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# A Discrete Spirocyclic ( $\text{H}_2\text{O}$ )<sub>9</sub> Cluster and 1D Novel Water Chain with Tetrameric and Octameric Clusters in Cationic Hosts

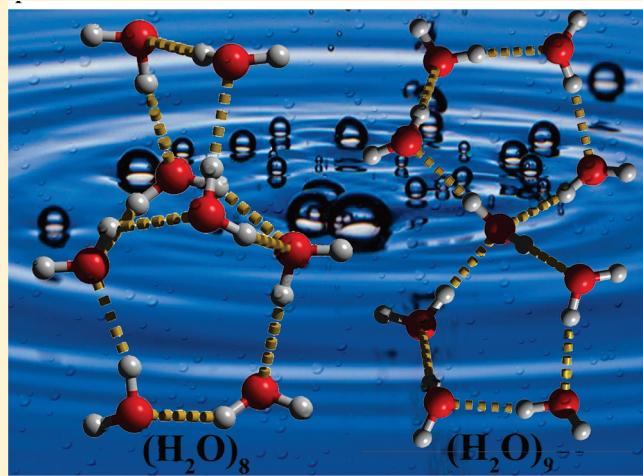
Geng-Geng Luo,<sup>\*,†</sup> Hong-Bo Xiong,<sup>†</sup> Di Sun,<sup>‡</sup> Dong-Liang Wu,<sup>†</sup> Rong-Bin Huang,<sup>‡</sup> and Jing-Cao Dai<sup>\*,†</sup>

<sup>†</sup>Institute of Materials Physical Chemistry, Huaqiao University, Xiamen, Fujian 361021, China

<sup>‡</sup>Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

 Supporting Information

**ABSTRACT:** Two mixed-ligand Ag(I) coordination polymers (CPs),  $[\text{Ag}_2(\text{bpp})_2(\text{suc}) \cdot 12\text{H}_2\text{O}]_n$  (**1**) and  $[\text{Ag}_2(\text{bpe})_2(\text{suc}) \cdot 9\text{H}_2\text{O}]_n$  (**2**) (where bpp = 1,3-bis(4-pyridyl)propane, bpe = 1,3-bis(4-pyridyl)ethane, and  $\text{H}_2\text{suc}$  = succinic acid), have been synthesized and structurally characterized. Both structures consist of cationic layers with  $\text{Ag} \cdots \pi$  interacted chains of alternating metal and bis(pyridyl) ligands. The noncoordinated succinate ( $\text{suc}^{2-}$ ) in **1** or **2** serves as an anionic template driving surrounding water molecules to aggregate into an ordered 2D water-suc anionic layer. The interlamellar anions and cationic layers are stacked through weak electrostatic interaction and hydrogen bonds. One novel 1D water chain constructed from alternating water tetramer with *uudd* configuration and rare octamer exists in the anionic layer of **1**. Each octameric water cluster consists of a pair of fused hexameric water clusters, and each water hexamer assumes a rare bag-shaped conformation. A discrete spirocyclic nonameric water cluster featuring two vertex-sharing pentamers, which shows a similar structure to organic hydrocarbon spiro[4.4] nonane, was observed in **2**. All water clusters have not been structurally documented so far and illustrate new modes of supramolecular association of water molecules. What is more important is that the present observations demonstrate that the spacer length of N-donor ligands has a significant influence on the final formation of water aggregates.



## INTRODUCTION

Water is the basis of life and plays a crucial role in many biological and chemical processes.<sup>1</sup> *Science* ranked the study of water among the top 10 breakthroughs in 2004.<sup>2</sup> However, some properties of water still remain anomalous<sup>3</sup> because of the different arrangements of hydrogen bonds and their tremendous fluctuations. Water clusters are the aggregations of water molecules held together by hydrogen bonds. The assembly and structural information of hydrogen-bonded small water clusters are not only the first step to understanding the unexplained behavior of bulk water<sup>4</sup> but also help to obtain insight into the processes that occur at the ice–liquid, ice–air, and liquid–air interfaces<sup>5</sup> and into the nature of water–water and water–solute interactions.<sup>5a</sup> It is this realization that has led to an upsurge in studying small water clusters in different surroundings. With the development of water clusters, they have been classified into two classes: discrete clusters and polymeric clusters. A variety of discrete water clusters ( $\text{H}_2\text{O}$ )<sub>n</sub> (where  $n = 2–11$ )<sup>6–15</sup> and larger water rings<sup>16</sup> have a vast number of reports describing these. Among the discrete small clusters, even-numbered water clusters are common within the lattice of a crystal host. However, surprisingly little is known of the discrete odd-numbered water

clusters, even though trimers<sup>7</sup> and pentamers<sup>9</sup> are familiar in crystal hydrates. Particularly, the higher nuclearity, odd-numbered nonamer cyclic water cluster seems to be a mysterious member and has rarely been captured in the host matrixes.<sup>13</sup> To obtain the water nonamer, it is crucial to construct appropriate crystal hosts that may offer suitable environments for the formation of water clusters. On the other hand, as compared to discrete water clusters, the physical properties of polymeric clusters, which structurally lie between small water clusters and bulk water/ice, are more closely associated with those of bulk water. To date, three morphologies of polymeric water clusters, including one-dimensional (1D) water chains or tapes,<sup>17,18</sup> two-dimensional (2D) water layers,<sup>19</sup> and three-dimensional (3D) water structures,<sup>20</sup> have been observed. Apparently, these observations have significantly promoted the elucidation of the interactions between water molecules, as well as between water molecules and hosts, and enriched the water chemistry. However, the aspects of water behavior are rather complex and so far

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still have been poorly understood for researchers from all branches of the natural sciences. Most water clusters are obtained occasionally, and the tunable construction of water clusters is still a challenging scientific endeavor for chemists because it is generally difficult to predict the shapes and structures of the water clusters in diverse surroundings.<sup>21</sup>

In previous work on the Cu(II)/bpp/aromatic dicarboxylate system,<sup>22</sup> through controlling water aggregates with different water morphologies by simple employment of tp<sup>2-</sup> and ip<sup>2-</sup> as anionic templates (where bpp = 1,3-bis(4-pyridyl)propane, tp<sup>2-</sup> = terephthalate, and ip<sup>2-</sup> = isophthalate), we did not take the influence of different spacer lengths on the assembly of water aggregates into account. As a continuation of our investigation on water structures, we choose two flexible bis(pyridyl) ligands of bpp and bpe as alternatives with different -(CH<sub>2</sub>)<sub>n</sub>- (*n* = 3 and 2) motifs and mainly focus on a program aimed at gaining important insights into the effect of N-donor ligands with different flexibility and conformational freedom endowing different capacities of spatial extension on the assembly of water clusters. In this context, we present both a novel 1D water chain and one discrete spirocyclic (H<sub>2</sub>O)<sub>9</sub> water cluster observed in two silver-based coordination polymers (CPs), [Ag<sub>2</sub>(bpp)<sub>2</sub>(suc) · 12H<sub>2</sub>O]<sub>n</sub> (**1**) and [Ag<sub>2</sub>(bpe)<sub>2</sub>(suc) · 9H<sub>2</sub>O]<sub>n</sub> (**2**) [where bpp = 1,3-bis(4-pyridyl)propane, bpe = 1,3-bis(4-pyridyl)ethane, and H<sub>2</sub>suc = succinic acid]. Attractively, herein, the formation of water clusters with different morphologies is well-controlled by modulating the spacer length of N-donor ligands, which may provide us with a simple and efficient synthetic route for the tunable construction of water clusters. Meanwhile, both complexes also exhibit the crystallographically structural cases of the anion cluster (suc)<sup>2-</sup> · (H<sub>2</sub>O)<sub>4</sub>.

