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Well-Resolved, New Water Morphologies Obtained by Modification of the Hydrophilic/Hydrophobic Character and Shapes of the Supporting Layers

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The planar coordination complexes $[Ag_2L_2]$ (L = ophen or obpy, where Hophen = 1*H*-[1,10]phenanthrolin-2-one and Hobpy = 1*H*-[2,2′]bipyridinyl-6-one) contain both hydrophilic and hydrophobic functional groups. Crystallization of these structurally related complexes in an aqueous medium gives $[Ag_2(ophen)_2]_2{\cdot}6H_2O$ (**1**), $[Ag_2(obpy)_2]_3{\cdot}18H_2O$ (**2**), and $[Ag_2(obpy)_2]_2{\cdot}14.5H_2O$ (**3**). Novel water morphologies are observed in these crystalline hydrates, similar 2D metal–organic layers in which the planar $[Ag_2L_2]$ complexes as building blocks are stacked alternately together and provide hydrogen bond acceptor sites (O atoms) for anchoring 1D water chains or 2D water layers on their surfaces. In the wavelike metal–organic framework of **1**, the wide hydrophobic region renders the formation of 1D water tapes containing four- and six-membered water rings, whereas more complex 2D water layers are sandwiched in **2** and **3**, owing to the fact that the surfaces of the supporting layers are more hydrophilic than **1**.

Introduction

Water has received intensive scientific interest in its gaseous, liquid, and solid states during the past few years for its unusual properties and importance in many physical, chemical, and biological processes.[1−16] Isolated small water clusters have been extensively studied both theoretically and experimentally as they can provide insight into the structure and characteristics of liquid water or ice.[1−10] Attention has also been paid to the infinite 1D and 2D water morphologies, which structurally lie between small water clusters and bulk water/ice.[11−16] Recent studies have focused on the morphologies of water clusters in diverse chemical environments to provide quantitative characterization of the hydrogen-bonded networks in liquid water or ice.[8−16]

Some individual examples of 2D water morphologies containing uniform $(H_2O)_6$, $(H_2O)_8$, $(H_2O)_{12}$, and $(H_2O)_{12}$ rings have been described to have structural similarity to

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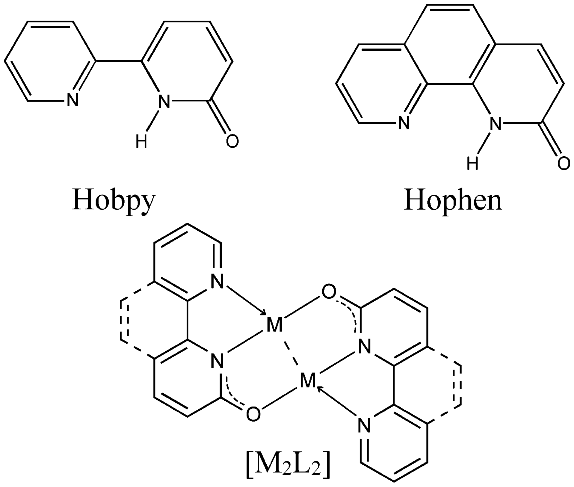
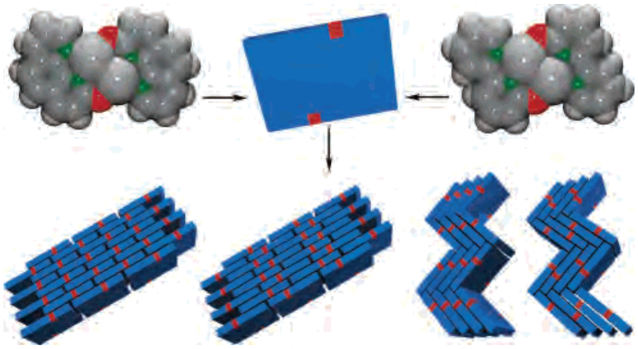
Chart 1



Scheme 1. Schematic Representation of Supporting Layers with Different Hydrophilic/Hydrophobic Characteristics Assembled by [M$_2$L$_2$] Building Blocks[a]



[a] Key: red, hydrophilic area; blue, hydrophobic area.

water or ice,[14−16] although liquid water should contain different small water clusters.[1] The formation of different 2D water morphologies may be due to a small change in the shape or distribution of the hydrophilic groups on the host frameworks. Therefore, a systematic variation of these backbones and determination of the corresponding water layers will improve our understanding of the structures of water.

