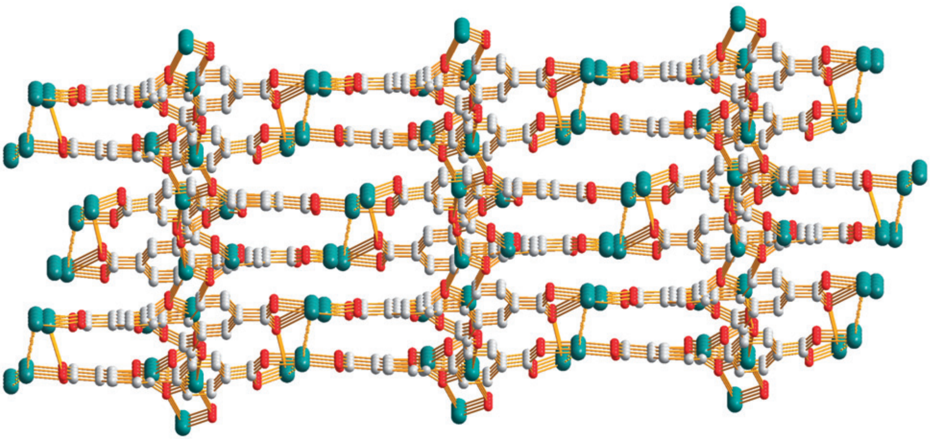

Figure 3. The 3-D framework in **1** along the *a*-axis. The 2,2′-bpy molecules and all hydrogen atoms are omitted for clarity.

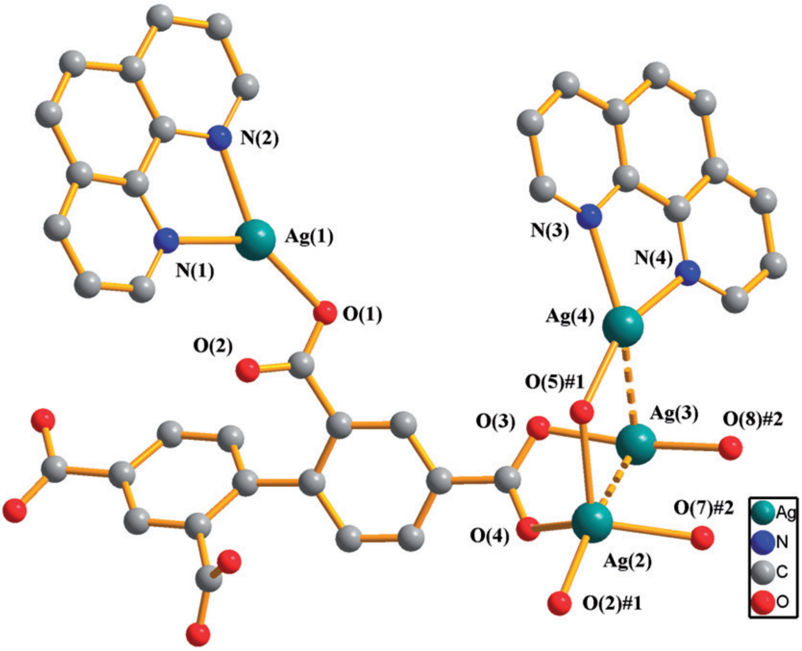

Figure 4. Coordination environment of Ag (I) in **2** (dotted lines indicate Ag···Ag interactions). All hydrogen atoms are omitted for clarity. Symmetry transformation codes: #1: $-x+1$, $y-1/2$, $-z+3/2$; #2: x, $y-1$, z.

As demonstrated by a comparison of **1** and **2**, nitrogen-containing chelating ligands (2,2′-bpy and phen) have a significant effect on the formation and structure of the resulting complexes. In this study, the final structure of the framework of **1** and **2** can be tuned by the influence of nitrogen-containing ligands on carboxyl coordination modes.

3.2. *TGA and XRPD analysis*

TGA of **1** and **2** were recorded in N_2 with a heating rate of $10^\circ C\,min^{-1}$ from 40°C to 900°C. The results indicate that **1** shows an initial weight loss of 17.25% from 253°C to 343°C, corresponding to removal of two 2,2′-bpy molecules per formula unit (Calcd 17.09%). Further increases in temperature cause the $[Ag_8(btc)_2]_n$ framework to collapse due to oxidization of $(btc)^{4-}$ (figure S2). Complex **2** loses 31.97% from 244°C to 317°C, corresponding to removal of two phen molecules per formula unit (Calcd 32.24%). Further increases in temperature cause the $[Ag_4(btc)]_n$ framework to decompose due to oxidization of the $(btc)^{4-}$ (figure S3). These results are consistent with the X-ray structure. All major peaks of experimental XRPD patterns match well with those of the simulated XRPD (figures S4 and S5), indicating reasonable crystalline phase purity of **1** and **2**.

