Accepted Manuscript

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PII:	80277-5387(18)30841-6			
DOI:	https://doi.org/10.1016/j.poly.2018.12.036			
Reference:	POLY 13653			
To appear in:	Polyhedron			
Received Date:	26 September 2018			
Revised Date:	14 December 2018			
Accepted Date:	19 December 2018			



Please cite this article as: Y-Y. Cui, J. Zhang, L-L. Ren, A-L. Cheng, E-Q. Gao, A functional anionic metal–organic framework for selective adsorption and separation of organic dyes, *Polyhedron* (2018), doi: https://doi.org/10.1016/j.poly.2018.12.036

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A functional anionic metal-organic framework for selective

adsorption and separation of organic dyes

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Keywords: anionic; metal-organic framework; intersecting channels; adsorption; organic dyes.

Abstract: A 3D porous anionic MOF, {[(CH₃)₂NH₂][Zn₆(μ_3 -OH)(μ_4 -O)(NSBPDC)₅(H₂O)₂] ·DMF·12H₂O}_n (**Zn-1**) (H₂NSBPDC = 6-nitro-2,2'-sulfone-4,4'-dicarboxylic acid), has been synthesized and characterized. **Zn-1** exhibits a rare 5-connected 'sqp' net and contains large 3D intersecting channels modified with functional groups. Notably, **Zn-1** can adsorb cationic dyes selectively and effectively, even for large molecules including Rhodamine B and Crystal Violet. The influences of the constant time and initial concentration of MB on the adsorption capacity of **Zn-1** have been studied in detail. Furthermore, the kinetic research indicates that the adsorption of MB matches well with the pseudo second-order model. In addition, the material of **Zn-1** is reusable, and the adsorbed dye (MB) can be released in saturated DMF/ethanol solution of LiNO₃.

1. Introduction

With the rapid development of dyeing and printing industry, more and more dye wastewater is generated and discharged into the environment [1]. As is well known, most organic dyes are difficult to degrade due to their stability against light and oxidation [2]. Unfortunately, many dyes are toxic and may cause a serious threat to the environment and human health [3-5]. Therefore, it is imperative to remove the dyestuffs before being discharged into the river. Thus far, several techniques, such as adsorption [6-8], membrane filtration [9-12], photocatalysis [5, 13, 14] and so on [15-17], have been adopted to remove organic dye pollutants. Among these methods, adsorption is recognized as one of the most feasible strategies due to its cost-effective and easy handling [18, 19]. Conventional

adsorbents such as activated carbons, zeolites and polymer-based porous materials have been widely applied to the removal of various dye mixtures, but they are unfit for selective adsorption of targeted dyes. It is hence significant to develop novel adsorption materials for selective adsorption and separation of organic dyes.

Metal-organic frameworks (MOFs) are a flourishing class of hybrid porous materials, which have attracted ever-increasing interest in the last two decades owing to their fascinating structural diversities and specific applications [20-26]. Compared with traditional adsorbents, MOFs have some advantages since their topological structures and pore characteristics can be tuned by the following strategies [27, 28]: I. Pore size/shape of MOFs can be adjusted by the judicious selection of metal ions (metal clusters) and bridging ligands. It facilitates the selective adsorption and separation of guest molecules of different sizes/shapes. II. It is feasible to construct frameworks with large cavities by employing polynuclear metal clusters as SBUs, which helps to encapsulate the large guest molecules (such as dye molecules and drug molecules). III. The internal surface of MOFs can be modified with uncoordinated metal centers or functional groups (such as -NH₂, -OH, -SO₃H, et al.) to improve the host-guest interactions. IV. MOFs with charged skeletons facilitate the adsorption of cationic or anionic dyes via electrostatic interactions and/or ion-exchange process. Recently, MOFs have been extensively used in the adsorption and separation of dye molecules [29-35], and the studies show that the charged MOFs are good candidates for selective adsorption of targeted dyes. Zhu, et al. constructed two nanocage anionic MOFs for rapid and selective adsorption of cationic dyes based on the ion-exchange [29]. Additionally, the studies in Zheng's group indicated that the adsorption efficiency of MOFs could be improved by modification of the pore surface with polar functional groups [30]. However, as far as we know, selective adsorption of dyes with charged MOFs modified with functional groups is still less explored.

