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PAPER

Simultaneous encapsulation of infinite T4(0)A(0)6(0) water tape and discrete water hexamer in a hydrogen-bonded Ag(I) supramolecular framework

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Self-assembly of Ag_2O, 1,4-bis(pyrid-4-yl)benzene (dpb) and 1,3-benzenedicarboxylic acid (H_2bdc) resulted in a one-dimensional mixed-ligand Ag(I) coordination polymer $[Ag_2(dpb)_2(bdc)\cdot 9H_2O]_n$ (**1**), in which infinite 1D T4(0)A(0)6(0) water tape and discrete water hexamer were simutaneously encapsulated. Chair-like water hexamer and D_{2h} water tetramer with two dangling water molecules are alternately hydrogen-bonded into the unprecedented 1D T4(0)A(0)6(0) water tape. Additionally, results about thermal stabiliy, UV-Vis absroption and photoluminescence spectra of **1** were discussed.

Introduction

Recently, water has received more scientific interest than any other substances, not only because it is a major chemical constitute of our planet's surface but also it plays important roles in many biological, chemical, and physical processes.[1] The study of water was ranked among the top ten breakthroughs by *Science* in 2004.[2] Hydrogen-bonded small water clusters are believed to be the subject of considerable theoretical, structural, spectroscopic and thermodynamic studies as it is possible to provide associated information to permit the anomalous behavior of bulk water to be better understood.[3] Many discrete water cluster and polymeric water aggregates with diverse sizes and shapes are captured in crystal lattice of organic or metal coordination compound during crystallization.[4] Although these findings have significantly advanced the understanding of the structure of bulk water, confining water arrays of particular shapes in crystal hosts is still a challenge and much work is required to reach this access. This consciousness has led to the exploration of several interesting water aggregates, such as trimers,[5] tetramers,[6] pentamers,[7] hexamers,[8] heptamer,[9] octamers,[10] nonamers[11] and decamers,[12] as well as one-dimensional (1D) chains with zigzag or helical motifs,[13] 1D tapes,[14] two-dimensional (2D) layers[15] and three-dimensional (3D) water structures.[16]

Among these small water aggregates, of particular interest is the 1D water morphologies, which lie between a 2D water sheet and discrete water cluster and are of great interest due to many fundamental biological processes.[17] Structural studies have shown that 1D water morphologies exist in gramicidin A membrane channels, bacteriorhodopsin, and □-amylase for rapid transport of protons and act as ''proton wires''.[18] Many infinite water tapes involving edge- or vertex-shared small water rings have been reported in the literatures. For example, six-membered and four-membered rings may be fused to form T4(2)6(2) water tape[19] by sharing one edge, four-membered rings may be connected by sharing a water to form a T4(1) tape[20] *etc*. In our previous work on Ag(I)/bipy/dicarboxylate system (bipy = 4,4'-bipyridine), we unmasked a 1D T7(2) water tape and a 1D water chain, and found that their structures could be adjusted by altering the lengths and geometries of the organic ligands.[21] In order to access more novel water aggregates, we extended above system by elongating bipy to dpb and coexistent infinite T4(0)A(0)6(0) water tape and discrete water hexamer were obtained. According to a CSD search (version 5.31, Feb. 2010)[22] with the method described by Infantes et al.,[23] there are only a few cases of 1D water aggregates formed by directly bonded without sharing corner or edge[24] and, to the best of our knowledge, no T4(0)A(0)6(0) water tape has been found. Herein we report the 1D mixed-ligand Ag(I) coordination polymer $[Ag_2(dpb)_2(bdc)\cdot 9H_2O]_n$ (1) as well as the interesting coexistent infinite T4(0)A(0)6(0) water tape and discrete water hexamer trapped in it.

Experimental

Materials and Methods

All the reagents and solvents employed were commercially available and used as received without further purification.

