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A new carboxyl-copper-organic framework and its excellent selective absorbability for proteins

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ABSTRACT

One-pot solvothermal treatments of $CuCl_2 \cdot 2H_2O$, H_2**L** (5-(3-methyl-5-(pyridin-4-yl)-4*H*-1,2,4-triazol-4-yl) isophthalic acid) and $Sm(NO_3)_3 \cdot 6H_2O$ in water yielded a rare carboxyl-copper-organic framework, $[Cu(HL)]_n \cdot nH_2O$ (**1**). The existence of carboxyl groups in compound **1** may be due to the interference of $Sm(NO_3)_3 \cdot 6H_2O$ at the relatively high temperature and autogenous pressure of the reaction. Compound **1** has been characterized by single-crystal X-ray diffraction, PXRD, IR, and elemental analysis. Compound **1** is a 3D coordination polymer, and an xfe-4-Fddd, ($4^2.6.8^3$) topology in **1** is created. In addition, the optical properties have been investigated. Rhodamine B dyeing experiments exhibited that there were residual carboxyl groups on the surface of compound **1**. UV–vis results showed that more lysozyme was adsorbed onto the surface of compound **1** than BSA at pH 7.4. At the same time, XPS spectra were also investigated to verify the results.

1. Introduction

Considerable attention has been paid to the study of transition metal coordination polymers not only because of non-linear optics [1,2], gas absorption [3–5], luminescence [6,33], magnetism [34], medicine [35], and catalytic properties [36,37], but also their fascinating architectures [38,39]. Many chemical functionalities are incompatible with the conditions for MOF assembly, and cannot be obtained covalently attached within MOF cavities via traditional synthetic routes. For example, MOFs with struts containing free carboxylic acids [7] or pyridines [8] remain rare, as these moieties often serve as the key coordinating elements of the MOF frameworks. This can be explained by the tendency of such reactive groups to engage in framework building through coordination or hydrogen bonding. The appeal of MOF materials that have free carboxylic acids is clear: they can be further modified using a wide range of reactions to afford new MOFs with different capabilities [9]. For example, such a MOF could be functionalized with a variety of metals, generating a series of new MOF materials with metal carboxylates in their pores, where each one can be used for a particular catalytic reaction [8,10]. Alternatively, the varying affinities that metal carboxylates have for different chemical species could be exploited to separate specific chemical mixtures [11–13]. In view of free carboxylic acids from the surface of MOF, we have considered the possibility of protein adsorption. In physiological media, most proteins carry a net charge, with the sign and magnitude of the net charge depending on the isoelectric point of the protein (pI). Electrostatic interactions between proteins and charged surfaces, therefore, often play a major role in the adsorption behavior of proteins [14–16]. Herein, we present a novel copper-based MOF $[Cu(HL)]_n \cdot nH_2O$ (**1**; H_2**L**=5-(3-methyl-5-(pyridin-4-yl)-4*H*-1,2,4-triazol-4-yl) isophthalic acid). The ligand H_2**L**, which can be obtained from cheap starting materials by a two-step synthesis in good yield, combines carboxylate, triazole, and pyridine functions and is adopted from a recently presented series of linkers. We investigated the amounts of bovine serum albumin (BSA, negatively charged at pH 7.4) and lysozyme (positively charged at pH 7.4) adsorbed onto negatively MOF to monitor the effect of electrostatic attraction and repulsion on the amount of adsorbed proteins. At the same time, XPS spectra were also investigated to verify the results.

2. Experimental section

2.1. Materials and physical measurements

Lysozyme was purchased from Sigma-Aldrich. Bovine serum albumin (BSA) was obtained from Amresco Inc. (Solon, OH).

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All commercially available chemicals and solvents were of reagent grade and used without further purification. The ligand 5-(3-methyl-5-(pyridin-4-yl)-4*H*-1,2,4-triazol-4-yl) isophthalic acid (H_2**L**) was synthesized according to the method reported previously [17]. X-ray powder diffraction (PXRD) intensities were measured on a Rigaku D/max-IIIA diffractometer (Cu-*K*α, $\lambda = 1.54056$ Å). The single crystalline powder samples were prepared by crushing the crystals and scanned from 3° to 60° with a scanning speed of 0.02°/s. Thermogravimetric analysis (TGA) were performed on a NETZSCH TG 209 instrument with a heating rate of 10 °C/min in the N_2 atmosphere. Flourescence spectroscopy data were recorded on HORIBA Jobin Yvon HJY-FL3-221-TCSPC spectrophotometer.

2.2. Preparation of coordination polymers

2.2.1. Synthesis of $[Cu(HL)]_n \cdot nH_2O$

$CuCl_2 \cdot 2H_2O$ (0.1 mmol, 0.017 g), H_2**L** (0.2 mmol, 0.0648 g) and $Sm(NO_3)_3 \cdot 6H_2O$ (0.1 mmol, 0.0444 g) were dissolved in 15 mL water, reacted for 20 min under the 100 W of ultrasound, transferred to a 25 mL Teflon-lined pot, and the reaction mixture was heated within 2 h up to 140 °C. The temperature was kept on a constant level for 3 days, and then the autoclave was cooled rapidly to room temperature. Brown block crystals of **1** were collected with a yield of 78% (based on Cu). Anal. calcd for $C_{16}H_{13}N_4O_5Cu$: C, 47.47; H, 3.24; N, 13.84. Found: C, 47.52; H, 3.14; N, 13.90. IR data (KBr pellet, ν[cm^{-1}]): 3419.61, 2362.76, 2342.41, 2026.88, 1619.15, 1544.96, 1373.96, 1306.30, 1251.18, 1132.83, 879.04, 840.91, 623.85, 488.66.