## EXPERIMENTAL SECTION

**Materials and General Methods.** All reagents and solvents for synthesis were purchased from commercial sources and used as received. The C, H, and N microanalyses were carried out with a CE instruments EA 1110 analyzer. The Fourier transform infrared (FT-IR) spectra were recorded from KBr pellets in the range of 4000–400 cm<sup>-1</sup> on a Nicolet AVATAT FT-IR360 spectrometer. Photoluminescence spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer (slit width, 5 nm; sensitivity, high). Thermogravimetric (TG) curves were performed from 25 to 800 °C on a NETZSCH TG 209 F1 instrument at a heating rate of 5 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere (100 mL/min). X-ray powder diffractions were measured on a Panalytical X-Pert Pro diffractometer with Cu Kα radiation equipped with an X'celerator detector.

**Synthesis of [Ag<sub>2</sub>(bpp)<sub>2</sub>(suc) · 12H<sub>2</sub>O]<sub>n</sub> (**1**).** A mixture of AgNO<sub>3</sub> (167 mg, 1 mmol), bpp (205 mg, 1 mmol), and H<sub>2</sub>suc (116 mg, 1 mmol) was treated in CH<sub>3</sub>OH–H<sub>2</sub>O mixed solvent (10 mL, v/v, 1:4) under ultrasonic treatment (160 W, 40 kHz) at ambient temperature for 10 min. Then, an aqueous NH<sub>3</sub> 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 colorless crystals of **1** (yield, 53%, based on AgNO<sub>3</sub>). They were washed with a small volume of cold CH<sub>3</sub>OH and diethyl ether. Anal. calcd (%) for C<sub>15</sub>H<sub>28</sub>AgN<sub>2</sub>O<sub>8</sub>: C, 38.99; H, 5.38; N, 6.50. Found: C, 39.08; H, 5.44; N, 6.57. FT-IR (KBr, cm<sup>-1</sup>): ν = 3420 (s), 3244 (br), 3028 (w), 2950 (w), 1612 (s), 1558 (s), 1420 (s), 1300 (m), 1222 (m), 1078 (m), 1018 (m), 832 (s), 677 (m), 551 (m) (see Figure S1b in the Supporting Information).

**Synthesis of [Ag<sub>2</sub>(bpe)<sub>2</sub>(suc) · 9H<sub>2</sub>O]<sub>n</sub> (**2**).** The reaction was carried out in a method similar to that for **1**, using bpe (193 mg, 1 mmol) instead of bpp ligand. Colorless crystals of **2** were obtained in 49% yield

**Table 1. Crystal Data and Structure Refinement for **1** and **2****

complex	<b>1</b> (CCDC 808721)	<b>2</b> (CCDC 808722)
empirical formula	C <sub>15</sub> H <sub>28</sub> AgN <sub>2</sub> O <sub>8</sub>	C <sub>28</sub> H <sub>46</sub> Ag <sub>2</sub> N <sub>4</sub> O <sub>13</sub>
M <sub>r</sub>	472.26	862.43
crystal system	monoclinic	orthorhombic
space group	C2/c	Fddd
<i>a</i> (Å)	30.181(6)	13.600(3)
<i>b</i> (Å)	9.092(2)	15.107(3)
<i>c</i> (Å)	17.920(4)	33.000(7)
β (deg)	125.66(3)	90
Z, D <sub>calcd</sub> (Mg/m <sup>3</sup> )	8, 1.570	8, 1.690
V (Å <sup>3</sup> )	3995(2)	6780(2)
μ (mm <sup>-1</sup> )	1.05	1.22
F(000)	1944	3520
total no. of reflns	11725	7788
no. of unique reflns	4364 ( <i>R</i> <sub>int</sub> = 0.032)	1481 ( <i>R</i> <sub>int</sub> = 0.024)
no. of variables	3599	1404
parameters	235	114
final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.036, <i>wR</i> <sub>2</sub> = 0.124	<i>R</i> <sub>1</sub> = 0.021, <i>wR</i> <sub>2</sub> = 0.053
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.045, <i>wR</i> <sub>2</sub> = 0.141	<i>R</i> <sub>1</sub> = 0.022, <i>wR</i> <sub>2</sub> = 0.054
goodness-of-fit on <i>F</i> <sup>2</sup>	1.087	1.066

<sup>a</sup> *R*<sub>1</sub> = Σ||F<sub>o</sub>| - |F<sub>c</sub>||/Σ|F<sub>o</sub>|. <sup>b</sup> *wR*<sub>2</sub> = [Σ*w*(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ*w*(F<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>.

based on AgNO<sub>3</sub>. Anal. calcd (%) for C<sub>28</sub>H<sub>46</sub>Ag<sub>2</sub>N<sub>4</sub>O<sub>13</sub>: C, 38.99; H, 5.38; N, 6.50. Found: C, 39.08; H, 5.44; N, 6.57. FT-IR (KBr, cm<sup>-1</sup>): ν = 3420 (s), 3244 (br), 3028 (w), 2950 (w), 1612 (s), 1558 (s), 1420 (s), 1300 (m), 1222 (m), 1078 (m), 1018 (m), 832 (s), 677 (m), 551 (m) (see Figure S1b in the Supporting Information).

