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A novel porous anionic metal–organic framework with pillared double-layer structure for selective adsorption of dyes

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ABSTRACT

A novel porous anionic metal–organic framework, $(Me_2NH_2)_2[Zn_2L_{1.5}bpy]\cdot 2DMF$ (**BUT-201**; H_4L=4,8-disulfonaphthalene-2,6-dicarboxylic acid; bpy=4,4-bipyridine; DMF=N,N-dimethylformamide), with pillared double-layer structure has been synthesized through the reaction of a sulfonated carboxylic acid ligand and $Zn(NO_3)_2\cdot 6H_2O$ with 4,4-bipyridine as a co-ligand. It is found that **BUT-201** can rapidly adsorb cationic dyes with a smaller size such as Methylene Blue (MB) and Acriflavine Hydrochloride (AH) by substitution of guest $(CH_3)_2NH_2^+$, but has no adsorption towards the cationic dyes with a lager size such as Methylene Violet (MV), the anionic dyes like C. I. Acid Yellow 1 (AY1) and neutral dyes like C. I. Solvent Yellow 7 (SY7), respectively. The results show that the adsorption behavior of **BUT-201** relates not only to the charge but also to the size/shape of dyes. Furthermore, the adsorbed dyes can be gradually released in the methanol solution of $LiNO_3$.

1. Introduction

Recently, as a class of organic–inorganic hybrid porous material, metal–organic frameworks (MOFs) [1–3] composed of organic ligands and metal ions (clusters) have received a considerable attention owing to their emerging applications in many areas, such as gas storage/separation [4–9], ion exchange [10,11], catalysis [12–14], and so on [15–19]. The structures and properties of MOFs usually depend on the organic ligands and metal ions (or metal clusters). Metal clusters [20,21], also called secondary building units (SBUs), are usually formed *in situ*. Generally, under given synthetic conditions [22–28], it is easy to predict the structures of the resulting SBUs after a long time efforts of this respect in MOFs field. On the other hand, organic ligands have usually been synthesized prior to MOFs' construction, thus the structures and properties of MOFs can be easily tailored for some pre-designed applications to some extent [29].

Charged MOFs are very appealing due to their inherent features such as easy guest substitution. Recent studies show that charged MOFs as a class of excellent porous materials, exhibit a potential application for dye removal by guest molecule substitution [30–38]. Dyes are widely used in some industries including medicine, paper, leather, plastics and textiles, leading to the existence of various dyes in industrial effluents which must be removed before discharged into natural environment. Compared with conventional techniques [39,40], the methods based on adsorption are promising because of their low energy consumption and ease to operate. A representative example was reported by Bu's group [30]. They synthesized a series of cationic indium MOFs and applied them into the adsorption and separation of organic dyes based on anionic guest substitution. Despite some examples were reported on the exploration of organic dye removal using MOFs based on guest molecule substitution [30–38], the study in this area is still at the early stage.

Many efforts have been focused on modifying the pore chemistry by incorporating functional moieties in order to optimize the adsorption performance of MOFs. Sulfonate groups ($-SO_3^-$) were often selected to endow the framework of porous materials with free Lewis base sites to make strong interactions between guest molecules and the framework skeleton. For MOFs' construction, when sulfonate and carboxylic groups coexist in a ligand, the carboxylic groups are expected to preferentially coordinate with metal ions (clusters) from first-row transition-metal because of their relatively stronger coordination ability [41]. In this context, the generated framework might leave the sulfonate groups free and possibly make the resulted MOF with negative charges. Herein, 4,8-disulfonaphthalene-2,6-dicarboxylic acid (H_4L), synthesized through functionalizing 2,6-dicarboxylic acid with sulfonate groups was advisedly selected as organic ligand reacting to Zn $(NO_3)_2\cdot 6H_2O$ under solvothermal conditions. A novel anionic