3.3. *Electrochemistry properties*

Electrochemical properties of **1** were studied by cyclic voltammetry. A conventional tri-electrode system was used with glassy carbon as working electrode, Pt as auxiliary

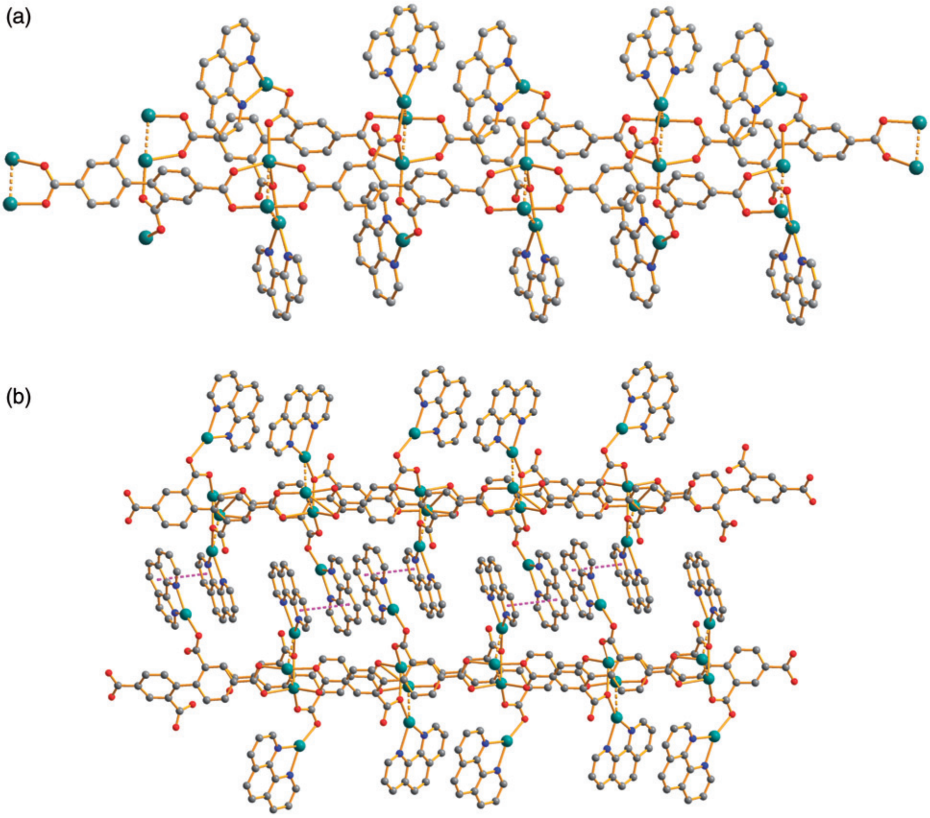

Figure 5. (a) View of the 1-D double-chain structure in **2** and (b) the 2-D supramolecular bilayer network of **2** forms π–π stacking interactions. All hydrogen atoms are omitted for clarity.

electrode, and saturated calomel electrode as reference electrode. The solvent is a mixture of methanol and water with complex concentration of $1.0 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$. KCl was used as supporting electrolyte. As depicted in figure 6, one reduction peak (−0.711 V) corresponds to the Ag (I) → Ag (0) single-electron reduction, the other oxidation peak (0.267 V) corresponds to Ag (0) → Ag (I) single-electron oxidation. Obviously, the transfer in the electrode reaction is irreversible. We can also deduce that the oxidizability of Ag (I) in **1** has been weakened. This study is significant for exploring the interrelation between structure and property, developing potential electronic functional materials.

4. Conclusion

We have synthesized two new Ag (I) coordination polymers constructed from the H_4btc and 2,2′-bpy or phen. For **1**, with 2,2′-bpy, a 3-D framework was obtained. In **2**, larger phen led to a 2-D supramolecular bilayer network structure. Our research demonstrates that the nitrogen-containing ancillary ligand has a significant effect on structure and

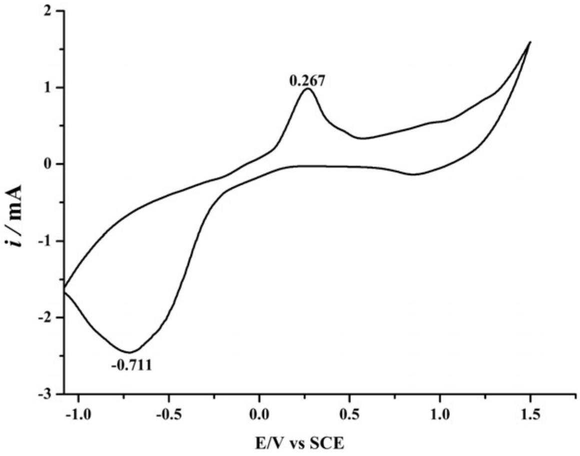

Figure 6. Cyclic voltammograms of **1**.

properties of the resulting coordination polymers. We will pursue our research on construction of MOFs of fascinating structures and specific properties through reaction of other related nitrogen-containing ancillary ligands, biphenyl-tetracarboxylic acid, and metals.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 873176 for **1** and CCDC 873177 for **2**. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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