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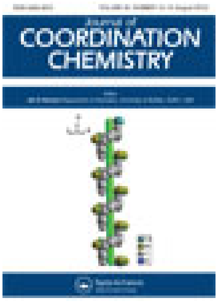

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Silver(I) coordination polymer based on anthraquinone-2,6-disulfonate: synthesis, crystal structure, and luminescent properties

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Silver(I) coordination polymer based on anthraquinone-2,6-disulfonate: synthesis, crystal structure, and luminescent properties

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Self-assembly of anthraquinone-2,6-disulfonic acid disodium salt (Na_2a-2,6-dad) and $AgNO_3$ under hydrothermal conditions resulted in an unprecedented coordination complex, which was characterized by single-crystal X-ray analyses, elemental analyses, IR spectra, TG analyses, and fluorescence investigations. Complex **1** is a 3-D coordination polymer, where a-2,6-dad and Ag–Ag bonds play vital roles. Two sulfonate groups of a-2,6-dad are μ_4- and μ_5-bridges. The unique packing environments of the Ag ions and Ag–Ag bonds lead to 1-D chains consisting of eight- and four-membered rings for Ag1 and Ag1, Ag2 and Ag2 connection, respectively.

Keywords: Silver; Sulfonate; Polymers; Fluorescence

1. Introduction

Construction of metal-organic frameworks (MOFs) based on coordination bonds and non-covalent interactions is of interest because of intriguing architectures and special properties such as magnetism, electric conductivity, heterogeneous catalysis, and fluorescence [1–7]. Selection of organic ligands and metal ions as building blocks is a key in assembling coordination polymers, using the stereo and interactive information stored in the ligands and coordination geometries of the metal ions [8]. Careful selection of suitable, polyfunctional organic ligands, and metal ions is important for constructing and tailoring MOF materials.

Many efforts have been devoted to use of rigid or flexible ligands containing oxygen or hybrid oxygen/nitrogen donors such as multi-carboxylates or their derivatives [9]. Fewer examples with sulfonates have been reported, probably from weak coordination [10]. Ligands containing sulfonate were used to investigate the lanthanide contraction effect [11] and coordination polymers of main group metals [12]. Yet, systematic studies of sulfonate ligands are lacking. Silver(I) is a favorable building block for many coordination architectures on account of its short M–M bond and variety of

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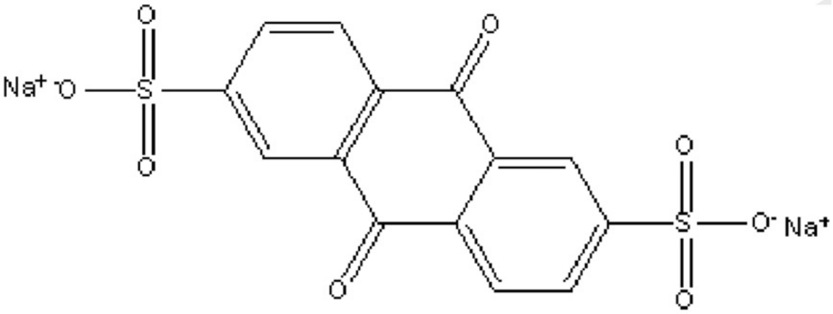

Scheme 1. Structure of anthraquinone-2,6-disulfonic acid disodium salt (Na_2a-2,6-dad).

coordination geometries such as linear, bent, trigonal planar, T-shaped, tetrahedral, trigonal pyramidal, and octahedral [13]. The diversity of MOFs, particularly involving metal silver(I) complexes that are constructed by sulfonates, has attracted interest, not only because of unusual structures, but also for important roles in functional materials.

We began to study the reactions of sulfonate ligands with silver salts by self-assembly with two goals: (i) to obtain coordination information on such ligands to construct coordination polymers and (ii) research potential as functional materials. In order to investigate the weak coordination ability of flexible sulfonate ligands, we selected rigid ligands of anthraquinone-2,6-disulfonic acid disodium salt (Na_2a-2,6-dad, scheme 1) as assembly ligands. To extend our work, we carried out systematic studies of Na_2a-2,6-dad, herein, describing the details of the preparation and characterization of the silver polymer $[Ag_2(\text{a-2,6-dad})(H_2O)]_n$ (**1**), which displays fluorescence properties at room temperature.