**X-ray Crystallography.** Single crystals of complexes **1** and **2** with appropriate dimensions were 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 were collected on a Rigaku R-AXIS RAPID Image Plate single-crystal diffractometer with a graphite-monochromated Mo Kα radiation source ( $\lambda$  = 0.71073 Å) operating at 50 kV and 90 mA in ω scan mode for **1** and **2**. A total of 44 × 5.00° oscillation images were collected, each being exposed for 5.0 min. Absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program.<sup>23</sup> In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELSX-97<sup>24</sup> and refined on *F*<sup>2</sup> by full-matrix least-squares procedures with SHELXL-97.<sup>25</sup> Atoms were located from iterative examination of difference *F* maps following least-squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times *U*<sub>eq</sub> of the attached C atoms. The hydrogen atoms attached to oxygen were refined with O–H = 0.85 Å, and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(O). The hydrogen atoms of O1W (H1WB and H1WC), O2W (H2WB and H2WC), O3W (H3WB and H3WC), and O6W (H6WB and H6WC) for **1** and O1W (H1WA and H1WC) and O2W (H2WB and H2WC) for **2** are disordered with equal occupancy over two orientations related by the 2-fold axis and inversion center for **1** and **2**, respectively. O3W in **2** is located in a special position with 0.25 occupancy. The C7 of suc<sup>2-</sup> in **2** is disordered over two sites with occupancy of 0.28 and 0.72. All structures were examined using the Addsym subroutine PLATON<sup>26</sup> to ensure that no additional symmetry could be applied to the models. Crystal structure views were obtained using Diamond v3.1<sup>27</sup> and rendered by POV-Ray v3.6. Simulated PXRD patterns were calculated with the Material Studio program<sup>28</sup> using the single crystal data. Some crystallographic data for **1** and **2** are summarized in

**Table 2.** Selected Bond Distances ( $\text{\AA}$ ) and Angles (deg) for **1** and **2<sup>a</sup>**

complex 1			
Ag1—N1	2.168(2)	Ag1—N2 <sup>i</sup>	2.160(2)
Ag1—O1W <sup>ii</sup>	2.692(2)	Ag1—O3W	2.715(2)
N2 <sup>i</sup> —Ag1—N1	159.56(9)	N2 <sup>i</sup> —Ag1—O1W <sup>ii</sup>	102.42(7)
N1—Ag1—O3W	101.35(8)	O1W <sup>ii</sup> —Ag1—O3W	74.57(6)
N1—Ag1—O1W <sup>ii</sup>	92.40(7)	N2 <sup>i</sup> —Ag1—O1W	96.18(7)
complex 2			
Ag1—N1	2.164(2)	Ag1—N1 <sup>i</sup>	2.164(2)
N1—Ag1—N1 <sup>i</sup>	180.0(1)		

<sup>a</sup> Symmetry codes: (i)  $x - 1/2, -y + 1/2, z - 1/2$ . (ii)  $-x, -y + 1, -z + 1$  for **1**. (i)  $-x + 1/2, -y + 1/2, -z$  for **2**.

**Table 3.** Hydrogen Bond Geometries ( $\text{\AA}$ , deg) Associated with Water Molecules in **1** and **2<sup>a</sup>**

D—H…A	D—H	H…A	D…A	D—H…A
complex 1				
O1W—H1WA…O1	0.85	1.93	2.771(3)	172
O1W—H1WB…O1W <sup>v</sup>	0.85	1.98	2.828(4)	180
O1W—H1WC…O2W	0.85	1.94	2.779(3)	168
O2W—H2WA…O6W	0.85	2.16	2.848(3)	138
O2W—H2WB…O1W	0.85	1.95	2.779(3)	166
O2W—H2WC…O6W <sup>v</sup>	0.85	1.96	2.757(3)	157
O3W—H3WA…O2 <sup>vi</sup>	0.85	1.88	2.711(3)	165
O3W—H3WB…O3W <sup>vii</sup>	0.85	2.08	2.795(4)	141
O3W—H3WC…O6W <sup>viii</sup>	0.85	1.95	2.783(3)	165
O4W—H4WA…O5W	0.85	2.04	2.878(3)	170
O4W—H4WB…O1	0.85	1.93	2.777(3)	176
O5W—H5WA…O2 <sup>ix</sup>	0.85	1.88	2.730(3)	174
O5W—H5WB…O4W <sup>x</sup>	0.85	1.92	2.763(3)	171
O6W—H6WA…O5W	0.85	1.98	2.807(3)	165
O6W—H6WB…O3W <sup>xi</sup>	0.85	1.95	2.783(3)	165
O6W—H6WC…O2W <sup>v</sup>	0.85	2.10	2.757(3)	133
complex 2				
O1W—H1WC…O1W <sup>v</sup>	0.85	1.87	2.705(4)	167
O1W—H1WB…O1	0.85	1.88	2.720(2)	170
O1W—H1WA…O2W <sup>vi</sup>	0.85	1.94	2.780(2)	167
O2W—H2WA…O	0.85	1.87	2.712(2)	173
O3W—H3WA…O2W	0.85	1.95	2.802(2)	178
O2W—H2WC…O1W <sup>vi</sup>	0.85	1.95	2.780(2)	167

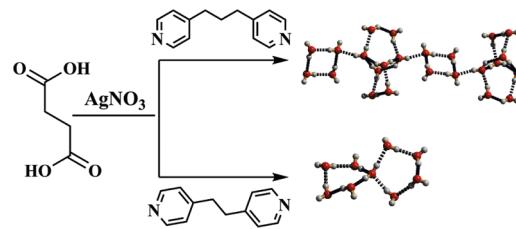
<sup>a</sup> Symmetry codes: (v)  $-x, y, -z + 1/2$ , (vi)  $x, -y + 1, z - 1/2$ , (vii)  $-x, y, -z + 1/2$ , (viii)  $x, -y, z - 1/2$ , (ix)  $x, y - 1, z$ , (x)  $-x + 1/2, -y + 1/2, -z + 2$ , (xi)  $x, -y, z + 1/2$  for **1**, (v)  $-x + 5/4, y, -z + 1/4$ , (vi)  $-x + 3/4, -y - 1/4, z$  for **2**.

Table 1. Selected bond lengths and angles for **1** and **2** are listed in Table 2. Hydrogen bond geometries for **1** and **2** are shown in Table 3.