In our ongoing investigation of the unique structures and properties of the metal complexes of α-hydroxylated 2,2′-bipyridine-like ligands, we discovered a family of robust molecular complexes [M$_2$L$_2$] (M = Cu^I or Ag^I; L = ophen or obpy, where Hophen = 1*H*-[1,10]phenanthrolin-2-one and Hobpy = 1*H*-[2,2′]bipyridinyl-6-one) (Chart 1).[17,18] As shown in Scheme 1, these neutral, planar complexes may serve as effective building blocks for the construction of various 2D supramolecular arrays for stabilization of water morphologies. Under hydrothermal or nonaqueous crystallization conditions, such metal−organic layerlike structures were observed as expected (see the Supporting Information) but pack efficiently via interlayer C−H···O hydrogen bonds to give anhydrous products. However, water molecules can be readily trapped within [Ag$_2$L$_2$] layers by crystallizing from an aqueous medium. In fact, a new water tape and a complex water layer were found in [Ag$_2$(ophen)$_2$]$_2$·6H$_2$O (**1**) and [Ag$_2$(obpy)$_2$]$_3$·18H$_2$O (**2**), respectively, which have not been described in our previous study on the competitive phenomena between metallophilic and $\pi-\pi$ interactions.[18] Since the water molecules are disordered in [Ag$_2$(obpy)$_2$]$_2$·0.5DMF·4.5H$_2$O,[18] we also attempted to synthesize other water morphologies hosted by [Ag$_2$(obpy)$_2$]$_2$. By employing a different crystallization condition, we isolated a new and ordered water layer in [Ag$_2$(obpy)$_2$]$_2$·14.5H$_2$O (**3**). We now describe the hydrogen-bonded water networks in **1**−**3** that are well resolved by X-ray crystallography.

Experimental Section

Materials and Physical Measurements. Commercially available reagents were used as received without further purification. Infrared spectra were obtained from KBr pellets on a Bruker EQUINOX 55 FT-IR spectrometer in the 400−4000 cm^{-1} region. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 elemental analyzer. Synthetic details for **1** and **2** are described in ref 18.

Synthesis of [Ag$_2$(obpy)$_2$]$_2$·14.5H$_2$O (**3**). An aqueous (5 mL) solution of AgNO$_3$ (0.170 g, 1.0 mmol) was added to a DMF (5 mL) solution of Hobpy (0.172 g, 1.0 mmol). The resulting clear solution was placed in the dark for several days to give pale-yellow platelike crystals (yield ca. 40%). Anal. Calcd for $C_{40}H_{57}Ag_4N_8O_{18.5}$: C, 34.88; H, 4.17; N, 8.14. Found: C, 34.95; H, 4.12; N, 8.20. IR: 3356m, 3082m, 2051w, 1655w, 1569s, 1471vs, 1366s, 1293m, 1172m, 990m, 771s, 735m cm^{-1}.

X-ray Crystallography. Data collection of **1**−**3** was performed with Mo Kα radiation (λ = 0.71073 Å) on a Bruker Apex CCD diffractometer at T = 123(2) K. Absorption corrections were applied by using the multiscan program SADABS.[19] The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program.[20] Hydrogen atoms on organic ligands were generated by the riding mode (C−H = 0.95 Å), and hydrogen atoms on water molecules were located from difference maps. Crystal data for **1** (CCDC-245548) and **2** (CCDC-245551) have been reported in ref 18. Crystal data for **3**: orthorhombic, *Ccca* (No. 68), a = 17.0202(13) Å, b = 21.3162(16) Å, c = 27.282(2) Å, V = 9898.2(13) Å^3, Z = 8, D_c = 1.849 g cm^{-3}, $F(000)$ = 5512, μ = 1.640 mm^{-1}, 21804 reflections measured, 6068 unique (R_{int} = 0.030), final $R1$ = 0.0550, $wR2$ = 0.0833, S = 1.018 for all data (refinement details for **3** in $P\bar{1}$; see the Supporting Information). The X-ray data can be retrieved from the Cambridge Crystallographic Data Centre using Deposition No. CCDC-254236.