2. Experimental

2.1. *Materials and methods*

Solvents and starting materials of analytical grade in the experiments were obtained from commercial sources and used without purification. Elemental analysis (C, H, N, S) was determined on a Perkin-Elmer 2400 type elemental analyzer. Infrared spectra were recorded in a Bruker EQUINOX-55 spectrophotometer from 400 to 4000 cm^{-1} using KBr disks. Thermogravimetric analyses were performed under nitrogen with a heating rate of 20°C min^{-1} using a NETZSCH STA 449 C thermogravimetric analyzer. Photoluminescence analyses of the solid samples were performed on an Edinburgh Instrument F920 fluorescence spectrometer at ambient temperature.

2.2. *Syntheses of $[Ag_2(\text{a-2,6-dad})(H_2O)]_n$ (1)*

A mixture of Na_2a-2,6-dad (0.4 mmol) and $AgNO_3$ (0.2 mmol) in water (15 mL) was sealed into a 25 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure heated at 180°C for 4 days and cooled to 20°C at 3°C h^{-1}; colorless

Table 1. Crystal data for **1**.

Temperature (K)	293(2)
Empirical formula	$Ag_2C_{14}H_8O_9S_2$
Formula weight	600.06
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	5.5936(9)
b	10.0770(19)
c	14.372(3)
α	106.966(4)
β	95.293(3)
γ	98.927(3)
Volume (Å^3), Z	757.3(2), 2
Calculated density (Mg m^{-3})	2.632
θ range for data collection (°)	3.1 to 25.5
Limiting indices	$-6 \le h \ge 5$, $-12 \le k \ge 11$, $-17 \le l \ge 17$
Wavelength (Å)	0.71075
Reflections collected	6094
Data/restraints/parameters	2782/253/2
$F(000)$	580
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0452$, $wR_2 = 0.1269$
R indices (all data)	$R_1 = 0.0534$, $wR_2 = 0.1304$

prismatic single crystals suitable for X-ray analyses were obtained. The crystals were collected by filtration, washed with distilled water and ethanol, and dried at room temperature. Yield 60% (based on Ag). Elemental analysis for $Ag_2C_{14}H_8O_9S_2$ (%) Found: C, 27.9; H, 1.4; S, 10.9. Calcd: C, 28.0; H, 1.3; S, 10.7. IR (KBr pellet, cm^{-1}): ν(O–H) 3420 (br. vs), 3353 (br. vs), 3270 (br. s); ν(S–O) 1280 (sh), 1270 (vs), 1230 (s), 1170 (vs), 1130 (s), 1128 (s); ν(C–S) 1043 (w), 1020 (s); ν(C–C) 1550 (w); δ(O–H) 1660; δ(C–H) 1445 (m), 1400 (m), 1380 (m).

2.3. *Crystal structure determination*

Crystal data were collected using a Bruker Smart-1000CCD diffractometer. Graphite monochromated Mo-Kα ($\lambda = 0.71075$ Å) radiation was used. The single crystal structure was solved by direct methods using SHELXS-97 and refined on F^2 by full-matrix least squares using the SHELXL-97 program package [14]. All non hydrogen atoms were refined anisotropically by full-matrix least squares. The C–H hydrogen atoms were calculated in idealized geometry riding on their parent; protic O–H were found and refined. The crystal data and refinement details are summarized in table 1.

3. Results and discussion

3.1. *Crystal structure of 1*

Single-crystal analysis reveals that **1** crystallizes in the triclinic space group $P\bar{1}$ and exhibits a 3-D network. The fundamental building unit of **1** consists of two silver(I) ions, two a-2,6-dad ligands, and one coordinated water. As shown in figure 1, there are

