View Article Online View Journal

CrystEngComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: H. Liu, G. Gao, J. Liu, F. Bao, Y. Wei and H. Wang, *CrystEngComm*, 2019, DOI: 10.1039/C9CE00065H.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/crystengcomm

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/



Huiyan Liu,* Guimei Gao, Jie Liu, Fenlin Bao, Yuhui Wei and Haiying Wang*

Based on varying solvents, two ionic indium-organic frameworks (1 and 2) were achieved. Both MOFs are constructed from the same indium monomer building units and amide-functionalized linker, but they present distinct topology along with varied channel size and shape. Importantly, the adsorption potential of two anionic frameworks towards organic dyes with different charge and size was thoroughly examined. Both frameworks exhibited highly selective adsorption towards cationic dye methylene blue (MB) based on preferential electronic affinity and size-excluded effect. Besides MB, 1 and 2 also exhibited uptakes towards cationic dyes rhodamine B (RhB) and rhodamine 6G (R6G) but inert action to cationic dye crystal violet (CV), and thus additional hydrogen-bonding interactions of amide groups and dyes over the adsorption were suggested. The results also revealed that the adsorption capacity and kinetic constant of 1 are greater than those of 2, showing the importance of porosity and pore structure during the adsorption. The adsorption capacity of 1 towards MB is as high as 281 mg g⁻¹ and can potentially serve as column-chromatographic filler for separating dye molecules.

Introduction

Published on 08 March 2019. Downloaded by University of Texas at Dallas on 3/8/2019 12:31:43 PM

Currently, organic dyes are extensively used in many industries with the advance of industrialization and, accordingly, the removal of organic dyes from waste water has been a severe issue from an environmental point of view.¹ So far, various methods have been explored for the remove of organic dyes, and adsorption has been regarded as one of the most competitive methods.^{1b, 2}

Metal-organic frameworks (MOFs) have been a fascinating class of hybrid materials for their intriguing structural diversities as well as promising potential applications in gas sorption and separation, molecular sensing and ion-exchange.³ Given their intrinsic features of high porosity and easy tenability of pore size and shape, MOFs towards high-performance in organic dyes decontamination have become a hot research subject more recently.⁴ Especially, ionic metal-organic frameworks, as a fraction of MOFs with either positively or negatively charged frameworks, have been attracting significant attentions.^{2e, 5} The charged species in these ionic architectures facilitate the improved interactions

School of Chemistry & Materials Science, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou 221116, P. R. China.

between the host and incoming guest molecules. Moreover, by the ion-exchange, ionic MOFs can be easily modified and accommodate other charged guest molecules, including ions, organic dyes or small coordinated molecules. Thus, such ionic MOFs materials are expected to be an ideal platform for different applications as functional materials. A handful of MOF materials have been evaluated to demonstrate adsorptive capabilities towards organic dyes.^{1,5} For efficient adsorption, not only adequate porosity/pore size but also pore functionality along with special interaction sites is suggested.⁶ Then, by tuning pore size and incorporating functionality groups into ionic frameworks permit the encapsulation of ionic receptors and thereby make it feasible to investigate the various host-guest interactions during the adsorption progress. Generally, for charged MOFs, strong electrostatic interactions are mainly interactions for efficiently and selectively separate dyes with different charges as demonstrated in many works. Meanwhile, non-valence interactions, such as hydrogen-bonding interactions and π - π stacking interactions are common intermolecular interactions which play important role in the preferred dyes adsorption processes.^{6a-c, 7} However, little has been known about the presence or how these weak forces combine or collaborate with strong electrostatic interactions during the dyes adsorption processes for the charged MOFs.

DOI:

Based on above consideration and as a continuation of our effort to construct polyfunctional carboxylate based MOFs for gas separation and molecular sensing,⁸ herein, by varying solvents we access two ionic frameworks,

E-mail: liuhuiyan72@163.com; wanghy@jsnu.edu.cn

^{*}Electronic supplementary Information (ESI) available: CCDC reference numbers 1863820 and 1881138. The supplementary tables, figures, and additional characterization data. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

ARTICLE

[(CH₃)₂NH₂][In(L)]·4H₂O·2DMF (1) and $[(CH_3)_2NH_2][In(L)] \cdot H_2O \cdot 3DMF$ (2) with amide-functionalized tetracarboxylate linker (5-(3,5-dicarboxybenzamido) isophthalic acid) (H₄L). Noticeably, incorporating amide functional group into framework not only accesses distinct network as well as modified pore structure, but also serves as special interaction sites for dyes adsorption.