Results and Discussion

The [Ag$_2$(ophen)$_2$]$_2$ molecules in **1** are closely stacked via intermolecular Ag···π and C−H···π interactions to form metal−organic layers on the (100) planes featuring wavelike

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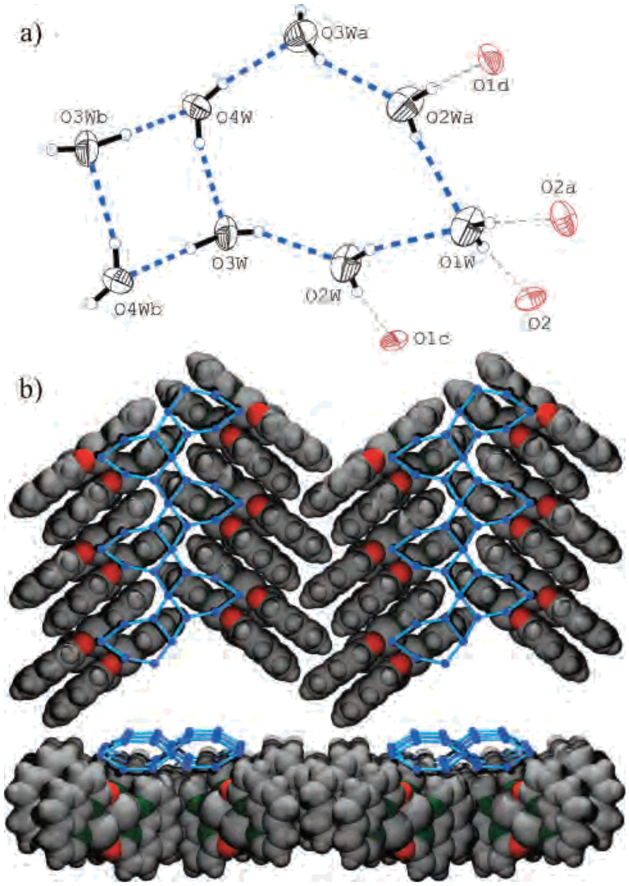

Figure 1. (a) ORTEP drawing (50%; a, $-x$, y, $0.5 - z$; b, $-x$, $-y$, $1 - z$; c, $0.5 - x$, $0.5 - y$, $1 - z$; d, $-0.5 + x$, $0.5 - y$, $-0.5 + z$) of the hydrogen-bonding environments of the water molecules and (b) top (along the *a*-axis) and side (along the *c*-axis) views of the metal−organic layer (space-filling; gray, silver, carbon, hydrogen; green, nitrogen; red, oxygen) and water tapes (ball-and-stick; water hydrogen atoms were omitted for clarity) in **1**.