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three-dimensional (3D) pillared double-layer MOF with the formula of $(Me_2NH_2)_2[Zn_2L_{1.5}bpy]\cdot 2DMF$ (**BUT-201**, BUT=Beijing University of Technology) was synthesized in the presence of 4,4-bipyridine (bpy) as a co-ligand. It was found that **BUT-201** can rapidly adsorb cationic dyes with a smaller size such as Methylene Blue (MB) and Acriflavine Hydrochloride (AH), but hardly adsorb such dyes as neutral Solvent Yellow 2 (SY2) and negative Methyl Orange (MO). Furthermore, the larger cationic dye, Methylene Violet (MV), was rarely adsorbed, and no uptake was found upon neutral (C. I. Solvent Yellow 7, SY7) and anionic dyes (C. I. Acid Yellow 1, AY1) with even smaller sizes compared with SY2 and MO [38], respectively.

2. Experimental

2.1. Materials and general methods

All the reagents and solvents (AR grade) for the synthesis were purchased from commercial sources and used without further purification. The ligand H_4L was synthesized according to the modified previous reports [41,42]. IR spectra were monitored with a Shimadzu IR435 spectrometer as KBr pellet (4000–400 cm^{-1}). Thermal analysis data were collected on a SHIMADZU DTG-60 thermal analyzer from 40 to 800 °C with a heating rate of 5 °C min^{-1} under N_2 atmosphere. Powder X-ray diffraction (PXRD) patterns were recorded on a PANalytical X'Pert PRO Diffractometer by using Cu-Kα radiation (λ=1.541874 Å) at room temperature. Simulation of the PXRD pattern was performed by the single-crystal data and diffraction-crystal module of the *Mercury* program. UV–vis spectra data were obtained with a SHIMADZU UV-2600 Spectrophotometer.

2.2. Synthesis of H_4L ligand

20 mL of fuming sulfuric acid (SO_3, 20 wt%) was slowly added to a 100 mL three-neck flask containing 4 g (18.5 mmol) naphthalene-2,6-dicarboxylic acid under stirring. Then the reaction mixture was stirred at 120 °C for 12 h. After cooling to room temperature, the mixture was transferred into concentrated HCl and the white power of acid H_4L was precipitated. The power was washed serveral times with concentrated HCl. Then pure product was collected by centrifuge and dried at 80 °C. Yield 6.0 g (~86%) based on naphthalene-2,6-dicarboxylic acid. IR (KBr pellet, cm^{-1}): 1287 (m), 1196 (s), 1113 (w), 1047 (m) (O=S=O of $-SO_3H$ group) [42], 623 (m).

2.3. Preparation of $(Me_2NH_2)_2[Zn_2L_{1.5}bpy]\cdot 2DMF$ (**BUT-201**)

A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (10 mg, 0.035 mmol), H_4L (13 mg, 0.035 mmol), bpy (3 mg, 0.019 mmol) and 1.6 mL DMF with 6 drops HBF_4 was sealed into a 5 mL vial and then heated at 100 °C for 48 h. After the reaction system was cooled down to room temperature, the products were washed with DMF twice to obtain the pure colorless block crystals. The as-synthesized **BUT-201** was hardly soluble in common organic solvents such as DMA, DMF, CH_2Cl_2, $CHCl_3$, MeOH, EtOH, and acetone. IR (KBr, cm^{-1}): 3475 (m), 3097 (w), 2812 (w), 2359 (w), 1714 (m), 1613 (s), 1395 (s), 1345 (s), 1194 (s), 1035 (s), 809 (m), 750 (w), 607 (s), 515 (m).

2.4. X-ray crystallography

The diffraction data for **BUT-201** were collected on an Agilent Technologies SuperNova Single Crystal Diffractometer that was equipped with graphite-monochromatized Mo-Kα radiation (λ=0.71073 Å) at −173 °C. Empirical absorption correction was

Table 1
Crystal data and structure refinement for **BUT-201**.