## RESULTS AND DISCUSSION

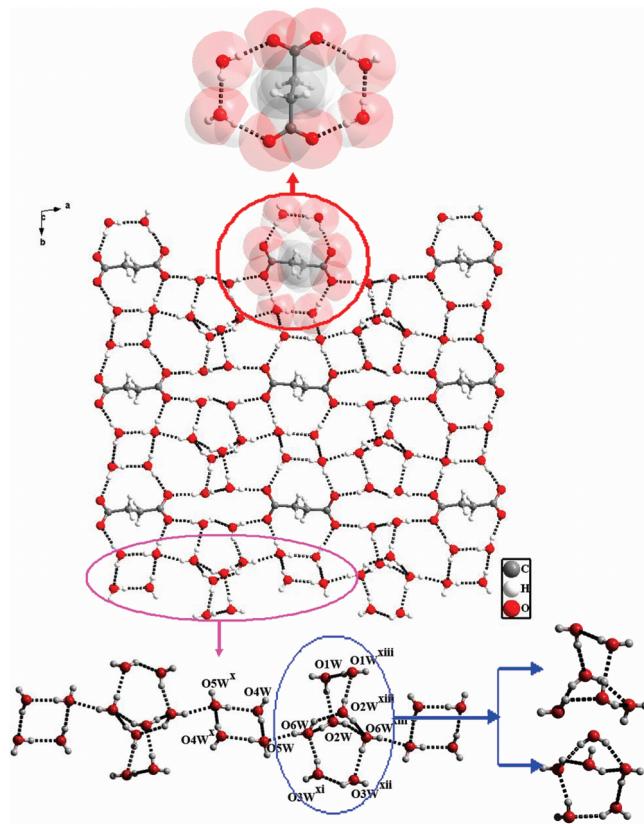
**Comments on the Synthesis.** The synthesis of **1** and **2** was carried out in darkness to avoid photodecomposition and is summarized in Scheme 1. It is well-known that the reactions of Ag(I) with carboxylates and/or neutral ligands in aqueous

**Scheme 1.** One-Dimensional Water Chain/Discrete ( $\text{H}_2\text{O}$ )<sub>9</sub> Cluster Dependent on the Spacer Lengths of Bis(Pyridyl) Ligands



solution often result in the formation of insoluble substances presumably because of the fast coordination of them to form polymeric structures,<sup>29</sup> making it difficult to grow good crystals of complexes. Hence, proper slowdown of the reaction rate or enhancing solubility, such as using ammoniacal conditions, layer–separation diffusion treatments, gel permeation, or even a microwave-assisted hydrothermal method may favor the formation of crystalline products.<sup>30</sup> In this paper, ultrasonic synthesis under the ammoniacal conditions has been used to synthesize these complexes, and good crystallines of **1** and **2** for structural data collection can be obtained within 1 week. Different molar ratios of AgNO<sub>3</sub>:H<sub>2</sub>suc:N-donors (1:1:1, 1:2:1, 2:1:1, 2:2:1, 1:3:1, and 3:1:1) have been explored, respectively, which showed that the formation of **1** and **2** is not significantly affected by changes of metal-to-ligand ratios, and the resultant crystals are stable in air and insoluble in water and other common organic solvents such as ethanol, benzene, acetone, and acetonitrile. The compositions of **1** and **2** were first documented from single-crystal X-ray crystallography at low temperature and further confirmed from elemental analysis, IR spectra, and thermogravimetric analysis (TGA). The phase purity of either **1** or **2** has been sustained by powder X-ray diffraction (PXRD) patterns (see Figure S2 in the Supporting Information).

**Structure Descriptions.** [Ag<sub>2</sub>(bpp)<sub>2</sub>(suc)·12H<sub>2</sub>O]<sub>n</sub> (**1**). X-ray single-crystal diffraction analysis reveals that **1** crystallizes in the monoclinic C2/c space group with an asymmetric unit containing one crystallographically independent Ag<sup>+</sup> cation, one bpp ligand, a half suc<sup>2-</sup> anion, two weakly coordinated water molecules, and four lattice water molecules (Figure S3 in the Supporting Information). Each Ag atom is coordinated by the pyridyl nitrogen atoms of two bpp ligands [Ag1—N1 = 2.168(2), Ag1—N2<sup>i</sup> = 2.160(2)  $\text{\AA}$ , and N1—Ag1—N2<sup>i</sup> = 159.56(9) $^{\circ}$ ]. Each Ag atom also interacts weakly with two oxygen atoms from two water molecules [Ag1—O1W<sup>ii</sup> = 2.692(2), and Ag1—O3W = 2.715(2)  $\text{\AA}$ ,<sup>31</sup> and two oxygen atoms adopt positions resulting in a narrow O—Ag—O angle [74.57(6) $^{\circ}$ ]. The result is an appreciably distorted tetrahedral geometry at the Ag center with a parameter  $\tau_4$  of 0.69.<sup>32</sup> As is well-known, the flexible bpp ligands can assume four different conformations defined by quite different N-to-N distances (TT, 9.1–10.1  $\text{\AA}$ ; TG, 8.6–9.2  $\text{\AA}$ ; GG', 6.7–8.6  $\text{\AA}$ ; and GG, 3.9  $\text{\AA}$ , where T = trans, and G = gauge).<sup>33</sup> Thus, in **1**, each bpp ligand adopts a TT conformation with N…N separation of 9.18  $\text{\AA}$  and bridges two different metal centers, yielding 1D sinusoidal cationic chains by repeating units of [Ag<sub>2</sub>(bpp)<sub>2</sub>] (period 24.52  $\text{\AA}$ ) (Figure S3 in the Supporting Information). Furthermore, adjacent 1D cationic chains further interact with each other through Ag…π interactions to generate a 2D cationic sheet of {[Ag<sub>2</sub>(bpp)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup>}<sub>n</sub> (Figure S4 in the Supporting Information), in which the shortest distance



**Figure 1.** View showing how a novel  $\{[(\text{suc}) \cdot 8\text{H}_2\text{O}]^{2-}\}_n$  layer (middle) assembled by the hydrogen-bonded network of the lattice water molecules and  $\text{suc}^{2-}$  anions fabricated through forming the “ $\phi$ ” fashion of  $\text{suc}^{2-} \cdot (\text{H}_2\text{O})_4$  anion clusters (up) and 1D water chain built of alternating water tetramers and octamers (bottom). Each octamer consists of a pair of fused water hexamers by sharing four hydrogen bonds, and each water hexamer assumes a rare bag-shaped conformation. Symmetry codes: (x)  $-x + 1/2, -y + 1/2, 2 - z$ . (xi)  $x, -y, 1/2 + z$ . (xii)  $-x, -y, 1 - z$ . (xiii)  $-x, y, -z + 3/2$ . Hydrogen bond lengths and angles are provided in Table 3.

from C to the Ag(I) ion ( $3.40 \text{ \AA}$ ) is at the upper limit of the  $2.89$ – $3.40$  range of  $\text{Ag}-\eta^6$  arene  $\pi$  interactions,<sup>34</sup> indicating weak interactions. Bond distances and bond angles involving the Ag(I) ion are closely similar to those observed in several related species.<sup>35</sup>