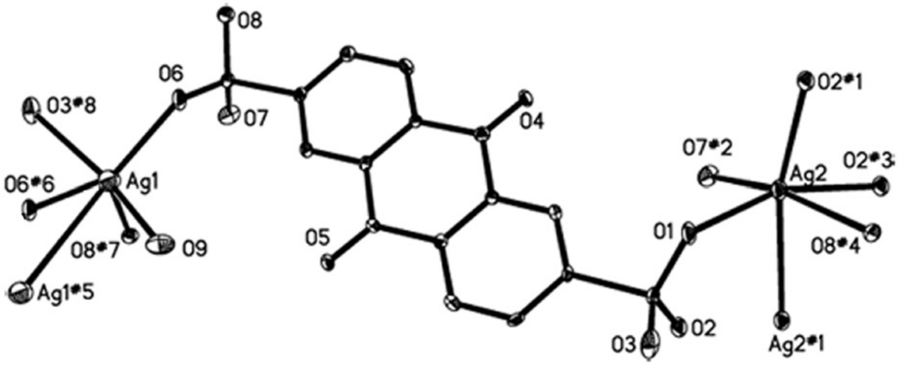

Figure 1. ORTEP drawing of $[Ag_2(a\text{-}2,6\text{-dad})(H_2O)]_n$ (**1**) at 30% probability level; hydrogen atoms are omitted for clarity. Symmetry codes: #1: $2-x$, $1-y$, $2-z$; #2: $1-x$, $-y$, $1-z$; #3: $1+x$, y, z; #4: $1+x$, $1+y$, $1+z$; #5: $-1-x$, $-y$, $-z$; #6: $-x$, $-y$, $-z$; #7: $-1+x$, y, z; #8: $-1+x$, $-1+y$, $-1+z$.

Table 2. Selected bond lengths (Å) and angles (°) of **1**.

Ag1–O9	2.340(6)	Ag1–O6	2.400(5)	Ag1–O6#6	2.672(14)
Ag1–O8#7	2.425(5)	Ag1–O3#8	2.440(5)	Ag1–Ag1#5	3.1966(13)
Ag2–O7#2	2.363(5)	Ag2–O1	2.404(5)	Ag2–O2#2	2.412(5)
Ag2–O2#1	2.440(4)	Ag2–O8#4	2.503(4)	Ag2–Ag2#1	2.9901(11)
O9–Ag1–O6	85.40(18)	O9–Ag1–O8#7	100.96(18)	O8#7–Ag1–Ag1#5	93.08(11)
O3#8–Ag1–Ag1#5	102.16(12)	O6–Ag1–O3#8	94.54(16)	O9–Ag1–O6#6	79.52(10)
O7#2–Ag2–O1	93.06(18)	O1–Ag2–O2#3	102.03(16)	O2–Ag2–O8#4	82.47(16)
O8#4–Ag2–O2#1	76.64(16)	O2#1–Ag2–Ag2#1	77.34(11)	O7#2–Ag2–Ag2#1	77.70(13)

Symmetry codes: #1: $2-x$, $1-y$, $2-z$; #2: $1-x$, $-y$, $1-z$; #3: $1+x$, y, z; #4: $1+x$, $1+y$, $1+z$; #5: $-1-x$, $-y$, $-z$; #6: $-x$, $-y$, $-z$; #7: $-1+x$, y, z; #8: $-1+x$, $-1+y$, $-1+z$.

two kinds of crystallographically unique silver(I) in the asymmetric unit, both having six-coordinate distorted octahedral geometries. Ag1 is formed by four oxygen atoms (O3#8, O6, O6#6, O8#7) from different a-2,6-dad anions, one oxygen (O9) from coordinated water and one symmetry-related Ag1#5 with the distance between Ag1 and Ag1#5 of 3.197 Å, far shorter than the sum of van der Waals radii (3.44 Å) yet close to the Ag–Ag distance in silver metal (2.89 Å) [15]. O6, O6#6, O8#7, and Ag1#5 constitute the equatorial plane and O9 and O3#8 occupy the apical sites with an angle of 156.70° of O9–Ag1–O3#8. (Ag2)(I) is coordinated by five oxygen atoms (O1, O2#1, O2#3, O7#2, O8#4) from five different a-2,6-dad ligands, and one symmetry-related silver(I) (Ag2#1, Ag2–Ag2#1 interactions: 2.990 Å). O1 and O2#1 take up the apical positions with O1–Ag2–O2#1 angle of 160.14°. The Ag–O bond lengths are 2.340(6) to 2.672(14) Å, consistent with values reported for Ag-sulfonate complexes [12a, 16]. Selected interatomic distances and angles for **1** are listed in table 2.

