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Regular Article

Selective adsorption activities toward organic dyes and antibacterial performance of silver-based coordination polymers

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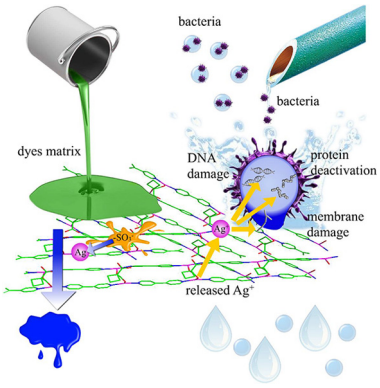
GRAPHICAL ABSTRACT

Silver-based coordination polymers were used to conduct efficiently selective uptake of organic dyes with —NH_2 & —SO_3^-. The controlled slow-release of Ag^+ ions from silver-based CPs leads to excellent antibacterial activities towards bacteria.



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ABSTRACT

Two silver-based coordination polymers, $[Ag_2(bpy)_2(cbda)]$ (**BUC-51**) and $[Ag_3(bpy)_3(cpda)]\cdot(NO_3)\cdot 9H_2O$ (**BUC-52**), have been successfully prepared by slow evaporation at room temperature. These coordination polymers exhibited good adsorptive performances toward series organic dyes with sulfonic groups, which could be ascribed to the Ag*cdots*O interaction between the silver(I) atoms in CPs and the oxygen atoms from sulfonic groups attached to organic dyes. Both **BUC-51** and **BUC-52** favoured slow release of Ag^+ ions resulting into outstanding long-term antibacterial abilities toward Gram-negative bacteria, *Escherichia coli* (*E. coli*), which was tested by a minimal inhibition concentration (MIC) benchmark and an inhibition zone testing method. Both scanning electron microscope (SEM) and transmission electron microscope (TEM) images demonstrated that these two Ag-based coordination polymers could destroy the bacterial membrane and further cause death. Additionally, the excellent stability in common solvents and good optical stability under UV–visible light facilitated their adsorptive and antibacterial applications.

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1. Introduction

Coordination polymers (CPs), as a new class of inorganic-organic hybrid materials, have great potential for wide range of applications like catalysis [1,2], anti-microbial [3], gas storage and separation [4], pollutants adsorption [5], sensing [6], fluorescence [7], magnetism [8], drug delivery [9], and so on [10,11], due to their diverse compositions, easily tailored structures, ultra-high surfaces and active sites [12]. Especially, CPs are promising absorbents for high-performance adsorptive removal of pollutants from aquoues solution resulting from their striking characteristics of cavities with regular size and shape, well-defined channels, surface charge, along with excellent stability [13,14]. Furthermore, some CPs were used to selectively adsorb and efficiently separate organic pollutants with different charges from their matrix due to the electronic interactions and/or guest-guest exchange interactions [15,16]. For instance, Wang and co-workers presented chemically stable graphene-like CP, which could achieve both high-performance adsorption toward anionic organic dyes such as congo red (CR) with adsorption capacity of 4923 mg/g and efficient separation of organic dyes with different charges from their matrix [17]. CPs also exhibited outstanding antibacterial activities with high durability, considering that they could be utilized as reservoirs to slowly release metal ions such as Ag^+, Zn^{2+}, Cu^{2+} or Cu^+ with the aid of organic ligands [3,18]. It was worthy to note that Ag^+ ions could be easily diffused into a bacterial membrane and further destroy cell membrane proteins [18,19]. From this point, it is important and necessary to design and prepare Ag-based CPs as excellent antibacterial agent candidates.

In this work, two new coordination polymers, $[Ag_2(bpy)_2(cbda)]$ (**BUC-51**) and $[Ag_3(bpy)_3(cpda)]\cdot(NO_3)\cdot 9H_2O$ (**BUC-52**) were synthesized from the reaction of 4,4′-bipyridine (bpy), 1,1-cyclopropanedicarboxylic acid (H_2cpda)/1,1-cyclobutane dicarboxylic acid (H_2cbda) via slow evaporation, and were characterized by TGA, XRD and FTIR. Their adsorptive performances toward different organic dyes and antibacterial activities along with the corresponding mechanisms were investigated.

