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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 LiNO₃.

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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

http://dx.doi.org/10.1016/j.jssc.2015.10.022 0022-4596/© 2015 Elsevier Inc. All rights reserved. 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 (-SO₃⁻) 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 (H₄L), synthesized through functionalizing 2,6-dicarboxylic acid with sulfonate groups was advisedly selected as organic ligand reacting to Zn (NO₃)₂·6H₂O under solvothermal conditions. A novel anionic

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three-dimensional (3D) pillared double-layer MOF with the formula of $(Me_2NH_2)_2[Zn_2L_{1.5}bpy]$ 2DMF (**BUT-201**, BUT=Beijing University of Technology) was synthesized in the presence of 4,4bipyridine (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 H₄L was synthesized according to the modified previous reports [41,42]. IR spectra were monitored with a Shimadzu IR435 spectrometer as KBr pellet ($4000-400 \text{ cm}^{-1}$). 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 N₂ atmosphere. Powder X-ray diffraction (PXRD) patterns were recorded on a PANalytical X'Pert PRO Diffractometer by using Cu-K α radiation (λ =1.541874 Å) at room temperature. Simulation of the PXRD pattern was performed by the singlecrystal 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 $H_{4}L$ ligand

20 mL of fuming sulfuric acid (SO₃, 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 H₄L 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 (\sim 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(NO₃)₂ · 6H₂O (10 mg, 0.035 mmol), H₄L (13 mg, 0.035 mmol), bpy (3 mg, 0.019 mmol) and 1.6 mL DMF with 6 drops HBF₄ 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-K α radiation $(\lambda = 0.71073 \text{ Å})$ at -173 °C. Empirical absorption correction was

Table 1

Crystal data and structure refinement for BUT-201.

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

^a $R_1 = \Sigma(||F_0| - |F_C||) / \Sigma |F_0|$ and

010-Zn2-05

N2^b-Zn2-O5^c

02^a-Zn2-012

^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.							
Zn1-011	1.932 (2)	Zn1-O1ª	1.944 (2)				
Zn1-09	1.974 (2)	Zn1-N1	2.005 (3)				
Zn2-010	1.954 (2)	Zn2-O2 ^a	1.959 (2)				
Zn2–N2 ^b	2.013 (3)	Zn2-O5 ^c	2.085 (3)				
Zn2-012	2.140 (3)	011-Zn1-01 ^a	111.9 (1)				
011-Zn1-09	102.0(1)	01 ^a -Zn1-09	129.9 (1)				
011-Zn1-N1	111.1 (1)	O1 ^a -Zn1-N1	103.4 (1)				
09-Zn1-N1	97.1 (1)	010-Zn2-02 ^a	146.3 (1)				
010-Zn2-N2 ^b	112.8 (1)	O2 ^a -Zn2-N2 ^b	100.7 (1)				

02^a-Zn2-05^c

010-7n2-012

N2^b-Zn2-O12

90.1 (1)

86.5(1)

92.0(1)

05°-Zn2-	-012	168.4	(1)		
Symmetry	transformations	used	to generate	equivalent	atoms:

87.5 (1)

99.6 (1)

89.4 (1)



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



Fig. 2. The PXRD patterns for simulated and as-synthesized BUT-201.

applied using spherical harmonics and implemented in *SCALE3 ABSPACK* scaling algorithm. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement using the *SHELXTL* software package [43]. All non-H atoms were refined anisotropically during the final cycles. Hydrogen atoms of ligands were calculated at idealized

positions with a riding model and refined isotropically. There are large solvent accessible pore volumes in the crystals of **BUT-201**, which are occupied by highly disordered solvent molecules. No satisfactory disorder model for these guest molecules could be achieved, and therefore the *SQUEEZE* program implemented in *PLATON* was used to remove the electron densities of these disordered species. Thus, all of the electron densities from free guest molecules have been "squeezed" out [45]. The details of structural refinement can be found in Table 1, while the selected bond lengths and angles are summarized in Table 2.

2.5. Dyes absorption and release

Dyes selective absorption: as-synthesized **BUT-201** crystals were successively washed with DMF and MeOH three times. Then the samples were transferred into MeOH solutions containing MB, AH, MV, MO, SY2, AY1, and SY7 with certain concentrations at the detectable range by UV–vis spectra in vials, respectively. After that, the concentrations of dyes were measured every several minutes with UV–vis to assess the adsorption property of **BUT-201**. In addition, the pure dye solution is replaced with the mixture of two different dyes, including MB&MO and MB&SY2, which were employed to further verify the selective uptake property of **BUT-201**.