There is one crystallographically unique a-2,6-dad in the structure and two coordination modes of sulfonate to silver, μ_4- and μ_5-bridges. As shown in figure 2, one sulfonate of a-2,6-dad binds to four different silver ions, with one oxygen of sulfonate binding to two different silver ions, while the remaining two oxygen atoms bind to only a single silver. The μ_5 sulfonate binds to five different silver ions, with two oxygen atoms binding to two different silver ions, while the remaining oxygen binds to only a single silver. Thus, each a-2,6-dad binds to nine silver ions. This is a highly

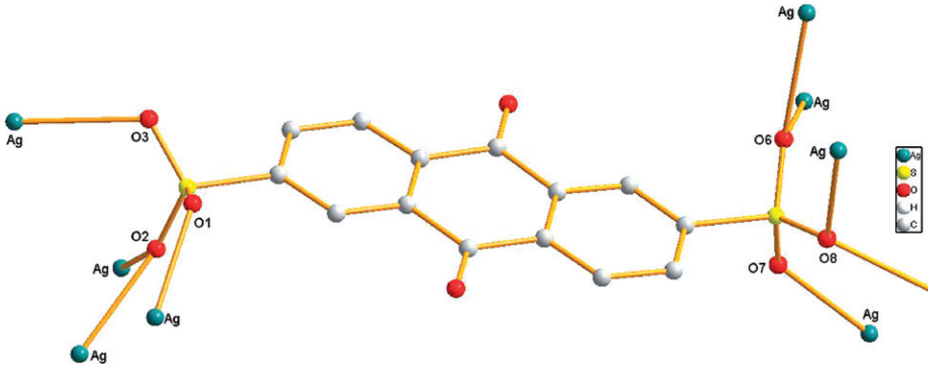

Figure 2. The coordination mode of a-2,6-dad.

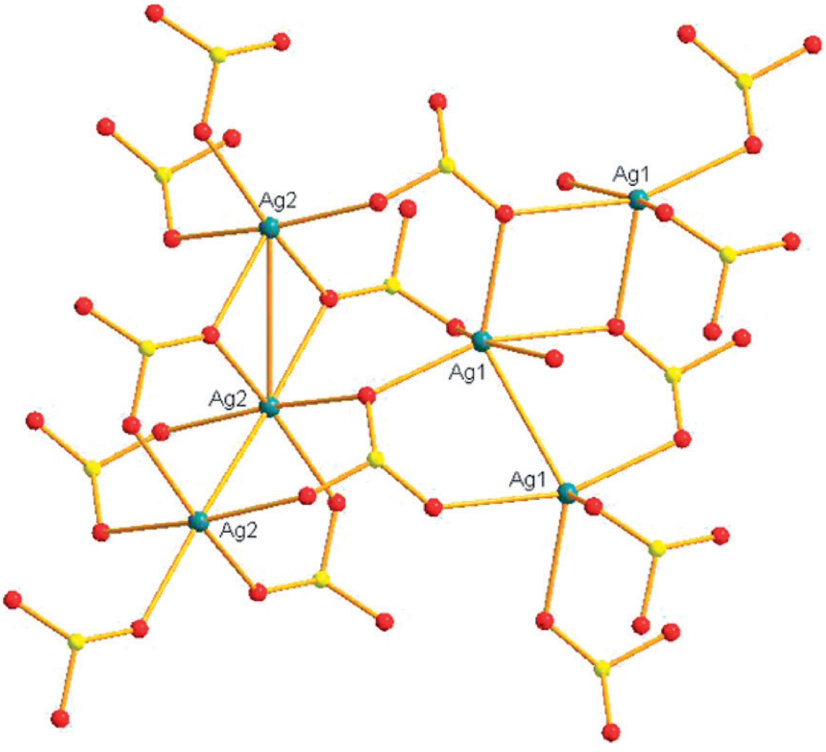

Figure 3. Coordination environment of silver in **1**.

unusual coordination mode for $R{-}SO_3^-$ [17]. The architectures and properties may be controlled by a-2,6-dad.