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† Electronic Supplementary Information (ESI) available: Synthetic and crystallographic details, additional measurements, figures and tables. CCDC 973454 (**1**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x.

Infrared spectra were recorded on a Nicolet AVATAT FT-IR330 spectrometer as KBr pellets in the frequency range 4000-400 cm^{-1}. The elemental analyses (C, H, N contents) were determined on a CE instruments EA 1110 analyzer. Photoluminescence measurements were performed on a Hitachi F-7000 fluorescence spectrophotometer with solid powder on a 1 cm quartz round plate. Thermogravimetric (TG) curves were measured from 15 to 800 ^oC on a NETZSCH TG 209 F1 Iris® Thermogravimetric Analyser at the heating rate 10 ^oC/min under N_2 atmosphere (20 mL/min). The UV-Vis spectra measurements (diffuse-reflectance mode) were carried on a Varian Cary5000 UV-VIS-NIR spectrophotometer equipped with an integrating sphere at 298 K.

Synthesis of $[Ag_2(dpb)_2(bdc)\cdot 9H_2O]_n$ (1)

Reaction of a mixture of Ag_2O (23.2 mg, 0.1 mmol), dpb (46.4mg, 0.2 mmol) and H_2bdc (33.2 mg, 0.2 mmol) in methanol-H_2O (6 mL, v:v = 2:1) under the ultrasonic condition (160W, 40 KHz, 40 min, room temperature). Then aqueous NH_3 solution (25%) was dropped into the mixture to give a clear solution. The resultant solution was allowed to evaporate slowly in darkness at room temperature for several days to give pale-yellow crystals of **1**. Anal. Calc. (found) for $C_{40}H_{46}Ag_2N_4O_{13}$: C, 47.73 (47.59); H, 4.60 (3.98); N, 5.57 (5.30) %. IR (KBr): ν(cm^{-1}) = 3422(s), 1943(w), 1607(s), 1551(s), 1481(m), 1428(m), 1371(s), 1231(w), 1073(w), 1043(w), 1008(w), 905(w), 859(w), 811(s), 800(s), 734(m), 715(m), 704(m), 656(w), 573(w), 481(w), 399(w)..

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

Empirical formula	$C_{40}H_{46}Ag_2N_4O_{13}$
Formula weight	1006.55
Temperature/K	173
Crystal system	triclinic
Space group	*P*-1
a/Å	11.2602(8)
b/Å	13.378(1)
c/Å	14.7418(10)
α/°	90.379(1)
β/°	102.681(1)
γ/°	111.435(1)
Volume/$Å^3$	2007.4(2)
Z	2
ρ_{calc} mg/mm^3	1.665
μ/mm^{-1}	1.047
F(000)	1024.0
Crystal size/mm^3	0.15 × 0.1 × 0.1
2Θ range for data collection	4 to 52°
Index ranges	$-7 \le h \le 13$, $-15 \le k \le 16$, $-18 \le l \le 15$
Reflections collected	10860
Independent reflections	7739[R(int) = 0.0170]
Data/restraints/parameters	7739/0/532
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R1 = 0.0354, wR2 = 0.0826
Final R indexes [all data]	R1 = 0.0486, wR2 = 0.0911
Largest diff. peak/hole / e $Å^{-3}$	0.78/-0.41

X-ray crystallography

Single crystal of the complex **1** with appropriate dimensions was chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data for them were collected on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections.[25] Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.[25] All structures were solved by direct methods using SHELXS-97[26] and refined on F^2 by full-matrix least-squares procedures with SHELXL-97.[27] Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C atoms. Crystallographic data collection and refinement parameters are collated in Table 1. Bond lengths and angles for **1** are collated in Table 2. The hydrogen bond geometries for **1** are shown in Table 3.

Table 2. Bond lengths (Å) and angles (°) for **1**.