Recently, two sulfone-functionalized anionic MOFs (UoC-1 and UoC-2) with large 3D intersecting channels have been reported by Trikalitis [36]. The two MOFs are both constructed from the ligand 2,2'-sulfone-4,4'-dicarboxylic acid (H₂SBPDC) based on polynuclear Zn(II) clusters. To evaluated the influences of functional groups on the packing modes of the networks as well as their related properties, 6-nitro-2,2'-sulfone-4,4'-dicarboxylic acid (H₂NSBPDC) was prepared by functionalizing H₂SBPDC with -NO₂ groups and was utilized as the bringing ligand, and a new anionic framework (**Zn-2**) with ultra-microporous channels decorated with functional groups has been assembled successfully [37]. **Zn-2** is based on novel tetranuclear Zn(II) clusters and shows selective gas adsorption properties. It is well known that the packing mode of the framework is also affected by the reaction conditions, including temperature, solvents and so on. In this work, a new 3D anionic porous framework, $[(CH_3)_2NH_2][Zn_6(\mu_3-OH)(\mu_4-O)(H_2O)_2(NSBPDC)_5]\cdot12H_2O$ (**Zn-1**) was synthesized by varying the reaction conditions. **Zn-1** is constructed from the predesigned ligand (H₂NSBPDC) based on hexanuclear $[Zn_6(\mu_3-OH)(\mu_4-O)(H_2O)_2(COO⁻)_{10}]^-$ clusters. The framework has large 3D intersecting channels decorated with functional groups show that the

structure of **Zn-1** collapses in the air, however, the crystalline can be regained by immersing the amorphous samples in DMF or ethanol. Additionally, adsorption studies show that **Zn-1** can adsorb and separate cationic dyes with high selectivity, even for Rhodamine B (RhB) and Crystal Violet (CV) molecules with large sizes.

2. Experimental section

2.1 Materials and measurements

The ligand 6-nitro-2,2'-sulfone-4,4'-dicarboxylic acid (H₂NSBPDC) was synthesized based on the literature method [38]. The reagents employed were commercially available and used directly. The detailed description of the physical measurements and X-ray crystallographic analysis can be seen in the supporting information. The crystal data and structure refinement for **Zn-1** are shown in Table S1. CCDC No.: 1866598.

2.2 Synthesis of {[(CH₃)₂NH₂][Zn₆(μ_3 -OH)(μ_4 -O)(NSBPDC)₅(H₂O)₂]·DMF·12H₂O}_n (Zn-1) Zn(NO₃)₂·6H₂O (60mg, 0.2mmol), H₂NSBPDC (35mg, 0.1mmol) and DMF (7ml) were mixed under stirring for about 20 min. The mixture was then transferred into a 23 mL Teflon-lined reactor and heated at 92 °C for 3 days. After slow cooling to room temperature, the orange plate-like crystals were obtained with a yield of 43% (based on H₂NSBPDC). Anal. Calcd. (%) for C₇₅H₆₉N₇O₅₇S₅Zn₆: C 35.6, H 2.74, N 3.87. Found: C 34.70, H 2.72, N 3.60 \circ IR (KBr, cm⁻¹): 1656, 1539, 1375, 1317, 1193, 1143.

2.3 Experimental details for dye adsorption/desorption

Adsorption experiments were carried out in the mixed solutions of EtOH and DMF (7:1, v/v) at room temperature. The freshly prepared samples of **Zn-1** (15 mg) were immersed into solutions (10 mg·L⁻¹, 2.5 mL) containing different kinds of organic dyes (MB, SD, MO, CV, RhB) without disturbance. The adsorption process of each dye was detected using a UV-Vis absorption spectroscopy at the maximum absorbance of the dye at specified time.

The adsorption capacity (Q_t) and removal efficiency (η) of **Zn-1** at time *t* were quantified using the following Eqs (1) and (2):

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% = \frac{A_0 - A_t}{A_0} \times 100\% \quad (2)$$

Where C_0 is the initial concentration of the dye, and C_t is the dye concentration at time t (mg·L⁻¹). A_0 and A_t represent the absorbance of the dye before and after the adsorption. V is the volume of the solution (L), and m is the mass of the adsorbent (g).