Dyes release: the **BUT-201** samples loaded with MB or AH (MB@BUT-201 or AH@BUT-201) were transferred into pure MeOH and MeOH solutions of LiNO₃ in vials, respectively. Then the releasing process was monitored by UV–vis.



Fig. 3. The structural presentation of BUT-201 (hydrogen atoms, dimethylaminecations, and solvent molecules are omitted for clearly): (a) Coordinaton environments of Zn^{2+} , H₄L and bpy ligands. *Symmetry codes*:A, (x, 1+y, z); B, (1-x, 1-y, 2-z); C, (1+x, y, z); D, (1-x, 2-y, 1-z); (b) View of the 2D layer assembled by Zn^{2+} , L⁴⁻ and bpy ligands; (c) 3D pillared double-layer structure of BUT-201, showing the rhombic channel along *b* axis; (d) The space-filling structure of BUT-201. Color scheme: Zn, cyan; N, blue; S, yellow; O, red; C, gray. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. Changes of UV-vis spectra in MeOH solutions of MB (a), AH (b), MO (c), SY2 (d), and MV (e) AY1 (f) SY7 (g) containing BUT-201 with the time past; the inset photographs for the changes of crystals color before and after adsorption in MeOH solutions towards the corresponding dyes.



Fig. 5. UV-vis spectra changes of dye mixture in the presence of BUT-201. (a) MB&MO; (b) MB&SY2. The inset photographs are before and after adsorption.



Fig. 6. UV-vis spectra monitored the process of dye release in a solution of MeOH with LiNO₃. (a) MB@BUT-201; (c) AH@BUT-201; (b) The release-rate comparison of MB from MB@BUT-201 in pure MeOH and in a MeOH solution of LiNO₃; (d) The release-rate comparison of AH from AH@BUT-201 in pure MeOH and in MeOH solution of LiNO₃.

3. Results and discussion

3.1. Synthesis and general characterizations of BUT-201

Transparent block crystals of **BUT-201** were prepared from H₄L, bpy, and $Zn(NO_3)_2 \cdot 6H_2O$ in DMF-HBF₄ mixed solution under solvothermal conditions. The TGA was employed to check the thermal stability of as-synthesized **BUT-201**. The curve of thermal gravimetric analysis in Fig. 1 shows that two processes of rapid weight loss are observed before 250 °C. The weight loss of 14% is corresponding to the calculated value (13%) for the removal of

DMF molecules, and then there is an additional weight loss of 10% which is in good agreement with the removal of dimethylamine molecules (calc. 8%). The dimethylamine molecules mentioned above should be from $(CH_3)_2NH_2^+$ with a proton transfer process between the counter cations and the anionic framework [41,44]. The host framework decomposes after an obvious platform and the thermal stability of **BUT-201** is up to ~380 °C. The phase purity of as-synthesized **BUT-201** was tested by PXRD. Fig. 2 shows that the experimental PXRD pattern is almost coincident with the simulated one from the single crystal data, suggesting the phase purity of as-synthesized **BUT-201**. The difference in reflection

intensities between the simulated and experimental patterns may be attributed to the variation in preferred orientation of the powder samples during the collection of the experimental PXRD data.

3.2. Structure of BUT-201

The formula of **BUT-201** is (Me₂NH₂)₂[Zn₂L_{1.5}bpy] · 2DMF obtained by single-crystal X-ray diffraction studies, thermal gravimetric analysis, and charge-balance theories. Single-crystal X-ray diffraction shows that **BUT-201** crystallizes in the triclinic space group *P*-1. In the structure, the crystallographically asymmetric unit contains two Zn^{2+} ions, one and a half L^{4-} , one bpv, two $(CH_3)_2NH_2^+$ cations, and two DMF molecules [Fig. 3(a)]. The $(CH_3)_2NH_2^+$ cations in pores should be originated from the decomposition of DMF during the reaction [38]. The Zn1 ion is surrounded by three O atoms of carboxylate groups from three different L⁴⁻ and one N atom from bpy, forming a distorted tetrahedral geometry. The Zn1–O bond distances range from 1.932 to 1.973(5) Å, and the Zn1–N bond distance is 2.005(4) Å. The Zn2 ion adopts a distorted trigonalbipyramid geometry finished by three O atoms of carboxylate groups and one O atom of sulfonate group from four independent L^{4-} , as well as one N atom from bpy. The Zn2-O bond lengths are between 1.954 and 2.084(5) Å, and the Zn2–N bond distance is 2.013(2) Å. Each carboxylate group bridges two Zn²⁺ ions in a syn-syn- μ^2 - η^1 : η^1 linking mode to form a dinuclar unit, which is connected by two L⁴⁻ and two bpy to generate a two-dimensional (2D) layer [Fig. 3(b)]. Meanwhile, Zn1 ions in one single layer are coordinated with O atoms of sulfonate groups of L⁴⁻ from adjacent layer resulting in a double-layered structure, which is further extended through L⁴⁻ to form a threedimensional (3D) pillared double-layer structure, featuring rhombic channels with a pore dimension of 12×12 Å (the distance between the atoms) [Fig. 3(c)], in which disordered (CH₃)₂NH₂⁺ cations accommodate. Topologically, the dinuclar Zn unit serves as a six-connected node and the L⁴⁻ as a three-connected linker, affording a (3,6)-connected binodal 3D structure with 3,6T24 topological type. After removing all of the guest molecules from the channels, the calculated total accessible volume is 47.7% by the PLATON.