Ag1-N1	2.126(3)	Ag2-N2	2.148(2)
Ag1-N4^i	2.123(3)	Ag2-N3	2.156(2)
N4^i-Ag1-N1	175.23(11)	N2-Ag2-N3	175.82(11)

Symmetry code: (i) $x-2, y+1, z-1$.

Table 3 The hydrogen bond geometries for **1**.

D-H···A	H···A	D···A	D-H···A
O1W-H1WA···O9W^{ii}	2.06	2.873(4)	160.5
O1W-H1WB···O3W	1.93	2.779(4)	178.2
O2W-H2WA···O8W^{ii}	2.00	2.826(4)	164.8
O2W-H2WB···O4	1.97	2.785(4)	160.8
O3W-H3WA···O7W	1.96	2.757(4)	155.2
O3W-H3WB···O3	2.00	2.788(4)	154.4
O4W-H4WA···O3	1.89	2.741(3)	173.6
O4W-H4WB···O1^{ii}	1.94	2.776(3)	165.6
O5W-H5WA···O2	1.83	2.676(3)	174.0
O5W-H5WB···O4W^{iii}	1.90	2.706(3)	158.7
O6W-H6WB···O1^{ii}	1.94	2.774(3)	168.1
O6W-H6WA···O4	1.88	2.707(3)	164.1
O7W-H7WA···O2	1.95	2.794(3)	175.8
O7W-H7WB···O1W^{iv}	1.91	2.754(4)	176.2
O8W-H8WB···O6W^{v}	1.97	2.808(3)	169.1
O8W-H8WA···O6W^{iii}	2.14	2.865(3)	143.6
O9W-H9WB···O5W	1.96	2.725(3)	148.7
O9W-H9WA···O5W^{vi}	2.00	2.780(3)	153.1

Symmetry code: (ii) $x+1, y, z$; (iii) $x-1, y, z$; (iv) $-x+1, -y, -z+1$; (v) $-x+1, -y+1, -z$; (vi) $-x, -y, -z+1$.

Result and discussion

Structure Description of $[Ag_2(dpb)_2(bdc)\cdot 9H_2O]_n$ (1).

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the space group *P*-1 with an asymmetric unit that contains two unique Ag(I) ions, two dpb ligands, one bdc^{2-} and nine lattice water molecules (Fig. 1a). Each Ag(I) ion exhibits a two-coordinated arrangement with two N atoms belonging to two different dpb ligands. In addition to the strong coordination bonds, the Ag···O weak interaction also exists (Ag1···O9W = 2.710(2) Å), which is a little longer but still falls in the secondary bonding range (the sum of Van der Waals radii of Ag and O is 3.24 Å).[28] The charge neutrality is achieved by bdc^{2-} anion. In two unique dpb ligands, the central phenyl rings are noncoplanar with

respect to other two terminal pyridyl rings, giving two pairs of dihedral angles of 27.73(17)°, 27.26(16)° and 27.74(16)°, 28.10(16)°, respectively. The Ag(I) ions are bridged by dpb ligands to form a 1D infinite polymeric chain structure in absence of Ag···Ag interaction due to the large displacement between Ag(I) atoms in adjacent chains. The 1D chains are bound together to form 2D sheet by the π···π interactions varying from 3.637(2) to 3.8642(19) Å (Fig. 1b and Table S1 in the ESI†), and C-H···π interactions (C11-H11A···Cg7^{iii} = 143°, H11A···Cg7^{iii} = 2.89 Å, Fig. S1 in the ESI†). Abundant O_{water}···O_{water} and O_{water}···$O_{carboxylate}$ hydrogen bonds extend the 2D sheet into a 3D supramolecular framework.