Empirical formula	$C_{38}H_{44}N_6O_{17}S_3Zn_2$
Formula weight	1083.7
Crystal system	Triclinic
Space group	*P*-1
a (Å)	12.6390 (3)
b (Å)	13.9706 (4)
c (Å)	16.2850 (4)
α (°)	68.414 (3)°
β (°)	83.532 (2)°
γ (°)	73.525 (2)°
Volume (Å^3)	2567.86 (12)
Z	2
Calculated density (mg m^{-3})	1.402
Independent reflections ($I>2\sigma(I)$)	9534
F (000)	1116
θ range for data collection	4.3–73.6°
Limiting indices	$-15\le h\le 15$ $-17\le k\le 15$ $-20\le l\le 20$
Goodness-of-fit on F^2	0.722
$R1^a$, $wR2^b$ [$I>2\sigma(I)$]	R_1=0.0583,wR_2=0.1623
$R1^a$, $wR2^b$ (all data)	R_1=0.0563,wR_2=0.1598
Largest diff. peak and hole (e Å^{-3})	1.38 and −1.11

[a] $R_1=\Sigma(||F_0|-|F_c||)/\Sigma|F_0|$ and
[b] $wR_2=[\Sigma w(|F_0|^2-|F_c|^2)^2/\Sigma w(F_0^2)]^{1/2}$

Table 2
Selected bond lengths (Å) and angles (°) for **BUT-201**.

Zn1–O11	1.932 (2)	Zn1–O1[a]	1.944 (2)
Zn1–O9	1.974 (2)	Zn1–N1	2.005 (3)
Zn2–O10	1.954 (2)	Zn2–O2[a]	1.959 (2)
Zn2–N2[b]	2.013 (3)	Zn2–O5[c]	2.085 (3)
Zn2–O12	2.140 (3)	O11–Zn1–O1[a]	111.9 (1)
O11–Zn1–O9	102. 0 (1)	O1[a]–Zn1–O9	129.9 (1)
O11–Zn1–N1	111.1 (1)	O1[a]–Zn1–N1	103.4 (1)
O9–Zn1–N1	97.1 (1)	O10–Zn2–O2[a]	146.3 (1)
O10–Zn2–N2[b]	112.8 (1)	O2[a]–Zn2–N2[b]	100.7 (1)
O10–Zn2–O5[c]	87.5 (1)	O2[a]–Zn2–O5[c]	90.1 (1)
N2[b]–Zn2–O5[c]	99.6 (1)	O10–Zn2–O12	86.5 (1)
O2[a]–Zn2–O12	89.4 (1)	N2[b]–Zn2–O12	92.0 (1)
O5[c]–Zn2–O12	168.4 (1)		

Symmetry transformations used to generate equivalent atoms:
[a] $x+1, y, z$;
[b] $x, y+1, z$;
[c] $-x+1, -y+1, -z+2$.

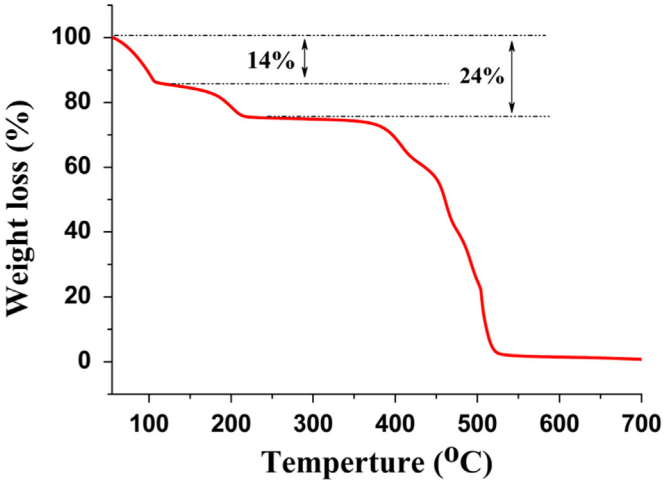

Fig. 1. TG curve of as-synthesized BUT-201.