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Silver carboxylate metal–organic frameworks with highly antibacterial activity and biocompatibility

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ABSTRACT

Two novel Ag-based metal–organic frameworks (MOFs) $[Ag_2(O\text{-}IPA)(H_2O)\cdot(H_3O)]$ (**1**) and $[Ag_5(PYDC)_2(OH)]$ (**2**) were synthesized under the hydrothermal conditions using aromatic–carboxylic acids containing hydroxyl and pyridyl groups as ligands ($HO\text{-}H_2IPA$ = 5-hydroxyisophthalic acid and H_2PYDC = pyridine-3, 5-dicarboxylic acid). Single crystal X-ray diffraction indicated that two compounds exhibit three-dimensional frameworks constructed from different rod-shaped molecular building blocks. Both compounds favor slow release of Ag^+ ions leading to excellent and long-term antimicrobial activities towards Gram-negative bacteria, *Escherichia coli* (*E. coli*) and Gram-positive bacteria, *Staphylococcus aureus* (*S. aureus*). Their antibacterial potency was evaluated by using a minimal inhibition concentration (MIC) benchmark and an inhibition zone testing. High-resolution transmission electron microscope images indicate that the Ag-based MOFs could rupture the bacterial membrane resulting in cell death. Hematological study showed that these MOFs exhibit good biocompatibility in mice. In addition, good thermal stability and optical stability under UV–visible and visible light are beneficial for their antibacterial application.

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1. Introduction

In the past decades, antibacterial agents have attracted increasing attention for the emergence of epidemics caused by different pathogenic bacteria [1–4]. Among chemical disinfectants, both inorganic and organic–inorganic hybrid materials containing silver ions or silver particles exhibit strong inhibitory and bactericidal effects on as many as species of microbes, including Gram-negative and Gram-positive bacteria [5,6]. They have been increasingly utilized in numerous consumer products and medical devices, such as cosmetics, ceramics, catheters, surgical devices and wound dressings [7,8]. Several works have been dedicated to explain that bactericidal action of silver-based materials arises from a release of biocidal Ag^+ ions into the surrounding environment [9,10], but it is still a great challenge to design and prepare new materials allowing Ag^+ ions to be delivered with controllable increased efficiency.

In recent years, as a new class of inorganic–organic hybrid materials, metal–organic frameworks (MOFs) have great potential for a wide range of applications, such as gas storage, catalysis, chemical sensing and drug delivery [11–18], but their bactericidal applications have rarely been explored until now [19]. Compared with traditional chemical disinfectants, MOF antibacterial agents have many advantages in wide antibacterial spectrum, long-term persistence, high effectiveness, and thermal–optical stabilities. K. Nomiya and co-workers firstly presented the argument that polymeric Ag(I)-N bonding compounds had the potential application in antibacterial materials against bacteria, yeast and mold [20]. Y. Cui [21] and C. Pettinari et al. [22] showed that Ag-based MOFs constructed from 4-pyridyldurylborane and 4,4′-bipyrazolyl ligands exhibited strong antimicrobial properties, although their antibacterial mechanisms were unclarified. To the best of our knowledge, MOFs can be considered as promising antibacterial materials because their inorganic and organic components can provide platforms to generate high potent bactericidal activity and biocompatibility [23–27]. More importantly, the antibacterial activity of silver-based MOFs may be correlated with their structures which can be facilely tuned by the choice of versatile organic ligands.

In our continuing research on synthesis and properties of MOFs constructed from polycarboxylate ligands [28,29], we are interested in self-assembling high-dimensional Ag-based MOFs which may be beneficial for sustaining antibacterial efficiency due to their stoichiometric frameworks controlling the release of Ag^+. Herein, we introduce aromatic–carboxylic acids containing hydroxyl and pyridyl groups as ligands, and two three-dimensional Ag-based MOFs, $[Ag_2(O\text{-}IPA)(H_2O)\cdot(H_3O)]$ (**1**) and $[Ag_5(PYDC)_2(OH)]$ (**2**) ($HO\text{-}H_2IPA$ = 5-

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hydroxyisophthalic acid, and H_2PYDC = 3,5-dicarboxylic pyridine) have been synthesized under hydrothermal conditions. **1** and **2** displayed high antibacterial activities towards both Gram-negative bacteria and Gram-positive bacteria with excellent biocompatibility towards blood cells. The release ability of Ag^+ ions, thermogravimetric analysis and optical stability of these compounds are presented as well.

2. Experimental

2.1. Materials and methods

All of the reagents are of reagent grade and were used without further purification. Elemental analysis was performed on a Perkin-Elmer 240C elemental analyzer. FT-IR spectra were recorded on a Bruker IFS 66 V interferometer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 7 unit with a heating rate of 10 °C·min^{-1}. The samples were characterized by X-ray diffraction (XRD) (Rigaku-DMax 2400) in reflection mode (Cu-Kα radiation). The shapes and structures of samples were observed by scanning electron microscope (SEM, JEOL-6360LV). The morphological changes of the bacteria were observed by transmission electron microscopy (TEM, Tecnai F30, made by FEI Company), operated at 20 kV. The release ration of Ag^+ ions was performed on inductively coupled plasma atomic emission spectrometer (ICP-AES) (Optima 200 DV, made by Perkin Elmer Company).