Mainly, the anionic nature of frameworks of 1 and 2 induces strong electrostatic affinity which facilitates outstanding sizeselective adsorption towards cationic organic dye methylene blue (MB). Moreover, besides the preferential electrostatic affinity observed, additional hydrogen-bonding interactions of amide groups and dye molecules were found, which show a beneficial effect on the dyes adsorption. Both frameworks, especially 1, display large adsorption capacity and can potentially serve as column-chromatographic filler for separating dyes molecule. In addition, the adsorption isotherms and kinetics characteristic of dye adsorption onto the two MOFs were also investigated.

Experimental section

General methods

Published on 08 March 2019. Downloaded by University of Texas at Dallas on 3/8/2019 12:31:43 PM

All reagents were commercially obtained and used as received. H₄L ligand was prepared according to the procedure reported with modification.^{3e} Elemental analyses (C, H and N) were performed on a PerkinElmer 240 analyzer. ¹H NMR spectra were recorded on a Bruker DRX-500 spectrometer. Thermogravimetric analyses (TGA) were carried out under N₂ atmosphere using a 2960 SDT thermogravimetric analyzer. IR spectra were obtained on a Bruker Tensor 27 spectrometer with KBr pellets in the range of 4000-400 cm⁻¹. UV-vis spectra were recorded on a UV-vis spectra were collected on a PerkinElmer Lambda 365 UV/VIS spectrophotometer. A Bruker D8 ADVANCE diffractometer with Cu K α radiation (λ = 1.5418 Å) was used to collected powder X-ray diffraction (PXRD) data at room temperature. NanoBrook 90PlusPALS size and zeta potential analyzer was used to determine the zeta potential.

Synthesis of H₄L ligand

3,5-bis(methoxycarbonyl)benzoic acid (2.38 g, 10 mmol) and SOCI₂ (50 mmol) were added to a mixture of CH₂Cl₂ (40 mL) and DMF (0.1 mL). Then the mixture was refluxed for 12 h $\,$ under N₂ atmosphere. The excess SOCl₂ was removed under The vacuum. resultant was dissolved in N,Ndimethylacetamide (DMA) (20 mL) and added dropwise to a solution of dimethyl 5-aminoisophthalate (2.09 g, 10 mmol) in DMA (20 mL) at 0 °C. After the completion of the addition, the mixture was stirred at 50 °C for another 12 h and then poured into water to obtain the crude product. The crude product was hydrolyzed by refluxing in LiOH (1 M) followed by acidification with HCl (3M) to afford H₄L (yield 90%). ¹H NMR (400 MHz, DMSO-d₆, δ ppm): 13.47 (s, COOH), 10.97 (s, NH), 8.82 (d, 2H, J = 4.0 Hz, ArH), 8.70 (d, 2H, J = 4.0 Hz, ArH), 8.65 (t, 1H, J = 4.0 Hz, ArH), 8.25 (t, 1H, J = 4.0 Hz, ArH). Anal. Calcd (Found) for C₁₇H₁₁NO₉: C, 54.70 (54.62); H, 2.97(2.86); N, 3.75 (3.82)%.

Selected IR data (KBr, cm⁻¹): 3311, 3057, 1709, 1606, 1550, 1505, 1446, 1334, 1241, 1103, 907, 763, 792,166539/C9CE00065H

Synthesis of 1

A mixture of In(NO₃)₃·6H₂O (10.0 mg, 0.024 mmol), H₄L (5.0 mg, 0.013 mmol) and $\rm HNO_3$ (0.6 mL, 2.7 M in DMF) in DMF (1 mL) was placed in a 23 mL glass vial and heated at 75 °C for 36 h. The colorless polyhedron crystals were obtained and washed with DMF (yield: 80% based on ligand). Anal. Calcd (Found) for C₂₈H₃₈InN₅O₁₃: C, 43.82 (43.78); H, 4.99 (5.02); N, 9.12 (9.22)%. Selected IR data (KBr, cm⁻¹): 3417, 3086, 2801 1624, 1559, 1443, 1363, 1283, 1190, 1104, 1019, 905, 777, 742.