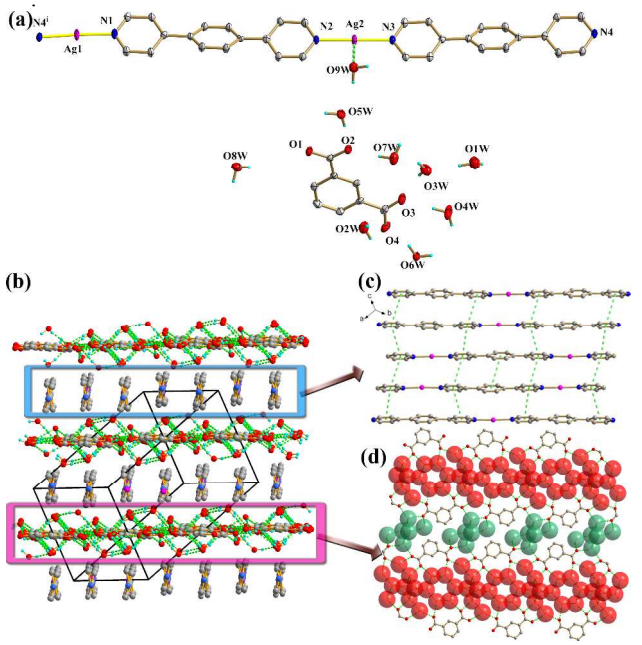

Fig 1. (a) Coordination environment of Ag(I) ion in **1** with the thermal ellipsoids at the 30% probability level. Hydrogen atoms were omitted for clarity. (b) Ball and stick view of 3D supramolecular framework incorporating hydrogen bonds. (c) A view of the 2D sheet forming by the weak π···π interactions (green dashed lines). (d) Ball and stick plot showing the 2D water-bdc anionic sheet incorporating infinite 1D water tape and discrete water hexamer. (Color legend: Ag, purple; N, blue; O, red; C, gray).

One of the most striking features of this complex is that, of the crystallizing water molecules are interconnected by hydrogen bonding to form a water tape based on $(H_2O)_{12}$ cluster (Fig. 2a) in which the $(H_2O)_{12}$ subunit involves one cyclic chair-like water hexamer (Fig. 2b) and one D_{2h} water tetramer (Fig. 2c) with two dangling water molecules as acceptors lying on its two opposite angles. Three water molecules O1W, O3W, O7W and their symmetry-related counterparts form a centrosymmetric chair-like water hexamer through hydrogen bonds. The O···O distances in the hexamer vary from 2.746(4) to 2.780(4) Å with an average O···O separation of 2.765 Å, which is comparable to the 2.74 Å in ice I_c and 2.76 Å in ice I_h [29] In the hexamer, each oxygen atom act as single hydrogen bond donor as well as acceptor. Thus, the overall $(H_2O)_6$ cluster can be represented by $R_6^6(12)$ in the graph set notation,[30] and *R*6 by water cluster notation.[31] The tetramer cyclic $(H_2O)_4$ is formed by O5W, O9W and their symmetry-related counterparts. In the tetramer, four water molecules are perfectly coplanar imposed by inversion center and two O5W molecules act as a double hydrogen bond acceptor while two O9W molecules act as a double hydrogen bond donor. The O···O distances in the tetramer fall in the range of 2.726(3)-2.779(3) Å with an average of O···O separation of 2.752 Å, being shorter than that of in hexamer. The overall $(H_2O)_4$ cluster can be represented by $R_4^2(6)$ in the graph set notation, and *R*4 by the water cluster notation. The hexamer and tetramer don't share any water molecules and are linked directly by strong hydrogen bonds between O1W···O9W to an extended tape with a T4(0)A(0)6(0) motif. Although some of water tapes consisting of hexamer and tetramer were reported, which are edge- or vertex-shared, including T4(1)6(1),[32] and T4(2)6(2),[33] T4(1)6(1)6(2)[34] and so on. To our best knowledge, no T4(0)A(0)6(0) has been structurally characterized up to now. The T4(0)A(0)6(0) water tape in **1** is also different from a strictly defined T4(0)A(0)6(0) water tape because it contains two dangling water molecules lying on its two opposite angles which connect as D_{2h} water tetramer.

