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# A 2D metal-organic framework for selective adsorptions on organic dyes

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ABSTRACT

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# 1. Introduction

Air, water and soil pollutions are always going along with the rapid development of industrialization [1]. Finding effective methods to handle the heavy-metal, pesticide, printing and dying waste in polluted water are hot research topics. The traditional ways to treat these are biological oxidation [2], and advanced oxidation [3]. Because of the simplicity, low cost and high efficiency, removing contaminants through adsorption is deemed as an adaptable method [4–5]. Generally, porous materials are thought to be good materials in adsorption, so porous materials, such as activated carbon and zeolites were studied in this area. However, these materials are generally poor at selective removing contaminants [6]. It is necessary to find new kind of porous materials to solve this problem.

The keys to success in achieving ideal adsorbents for selectively removing contaminants are the following: (1) A framework shows stable and flexible properties, which are important for accommodating guests [7]. (2) The framework could interact with guests through some interactions, such as ionic interactions [8–9], hydrogen bonding [10],  $\pi$ – $\pi$  interactions [11]. Metal–organic frameworks (MOFs) also known as porous coordination polymers (PCPs) are one class of porous materials constructed from metal-containing nodes and organic linkers [12]. Due to their variable structures, ultrahigh porosity and large specific surface area [13],

MOFs have been considered as a promising adsorbent materials for gas [14] and hazardous substance [15].

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Removal of organic dyes has become an important issue from the biological and environmental

standpoint. A metal-organic framework  $\{[Zn_2(L)(H_2O)(DMA)] \cdot DMA \cdot H_2O\}_n$  (1)  $(H_4L = 9 - (3, 5 - Dicarboxy - 1))$ 

benzyl)-9H-carbazole-3,6-dicarboxylic acid, DMA = N,N'-dimethylacetamide) has been synthesized

based on a multicarboxylate ligand through solvothermal reaction. Compound 1 has a 2D bilayered

structure and exhibits effective adsorption on organic dyes. The adsorbing capacity of MB and MO are 139.6 mg/g and 116.9 mg/g, respectively. The selective adsorption properties on dyes were studied.

Considering many dyes have the conjugated system, we convinced that a ligand with the large conjugated system, such as carbazole derivatives, could stabilize the dyes through  $\pi$ - $\pi$  interactions/stacking with dyes. In addition, variable interactions between the framework and different dyes, could facilitate the separation of dyes. Herein, a semi-rigid ligand 9-(3,5-Dicarboxy-benzyl)-9H-carbazole-3,6-dicarboxylic acid (H<sub>4</sub>L, Scheme 1) that has a large conjugation system has been designed to build a 2D MOF {[Zn<sub>2</sub>(L)(H<sub>2</sub>O)(DMA)]·DMA·H<sub>2</sub>O}<sub>n</sub> (1). The selective adsorption properties for dyes were studied.

# 2. Experimental

# 2.1. Materials and methods

3,6-Diacetyl-9H-carbazole [16] and 5-Bromomethyl-isophthalic acid diethyl ester [17] were prepared according to the literature method. All other materials were purchased as reagent grade and used without any further purification. The IR spectra were obtained as KBr disks on a NICOLET 380 spectrometer. Elemental analyses were performed on a Perkin Elmer240C elemental analyzer. The solution UV–Vis absorbance spectra were collected on a Cary-300 UV–Vis spectrophotometer. Powder X-ray diffraction patterns (PXRD) were determined with Rigaku-D/Max-2200 X-ray diffractometer. The field-emission scanning electron microscopy (SEM) images were obtained by using a JEOL JSM-6700F





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Scheme 1. The chemical structure of the ligand H<sub>4</sub>L.

scanning electron microscope. <sup>1</sup>H NMR spectrum was recorded on a spectrometer (Bruker AVANCE DPX 300).