Synthesis of 2

A mixture of In(NO₃)₃·6H₂O (40.0 mg, 0.096 mmol), H₄L (10.0 mg, 0.026 mmol) and HNO₃ (0.09 mL) in a mixed solvents of DMSO (1mL) and DMF (1 mL) was placed in a 23 mL glass vial and heated at 85 °C for 36 h. The colorless polyhedral crystals were obtained and washed with DMF (yield: 80% based on ligand). Anal. Calc. (Found) for C₂₅H₃₇InN₄O₁₅: C, 40.12 (40.22); H, 4.98 (5.08); N, 7.49 (7.40)%. Selected IR data (KBr, cm⁻¹): 3078, 2806, 1622, 1557, 1503, 1361 1281, 1238, 1197, 1104, 1018, 777, 740.

X-ray Crystallography

The X-ray diffraction data for 1 and 2 were performed on a Bruker Apex II CCD diffractometer at 291 K using graphite monochromated Mo K α radiation (λ = 0.71073 Å) and Bruker SAINT program was used to data reduction.9a The structure was solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package.^{9b} Displacement parameters were refined anisotropically, and the positions of the hydrogen atoms were generated geometrically assigned isotropic thermal parameters and allowed to ride on their parent carbon atoms before the final cycle of refinement. The diffused electron densities resulting from highly disordered solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated. The contents of the solvent region are not represented in the unit cell contents in the crystal data. Details of the crystal parameters, data collection, and refinements for 1 and 2 are summarized in Table 1 (CCDC reference numbers 1863820 (1) and 1881138 (2)).

Dye absorption and separation measurements

Freshly prepared crystalline samples of 1 and 2 (15 mg) were transferred into solution of methylene blue (MB), methyl orange (MO), solvent yellow 2 (SY2), acid red 2 (AR2), crystal violet (CV), rhodamine B (RhB) and rhodamine 6G (R6G) in MeOH (5 mL), respectively. The concentration of dyes was 40 mg L⁻¹. The selective dyes adsorption ability was carried out by placing fresh crystalline samples (15 mg) in the mixed dyes solutions with the same concentration (10 mL). UV-vis spectra were used to measure the adsorption ability towards dyes and selective adsorption ability of 1 and 2.

CrystEngComm Accepted Manuscrip

Dye-releasing experiments were performed by immersing the fully MB loaded samples (**MB@1** and **MB@2**) in pure MeOH or DMF and a saturated solution of NaCl in MeOH or DMF, respectively. UV-vis spectra were also used to measure the release ability of two frameworks.

Reusability experiments for MB adsorption were further conducted. The sample after MB fully released was filtered out and washed thoroughly, and the above adsorption–desorption cycle was repeated.

The equilibrium adsorption capacity (q_e) is calculated based on the difference in the dye concentrations in solution before and after the adsorption process according to the following equation $1.^{1g,\ 10a}$

(1)

where
$$c_e,$$
 V, and m denote the equilibrium concentration of view Article Online adsorbate, the volume of system and the that confided adsorbent, respectively.

The experiment data for adsorption of two MOFs were fitted with the Langmuir isotherm model, which is represented by equation $2.^{10a}$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad (2)$$

where q_m (mg g^{-1}) and K_L (L mg $^{-1}$) are the maximum adsorption capacity of the adsorbent and Langmuir constant, respectively. The values of q_m and K_L were calculated from the slope and intercept of the C_e/q_e vs C_e plot.