In the structure of **1** (figure 3), each Ag1 is surrounded by four a-2,6-dad anions and Ag2 is surrounded by five a-2,6-dad groups. Between Ag1 and Ag1, Ag1 and Ag2, Ag2 and Ag2, there are two connection methods, μ_2-O or μ_2-SO_2 of sulfonate. Each pair of

Ag1 ions is bridged by two sulfonate oxygen atoms (μ_2-O) and two μ_2-SO_2 of sulfonate to form a four-membered ring (Ag_2O_2) and an eight-membered ring ($Ag_2O_4S_2$). A binding interaction exists between Ag1 and Ag1 with Ag–Ag distance of 3.197 Å in the eight-membered ring. Ag2 and Ag2 are bridged by four μ_2-SO_2 of sulfonate to form two eight-membered rings ($Ag_2O_4S_2$) and further bridged by two μ_2-O to form a four-membered ring (Ag_2O_2); the distances of Ag2 and Ag2 to neighboring silver ions are 2.290 and 3.392 Å in eight- and four-membered ring, indicating there is strong Ag–Ag binding. Neighboring Ag1 and Ag2 are connected by μ_2-O and a μ_2-SO_2 of sulfonate with distances of Ag1 and Ag2 to neighboring silver ions larger than 3.7 Å, indicating no Ag–Ag binding.

In the structure of **1**, each Ag1 is bridged by two methods to form a 1-D chain. There are four-membered and eight-membered rings in the 1-D chains. Similarly, Ag2 and Ag2 are bridged by two methods to form 1-D chains, with two eight-membered rings and a four-membered ring present in the 1-D chains. Each 1-D chain is connected to two neighboring chains through coordination of the sulfonic oxygen to silver of the neighboring polymeric chain along the *b*-axis to form a 2-D network (figure 4) in the *a* and *b* plane. Two different 1-D chains are present (figure 5), which are like a tree branch in a 2-D network. The 2-D networks *via* sulfonates of a-2,6-dad interact by μ_4- and μ_5-bridges, forming a 3-D framework structure (figure 6). $\pi \cdots \pi$ interactions are present (figure S1, table 3) in the 3-D structure of **1**, which exhibits a short centroid···centroid

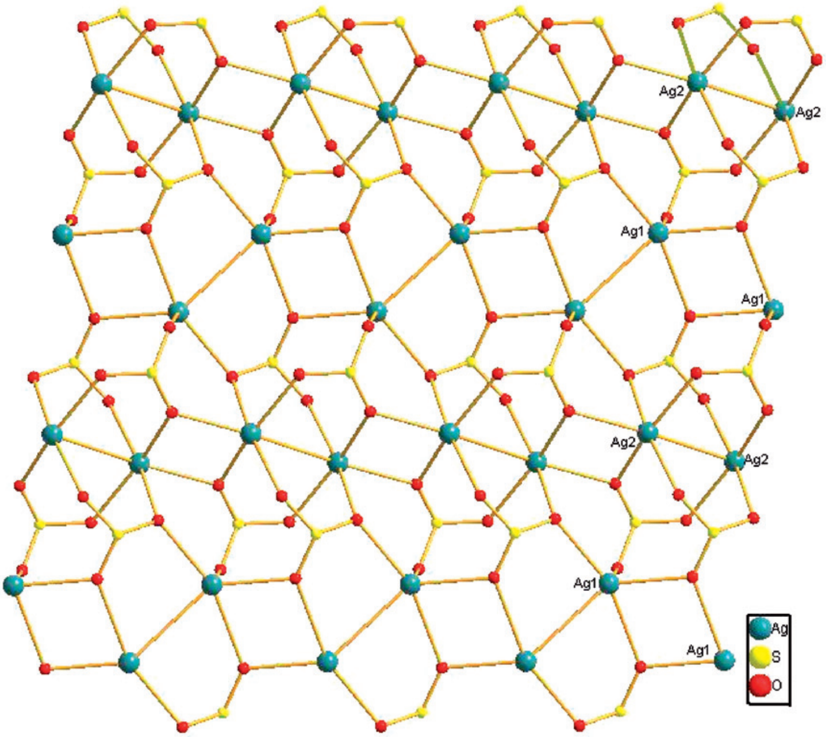

Figure 4. 1-D chain and 2-D framework of **1**.

distance (3.42 Å and 3.49 Å). The π-stacking interactions can be viewed as medium-to-strong if they exhibit short centroid···centroid distances (<3.8 Å) together with large slip angles (β, $\gamma < 25°$) and vertical displacements ($d < 1.5$ Å); weak π stacking shows quite short centroid···centroid contacts (>4.0 Å), small slip angles ($\beta > 30°$), and vertical displacements ($d > 2.0$ Å), which translate into a sizeable overlap of the aromatic planes [18]; coordinated water (O9) as well as uncoordinated sulfonato oxygen atoms (O3#10) form hydrogen bonds (O9–H···O3#10).