To assess the adsorption selectivity of **Zn-1**, crystals of **Zn-1** (15 mg) were immersed into 2.5mL solutions containing dye mixture (MB/RB or MB/BR₂), and the original concentration ratio of each dye mixture was set to be 1:1 (10 mg·L⁻¹/10 mg·L⁻¹/10

¹). The absorbance change of each dye was detected using the UV-Vis adsorption spectra.

To evaluate the effect of initial concentration of dyes on the adsorption capacity, 15 mg of **Zn-1** were soaked in 50 mL MB solutions with different concentrations (4, 8, 12, 16 mg·L⁻¹) under agitation for 3 days at room temperature. The reaction suspension was centrifuged to remove the particles, and the supernatant was further measured using the UV-Vis absorption spectra.

Dye release experiment was performed in saturated EtOH/DMF (7/1 v/v) solution of $LiNO_3$.

3. Results and discussion

3.1 Synthesis and structure description

X-ray diffraction analysis reveals that the structure of Zn-1 is similar with that of UoC-2. However, the values of the cell parameters of the two compounds were somewhat different, which might be due to the introduction of nitro groups. Zn-1 crystalizes in the triclinic system, the $P\overline{1}$ space group, and features a non-interpenetrated anionic framework based on hexanuclear $[Zn_6(\mu_3-$ OH)(μ_4 -O)(COO)₁₀(H₂O)₂] clusters. As shown in Fig. 1, each cluster, consisting of two octahedral and four tetrahedral Zn²⁺ ions, is linked by five pairs of NSBPDC²⁻ ligands to form a five-connected pseudo-square pyramidal geometry. In each direction, two ligands are parallel with each other and stabilized by weak π - π interactions, with the interplanar and centroid–centroid distances of about 3.8 Å and 4.0 Å, respectively. In other words, each pair of ligands can be seen as a double linker. Thus, the five connected hexanuclear clusters are linked by the double linkers to form a threedimensional network. The structure has large 3D intersecting channels with dimensions of about 17 Å $\times 12$ Å along the *a* axis. The solvent accessible volume calculated with PLATON comprises 71.5% of the crystal volume [39], in which the disordered $[(CH_3)_2NH_2]^+$, H₂O and DMF molecules are included. Topologically, if the hexanuclear clusters and double linkers can be regarded as 5connected nodes and rods, respectively, the overall structure can be simplified as a 3D uninodal 5connected 'sqp' network with the Schläfli symbol of $(4^{4}6^{6})$ [40].



Fig.1 (a) the hexanuclear [Zn₆O(OH)(COO)₁₀(H₂O)₂] SBU in Zn-1; (b) the pseudo-square pyramidal connectivity of five SBUs in Zn-1. All hydrogen atoms are omitted for clarity.



Fig. 2 (a) the 3D structure of Zn-1 with channels along the *a* axis; (b) the five-connected uninodal net of Zn-1.

The experimental PXRD patterns of **Zn-1** agree well with the simulated patterns generated from the single crystal data, indicating the good purity of **Zn-1** (Fig. S6). The thermal stability of **Zn-1** was explored by thermo-gravimetric analysis (TGA). The TG curve of **Zn-1** shows a weight loss of 11.3 % between 50°C ~220°C, corresponding to the release of one DMF and twelve H₂O guest molecules (cal. 11.4%), and the framework breaks down at about 250°C (Fig. S7). Additionally, the crystals of **Zn-1** become opaque gradually in the air, and PXRD studies show that the samples of **Zn-1** lose its crystallinity along with the release of guest molecules. However, the crystallinity of **Zn-1** can be regained by immersing the amorphous samples in DMF or ethanol. The results show that the structure of **Zn-1** can be collapsed and recovered reversibly (Fig. S6).

3.2 Dye adsorption and separation properties

Inspired by the high porosity and negative electrical skeleton of Zn-1, we explored its potential application in adsorption and separation of positively charged dyes. Compared with other reported MOFs for adsorption, Zn-1 does not require any activation process. In consideration of the integrity of the framework of Zn-1, a mixed solution of EtOH/DMF (7/1, 1/1) was prepared and used in the following dye adsorption and separation experiments.