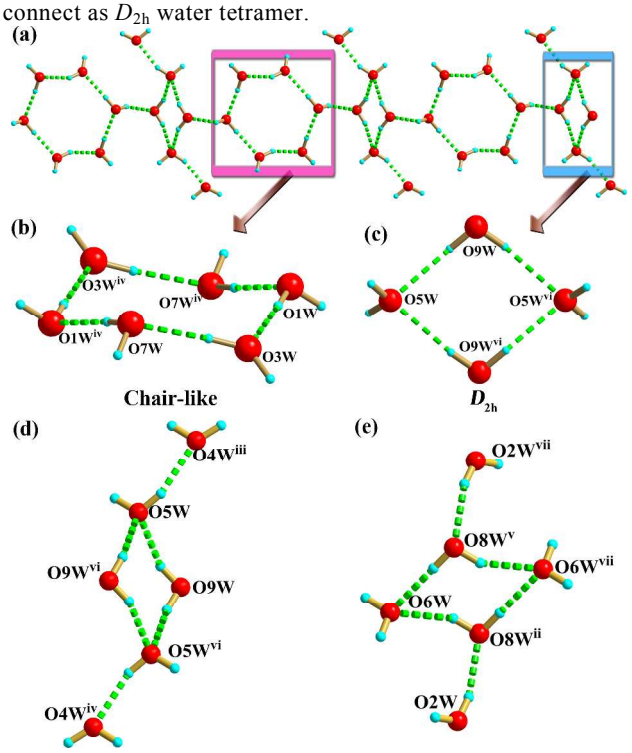

Fig 2. (a) A T4(0)A(0)6(0) water tape containing the chair conformation of hexamer water and D_{2h} water tetramer with two dangling water molecules. (b) Chair-like water hexamer. (c) D_{2h} water tetramer. (d) water hexamer in 1D water tape. (e) discrete water hexamer. (Color legend: O, red. H, cyan) (symmetry codes: (ii) *x*+1, *y*, *z*; (iii) *x*−1, *y*, *z*; (iv) −*x*+1, −*y*, −*z*+1; (v) −*x*+1, −*y*+1, −*z*; (vi) −*x*, −*y*, −*z*+1; (vii) −*x*+2, −*y*+1, −*z*)

Another notable feature is a similar discrete water hexamer that is also comprised of one D_{2h} water tetramer (O6W O8W and their counterparts) with two dangling water molecules (O2W and its counterpart), which, however, act as hydrogen bond donors instead of acceptors in the 1D water tape (Fig. 2d and 2e). Mixed water aggregates in one supramolecular framework such as *S*4 and D_{2h} tetrameric water rings[35a] in a Co(II) crystal host, water dimer and hexamer in a 3D Ln-MOF[35b] are rarely observed due to the difficulty in accessing two or more different hydrophilic voids.

Comparison of encapsulated water clusters in silver(I)/bipyridine-based ligand/carboxylate system

As indicated by previous reports about the system composed of Ag(I), bipyridine-based ligand (including 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethane, and 1,3-bis(4-pyridyl)propane) and dicarboxylic acids (including aliphatic and aromatic ones), there are usually voids with strong hydrophilicity and some interesting examples of water clusters have been disclosed in them (see Table S2†). Cao et.al., firstly reported a novel water tape containing $(H_2O)_{18}$ cluster units in the lattice of $[Ag(4,4'\text{-bipyridine})]_3\cdot(\text{succinate})_{1.5}\cdot 10H_2O$, in which each $(H_2O)_{18}$ cluster consists of one $(H_2O)_{12}$ and two $(H_2O)_5$ subunits.[36] Following their work, we varied aliphatic dicarboxylates from oxalate, adipate, suberate to azelate in Ag(I)/4,4'-bipyridine/dicarboxylate system and four different water clusters including 1D water chain, tape, discrete water decamer and hexamer were captured and modulated.[21,37] Of particular interest, when oxalate used, coexisted 1D *C*4 water chain and 1D T7(2) water tape constructed from edge-sharing heptamer water clusters were well resolved. Altering the bipyridine-based ligands, the captured water clusters could be also modulated. When bipyridine-based ligands varied from 1,3-bis(4-pyridyl)propane to 1,2-bis(4-pyridyl)ethane, the water clusters were correspondingly changed from discrete spirocyclic water nonamer featuring two vertex-sharing pentamers to 1D water chain comprised of alternating water tetramer and octamer.[38] The anion-template effect of different dicarboxylates or different hydrophilic environment responsible for the formation of different water clusters are also proposed.[39] Compared to above mentioned water clusters, infinite 1D T4(0)A(0)6(0) water tape and discrete water hexamer simultaneously encapsulated in **1** is clearly unique. The suitable size and hydrophilic environment of the formed voids in **1** are responsible for the formation of such novel mixed water clusters.