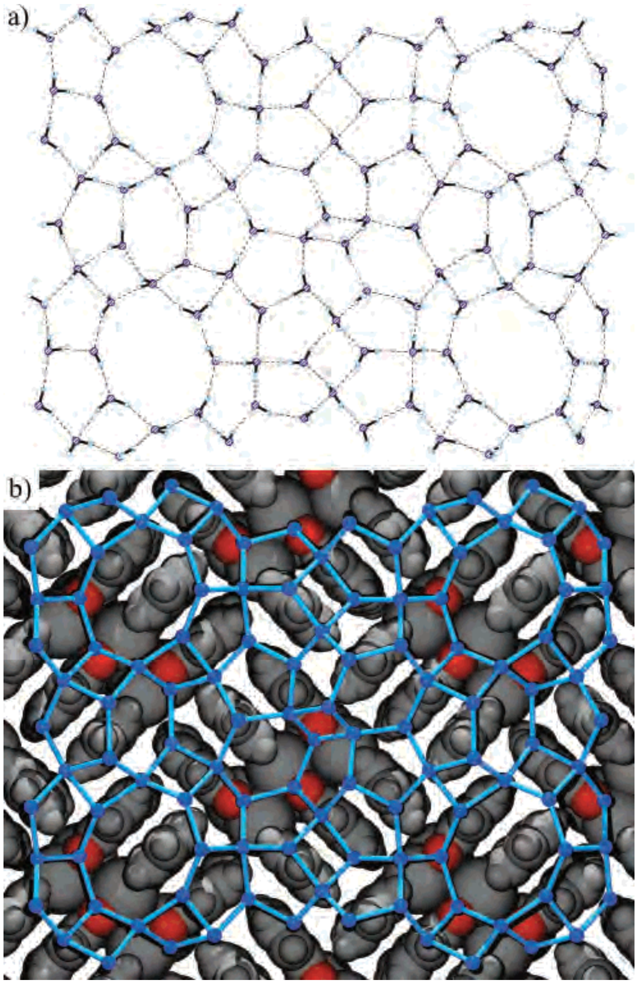

Figure 2. (a) Hydrogen-bonded network of the water molecules and (b) top view (along the *c*-axis) of the metal−organic layer (space-filling) and water network (ball-and-stick) in **2**.

surfaces. Two of the four crystallographically independent water molecules (O1W, O4W) are located at the 2-fold rotation axes. O1W and O2W are hydrogen-bonded to the ophen oxygen atoms that are pointing away from the surfaces of the metal−organic framework (O1W···O2 = 2.710(4) Å, O2W···O1 = 2.719(5) Å). O3W and O4W have no significant supramolecular interaction with the metal−organic layers, but they are hydrogen-bonded to each other (O3W···O4W = 2.708(5) Å, O4W···O3W = 2.799(5) Å) and O2W (O3W···O2W = 2.696(5) Å). These water molecules joined together to form an unusual quasi-planar cyclic hexamer with C_2 symmetry (Figure 1a).[5,6,9,10] Adjacent hexamers are assembled in a head-to-head fashion via O3W···O4W hydrogen bonds along the *c*-axis to give an extended water tape occupying the groove region of the surface. This new 1D water morphology consists of fused four- and six-membered rings, as well as corner-sharing four-membered rings.[11] The O···O distances and O···O···O angles between water molecules range from 2.696(5) to 2.832(5) Å and from 82.7° to 144.7°, respectively. These values indicate that the configuration of the water tape is strongly enforced by the shape of the supporting backbone. The water tapes are separated far from each other (>10 Å) by the bulging hydrophobic backbone (Figure 1b). There are only weak van der Waals interactions found between the bulging areas of the adjacent metal−organic layers.

In **2**, $[Ag_2(obpy)_2]_3$ molecules are held together by $\pi\cdots\pi$, C−H···π, and C−H···Ag interactions and form metal−organic layers parallel to the (001) plane. The hydrophilic keto group of the obpy ligand is evenly distributed on the surface of the scaffold, and the hydrophobic region is smaller than that found in **1**. All six oxygen atoms of $[Ag_2(obpy)_2]_3$ are involved in the hydrogen-bonding interactions with the water layer [O−H···O = 2.655(4)−2.763(4) Å]. Furthermore, a complex water layer is constituted by 18 independent water molecules (Figure 2). Most of the O···O distances and the O···O···O angles fall within 2.75−2.85 Å and 100−120°, respectively. The average O···O distance is 2.824 Å and the O···O···O angle 109.7°, which are also close to the values found in liquid water.[1] This complex 2D water layer consists of fused four-, five-, six-, and eight-membered rings in a ratio of 6:14:3:1. Molecular dynamics simulations suggested that liquid water is composed of small cyclic water clusters with different sizes, in which the cyclic water pentamer is the dominant species.[1b,4] In addition, the O···O distances and O···O···O angles measured in the water layer of **2** are very close to those found in the bulk water.[1]