To evaluate the selective adsorption ability of **Zn-1** towards cationic dyes, three organic dyes possessing similar size but different charges, positively charged methylene blue (MB), electrically neutral sudan I (SD), negatively charged methyl orange (MO), have been carefully selected as the models. Typically, 15 mg of **Zn-1** were soaked in dye-containing solutions (10 mg·L⁻¹, 2.5 mL) without disturbance, and the content of the dye in each solution was detected using a UV-Vis absorption spectroscopy at certain time intervals. As can be seen, the corresponding absorbance of the cationic dye solution (MB) decreased gradually, and up to 94% of MB could be removed after 55h (Fig. 3a). Meanwhile, the color of the solution changed from blue to colorless and the color of crystals of **Zn-1** changed from orange to green (Fig S12). In contrast, the absorbance of the anionic



and neutral dye solutions remained unchanged (Fig. 3b-3c). These results indicated that **Zn-1** has good absorption selectivity for MB.

Fig. 3 UV-Vis spectra changes of dyes in EtOH/DMF solutions in the presence of Zn-1: (a) MB; (b) MO; (c) SD;(D) RhB; (e) CV. The inset photographs show the colors of the dye solutions before (left) and after (right) adsorption.

Up to now, much attention has been paid to the adsorption and separation of dyestuffs by MOFs. However, to the best of our knowledge, due to the restriction of the pore size of the adsorbents, only a handful of studies focused on the adsorption of large dye molecules [41, 42]. To evaluate the adsorption ability of **Zn-1** for large cationic dyes, two other dyes with large sizes (CV and RhB)

were selected for further study. The results are shown in Fig 3d, 3e and S12, both of CV and RhB can be adsorbed by **Zn-1** effectively, and the color of crystals of **Zn-1** changed from orange to rose red and red. The absorbance of the dye solutions decreased gradually, and the removal efficiency was about 94% and 90% after 55h, respectively (Fig. 5). By careful comparison, it can be found that though the removal efficiency of CV and RhB was similar with that of MB after 55h; however, the removal efficiency of CV and RhB was relatively lower during the first 24h, which might be caused by the size effect of the host and guest molecules.

Motivated by the good adsorption selectivity of **Zn-1** for cationic dyes, **Zn-1** was further used for separating MB from mixtures of MB/SD and MB/MO. As expected, **Zn-1** can adsorb cationic dye molecules (MB) selectively from the mixed dye solutions, and the residual solutions exhibited the color of SD or MO (Fig. 4). These results revealed that **Zn-1** could selectively capture cationic dyes. Compared with the removal efficiency of MB in the single dye solution, the removal efficiency in mixed dye solutions was lower at the first 24h. As time went on, the removal rate increased gradually and was up to 95% after 55h (Fig. 5). Therefore, **Zn-1** can be a potential candidate for selective adsorption and separation of dye mixtures.



Fig. 4 UV-Vis spectra changes of dyes in EtOH/DMF solutions in the presence of **Zn-1**: (a) MB/MO; (b)MB/SD. The inset photographs show the colors of the dye solutions before (left) and after (right) adsorption.



Fig. 5 Effect of constant time on the removal efficiency of cationic dyes (MB, RhB, CV, MB/SD and MB/MO).

3.3 The effect of initial concentration

To evaluate the effect of initial concentration of dyes on the adsorption capacity, crystals of **Zn-1** (15 mg) were immersed in 50 mL solutions of MB (4, 8, 12, 16 mg·L⁻¹) and stirred at room temperature for 3 days. As shown in Fig. 6, as the initial concentration of MB increased from 4 mg·L⁻¹ to 16 mg·L⁻¹, the adsorption capacity of **Zn-1** increased significantly from 20.6 mg·g⁻¹ to 100.6 mg·g⁻¹. The results indicated that the initial concentration of dyes was one of the key influence factors in the adsorption properties of the adsorbents. As the initial concentration increased to 500 mg·L⁻¹, the maximum adsorption amounts were found to be 180 mg·g⁻¹ and 147 mg·g⁻¹ for MB and RhB, respectively. As listed in Table S2, **Zn-1** exhibits competitive adsorption capacities with respected to the previously reported porous adsorbents [29, 43-50].



Fig. 6 Effects of initial concentration and contact time on the adsorption of MB.

3.4 Adsorptive Kinetics

To understand the kinetics of the adsorption of MB, the experimental kinetic data obtained in Fig. 6 ($C_{0, MB}$ = 16 mg·L⁻¹) were used to evaluate the effect of contact time on the adsorption capacity of **Zn-1** for MB. As can be seen, the adsorption capacity for MB increased rapidly in the first 50 hours, and then gradually slowed down and reached equilibrium. Additionally, to evaluate the adsorption mechanism and rate, the above kinetic data were analyzed using the pseudo-first-order and pseudo-second-order kinetic models (Eqs 3 and 4).