3.2. *Spectroscopic properties*

The solid-state emission and excitation spectra of **1** and H_2a-2,6-dad at room temperature are depicted in figure 7 and figure S2. H_2a-2,6-dad displays emission at 423 nm under 363 nm radiation. Complex **1** exhibits intense emission maximum at 403 nm upon excitation at 330 nm. The emissions are similar to that of H_2a-2,6-dad, indicating that luminescence should originate from transitions between energy levels

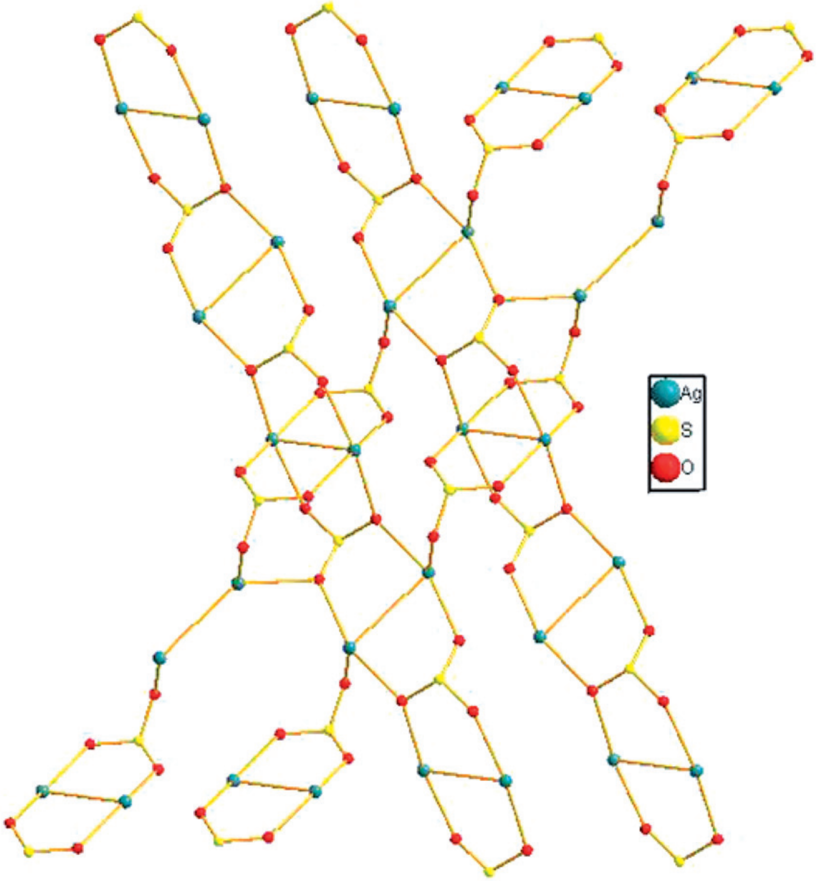

Figure 5. Two infinite 1-D intersection chains in **1**.

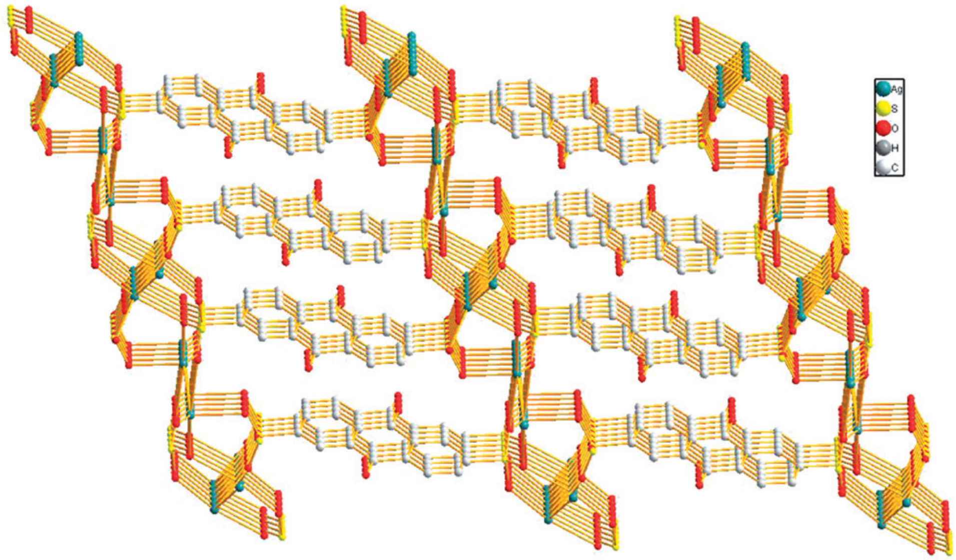

Figure 6. 3-D framework of **1**.