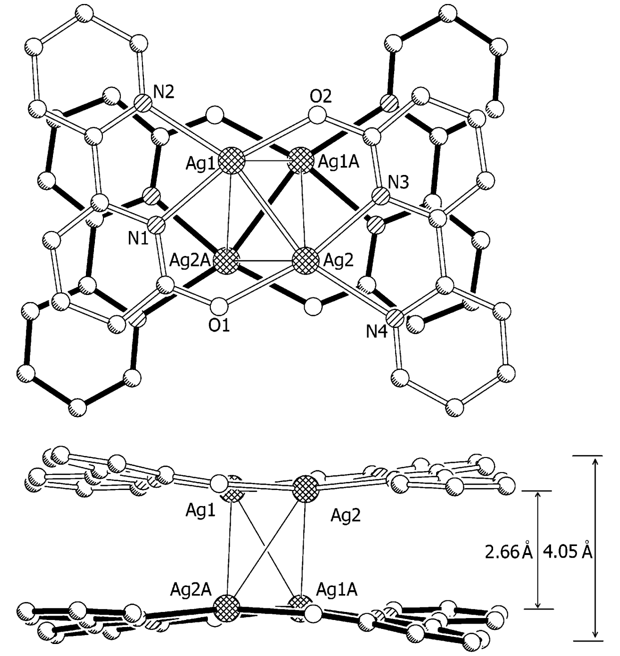

Figure 3. Top (top) and side (bottom) views of $[Ag_2(obpy)_2]_2$ in **3**. Selected interatomic distances (Å): Ag1···Ag2, 2.7716(4); Ag1···Ag1A, 3.0757(6); Ag2···Ag2A, 3.1859(6); Ag1···Ag2A, 3.4729(4); Ag1−O2, 2.172(2); Ag1−N1, 2.220(3); Ag1−N2, 2.357(3); Ag2−O1, 2.182(2); Ag2−N3, 2.223(3); Ag2−N4, 2.372(3) (symmetry code A: $1 - x$, $-0.5 - y$, z).

The C_2 symmetric $[Ag_2(obpy)_2]_2$ complex in **3** has a dimer-of-dimers configuration similar to that of the previously described C_1 $[Ag_2(obpy)_2]_2$ complex.[18] The molecular structure of $[Ag_2(obpy)_2]$ in **3** is similar to those of the reported analogues, featuring short Ag···Ag contacts (Figure 3). The attractive nature of interdimer Ag···Ag interactions can be shown by the fact that the edges of the ligands are bent outward, with two pairs of silver atoms crossing over each other. The average intermolecular Ag···Ag separation in **3** is 3.302 Å, which is comparable to the value of 3.283 Å found in its C_1 analogue. It should be noted that the shortest interdimer Ag···O distance 2.963 Å in **3** is significantly longer than that in the C_1 analogue (2.717 Å). This evidence further supports our viewpoint that in this family of oligomers-of-dimers the short metal···metal contact does not depend on the short metal···ligand contact.

Similar to those of other $[M_2L_2]$ analogues, the $[Ag_2(obpy)_2]_2$ molecules in **3** stacked together by Ag···π and π···π interactions to form a layerlike structure parallel to the (001) family of planes (Figure 4). Notably, the positions of the hydrogen atoms on the water molecules cannot be rationalized regarding the high space group symmetry *Ccca*, since the high crystallographical symmetry requires some of the water protons to be disordered in the lattice. For instance, the two protons of O9W must be disordered at four positions featuring a tetrahedral arrangement as the oxygen center resides at a crystallographical 222 site. However, the protons in the water layer of **3** may be ordered as a reasonable hydrogen-bonding scheme can be obtained after the space group symmetry is lowered to $P\bar{1}$ (see the Supporting Information). The average O···O distance is 2.76 Å, and the average O···O···O angle is 108.8°, which are close to those determined in ice I_h. In contrast to **1**, there is no direct contact between adjacent metal−organic layers in **2** or **3**. Furthermore, the hydrogen-bonding parameters between the water layer and the metal−organic backbone are similar in **2** and **3**.