# 2.2. Systhesis of 9-(3,5-Dicarboxy-benzyl)-9H-carbazole-3,6-dicarboxylic acid (H<sub>4</sub>L)

3,6-Diacetyl-9H-carbazole (0.75 g, 3 mmol) was dissolved in 50 mL acetone, then K<sub>2</sub>CO<sub>3</sub> (0.42 g, 3 mmol) was added under stirring. The mixture was refluxed for 1.5 h before dropping 5-bromomethyl-isophthalic acid diethyl ester (1.05 g, 3.3 mmol) and kept at 60 °C overnight. Then, the mother solution was evaporated to give the crude product, which was purified by column chromatography (pet. ether: ethyl acetate = 1:1). 5-(3,6-Diacetylcarbazol-9-ylmethyl)-isophthalic acid (0.65 g, 1.5 mmol) was obtained by hydrolyzed in NaOH solution and acidified with HCl. Pure H<sub>4</sub>L was obtained through bromoform reaction according to the literature method [18] (Scheme S1). IR (KBr, cm<sup>-1</sup>): 3445.1 (m), 2981.9(w), 1693.4(s), 1629.6(s), 1598.5(s), 1485.2(m), 1418.2(s), 823.4(m), 769.0(s), 650.1(s), 543.0(s). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): 5.86–5.90 (2H, d, J = 16 Hz), 7.66–7.67 (4H, dd, J = 4 Hz), 7.90-7.92 (2H, d, J = 8 Hz), 8.33 (1H, s), 8.54-8.61 (2H, d, I = 28 Hz).

## 2.3. Synthesis of compound $\{[Zn_2(L)(H_2O)(DMA)] \cdot DMA \cdot H_2O\}_n$ (1)

A mixture of  $Zn(NO_3)_2$ ·6H<sub>2</sub>O (36 mg, 0.12 mmol), H<sub>4</sub>L (25.8 mg 0.06 mmol), DMA (3 mL), EtOH (6 mL) and H<sub>2</sub>O (6 mL) was placed in a flask and stirred for 30 min at room temperature, then it was transferred to a Teflon-lined autoclave (25 mL), the block crystal was obtained after 3 days at 90 °C (yield, 40%, based on ligand). Calc. for  $C_{31}H_{33}N_3O_{12}Zn_2$ : C, 56.34; H, 4.28; N, 5.45. Found: C, 56.68; H, 4.86; N, 5.39%. IR (KBr, cm<sup>-1</sup>): 3412.5(s), 1603.5(s), 1448.9(w), 1397.5(s), 1303.5(m), 1263.7(w), 1211.8(m), 1147.7 (m), 780.5(s), 724.8(m), 664.3(m), 599.1(w).

## 2.4. X-ray crystallography

Single crystal of compound **1** was tested on a Bruker APEX II DUO CCD diffractometer equipped with graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at room temperature, cell parameters were refined on all observed reflections using the Bruker SAINT (Bruker AXS, 2013). The collected data were reduced by the program Bruker SAINT, and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined on F<sup>2</sup> by full matrix least squares using SHELXTL [19]. There were some guest solvent molecules were chemically featureless to refine, to solve the issue, the sQUEEZE program implemented PLATON was used to remove contribution of these solvent electron densities, the void volume and void count electrons are 581.4 and 211.7, which indicate the presence of one

#### Table 1

Crystal data and structure refinements for compound 1.

Compound	1
Formula	C <sub>31</sub> H <sub>33</sub> N <sub>3</sub> O <sub>12</sub> Zn <sub>2</sub>
Formula weight	770.37
T (K)	296(2)
Crystal system	monoclinic
Space group	P2(1)/n
a (Å)	11.8370(15)
b (Å)	14.6492(19)
c (Å)	21.388(3)
V (Å <sup>3</sup> )	3676.0(8)
Ζ	4
$D_{\text{calc}} (\text{g cm}^{-3})$	1.202
$\mu$ (mm <sup>-1</sup> )	1.350
F (000)	1352
R <sub>int</sub>	0.0650
Goodness-of-fit (GOF) on $F^2$	1.089
$R_1 \left[ I > 2\sigma(I) \right]^a$	0.0677
$wR_2 [I > 2\sigma(I)]^a$	0.1964
$R_1$ (all data) <sup>a</sup>	0.0863
$wR_2$ (all data) <sup>a</sup>	0.2141

<sup>a</sup>  $R_1 = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$ ,  $wR_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0^2]^{1/2}$ .



**Fig. 1.** (a) Coordination environment of Zn1 and Zn2. (b) View of compound **1** along the *a*-axis (the purple chain is the zigzag chain linked by carbazolyl). (c) Packing diagram of compound **1** viewed along the *b*-axis. Symmetry codes: A = x, -1 + y, z; B = x, 1 + y, z; C = 1/2 - x, -1/2 + y, 3/2 - z; D = 1/2 - x, 1/2 + y, 3/2 - z; E = 1 - x, 3 - y, 2 - z; F = -1/2 + x, 3/2 - y, -1/2 + z; G = -1/2 + x, 5/2 - y, -1/2 + z; H = 1/2 + x, 3/2 - y, 1/2 + z.