Table 1 Crystallographic data for 1 and 2.		
MOFs	1	2
empirical formula	$C_{38}H_{30}In_2N_4O_{18}$	$C_{19}H_{15}InN_2O_9$
formula wt	1060.30	530.15
cryst syst	monoclinic	monoclinic
space group	P21/c	C2/c
<i>a</i> (Å)	9.957(2)	14.212(2)
<i>b</i> (Å)	24.444(2)	14.062(2)
<i>c</i> (Å)	35.537(2)	22.5060(11)
β(deg)	90.337(3)	91.135(3)
V (ų)	8649.2(19)	4496.9(10)
Z	4	4
$ ho_{ m calcd}$ (g cm ⁻³)	0.814	0.783
μ (mm ⁻¹)	0.572	0.551
F(000)	2112	1056
index ranges	$-12 \le h \le 12$ $-24 \le k \le 31$ $-35 \le l \le 46$	$-18 \le h \le 18$ $-18 \le k \le 15$ $-29 \le l \le 29$
R _{int}	0.0900	0.019
T _{max} , T _{min}	0.875, 0.894	0.880, 0.900
data/restraints/parameters	19754/1/563	5124/1/149
Goodness of fit	1.025	1.095
$R_1^{a}, w R_2^{b} (I > 2\sigma(I))$	0. 0440, 0.1042	0.0488, 0.1427
R_1 , wR_2 (all data)	0. 0497, 0.1055	0.0521, 0.1455
$(\Delta ho)_{max}$, $(\Delta ho)_{min}$ (e A ⁻³)	1.71, -1.39	0.884, -0.986

J. Name., 2013, 00, 1-3 | 3

View Article Online

DOI: 10.1039/C9CE00065H

The pseudo-first-order and the pseudo-second-order kinetic models were applied to fit kinetic data obtained. The models can be expressed as equation 3 and equation 4, respectively.^{10b}

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

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

ARTICLE

where $q_e \ (mg \ g^{-1})$ and $q_t \ (mg \ g^{-1})$ are the amount of dyes adsorbed at equilibrium and at any time (min), respectively. K_1 and K_2 are the rate constants of the pseudo-first-order (min⁻¹) and pseudo second-order adsorption (g mg⁻¹ min⁻¹) models, respectively.

Chromatographic column is made of bottomless NMR sample tube and samples were filled in the NMR sample tube as stationary phase. The MeOH solutions of mixed dyes were passed through the chromatographic column at room temperature. Then pure MeOH were traversed the chromatographic column.

Results and discussion

Crystal structure and framework stability

Solvothermal reaction between H₄L and In(III) in different solvents afforded crystals of 1 and 2, respectively. Both structures are based on the same indium monomer building units but present distinctly different frameworks (Figs. 1 and 2). Single-crystal structure analysis reveals that 1 is crystallized in the monoclinic P21/c with cell parameters a = 9.957(2) Å, b = 24.444(2) Å, c = 35.537(2) Å and V = 8649.28(19) Å³, while **2** is crystallized in the monoclinic C2/c with cell parameters a = 14.212(2) Å, b = 14.062(2) Å, c = 22.506(11) Å and V = 4496.9(9) $Å^3$ (Table 1). Both anionic frameworks of **1** and **2** are constructed from negatively charged [In(CO₂)₄] building blocks, and contain $(CH_3)_2NH_2^+$ cations to balance the charge. Each In(III) center is eight-coordinated by bi-dentate chelating carboxylate oxygen atoms from four separate L⁴⁻ ligands, while each ligand binds to four separate In(III) centers (Figs. 1a and 2a). Notably, both frameworks contain amide functional groups in the channels, which are expected to serve as special sites and facilitate selectively adsorption of organic dyes.

In **1**, viewing along *a* axis, there exist two types of channels, rectangular and triangular in shape and measure about 7.2 × 5.4 Å² and 5.4× 5.0 Å², respectively (point-to-point and excluding van der Waals radii) (Figs. 1c and S1). After applying symmetry operation, there are two types of bridging L⁴⁻ ligands as well as two types of In(III) ions in **1**, but which can be topologically simplified as equal square-planar nodes and tetrahedral nodes, respectively (Fig. S2). Consequently, **1** adopts a distinct 4,4,4,4-connnected network with the topological point symbol of $(4 \cdot 6^2 \cdot 8^3) (4 \cdot 6^3 \cdot 8^2) (4^2 \cdot 6^2 \cdot 8^2) (4^2 \cdot 8^4)$ (Figs. 1d and 1e).



Fig. 1 (a) The monomeric $[In(CO_2)_4]$ building-block in **1**. (b) The coordination mode of the L⁴⁻ ligand. (c) Space-filling representation of the framework of **1** showing the channels along the [100] direction. (d, e) Ball-and-stick and natural tiling representations of (4,4,4,4)-connected net of **1**. (color code: In, turquoise; C, gray; O, red; N, blue).