The noncoordinated  $\text{suc}^{2-}$  anions, which play templating and charge-compensating roles in the structure, induce surrounding lattice water molecules to aggregate into an ordered 2D hydrogen-bonded-driven water-suc anionic layer  $\{[(\text{suc}) \cdot 8\text{H}_2\text{O}]^{2-}\}_n$  that is observed parallel to the above host  $\{[\text{Ag}_2(\text{bpp}) \cdot (\text{H}_2\text{O})_4]^{2+}\}_n$  sheet along the  $\sim[010]$  direction. Generally,  $\text{suc}^{2-}$  anion possesses a two-carbon aliphatic backbone, and there exist three potential conformations: *anti*–*anti*, *syn*–*anti*, and *syn*–*syn*.<sup>36</sup> In complex 1, each  $\text{suc}^{2-}$  anion adopts the *anti*–*anti* mode with a torsion angle of  $180.0^\circ$ , and the orientation of the carboxylate moiety with respect to the backbone line generates an angle of ca.  $66.78^\circ$ . The carbon backbone of the  $\text{suc}^{2-}$  anion is surrounded by two pairs of water molecules to form a  $\text{suc}^{2-} \cdot (\text{H}_2\text{O})_4$  cluster with two equivalent hydration shells almost distributed uniformly in both sides along the carbon backbone dividing line, displaying a beautiful shape of “ $\phi$ ” motif, where the deprotonated carboxyl groups of  $\text{suc}^{2-}$  act as hydrogen bond

**Table 4.** Bond Angles and Torsion Angles (deg) for the 1D Water Chain and Water Nonamer in 1 and 2<sup>a</sup>

	complex 1
O4W...O5W <sup>x</sup> ...O4W <sup>x</sup>	87.64(9)
O5W...O4W <sup>x</sup> ...O5W	92.36(9)
O4W...O5W...O6W	93.47(1)
O6W...O2W...O6W <sup>xiii</sup>	82.88(6)
O6W...O3W <sup>xi</sup> ...O3W <sup>xii</sup>	96.01(8)
O1W...O2W...O6W <sup>xiii</sup>	116.49(9)
O1W...O2W...O6W	97.59(8)
O1W <sup>xiii</sup> ...O1W...O2W	93.36(1)
O2W...O2W <sup>xiii</sup> ...O6W <sup>xiii</sup>	77.49(1)
O2W...O6W...O3W <sup>xi</sup>	111.99(8)
O2W <sup>xiii</sup> ...O6W...O3W <sup>xi</sup>	97.64(8)
O4W...O5W...O6W...O2W <sup>xiii</sup>	31.7(2)
O4W...O5W...O6W...O2W <sup>xiii</sup>	-95.3(2)
O4W...O5W...O6W...O3W <sup>xi</sup>	150.81(1)
	complex 2
O3W...O2W...O1W <sup>vi</sup>	98.979(5)
O2W...O1W <sup>vi</sup> ...O1W <sup>vii</sup>	96.406(5)
O2W...O3W...O2W <sup>iv</sup>	95.544(5)
O2W...O3W...O2W <sup>ix</sup>	129.420(6)
O2W...O1W <sup>vi</sup> ...O1W <sup>vii</sup> ...O2W <sup>viii</sup>	65.166(6)
O1W <sup>vi</sup> ...O1W <sup>vii</sup> ...O2W <sup>viii</sup> ...O3W	-51.509(6)
O1W <sup>vi</sup> ...O2W <sup>viii</sup> ...O3W...O2W <sup>iv</sup>	130.205(7)
O2W <sup>viii</sup> ...O3W...O2W <sup>ix</sup> ...O1W <sup>x</sup>	-114.400(6)

<sup>a</sup> Symmetry codes: (x)  $-x + 1/2, -y + 1/2, 2 - z$ . (xi)  $x, -y, 1/2 + z$ . (xii)  $-x, -y, 1 - z$ . (xiii)  $-x, y, -z + 3/2$  for 1. (iv)  $-x, -y + 1, -z + 1/2$ . (vi)  $-x + 3/4, -y - 1/4, z$ . (vii)  $x - 1/2, -y - 1/4, -z + 1/4$ . (viii)  $-x + 1/4, y, -z + 1/4$ . (ix)  $-x + 1/4, -y + 1/4, z$ . (x)  $x - 1/2, y + 1/2, z$ . (xi)  $-x + 3/4, y + 1/2, -z + 1/2$  for 2.

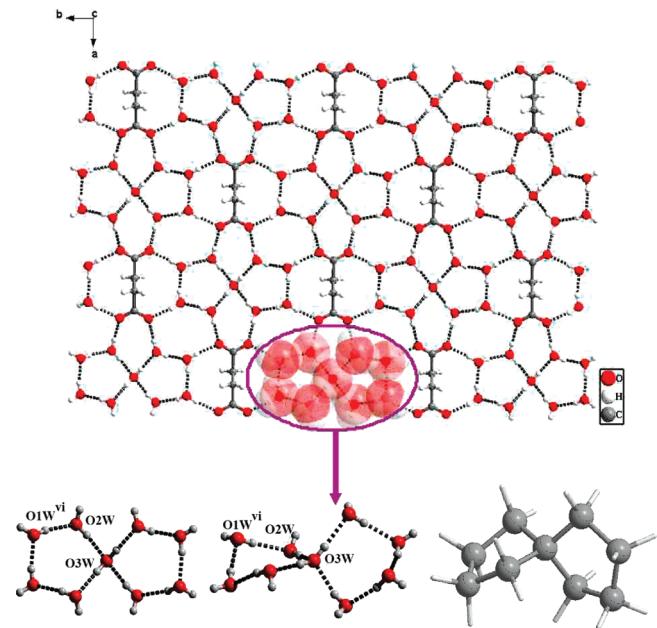
acceptors, while the lattice water molecules serve as hydrogen bond donors. According to graphset analysis nomenclature,<sup>37</sup> hydrogen motifs with in the  $\text{suc}^{2-} \cdot (\text{H}_2\text{O})_4$  cluster can be assigned to be  $R_3^3(11)$ .

A notable feature within the water-suc anionic layer is the presence of a 1D novel water chain with alternating  $(\text{H}_2\text{O})_8$  and  $(\text{H}_2\text{O})_4$  clusters. Four water molecules ( $\text{O}1\text{W}$ ,  $\text{O}2\text{W}$ ,  $\text{O}3\text{W}$ , and  $\text{O}6\text{W}$ ) and their symmetric equivalents form a  $(\text{H}_2\text{O})_8$  cluster (Figure 1). As a matter of fact, each water octamer is constructed of a pair of fused hexameric water clusters through sharing four hydrogen bonds, and each water hexamer can be viewed as either a combination of a butterfly-shaped water tetramer and a dimer or two pentamers fused together by sharing three hydrogen bonds. Interestingly, each hexamer assumes a rare bag-shaped conformation, which is structurally similar to a simple bridged hydrocarbon bicyclo[2.2.1] hexane (Figure S6). There is a crystallographic 2-fold axis along the  $c$ -axis passing through the octamer through the midpoint of  $\text{O}1\text{W}$  and  $\text{O}1\text{W}^{xiii}$ ,  $\text{O}2\text{W}^{xiii}$ , and  $\text{O}2\text{W}$ ,  $\text{O}3\text{W}^{xi}$ , and  $\text{O}3\text{W}^{xii}$ , respectively. As a result, the hydrogen atoms of water octamer are disordered. The  $\text{O} \cdots \text{O}$  distance within the octamer ranges from  $2.757(3)$  to  $2.848(3) \text{ \AA}$  with an average value of  $2.797(3) \text{ \AA}$ , which is shorter than those observed in liquid water ( $2.854 \text{ \AA}$ ),<sup>38</sup> but can be compared with the corresponding value in ice  $I_c$  ( $2.75 \text{ \AA}$ ) and ice  $I_h$  ( $2.759 \text{ \AA}$ ), determined at  $-130$  and  $-90^\circ\text{C}$ .<sup>4a,39</sup> As listed in Table 4, the  $\text{O} \cdots \text{O} \cdots \text{O}$  angles are in the range of  $77.49$ – $111.99^\circ$ ,

considerably deviating from the preferred ideal tetrahedral geometry of water.