2.2. Synthesis of single crystal $[Ag_2(O\text{-}IPA)(H_2O)\cdot(H_3O)]$ (1)

A mixture of $AgNO_3$ (0.16 g, 0.94 mmol), HO-H_2IPA (0.05 g, 0.27 mmol), and H_2O (10 mL) was sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 160 °C for 72 h. After cooling to room temperature, the colorless crystals were obtained in yield of 43% based on Ag. Element analysis calcd (%) for $C_8H_8O_7Ag_2$ (431.88): C, 22.23; H, 1.85. Found (%): C, 22.29; H, 1.88. IR (KBr, cm^{-1}) data: 3571(w), 3082(w), 2367(m), 1714(m), 1554(vs), 1383(m), 1201(vs), 763(s).

2.3. Synthesis of single crystal $[Ag_3(PYDC)(OH)]$ (2)

A mixture of $AgNO_3$ (0.16 g, 0.94 mmol), H_2PYDC (0.05 g, 0.30 mmol) and H_2O (10 mL) was sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 120 °C for 72 h. After cooling to room temperature, the colorless crystals were obtained in yield of 40% based on Ag. Element analysis calcd (%) for $C_{14}H_7N_2O_9Ag_5$ (886.57): C, 18.95; H, 0.79; N, 3.16. Found (%): C, 18.90; H, 0.78; N, 3.18. IR (KBr, cm^{-1}) data: 3384(w), 3085(w), 1613(m), 1553(vs), 1369(vs), 1138(m), 919(w), 759(s).

2.4. Single-crystal X-ray crystallography

The crystal structures of compounds **1** and **2** were determined by single-crystal X-ray diffraction experiment. The reflection data were collected on a Bruker-AXS SMART CCD area detector diffract meter with the crystals glued at the end of a glass fiber. Data collections were carried out at 293 K using a ω-scan and Mo-K_α radiation (λ = 0.71073). Empirical absorption correction was applied for all data. The structures were solved by direct methods and further refined by full-matrix least-square refinements on the basis of F^2 using SHELXTL program [30]. The heaviest atoms were firstly found. O, N and C atoms were subsequently located in difference Fourier maps. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of **1** and **2** were calculated by geometrical models. Experimental details for the structure analysis are given in Table 1. The selected bond distances and angles are listed in Table S1, and the hydrogen bonds are listed in Tables S2.

Table 1
Crystallographic data and structure refinements for **1** and **2**.

	1	2
Empirical formula	$C_8H_8O_7Ag_2$	$C_{14}H_7N_2O_9Ag_5$
Formula weight	431.88	886.57
Crystal system	Triclinic	Orthorhombic
Space group	*P-1*	*Pccn*
a (Å)	6.7037(3)	6.7533(13)
b (Å)	8.5829(4)	11.913(2)
c (Å)	9.9334(4)	20.834(4)
α (°)	96.775(4)	90
β (°)	109.688(3)	90
γ (°)	110.227(3)	90
Volume (Å^3)	486.84(4)	1676.1(5)
Z	2	4
D_{Calc}(mg/m^{-3})	2.946	3.513
μ (mm^{-1})	4.044	5.798
$F_{(000)}$	412	1648
R_{int}	0.0203	0.0182
GOF on F^2	1.030	1.038
R_1 [$I > 2\sigma(I)$]*	0.0314	0.0442
wR_2 [$I > 2\sigma(I)$]*	0.0849	0.1327
R_1 (all data)*	0.0327	0.0456
wR_2 (all data)*	0.0866	0.1335

* $R_1 = \Sigma(||F_o| - |Fc||)/\Sigma|F_o|$; $wR_2 = \{\Sigma w[(F_o^2 - F_c^2)] / \Sigma w[(F_o^2)^2]\}^{1/2}$

2.5. Optical stability test

The powders of **1** and **2** were exposed under visible light and UV–visible (UV–vis) light at room temperature in air atmosphere. Solid ultraviolet visible spectrum of **1** and **2** was tested at 24 h, 48 h and 120 h, and the powders in dark were also measured as blank.

The optical stability of compounds in aqueous solutions was tested according to the reported literature [31]. Filter papers (diameter of 10 mm) were impregnated with aqueous solutions of $AgNO_3$, **1** and **2**, respectively. The filter papers were dried at room temperature. And then they were exposed to air and irradiated with visible light for 24 h. The blank filter paper was treated as a comparative sample.

2.6. Antibacterial test

The antibacterial activities of the compounds were tested against *Escherichia coli* (F 1693) and *Staphylococcus aureus* (F 1557) by determining the minimal inhibitory concentration (MIC), growth inhibition assay and zone of inhibition technique. All bacterial routine handlings were conducted with Luria Bertani (LB) broth at 37 °C, and long term storage was performed in glycerol stocks stored at −20 °C. The medium was made up by dissolving agar and LB broth in distilled water.

2.6.1. MIC

The stock solutions of the synthesized samples were prepared in aqueous solution, and graded quantities of the test particles were incorporated in a specified quantity of sterilized liquid medium. Bacteria were maintained on general LB liquid media and were shaken at 37 °C overnight. Diluted overnight bacterial and LB liquid cultures were treated with serial dilutions of metal compounds for 24 h while shaking at 37 °C. And the optical density was measured at 600 nm (OD_{600}) to determine the MIC.

2.6.2. Growth inhibition assay

Diluted bacteria and LB liquid cultures were treated with different concentrations of commercial Ag nanoparticles (Ag-NPs), compounds **1** and **2** for 48 h while shaking at 37 °C, respectively. OD_{600} was measured for all samples through a UV–vis spectrometer at predetermined time intervals to draw the growth curves of bacteria. The growth curves of *E. coli* and *S. aureus* without antibacterial agents were also measured as blank.

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