The framework of **2** displays 1D square channels along *c* axis with an aperture size of approximately 6.0×6.0 Å² (Fig. 2c and S3). The bridging L⁴⁻ ligands and In(III) ions in **2** can be topologically simplified as square-planar nodes and tetrahedral nodes, respectively, giving **PtS** network with the topological point symbol of (4²·8⁴) (Figs. 2d and 2e).

Two nets are constructed from the same indium monomer building units with four carboxylate groups bind the metal in a chelating fashion. Evidently, the generation of different networks of **1** and **2** is related to conformational flexibility of the organic ligands originated from the incorporation of amide group into ligand (Fig. S4), which leads to different configurations in the interconnection of metal ions and thus different 3D nets. The total potential solvent-accessible volumes for **1** and **2** were 61.8 % and 53.6 %, respectively, as estimated by PLATON software.

Fig. 2 (a) The monomeric $[In(CO_2)_4]$ building-block in **2**. (b) The coordination mode of the L^{4–} ligand. (c) Space-filling representation of the framework of **2** showing the channels along the *b* and *c* direction, respectively. (d, e) Ball-and-stick and natural tiling representations of **Pts** net of **2**.

The thermal stability of 1 and 2 has been evaluated in the temperature range of 25–600 °C (Fig. S5). TG curve reveals a

weight loss of 35.3% (calcd 35.7%) for **1** and $36_{\text{M}}9\%_{\text{cl}}$ (calcd 36.7%) for **2** between 25 and 200 °C, corresponding to the loss of (CH₃)₂NH₂⁺ cations, and guest H₂O and DMF molecules in the cavity. Further heating above 300 °C may lead to the release of organic ligands. The bulk identity of **1** and **2** were confirmed by powder X-ray diffraction (PXRD) measurements (Fig. S7). The PXRD patterns for as-synthesized samples match well with the simulated patterns from crystal data, demonstrating that the crystal is representative of the pure bulk sample.

ARTICLE

Organic dye adsorption and separation

To explore the potential application of two anionic frameworks in organic dye removal, **1** and **2** were employed to capture different types of dyes in MeOH solutions. In addition, size and charge of the organic dye are the two most important factors during the process of dye capture. Based on these consideration, seven organic dyes were chosen for this study including methylene blue (MB), solvent yellow 2 (SY2), acid red 2 (AR2), methyl orange (MO), crystal violet (CV), rhodamine B (RhB) and rhodamine 6G (R6G) (Scheme S1).

At first, four types of dyes (MB, SY2, AR2 and MO) featuring the similar size and molecular weight but different charges were selected to conduct adsorption process. The crystalline samples of **1** and **2** were immersed in MeOH solution of different kinds of dyes, respectively. The content of dyes in the solution was monitored by certain time intervals through UVvis spectroscopy. As shown in Fig. 3, two frameworks can adsorb 99.6% in 90 mins and 94.5% of MB in 120 mins, respectively, demonstrating rapid and high-efficiency removal capacity of MB. At the same time, the color of the solution gradually becomes transparent. On the contrary, the neutral SY2 and AR2, and anionic MO cannot be effectively adsorbed (Figs. S8a-S8c and S9a-9c).



Fig. 3. UV-vis spectra of MB in MeOH solution at different time during the adsorption with 1 (a) and 2 (b) as the host. The insets are the corresponding photographs before and after adsorption.

The desirable adsorbent material should possess not only the outstanding adsorption property towards the dyes but also the eminent capability of selective removal and separation. Then the mixtures of MB/SY2, MB/AR2 and MB/MO solutions were used to further demonstrate the selective adsorption ability of **1** and **2** (Figs. 4a-4c and 5a-5c). As expected, only the cationic MB was effectively absorbed in the mixture solutions. The color of the solutions essentially came to as the same as the pure SY2, AR2 and MO solution after 30 mins. Meanwhile, the color of samples changed from colorless to blue, indicating selective trapping of MB within the pore. The selective

absorption of cationic dyes could be attributed to enhanced interaction between the anionic frameworks and cationic dyes, as well as the ion-exchange between free $(CH_3)_2NH_2^+$ cations present in the framework and cationic dyes. Therefore, by ion-exchange processes, **1** and **2** can be a potential material for selectively separating the organic dyes with similar sizes but different charges.