As we know, several different isomers for the water hexamers, such as ring, book, bag, cage, and prism topologies, which have energies that are within 0.7 kcal mol<sup>-1</sup> of each other, have been found from extensive theoretical calculations.<sup>40</sup> Until now, although the less stable cyclic conformers including “boat”,<sup>10d</sup> “chair”,<sup>10h,j</sup> “ring”,<sup>10i</sup> and “book”<sup>10j</sup> have been characterized by X-ray crystallographic analysis, the high-energy water “bag” hexamer predicted by theoretical calculations,<sup>41</sup> to our knowledge, has not yet been experimentally observed in any host matrixes. The high-energy bag-shaped water hexamers can still survive in the specific surrounding host environment, which may offer additional stabilization energy for them. Obviously, the present octameric cluster with a basketlike conformation is different from previously identified octameric cubane,<sup>12a</sup> cyclic ring,<sup>12b</sup> opened-cubane,<sup>12c</sup> and staircase<sup>12d</sup> structures observed in organic or organo-inorganic host matrixes and represents a novel conformation of water octamer not yet predicted and reported. The cyclic (H<sub>2</sub>O)<sub>4</sub> cluster is formed by O4W and OSW and their centrosymmetrically related atoms. The water tetramer adopts the up-up-down-down (uudd) configuration with four free hydrogen atoms in an uudd fashion. Although the uudd configuration is energetically less stable as compared to the energy minimum up-down-up-down (udud) configuration,<sup>42</sup> it has been observed in the crystalline solids of metal complexes.<sup>43</sup> The octamers and tetramers are linked through O6W-H $\cdots$ O5W hydrogen bonds to produce an extended water chain. A quick search of the Cambridge Structural Database (CSD)<sup>44</sup> revealed no corresponding crystal structure exhibiting this kind of water chain. Therefore, we believe that this motif of association of the water molecules has not even been described so far. It is worth noting that leaving the water molecules from the coordination spheres out of consideration, the presented 1D water chain can be represented by a T4(0)A(0) unit by water cluster notation,<sup>45a</sup> which is made up of alternating planar and butterfly-shaped (H<sub>2</sub>O)<sub>4</sub> clusters.

[Ag<sub>2</sub>(bpe)<sub>2</sub>(suc)<sub>·</sub>9H<sub>2</sub>O]<sub>n</sub> (**2**). When quasi-flexible bpe with a -(CH<sub>2</sub>)<sub>2</sub>- spacer was used instead of flexible bpp, complex **2** could be generated. Single-crystal X-ray diffraction analysis reveals that **2** crystallizes in the orthorhombic system with space group *Fddd* and is also a cationic 1D metal-organic host with infinite chains composed of alternating silver(I) centers and bpe organic linkers. In the asymmetric unit of **2**, there is one crystallographically independent Ag<sup>+</sup> ion, one bpe, half of a suc<sup>2-</sup> anion, and three lattice water molecules, as shown in Figure S7 in the Supporting Information. A fragment with the formula [Ag<sub>2</sub>(bpe)<sub>2</sub>(suc)<sub>·</sub>9H<sub>2</sub>O] was generated using an inversion symmetry operator. Unlike that in complex **1**, the Ag(I) ion in **2** displays a different coordination mode. Each two-coordinated Ag(I) center lying on a special position of  $\bar{1}$  site symmetry adopts a perfect linear geometry completed by two symmetry-related N donors from two bpe ligands [Ag1-N1 = 2.164(2), Ag1-N1<sup>i</sup> = 2.164(2) Å, and N1-Ag1-N1<sup>i</sup> = 180.0(1) $^\circ$ ]. In addition to the strong coordination bonds, weak Ag $\cdots$ O interactions also exist (Ag1 $\cdots$ O2W = 2.940 Å), which are shorter than the van der Waals contact (the sum of van der Waals radii of Ag and O is 3.24 Å)<sup>46</sup> but well outside the range expected for covalent bonding. In general, bpe exhibits two different conformations, *gauche* and *anti*.<sup>47</sup> In **2**, each bpe adopts a bis-monodentate bridging mode with *anti*-conformation [C8-C7-C7<sup>v</sup>-C8<sup>iii</sup>] dihedral angle of 180°; symmetry codes: (iii) -x + 5/4, -y + 1/4, z; (v) -x + 5/4,

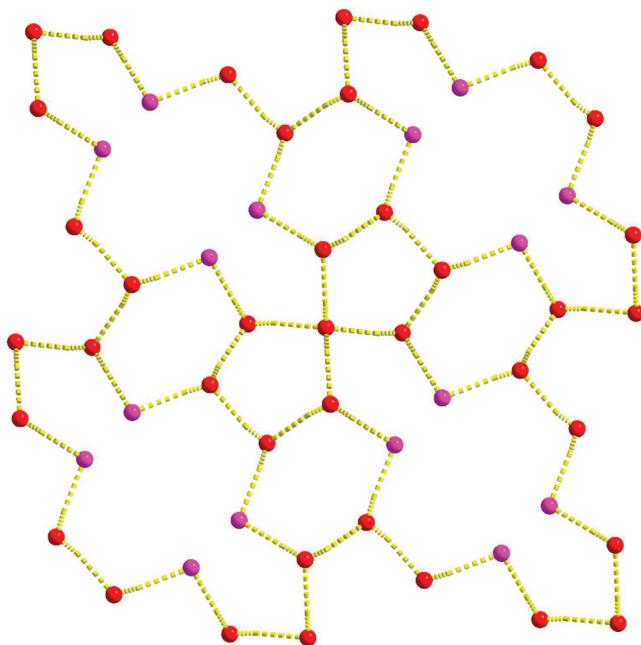


**Figure 2.** View showing how a  $\{[(\text{suc}) \cdot 9\text{H}_2\text{O}]^{2-}\}_n$  layer (top) assembled by the hydrogen-bonded network of the lattice water molecules and suc<sup>2-</sup> dianions fabricated through forming the “φ” fashion of suc<sup>2-</sup>·(H<sub>2</sub>O)<sub>4</sub> anion clusters and a discrete spirocyclic (H<sub>2</sub>O)<sub>9</sub> water cluster. Top view (bottom, left) and side view (bottom, middle) of the nonamer water cluster. Symmetry codes: (vi) -x + 3/4, -y - 1/4, z. Hydrogen bond lengths and angles are provided in Table 3. Ball and stick plot showing the structure of spiro[4.4] nonane (bottom, right).