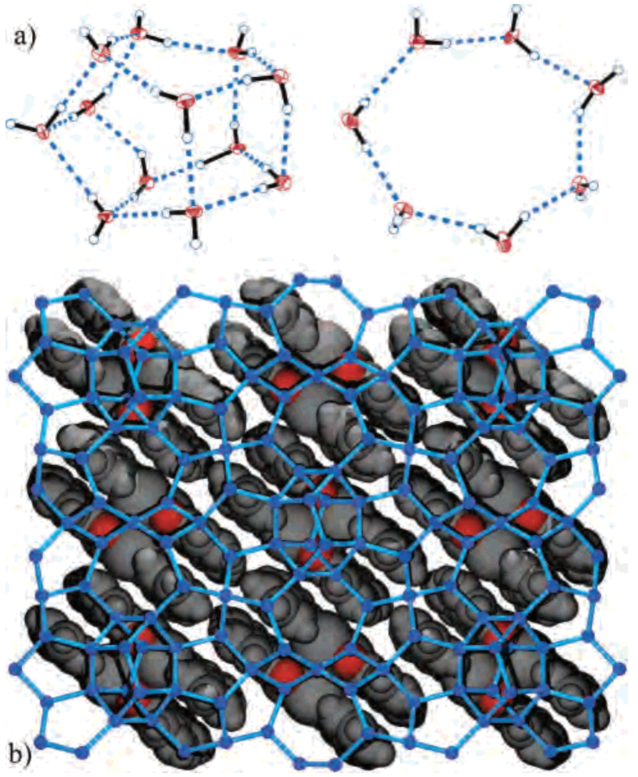

Figure 4. (a) ORTEP drawing (30%) of the W_{12} and W_7 clusters in **3**. (b) Top (along the *c*-axis) view of the metal−organic layer (space-filling) and water network (ball-and-stick).

Most of the cyclic water clusters from $(H_2O)_3$ to $(H_2O)_{18}$ have been widely studied. However, the cyclic water heptamer has never been characterized before.[8−16] The seven-membered ring observed in **3** has a quasi-planar conformation, which was calculated to be only 1 kcal/mol above the energy minima of its most stable 3D isomers.[3] One may notice that **3** contains more lattice water molecules than **2** by comparing their formulas. The additional water molecules give more 3D character to the water layer, which contains embedded 3D $(H_2O)_{12}$ clusters. The $(H_2O)_{12}$ cluster in **3**, being composed of four pairs of edge-sharing $(H_2O)_4$ and $(H_2O)_5$ rings with eighteen hydrogen bonds, has not been either experimentally observed or theoretically proposed. Theoretical calculations have predicted that the most stable conformations for $(H_2O)_{12}$ are face-sharing $(H_2O)_8$ cubes (20 hydrogen bonds) or two $(H_2O)_6$ rings directly coupled together in a face-to-face (18 hydrogen bonds) fashion.[1c,2] Some water networks containing fused cyclic $(H_2O)_{12}$ rings have also been structurally characterized.[14,15]

Although significant progress has been made in the structural determination of infinite water morphologies, no systematic effort has been focused on the modification of the supporting scaffolds and the resulting water morphologies. The structurally related metal−organic layers in **1**−**3** exhibit different degrees of hydrophilicity and distributions of the hydrophilic sites upon modification of the orientation and size of the aromatic ligand. The new and complex water morphologies in **1**−**3** strongly suggest that water layers may be formed easily on more hydrophilic surfaces (**1** vs **2** and **3**). The large discrepancy in the O···O distances and O···O···O angles as well as the complicated connectivities of these water networks can be attributed to the flexibility of the tetrahedrally hydrogen-bonded character of water molecules. This may adapt to various hydrophilic/hydrophobic hybrid surfaces for the formation of the first hydration shell. It should be mentioned that the statistical parameters for the O···O distances, O···O···O angles, and network connectivities of these water morphologies are consistent with the dynamic nature of liquid water. On the other hand, the simple, regular, infinite water morphologies should have more similarity to the structures of ice.[14−16]

Conclusions

We have developed a new strategy for constructing a series of structurally related metal−organic scaffolds to stabilize different water morphologies. New water morphologies varying from 1D, 2D, to 2D with 3D character have been observed by changing the hydrophobic property of the ligands, the method of crystal packing, and the shapes of the supporting layers.

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Supporting Information Available: Hydrogen bonding parameters and additional plots (PDF) and X-ray data files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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