DMA and one water molecule in the asymmetric unit. The crystallographic and refinement details are listed in Table 1. Selected bond lengths and angles are given in Table S1.

## 2.5. Dye adsorption experiments

In order to investigate the ability of compound **1** for dye adsorption, 10 mg of compound **1** was immersed in a vial containing 0.25 mg/mL methylene blue (MB) (5.6 mL) and methyl orange (MO) (5.6 mL) respectively. Each of the solution was stirred for 4 h and precipitate was filtrated through centrifuge. 100  $\mu$ L solution was taken out from the filtrate and diluted into 2 mL with water. The abilities of the compound to adsorb dyes from aqueous solution were determined through UV spectrophotometry.

# 3. Results and discussion

## 3.1. Structure description of compound 1

Compound **1** crystallizes in the monoclinic space group  $P_{2_1/n}$  and has an asymmetry unit consisting of one  $L^{4-}$  ligand, two Zn (II) ions, one coordinated water and DMA molecule. Zn1 has distorted trigonal bipyramid geometry that was coordinated by (O1I and O3B) from different carboxylates of different carbazolyl groups, (O6E and O7) from carboxylates of different phenyl groups

and O10 from water. Zn2 has tetrahedral geometry that was coordinated by (O2, O4F) from two carboxylates of different carbazolyl groups, O5C from carboxylate of phenyl and O9 from DMA. Zn1 and Zn2 atoms are bridged by three carboxylates into a dimer with Zn1…Zn2 distance of 3.24 Å. These dimers are linked by carbazolyl groups into a zigzag chain along the *b*-axis. Adjacent chains are joined together through one phenyl carboxylate into one plane. Adjacent planes are linked by the other phenyl carboxylate into a double layer (Fig. 1b). Both carboxylates from carbazovl group adopt  $\mu_2$ - $\eta^1$ , $\eta^1$  bidentate bridging coordination mode, while one carboxylate group from the phenyl group adopts monochelate coordination mode and the other one adopts  $\mu_2$ - $\eta^1$ , $\eta^1$ bidentate bridging coordination mode.  $\pi$ - $\pi$  stacking interactions were observed between the adjacent double layers with shortest centroid to centroid distance of phenyl groups of 3.6 Å (Fig. S1). which stabilizes the 3D structure.

### 3.2. Dye adsorption of compound 1

Adding compound **1** into the dye solution caused a large adsorption (Fig. 2), which could see from the obviously lighted solution color. The removal of MB and MO can reach 99.4% and 83.5% respectively (Table S2). Thus, the general formula of the resulting precipitates can be proposed as **1**.0.29MB and **1**.0.28MO. The contrast test of ligand (10 mg) on the adsorption



**Fig. 2.** (a) UV–Vis absorption spectra of MB solution with the use of ligand (MB@L, black), compound **1** (MB@**1**, red) and the control experiment without compound **1** (blue). (b) UV–Vis absorption spectra of MO solution with the use of ligand (MO@L, black), compound **1** (MO@**1**, red) and the control experiment without compound **1** (blue). (c) UV–Vis absorption spectra of adsorption of MB–MO mixture solution with the use of compound **1** (red) and the control experiment without compound **1** (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** The SEM of compound **1** after different treatments: (a) immersed in water (b) MB adsorption (c) MO adsorption.



**Fig. 4.** The PXRD patterns for compound **1**: (A) simulated, (B) experimental, (C) immersed in water, (D) after adsorption on MO and (E) after adsorption on MB.