y, -z + 1/4] to link adjacent Ag ions forming one 1D polycationic chain. Similarly, the Ag(I)-bpe chains are arranged into close-packed cationic layers  $\{[\text{Ag}_2(\text{bpe})_2]^{2+}\}_n$  by Ag $\cdots$ π interactions between adjacent 1D chains (Figure S8 in the Supporting Information), in which the shortest distance from C to Ag(I) ion (3.314 and 3.351 Å) is slightly shorter than that of **1**.

Similar to **1**, the H<sub>2</sub>suc guest in **2** completely deprotonates to balance the polymeric host charge, whereas it does not participate in coordinating to any Ag(I) cation. The amphiphilic behavior of suc<sup>2-</sup> anions makes lattice water molecules aggregate to form an ordered 2D water-suc anionic layer  $\{[(\text{suc}) \cdot 9\text{H}_2\text{O}]^{2-}\}_n$  with novel hydrogen-bonding linkage system. As shown in Figure 2, a closer look at the 2D water-suc anionic layer reveals the presence of a discrete cyclic (H<sub>2</sub>O)<sub>9</sub> water cluster, showing a similar structure to the simple hydrocarbon spiro[4.4] nonane. In detail, there is one O3W, which is located on the special position, and four symmetry-related O1W and O2W in this water cluster. It may appear from Figure 2 that the nonamer is formed by “corner-sharing pentamers”, where the two fused pentamers lie in two nearly perpendicular planes. A C<sub>2</sub> axis passes through O3W, giving the (H<sub>2</sub>O)<sub>9</sub> cluster a C<sub>2</sub> symmetry. As imposed by the symmetry, the hydrogen atoms of the (H<sub>2</sub>O)<sub>9</sub> cluster are disordered, as commonly observed in the ice structure.

This reflects the anomalous nature of water due to flexible hydrogen bonds. In the nonamer, each water molecule is involved in two hydrogen bonds, except the bridging O3W having a typical tetrahedral geometry (four hydrogen bonds), giving a total of 10 hydrogen bonds. The overall spirocyclic (H<sub>2</sub>O)<sub>9</sub> structure can be represented by the graph set notation R<sub>S</sub><sup>5</sup>(10)R<sub>S</sub><sup>5</sup>(10).<sup>37</sup> As we know, hitherto, only three structurally



**Figure 3.** View of a layer L5(6)6(4)14(12) in **2** when the contacts between the water nonamers and the carboxylic oxygen atoms of  $\text{su}c^{2-}$  are taken into account. For clarity, all hydrogen atoms are omitted. Yellow dotted lines for hydrogen bonds, red color atoms for oxygen from water, and pink color atoms for carboxylic oxygen of  $\text{su}c^{2-}$ .

characterized discrete nonamer water aggregates have been reported: The first case exhibits a finite zigzag water chain,<sup>17m</sup> the second can be described as an S-shaped water hexamer connecting a near linear water trimer,<sup>13a</sup> and the third can be considered as fused boatlike six-membered rings sharing two hydrogen bonds, showing a similar structure to the simple bridged hydrocarbon bicyclo[3.3.1] nonane with a crownlike conformation.<sup>13b</sup> Consequently, the presented nonameric water cluster in **2** is a novel one. The hydrogen-bonded O···O separations in the nonamer span the 2.705–2.802 Å with an average value of 2.762 Å, which is substantially the same as the distance of 2.758 Å generated from the ab initio calculations. The O···O···O angles also vary widely (range 95.54–129.42°) with an average of 103.04°, which is a deviation of ca. 6° from the corresponding value of 109.5° in ice  $I_c$  or 109.3° in ice  $I_h$ .<sup>16c</sup> The O···O···O···O torsion angles have values of –114.40, –51.51, 65.17, and 130.21°, indicating a twisted one (Table 4). Furthermore, it is noteworthy that the overall extended 2D layer can be described as a L5(6)6(4)14(12) according to the classifying law of Infantes and Motherwell<sup>45b</sup> when the contacts of nonameric water clusters with carboxylic oxygen atoms of  $\text{su}c^{2-}$  are considered (Figure 3).

Theoretical calculations<sup>48</sup> on discrete  $(\text{H}_2\text{O})_9$  cluster indicate that there are five low-energy structural isomers, and one of them with one water molecule hydrogen bonded to a  $D_{2d}$  cubic octamer is found to be the most stable. This minimum energy structure has 13 hydrogen bonds and has a stabilization energy of 85.05 kcal/mol based on the HF/6-31G(d,p) level.<sup>48a</sup> Alternatively, it can be also built up from a pentamer and a tetramer, which are fused together by sharing four hydrogen bonds. Clearly, theoretical predictions of the geometry of water cluster have little bearing on the liquid or solid state, where there is a subtle interaction between the formation of a low-energy

configuration and its interaction with its surrounding environment. Hence, although the nonameric cluster in **2** with 10 hydrogen bonds may be a high-energy configuration, the specific chemical environment may offer additional stabilization energy for it.

The 2D cationic and anionic sheets in **1** and **2** are stacked along the ~[001] direction following the alternating –ABAB– sequence (where A and B represent, for **1**,  $\{[\text{Ag}_2(\text{bpp})_2(\text{H}_2\text{O})_4]^{2+}\}_n$  cationic sheet and  $\{[(\text{suc}) \cdot 8\text{H}_2\text{O}]^{2-}\}_n$  anionic layer, and for **2**,  $\{[\text{Ag}_2(\text{bpe})_2]^{2+}\}_n$  cationic sheet and  $\{[(\text{suc}) \cdot 9\text{H}_2\text{O}]^{2-}\}_n$  anionic layer, respectively). In other words, those water–anion layered species are occupied in the interlayer spacing between two metallo-organic networks. Consequently, the overall structure either **1** or **2** also could be considered as a 2D metallo-supramolecular sandwich lamellar network (Figures S5 and S9 in the Supporting Information). Each anionic layer counterbalances the positive charges of the cationic sheet via nonclassic C–H···O hydrogen bonds [C···O distances range from 3.321 to 3.535 Å for **1** and from 3.341 to 3.470 Å for **2**] and interlayer Ag···O<sub>water</sub> interactions. Moreover, extensive O–H···O hydrogen bonds are also observed in **1** between each coordinated water molecule and anionic sheet, with the former providing hydrogen bond donors and the latter serving as hydrogen bond acceptors (Table 3).