 $\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$

 $\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t$ (4)

Where $q_e (mg \cdot g^{-1})$ and $q_t (mg \cdot g^{-1})$ are the adsorption amount at equilibrium and at time *t* (h). k_1 (h⁻¹) is the pseudo-first-order rate constant, while k_2 (mg \cdot g^{-1} \cdot h^{-1}) is the rate constant for pseudo-second-order. The $q_{e,exp}$ and q_t can be calculated using equation (1) at equilibrium and time t. $q_{e,exl}$, k_1 and k_2 can be obtained from the parameters by analyzing the data in Fig. 6 (C_{0, MB} = 16 mg \cdot L^{-1}) using equation (3) and (4). The fitting curves are shown in Fig. S14 and the relevant kinetic parameters are summarized in Table 1.

Kinetics model	Initial concentration	$q_{e^{*}exp}(\text{mg}\cdot\text{g}^{-1})$	$q_{e,cal}(\mathrm{mg}\cdot\mathrm{g}^{-1})$	k_{l} (h ⁻¹)	R^2
	$(mg \cdot L^{-1})$			$/k_2(\mathrm{mg}\cdot\mathrm{g}^{-1}\cdot\mathrm{h}^{-1})$	
Pseudo-first-order	16	100	93.21	0.0266	0.8678
model					
Pseudo-second-order	16	100	102.56	3.465×10-4	0.9407
model					

Table 1. Kinetic parameters and coefficients for the Pseudo-first-order and Pseudo-second-order model.

The correlation coefficient (R^2) calculated by pseudo-second-order model (0.9407) was higher than that of pseudo-first-order kinetic model (0.8678), which suggested that the adsorption of MB on **Zn-1** fitted the pseudo-second-order model well. Besides, the calculated q_e obtained by analyzing pseudo-second order model was much closer to the experimental q_e , which further proved that pseudo-second order model was more reasonable.

3.5 Regeneration of Zn-1

The regeneration of adsorbents is an important standard for commercial feasibility. Dye release experiment was performed in a saturated solution (EtOH/DMF, 7/2, v/v) of LiNO₃, and the concentration of the released MB at different time intervals was monitored by UV-Vis spectra. The results are shown in Fig. 7, which indicated that the adsorbed MB could be gradually released from MB@Zn-1 in the saturated LiNO₃ solution, whereas the dye molecules were scarcely released in the pure EtOH/DMF solution. It was speculated that the small Li⁺ ions entered into the channels of Zn-1 and released the cationic MB through cation-exchange, which in turn confirmed that the selective adsorption of MB on Zn-1 was an ion-exchange process. Additionally, the desorption experiment showed that the release ratio of MB was about 80% within 12 hours. The recycled Zn-1 was reused for MB adsorption, and about 80% adsorption capacity was still achieved after three adsorption-desorption cycles (Fig. S15). Furthermore, PXRD patterns of dyes@Zn-1 and dye-released samples are almost identical with the as-synthesized ones, indicating that the structural integrity of Zn-1 was maintained during the dye adsorption and desorption processes (Fig. S13 and





Fig 7. Temporal evolution of UV-Vis absorption spectra of MB@Zn-1 at certain time

Conclusion

In conclusion, a new anionic 3D framework (**Zn-1**) has been constructed from a predesigned functional ligand ($H_2NSBPDC$) and $Zn(NO_3)_2$. The structure of **Zn-1** is based on five-connected hexanuclear SBUs, which possesses large 3D intersecting channels decorated with functional groups. **Zn-1** exhibits selective adsorption and separation of cationic dyes, including dyes with large molecular size such as CV and RhB. Additionally, the kinetic studies indicate that the adsorption of MB follow the pseudo second-order model, and the adsorbed dye (MB) can be released in the saturated LiNO₃ solution.

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Graphical Abstract

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A functional anionic metal–organic framework for selective adsorption and separation of organic dyes

Ying-Ying Cui,^a Juan Zhang,^a Ling-Ling Ren,^a Ai-Ling Cheng,^{*a} En-Qing Gao^b

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