of MB and MO were performed. It is found that the removal of MB and MO can reach 98.7% and 22.2% respectively. Thus, the general formula of the resulting precipitates can be proposed as L-0.16MB

and L-0.04MO. The stability of MB@1 and MB@L was further checked by immersing the samples in water and methanol. It is found that both MB@1 and MB@L are stable in water. In the case of methanol, the adsorbed MB could be released from MB@L completely, while seldom MB could be released from MB@1 (Fig. S2). This result indicates that the interactions between MB and the framework are strong. To explore the adsorption mechanism, we examined the release performance of MB@1 and MB@L in water under external stimulus, for example the salt response of the composite. In this test, the loaded dye molecules are barely released in water solution of LiNO<sub>3</sub> [20], which exclude the guest cationic substitution-driven process. Thus we convinced the  $\pi$ - $\pi$  interactions between dyes and framework play the key role in the adsorption process. Relatively, MO@1 and MO@L are not stable in water and methanol, which would release MO molecules readily (Fig. S2). This may be explained by the fact that the MO that has the smaller conjugated structure could form weaker  $\pi - \pi$  interactions with the framework than MB do. The different adsorption ability of ligand on MB and MO also indicates that the main factor of the adsorption of compound **1** on dyes is  $\pi$ - $\pi$  interaction.

To check the stability of compound 1, the SEM images of different samples were investigated (Fig. 3), the crystal could maintain their morphologies after different treatments, indicating the framework is stable. Then the samples were further checked by powder X-ray diffraction (PXRD) (Fig. 4). After being immersed in water, the crystals still maintain their crystalline character with peaks move to higher angles. This indicates that compound 1 is stable and shrinked after exchanging of DMA and water molecules in water. After dye adsorption, the peaks move to the lower angle compared with that immersed in water one. This evidence means that the dyes entered into the pores of crystals and expanded the framework [21-23]. Because the different interactions between MB/MO and frameworks, the selective adsorption was performed. Compound 1 (10 mg) was immersed in a 13.4 mL MB-MO mixed solution containing MB (0.25 mg/mL, 5.6 mL) and MO (0.25 mg/mL, 2.8 mL) and the mixture was stirred for 4 h, the color of the solution changed from indigo to orange. From Fig. 2c, the peaks of MB disappeared after adsorption, while the peaks of MO still maintain. Thus compound **1** has the selective adsorption ability on the separation of MB-MO.

## 4. Conclusions

In this work, a tetracarboxylic acid bearing carbazolyl group was designed to build a flexible bilayered compound, in which  $\pi$ - $\pi$  interactions were observed between adjacent layers. The compound could function not only as absorbent materials for MB and MO, but also as selective absorbent for MB from MB–MO solution. Thus, we believe the introduction of bulky ligands with  $\pi$  conjugation system can help to design many flexible MOFs that have dye adsorption function. This study will widen the field of porous nano-species science. Further work is in progress to construct new MOFs with the combination of H<sub>4</sub>L and copper clusters.

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## Appendix A. Supplementary material

CCDC 1444629 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via

www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at http:// dx.doi.org/10.1016/j.ica.2016.03.024.

#### References

- [1] V.K. Gupta, I. Ali, T.A. Saleh, A. Nayak, S. Agarwal, RSC Adv. 2 (2012) 6380.
- [2] B.S. Souza, F.C. Moreira, M.W.C. Dezotti, V.P. Vilar, R.A.R. Boaventura, Catal. Today 209 (2013) 201.
- [3] A.D. Bokare, W. Choi, J. Hazard. Mater. 275 (2014) 121.
- [4] L.-L. Fan, C.-N. Luo, M. Sun, H.-M. Qiu, X.-J. Li, Colloids Surf. B 103 (2013) 601.
   [5] H.-X. Guo, F. Lin, J.-H. Chen, F.-M. Li, W. Weng, Appl. Organomet. Chem. 29
- (2015) 12.
- [6] Y.-C. He, J. Yang, W.-Q. Kan, H.-M. Zhang, Y.-Y. Liu, J.-F. Ma, J. Mater. Chem. A 3 (2015) 1675.
- [7] (a) E. Barea, C. Montoro, J.A.R. Navarro, Chem. Soc. Rev. 43 (2014) 5419;
   (b) S. Mukherjee, B. Joarder, A.V. Desai, B. Manna, R. Krishna, S.K. Ghosh, Inorg. Chem. 54 (2015) 4403;
  - (c) J.-P. Lang, Angew. Chem. Int. Ed. 43 (2004) 4741;
- (d) M. Dai, T.-Y. Gu, X. Zhao, H.-X. Li, J.-P. Lang, CrystEngComm 17 (2015) 8345. [8] (a) B. Wu, W.-H. Zhang, Z.-G. Ren, J.-P. Lang, Chem. Commun. 51 (2015) 14893;
- (b) Y.-X. Tan, Y.-P. He, J. Zhang, RSC Adv. 4 (2014) 1480.
- [9] (a) J.-M. Yang, Q. Liu, Y.-S. Kang, W.-Y. Sun, CrystEngComm 17 (2015) 4825;
   (b) D. Liu, H.-X. Li, Z.-G. Ren, Y. Chen, Y. Zhang, J.-P. Lang, Cryst. Growth Des. 9 (2009) 4562.
- [10] (a) B. Liu, F. Yang, Y.-X. Zou, Y. Peng, J. Chem. Eng. Data 59 (2014) 1476;
  (b) F.-L. Hu, Y.-X. Shi, H.-H. Chen, J.-P. Lang, Dalton Trans. 44 (2015) 18795;
  (c) L.-L. Liu, Z.-G. Ren, L.-M. Wan, H.-Y. Ding, J.-P. Lang, CrystEngComm 13 (2011) 5718;
  - (d) W.-H. Zhang, D. Liu, H.-X. Li, Z.-G. Ren, Y. Zhang, J.-P. Lang, Cryst. Growth Des. 10 (2010) 3.