Table 3. The hydrogen bond geometries and $\pi\cdots\pi$ interactions in **1**.

D–H···A	*d* (D–H) (Å)	*d* (H···A) (Å)	*d* (D–H···A) (Å)	∠DHA (°)
O9–H···O3#10	0.88(6)	2.30(3)	2.857(4)	122(2)
Ring(i) → ring(j)	*d* [$C_g\cdots C_g$]	*d* [C_g(i) → ring(j)]	*d* [C_g(j) → ring(i)]	β (°)
C_g(1)···C_g(2)#2	4.22	3.49	3.42	35.9
C_g(3)···C_g(4)#2	4.22	3.42	3.49	34.2

C_g(1): C9–C10–C11–C12–C13–C14; C_g(2): C3#2–C4#2–C7#2–C8#2–C9#2–C14#2; C_g(3): C3–C4–C7–C8–C9–C14; C_g(4): C9#2–C10#2–C1#2–C12#2–C13#2–C14#2.
Symmetry codes #2: $1-x$, $-y$, $1-z$; #10: $-x$, $1-y$, $1-z$.

of sulfonate [1, 19]. Compared to the emission of H_2a-2,6-dad, blue-shift of **1** is attributed to deprotonation of sulfonic acid and coordination of sulfonate to Ag [20].

3.3. *Thermogravimetric analysis*

Thermogravimetric analysis for **1** was performed under nitrogen at a heating rate of 20°C min^{-1} (figure S3). The TGA trace shows two weight loss steps: the first of 3.1% (Calcd 3.0%) is equivalent to loss of coordinated water from 110–190°C and the second begins at 380°C and ends above 620°C, implying that the a-2,6-dad decomposes with AgO the final residue (20.1%), supported by the expected value of 20.64%. These results are consistent with the X-ray structure.

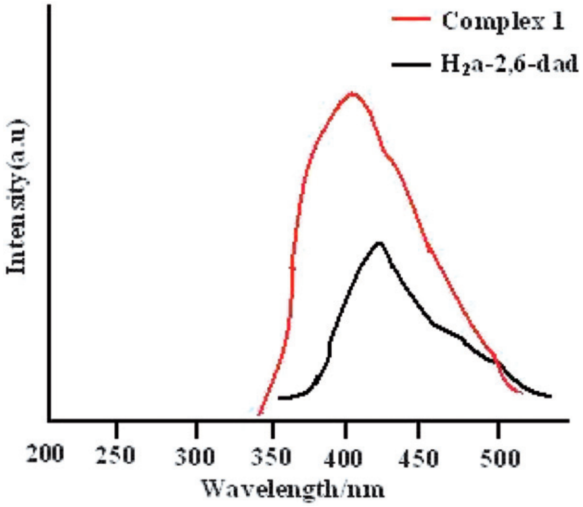

Figure 7. Emission spectra of **1** and H_2a-2,6-dad in the solid state at room temperature.

4. Conclusion

The silver polymer $[Ag_2(\text{a-2,6-dad})(H_2O)]_n$ (**1**) was synthesized by self-assembly of a-2,6-dad and $AgNO_3$. Contrary to previous reports of sulfonate ligands or silver coordination polymers [9(e,f), 12(a), 21], the a-2,6-dad are μ_4- and μ_5-bridges, controlling the architecture and properties of the polymer. The packing environments of Ag ions and Ag–Ag bonds lead to 1-D chains consisting of eight- and four-membered rings. Therefore, **1** displays a 3-D structure in its solid state. Photoluminescence measurements indicate that the compound has strong blue luminescence. The work may offer a strategy for combinations of different connectivity within a net structure, and may also enrich the family of coordination chemistry.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 864080 for **1**. Copies of the 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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