ARTICLE

To demonstrate the size effect, another two kinds of cationic dyes, CV and RhB, with the same charge but different molecular sizes, were chosen to carry out the absorption experiments. Compared with the results in Fig. 3, for the large size CV and RhB, an unexpected and different adsorption behavior was observed (Figs. S8d-8e and S9d-9e). Although the size of RhB is slightly large than that of CV, **1** and **2** show somewhat slow but complete RhB removal after 20 h, while no obvious adsorption towards CV even after 12 h, indicating that

the molecule size might not the major way to control the uptake of RhB. DOI: 10.1039/C9CE00065H It is evident from literature that the amide groups on the linkers are both hydrogen-bonding donors and acceptors that can facilitate hydrogen bonding interactions in MOFs.^{3e, 5b, 11} It is reasonable to speculate that the presence of amide groups within the pore surfaces and carboxylate groups in RhB might contribute to form hydrogen-bonding interactions and further facilitate RhB adsorption. To further confirm this claim, another cationic R6G with large size was employed to compare the adsorption performance. As same to that of RhB, 1 and 2 show somewhat slow but complete R6G removal after 24 h (Figs. S8f and S9f). These results further confirm that the formation of hydrogen-bonding interactions may be beneficial for the adsorption of dye molecules.



Fig. 4 UV-vis spectra of MB/SY2 (a), MB/AR2 (b), MB/MO (c), MB/CV (d), MB/RhB (e) and MB/R6G (f) in MeOH solution at different time during the adsorption with 1 as the host. The insets are the corresponding photographs before and after the adsorption.

The capture abilities were further inspected under mixed solution of MB/CV, MB/RhB and MB/R6G. As shown in Figs.

4d-4f and Figs. 5d-5f, only characteristic peaks of MB decreased significantly, while that of the CV remain unchanged.

CrystEngComm Accepted Manuscrip

However, for the mixed solution of MB/RhB and MB/R6G, the MB was almost completely adsorbed after about 30 min while only a very small amount of the RhB or R6G can be adsorbed. The removal efficiency of MB in mixed solution of MB/RhB and MB/R6G is lower than that in the single MB solution, which may be due to the competitive adsorption of RhB and R6G.

To further confirm that selective adsorption is mainly due to ionic interaction of dye with the anionic framework, dyereleasing experiment with MB were carried out and indicated by UV-vis spectroscopy (Figs. 6a and S10). As shown in Fig. 6a, the dye molecules in **MB @1** can be efficiently released in the presence of NaCl and the color of the solution gradually turned back to blue again. In contrast, the dye molecules are difficult to release in pure MeOH and DMF for **1** and **2**, respectively (Fig. S11). It is worth noting that the integrity of the framework is maintained throughout the absorption process, and normaling changes to the PXRD and IR patternsDof: ManaworksDowere detected after the exchange of dyes, as demonstrated by PXRD and IR studies (Figs. S7 and S12).Furthermore, PXRD of **1** and **2** after release experiment confirmed their high stability (Fig. S13). This high stability and reversible adsorption feature were crucial to the MB removal application.

The reusability experiments of **1** for MB adsorption show that **1** was found to be operational for three cycles with somewhat lowered adsorption efficiency for MB (Fig. S14). The PXRD patterns indicate that the framework of **1** is basically unchanged after three adsorption-desorption cycles for MB (Fig. S13).



Fig. 5 UV-vis spectra of MB/SY2 (a), MB/AR2 (b), MB/MO (c), MB/CV (d), MB/RhB (e) and MB/R6G (f) in MeOH solution at different time during the adsorption with 2 as the host. The insets are the corresponding photographs before and after the adsorption

Published on 08 March 2019. Downloaded by University of Texas at Dallas on 3/8/2019 12:31:43 PM

Journal Name



Fig. 6 (a) The MB released from the MB@1 in a saturated solution of NaCl in MeOH monitored by UV-vis spectra. (b) Langmuir fitting plots for the adsorptions of MB on 1.

From the combined information on the above dyes adsorption experiments, it is realized that the different interactions are combined or collaborative during dyes adsorption progress as summarized in Table S1. The main and preferential electrostatic affinity facilitated highly sizeselective and rapid adsorption towards cationic MB. Meanwhile, inserting amide groups in frameworks may serve as special interaction sites through hydrogen-bonding interactions, which favored the adsorption towards cationic RhB and R6G with large size. However, compared with the strong electrostatic affinity, hydrogen-bonding interactions were much smaller in this work and do not make such a big contribution for adsorption, which resulted in that the adsorption capacity of cationic RhB and R6G is very low.