3.3. Dyes absorption and release of BUT-201

In this work, BUT-201 was studied for adsorption of organic dyes owing to its porous anion framework nature. Four dyes were selected to assess the adsorption property of BUT-201, which possess the similar size but different charges: positively charged MB and AH, electrically neutral SY2 and negatively charged MO. The as-synthesized BUT-201 was immersed in MeOH solutions containing the above dyes at room temperature respectively. It was observed that the solutions containing MB and AH were obviously faded after several minutes, meanwhile the colorless crystals of BUT-201 turned blue of MB and yellow of AH, respectively (Fig. 4). However, the colors of solutions with negatively charged MO and electrically neutral SY2 remained unchanged (Fig. 4). These phenomena coincide with the measurement results by UV-vis spectra (Fig. 4). The results could be attributed to ionic interaction between anionic framework and cationic guest molecules, as well as cationic guest substitution occurring between (CH₃)₂NH₂⁺ and different cationic dye molecules.

Mixed dyes, namely MB&MO and MB&SY2, were chosen in order to further verify the selective uptake property of **BUT-201**. Experimentally, the solutions gradually turned intrinsic color of pure MO or SY2. Meanwhile the original crystals became blue of MB. The UV–vis spectra also demonstrated that **BUT-201** can rapidly and selectively adsorb cationic dyes, but has no adsorption

towards the anionic and neutral dye molecules in solutions (Fig. 5). For comparison, the adsorption of another cationic dye with a larger size and different shape, namely MV, was examined [Fig. 4 (e)]. But no incorporation was observed, and the size/shape exclusion effect may be the dominant factor. All tested results suggest that the adsorption behavior not only follows a charge but also a size/shape exclusion effect. In addition, we also tested dyes with even smaller sizes (compared with MB and AH [38]): anionic AY1 [Fig. 4(f)] and neutral SY7 [Fig. 4(g)], and no obvious adsorption was found by UV–vis spectra, even though the selected dyes seem to be able to accommodate pore considering the size. It further suggests that cationic guest molecule substitution may be the dirven-force and plays a primary role.

The reversibility of the dyes adsorption is extremely vital for application in practice, so dye release processes were also investigated in pure MeOH and a saturated MeOH solution of LiNO₃, respectively (Fig. 6). It was found that, the loaded dye molecules are barely released in pure MeOH, but can be readily released in saturated MeOH solution of LiNO₃, which is demonstrated that dye release in this work is also a guest cationic substitution-driven process. Furthermore, the processes of dye release recorded by UV–vis spectra were quickly achieved an equilibrium towards MB@BUT-201 and AH@BUT-201 over a period of time, and after that the release rate of dye molecules became slower, with the concentrations of released dyes in solutions increased (Fig. 6).

4. Conclusions

In summary, a novel anionic MOF with pillared double-layer structure was successfully synthesized, structurally characterized, and used in selective adsorption of dyes. **BUT-201** can rapidly and selectively adsorb the cationic dyes with a smaller size (MB and AH) by cationic guest molecule substitution, being controlled by charge and size/shape exclusion effect. Moreover, dye release is realized in a saturated MeOH solution of LiNO₃. Dye adsorption and release studies reveal that **BUT-201** possesses potential applications in selectively removing cationic dyes with a smaller size from effluents, which is very meaningful for environmental cleaning.

Supplementary data

Crystallographic data for the structure reported in this paper has been deposited on the Cambridge Crystallographic Data Center (CCDC No. 1416214). The material can be obtained free of charge via https://www.ccdc.cam.ac.uk/deposit.

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