- [11] (a) Z. Hasan, S.H. Jhung, J. Hazard. Mater. 283 (2015) 329;
   (b) X.-X. Wang, Z.-X. Li, K. Hecke, G.-H. Cui, Inorg. Chem. Commun. 54 (2015) 9;
- (c) D. Liu, J.-P. Lang, B.F. Abrahams, J. Am. Chem. Soc. 133 (2011) 11042–11045. [12] (a) H.-C. Zhou, S. Kitagawa, Chem. Soc. Rev. 43 (2014) 5415;
- (b) H. Furukawa, K.E. Cordova, M. O'Keeffe, O.M. Yaghi, Science 341 (2013) 74. [13] (a) H.-C. Zhou, J.R. Long, O.M. Yaghi, Chem. Rev. 112 (2012) 673;
- (b) S. Furukawa, J. Reboul, S. Diring, K. Sumida, S. Kitagawa, Chem. Soc. Rev. 43 (2014) 5700.
- [14] (a) W.-G. Lu, D.-Q. Yuan, T.A. Makal, J.-R. Li, H.-C. Zhou, Angew. Chem. Int. Ed. 51 (2012) 1580;
   (b) B. Chen, Z.-P. Lv, C.F. Leong, Y. Zhao, D.M. D'Alessandro, J.-L. Zuo, Cryst.
  - Growth Des. 15 (2015) 1861; (c) M.C. Das, Q.-S. Guo, Y.-B. He, J. Kim, C.-G. Zhao, K.-L. Hong, S.-C. Xiang, Z.-J. Zhang, K.M. Thomas, R. Krishna, B.-L. Chen, J. Am. Chem. Soc. 134 (2012) 8703.
- [15] (a) L.-T. Xie, D.-H. Liu, H.-L. Huang, Q.-Y. Yang, C.-L. Zhong, Chem. Eng. J. 246 (2014) 142;
- (b) W. Morris, C.J. Doonan, O.M. Yaghi, Inorg. Chem. 50 (2011) 6853.
- [16] N.P. Buu-Hoi, R. Royer, J. Org. Chem. 16 (1951) 1198.
- [17] J.P. Collman, X.-M. Zhang, K. Wong, J.I. Brauman, J. Am. Chem. Soc. 116 (1994) 6245.
- [18] L.-D. Kong, R.-Y. Zou, W.-Z. Bi, W.-J. Mu, J. Liu, R.P.S. Han, R.-Q. Zou, J. Mater. Chem. A 2 (2014) 17771.
- [19] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
- [20] S.-N. Sheng, Y. Han, B. Wang, C. Zhao, F. Yang, M.-J. Zhao, Y.-B. Xie, J.-R. Li, J. Solid State Chem. 233 (2016) 143.
- [21] V. Finsy, C.E.A. Kirschhock, G. Vedts, M. Maes, L. Alaerts, Chem. Eur. J. 15 (2009) 7724.
- [22] S. Heneke, A. Schneemann, A. Wütscher, R.A. Fischer, J. Am. Chem. Soc. 134 (2012) 9464.
- [23] V. Bon, J. Pallmann, E. Eisbein, H.C. Hoffmann, I. Senkovska, I. Schwedler, A. Schneemann, S. Henke, D. Wallacher, R.A. Fischer, G. Seifert, E. Brunner, S. Kaskei, Microporous Mesoporous Mater. 216 (2015) 64.