Powder X-ray diffraction and thermal stability analysis

Phase purity of **1** was sustained by its powder X-ray diffraction pattern (Fig. S2, ESI†), which is consistent with that simulated on the basis of the single-crystal X-ray diffraction data. The differences in intensity may be due to the preferred orientation of the crystalline powder samples.

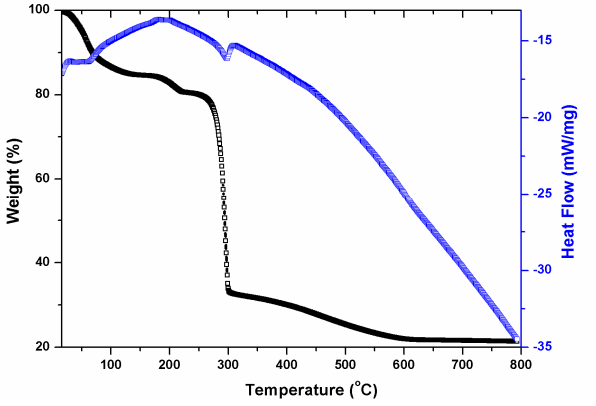

Fig. 3 Thermal gravimetry curve (left scale) and differential scanning calometry curve (right scale) for complex **1**.

The thermogravimetric (TG) analysis was performed in N_2 atmosphere on polycrystalline samples of complex **1** (Fig. 3). The TG curve of **1** shows the first weight loss of 15.83% in the temperature range of 25 °C to 153 °C, which indicates the loss of lattice water molecules (calcd: 16.11%). The broad endothermic peak ranging from 80 to 200 °C in the DSC curve corresponds to the loss of water molecules. The second loss of 4.10 % (calcd: 4.37%) corresponds to the loss of CO_2 because of the decarboxylation of one carboxyl of H_2bdc from 154 °C to 224 °C. And then the structure starts to decompose accompanying loss of organic ligands. The residual weight of 21.68 % is consistent with that of 21.43 % calculated for metallic silver.

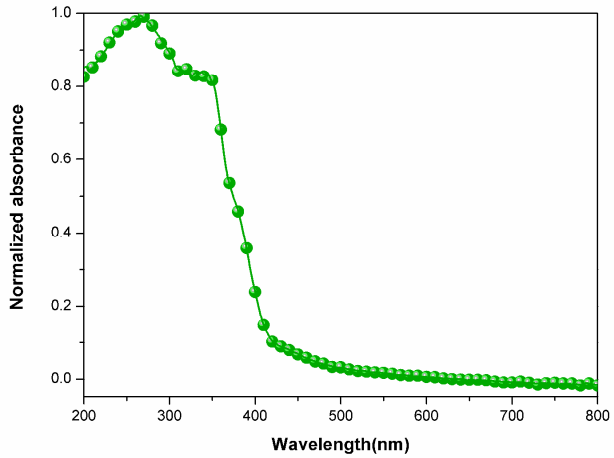

Fig. 4 UV-Vis spectrum of **1**.