**Influence of the Flexible Bis(Pyridyl) Ligands with Different Spacer Lengths on Arrays of Water Aggregates.** In this work, we select two kinds of flexible bis(pyridyl) ligands, bpp and bpe, intending to observe their effect on the assembly of water clusters by alteration of the spacer lengths of the organic units. Both complexes are based on  $\text{su}c^{2-}$  anions and Ag(I) ions, and the sole difference rests on the  $-(\text{CH}_2)_n-$  ( $n = 3, 2$ ) spacers of bis(pyridyl) ligands, which leads to 1D novel water chains in **1** and 0D discrete  $(\text{H}_2\text{O})_9$  clusters in **2**.

In **1**, the bpp molecule with a  $-(\text{CH}_2)_3-$  spacer has more flexibility and conformational freedom. This feature allows bpp to adopt the TT conformation to coordinate to Ag(I) ion and with two additional coordinated water molecules to give four-coordinated Ag(I) ion with distorted tetrahedral geometry. These coordinated water molecules further affect other non-coordinated water molecules around  $\text{su}c^{2-}$  anions through nonrandom hydrogen-bonding interactions to aggregate and form the 1D novel water chain. In **2**, the quasi-flexible bpe molecule with a  $-(\text{CH}_2)_2-$  spacer assumes an anti fashion, which makes it linearly coordinate to Ag(I) ion, giving the Ag(I) ion perfect linear geometry. The Ag(I) ions are negligibly coordinated with lattice water molecules. As a result, the lattice water molecules are only influenced and orderly driven by  $\text{su}c^{2-}$  anions to form the discrete  $(\text{H}_2\text{O})_9$  cluster. Comparing these experimental results, it is comprehensible that along with the length decrease of the  $-(\text{CH}_2)_n-$  spacer, the coordination number of Ag(I) ion reduces gradually, which finally modulates different water aggregates. Additionally, when a rigid bpy molecule with the shortest  $-(\text{CH}_2)_0-$  spacer length was chosen in place of longer and flexible bpp or bpe under the similar synthetic conditions,  $[\text{Ag}_3(\text{bpy})_3(\text{su}c)_{1.5} \cdot 10\text{H}_2\text{O}]$  (**3**, bpy = 4,4'-bipyridine) as a final member of this series was formed, which was previously reported by another synthetic method.<sup>49</sup> One 1D water tape containing  $(\text{H}_2\text{O})_{18}$  cluster units has been observed in **3**, in which each  $(\text{H}_2\text{O})_{18}$  cluster consists of  $(\text{H}_2\text{O})_{12}$  and two  $(\text{H}_2\text{O})_5$  subunits. Besides N-donor ligand effects, however, one more complicated phenomenon is that  $\text{su}c^{2-}$  anions in **3** adopt two different conformations (gauche and anti-gauche), which is

completely different from those observed in **1** and **2** (both adopt similar *anti-anti* modes). The effect of anionic templates with different conformations on assembly of water clusters will be the next subject of our study.

**IR Characterization and Thermal Analysis.** The solid-state IR spectra of **1** and **2** are quite similar and exhibit characteristic bands of suc<sup>2-</sup>, bpp, and bpe ligands in the region 4000–400 cm<sup>-1</sup> (Figure S1 in the Supporting Information). The O–H stretching frequency of the water cluster is observed at about 3425 and 3250 cm<sup>-1</sup> for **1** (3421 and 3244 cm<sup>-1</sup> for **2**). Generally, the IR spectrum of ice shows the O–H stretching band at 3220 cm<sup>-1</sup>, while this stretching vibration in liquid water appears at 3490 and 3280 cm<sup>-1</sup>.<sup>4a,10h</sup> This suggests that the water clusters in **1** and **2** show O–H stretching vibrations similar to that of liquid water, and the slight difference is attributable to the environment in which the clusters are.<sup>17h,50</sup> The peaks around 1610, 1560, and 1420 cm<sup>-1</sup> for **1** and **2** can be attributed to the asymmetric and symmetric vibrations of the carboxylate groups. There are no bands in the region 1690–1730 cm<sup>-1</sup>, indicating complete deprotonation of the H<sub>2</sub>suc molecules.<sup>51</sup> These are consistent with the results of the X-ray diffraction analysis.

To assess the thermal stability of the two title complexes, TG analysis has been performed on single-phase polycrystalline samples of **1** and **2** between 25 and 800 °C (Figure S10 in the Supporting Information). The results indicate that **1** showed an initial weight loss of 21.82% from ~25 to ~105 °C corresponding to the removal of 12 water molecules per formula unit (calcd, 22.59%), and then, the framework starts to decompose accompanying loss of organic ligands. For **2**, the TG curve is similar to that of **1**: The weight loss of 18.79% below ~108 °C (calcd, 18.45%) is attributed to loss of nine lattice water molecules, and then, the framework of **2** begins to collapse in the temperature range 110–300 °C.

## CONCLUSIONS

In summary, we have crystallographically characterized two novel water clusters in the two silver-based cationic hosts (**1** and **2**). By simply modulating the -(CH<sub>2</sub>)<sub>n</sub>- (*n* = 3 and 2) spacer lengths of bis(pyridyl) ligands, we succeeded in tuning different water morphologies. The 1D water chain in **1** is constructed from alternating water tetramer with uudd configuration and octamer. Each water octamer contains a pair of fused hexameric water clusters, and each hexamer assumes a rare bag configuration. The spirocyclic (H<sub>2</sub>O)<sub>9</sub> cluster in **2** provides a rare example of a high nuclearity, odd-numbered water cluster completely different from ones found experimentally or predicted theoretically. The present discovery gives novel cases of the formation of tunable water structures, which is very vital for gaining insight into hydrogen-bonding motifs of the aqueous environment in living systems and better understanding of the aspects of bulk water. That other factors such as anionic templates with different conformations affect assembly of water clusters is currently under way in our laboratory.

## ASSOCIATED CONTENT

**S Supporting Information.** Figure S1–S11 including the views of the building units and the host polymers as well as the 2D metalloc-supramolecular sandwich lamellar networks, FT-IR spectra, powder X-ray diffraction (PXRD) patterns, TGA traces

and emission spectra for **1** and **2**, and additional crystallographic data in CIF files (that has been also deposited as CCDC –808721 for **1** and –808722 for **2** in the Cambridge Crystallographic Data Centre). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*Tel/Fax: +86-595-22690569. E-mail: ggluo@hqu.edu.cn (G.-G.L.) and djc@hqu.edu.cn (J.-C.D.).

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