2.3. Analysis of the residual carboxyl groups of compound *1*

Compound **1** was first immersed in rhodamine B (0.1 wt%) in sodium phosphate buffer (0.1 M, pH 8) for 5 min. After rinsing with DI water and drying in a stream of nitrogen, the rhodamine B stained compound **1** was imaged using fluorescent microscopy (excitation 540 ± 20 nm, emission 625 ± 20 nm) [14].

2.4. Protein adsorption analysis

Protein adsorption assay was performed following the method previously reported [14]. Protein solutions were freshly prepared by dissolving BSA or lysozyme in phosphate-buffered saline (PBS, 0.01 mol/L, pH 7.4) to give a final concentration of 20 mg/mL. Compound **1** (40 mg) was placed in 5 mL centrifugal tubes, to which 2 mL of the freshly prepared BSA or lysozyme was added. Adsorption was allowed to proceed at 37 °C for 2 h under gentle shaking. The suspension was then centrifuged and washed with PBS five times. The supernatant was collected together, filtered through a membrane of 0.45 μm pore diameter, and diluted to 500 mL with PBS buffer. The supernatant was analyzed by ultraviolet absorbance at 280 nm to determine the adsorption amount of protein. Three repetitions were performed for all samples. The adsorption of protein, P (mg/g), on compound **1** was calculated according the following formula:

$$P = \frac{[C_i]V_i - [C_r]V_r}{m}$$

where $[C_i]$ is the protein concentration in the initial solution ($mg_{Protein}/mL_{solution}$), $[C_r]$ is the residual concentration of protein in solution ($mg_{Protein}/mL_{solution}$), and m is the mass of compound **1** (g).

2.5. X-ray photoelectron spectroscopy (XPS) analysis

XPS spectra were recorded using a Kratos Axis Ultra DLD spectrometer employing a monochromated Al-*K*α X-ray source ($h\nu = 1486.6$ eV). The vacuum in the main chamber was kept above 3×10^{-6} Pa during XPS data acquisitions. General survey scans (binding energy range: 0–1200 eV; pass energy: 160 eV) and high-resolution spectra (pass energy: 40 eV) in the regions of N1*s* were

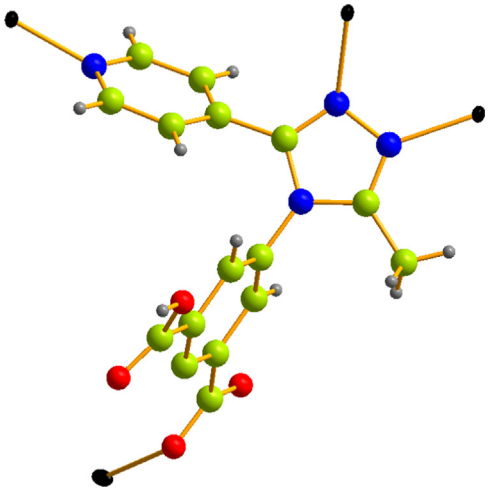
Table 1
Crystal data and structure refinements for compound 1.

Identification	Compd **1**
Empirical formula	$C_{16}H_{13}CuN_4O_5$
Formula weight	404.84
T (K)	293(2)
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	17.035(3)
b (Å)	10.172(2)
c (Å)	19.396(4)
α (°)	90
β (°)	113.62(3)
γ (°)	90
Z	8
ρ_{calc} (g cm^{-3})	1.747
μ (mm^{-1})	1.458
F(0 0 0)	1648
2θ scan range	4.58 to 50.02°
Reflections collected	12,530
R_{int}	0.1068
Independent reflections	2705
Parameters	240
Goodness-of-fit on F^2	1.093
R_1,wR_2[$I > 2\sigma(I)$]	0.0428, 0.0975
R_1,wR_2[all data]	0.0491, 0.1036

Table 2
Selected bond lengths [Å] and angles [°] for **1**

Selected bonds (Å) and angles (°)			
N(3)–Cu(1)#1	1.970(2)	N(2)–Cu(1)–N(3)#2	131.60(9)
Cu(1)–N(2)	1.965(2)	N(2)–Cu(1)–N(4)#3	113.23(9)
Cu(1)–N(3)#2	1.970(2)	N(3)#2–Cu(1)–N(4)#3	110.50(9)
Cu(1)–N(4)#3	2.068(2)	N(2)–Cu(1)–O(3)#4	90.87(9)
Cu(1)–O(3)#4	2.220(2)	N(3)#2–Cu(1)–O(3)#4	109.30(9)
N(4)–Cu(1)#3	2.068(2)	N(4)#3–Cu(1)–O(3)#4	89.60(8)
O(3)–Cu(1)#5	2.220(2)	N(2)–N(4)–Cu(1)#3	114.46(16)
		N(4)–N(2)–Cu(1)	122.61(17)

Symmetry transformations used to generate equivalent atoms: #1$x-1/2, y-1/2, z$; #2$x+1/2, y+1/2, z$; #3 $-x+3/2, -y+1/2, -z$; #4 $x, -y, z-1/2$; #5 $x, -y, z+1/2$.



Scheme 1. Coordination Modes of the ligand HL^- in compound **1**.