To investigate the effect of the water clusters to the framework of **1**, PXRD of as-prepared and dehydrated samples were measured (Fig. S2, ESI†). The dehydrated sample was obtained by heating crystals of complex **1** at 150 °C for 2h. The PXRD patterns of **1** before and after water expulsion show significant changes in peak position and their intensities, suggesting collapse of the host framework once the water molecules are removed. The dehydrated sample was soaked in water for three days, then subjected to the PXRD measurement. The PXRD pattern could not recovery to the simulated one, indicating impossibility of transformation from dehydrated samples to the original **1**. The IR and elemental analysis for dehydrated and rehydrated **1** were also performed to prove the different compositions, especially the contents of lattice water molecule between them and original **1** (see ESI†). These observations clearly indicate that water molecules are difficult to be rearranged in the crystal lattice of dehydrated sample.

UV-Vis spectum and luminescence properties

The absorption spectrum of **1** was measured in solid state at room temperature. As shown in Figure 4, **1** shows the high-energy absorption band at 265 nm and low-energy absorption band at 343 nm as a shoulder which are ascribed to the intraligand $\pi^*\rightarrow\pi$ transitions of the dpb moiety. The photoluminescence spectrum of **1** was shown in Figure 5. The free ligands dpb display photoluminescence with emission maxima at 367 nm (λ_{ex} = 300 nm).[40] It can be presumed that these peaks originate from the $\pi^*\rightarrow$n or $\pi^*\rightarrow\pi$ transitions. Upon complexation of these ligands with Ag(I) ion, intense emission is

observed at 419 nm (λ_{ex} = 365nm) for **1**. To the best of our knowledge, the emission of dicarboxylate belongs to π*→n transition which is very weak compared to that of the π* → π transition of the dpb, so the dicarboxylate almost have no contribution to the fluorescent emission of as-synthesized **1**. Therefore, the emission band of **1** originates from the intraligand π*→π transition modified by metal coordination. This observation indicates that **1** may be excellent candidate for potential photoluminescent material.

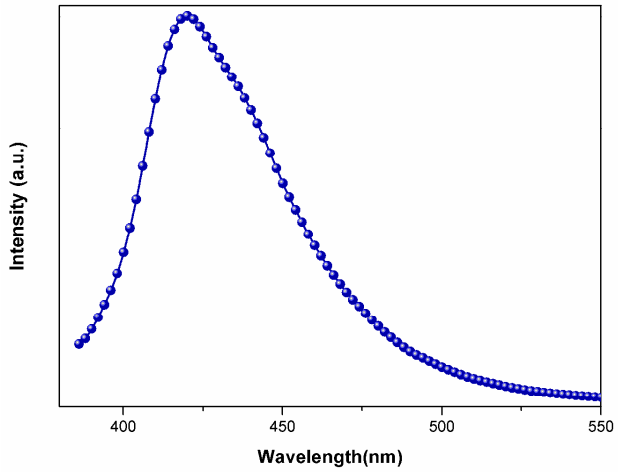

Fig 5. Emission spectrum of **1** at 298 K.

Conclusions

In summary, we have characterized well-resolved coexistent infinite water tape and water hexamer encapsulated in a silver(I) supramolecular framework. The water tape is a T4(0)A(0)6(0) type that consists of six-membered water rings with chair conformation and D_{2h} tetramer with two dangling water molecules. The cooperative association of the water aggregates and crystal host plays an important role in stabilizing the water aggregates.

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Graphical Abstract

In a one-dimensional mixed-ligand Ag(I) coordination polymer, infinite 1D T4(0)A(0)6(0) water tape and discrete water hexamer were simutaneously encapsulated. Chair-like water hexamer and D_{2h} water tetramer with two dangling water molecules are alternately hydrogen-bonded into the unprecedented 1D T4(0)A(0)6(0) water tape.