2. Experimental

2.1. Materials and methods

All GR chemicals and solvents were commercially available from J&K Chemical Ltd. and used without any further purification. *Escherichia coli* (CICC 23429) were purchased from the China Centre of Industrial Culture Collection (Beijing, China). Elemental analyses of C, H and N of the CPs were performed on Elementar Vario EL-III instrument. FTIR spectra in the region of 4000–400 cm^{-1} were recorded on a Nicolet 6700 FTIR spectrophotometer with KBr pellets. Thermogravimetric analyses were performed from 90 °C to 800 °C in air stream at a heating rate of 10 °C min^{-1} on a DTU-3c thermal analyser using α-Al_2O_3 as reference. Powder X-ray diffraction patterns were recorded using a Dandonghaoyuan DX-2700B diffractometer with Cu Kα radiation. X-ray photoelectron spectra measurement was conducted with Thermo ESCALAB 250XI. The elemental mapping was obtained on a Hitachi SU8020 scanning electron microscope. The change of bacteria was observed with the aid of microscope with Axio Imager A^2. The release rate of Ag^+ ions was tested on iCAP 7000 inductively coupled plasma optical emission spectrometer. The surface morphologies of samples were observed by JEOL-6360LV scanning electron microscope. The morphological changes of the bacteria were observed by Hitachi-HT7700 transmission electron microscopy operated at 20 kV.

2.2. Synthesis

2.2.1. $[Ag_2(bpy)_2(cbda)]$ (BUC-51)

An ammonia solution (125 mL, 0.5 mol/L) containing $AgNO_3$ (1.25 mmol, 0.21 g) and 1,1-cyclobutane dicarboxylic acid (H_2cbda, 1.25 mmol, 0.18 g) was added dropwise to an EtOH solution (125 mL) of 4,4′-bipyridine (bpy, 1.25 mmol, 0.20 g), and the mixture was stirred for 15 min, then allowed to evaporate slowly at room temperature in the dark. Block-like white crystals of $[Ag_2(bpy)_2(cbda)]$ (1) were obtained after 2 weeks (yield 90% based on $AgNO_3$). Anal. Calcd. for $C_{26}H_{22}Ag_2N_4O_4$ (%): C, 46.6; H, 3.3; N, 8.4. Found: C, 46.6; H, 3.4; N, 8.5. IR (KBr)/cm^{-1}: 3418, 1598, 1527, 1488, 1410, 1384, 1226, 1070, 805, 732, 621, 564, 510.

2.2.2. $[Ag_3(bpy)_3(cpda)]\cdot(NO_3)\cdot 9H_2O$ (BUC-52)

The synthesis of block-like white crystals of $[Ag_3(bpy)_3(cpda)]\cdot(NO_3)\cdot 9H_2O$ (**BUC-52**) followed the same procedure as for **BUC-51** except that H_2cbda was replaced with H_2cpda (yield 88% based on $AgNO_3$). Anal. Calcd. for $C_{35}H_{46}Ag_3N_7O_{16}$ (%): C, 36.7; H, 4.0; N, 8.6. Found: C, 36.8; H, 4.0; N, 8.7. IR (KBr)/cm^{-1}: 3396, 1600, 1532, 1488, 1417, 1383, 1222, 1064, 805, 727, 617, 565, 507.

2.3. Adsorption experiments

Anionic methyl orange (MO), anionic congo red (CR), cationic methylene blue (MB) and cationic rhodamine B (RhB) were selected as model pollutants to evaluate the adsorption performance of **BUC-51** and **BUC-52**. A solid sample powder (50 mg) of **BUC-51** and **BUC-52** were added to 200 mL of MO (10 mg/L), CR (50 mg/L), MB (10 mg/L) and RhB (10 mg/L) aqueous solution in a 300 mL breaker, respectively. The mixtures were vibrated in water bath shaker with speed of 150 r/min at 293 K. 1 mL aliquots were extracted using a 0.45 μm syringe filter (Tianjin Jinteng) at regular intervals for analysis. A Laspec Alpha-1860 spectrometer was used to monitor the MO, CR, MB and RhB concentration changes by the maximum absorbance at 463, 493, 664 and 552 nm, respectively.

2.4. Antibacterial activities

The antibacterial performances of **BUC-51** and **BUC-52** were used tested by agar plate diffusion assay method agar plate diffusion assay suggested by the National Committee for Clinical Laboratory Standards [20,21]. Surface water collected from Minghu Lake in BUCEA was used to investigate the antibacterial properties of **BUC-51** and **BUC-52**. Two micrograms of **BUC-51** and **BUC-52** were added to 200 mL lake water, and the control experiment was conducted at the same time without **BUC-51** and **BUC-52**. After 4 h cultivation, the supernatant was vaccinated onto Agar plate to observe the growth status of bacterial colony. Meanwhile, antibacterial activities of these two CPs were tested against *Escherichia coli* (CICC 23429) 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 −30 °C. The medium was made up by dissolving agar and LB broth in distilled water.

2.4.1. Minimum inhibitory concentration (MIC)

Bacteria were placed in general LB liquid media and were agitated at 37 °C overnight. Diluted overnight bacterial and LB liquid cultures were treated with serial dilutions of **BUC-51** and **BUC-52** for 24 h while shaking at 37 °C, respectively. The MIC values were determined by the optical density measured at 600 nm (OD_{600}, Fig. S1).