In all, as shown in Fig. 7, the possible mechanisms involved in the adsorption process could clarify its highly selective adsorption towards MB as well as different adsorption performance towards different dyes.



Fig. 7 Proposed interaction mechanism during adsorption of dyes on 1.

Dye adsorption capacity is commonly influenced by the concentration of the dye solutions. Therefore, by using UV-vis spectroscopy to test the adsorption amount at different initial dye concentrations for 24 h at room temperature, the adsorption capacity of 1 and 2 towards MB can be deduced from the dependence of saturate adsorption amount (q_e) on the initial concentration of adsorbate (c₀) according to the equation 1. In addition, Langmuir and Freundlich models are used to fit the maximum adsorption isotherms and it is found that the adsorptions can be described well by the Langmuir isotherm model (Figs. 6b and S15). The maximum adsorption amount for MB is 281 mg g⁻¹ for 1 and 181 mg g⁻¹ for 2, which are really higher than other reported carbonaceous materials (activated carbon, graphene oxide, and carbon nanotubes),^{2b,} ^{6c, 12a} and oxidized nanodiamond (OND-4.5) (Table S2). This values are also higher than or comparable with that of various MOFs, such as UiO-66 (90.9 mg g⁻¹)^{10b}, MOF-235 (187 mg g^{-1}),^{12b} NH₂-MIL-101-SO₃H (141 mg g^{-1}),^{6c} JLU-liu39 (308 mg g⁻¹),^{12c} {[Cd₄(BPTC)₂(DMA)₄(H₂O)₂](DMA)}n (79.4 mg g⁻¹),^{12d} [(CH₃)₂NH₂]_{1.5}[Tb_{1.5}(TATAT)(H₂O)_{4.5}]•x(solvent) (147 mg and g⁻¹)^{12e} (Table S2). In order to examine the adsorption mechanism, the pseudo-first-order and the pseudo-secondorder kinetic models were applied to analyze data obtained (Figs. S16 and S17). As indicated in Table S3, it is evident that the fitting with pseudo-second-order kinetic model matches well with experimental data by comparing the fitting coefficient.

At the same time, it is worth noted that the adsorption capacity and adsorption kinetic constant of **1** are greater than those of **2**, demonstrating the effect of porosity and pore structure during the adsorption.

Generally, zeta potential of adsorbents is another key factor affecting their adsorption capacity.^{6b,10b} Thus, we further tested the zeta potential of two MOFs. The zeta potential of **1** and **2** are about -15.38 and -10.37 mV, respectively. The result further demonstrated that the higher efficiency removal of cationic dye may be attributed to the electrostatic attraction interactions between the adsorbents and cationic dye.

Adsorption isotherm and kinetics for MB adsorption

gComm Accepted Manuscri

Published on 08 March 2019. Downloaded by University of Texas at Dallas on 3/8/2019 12:31:43 PM.

Journal Name

Ion chromatographic column filler for dyes separation

Encouraged by the excellent adsorption and separation performance towards cationic dyes on two frameworks, we used **1** and **2** as the stationary phase of an ion chromatographic column (Fig. 8). The mixed solutions of MB/MO, MB/AR2, MB/RhB, MB/CV and MB/SY2 with the same concentration were injected into the chromatographic column, respectively. As displayed in Fig. 8, MB was adsorbed into samples for a long time along with the MeOH stream, while MO, AR2, RhB, CV and SY2 were passed through the column. Consequently, the two kinds of dyes can be successfully separated by passing through chromatographic column, which could be easily observed by the naked eye. These experiments highlight the potential of **1** and **2** serving as column-chromatographic filler for the separation of dyes.



Fig. 8 Photograph for (left) 1-filled and (right) 2-filled column-chromatographic (a); separation process for MB/SY2 (b), MB/AR2 (c), MB/MO (d), and MB/CV (e).

Conclusions

Based on varying solvents, two ionic indium-organic frameworks were achieved with the amide-functionalized tetracarboxylate linkers (H_4L). Notably, incorporating amide functional group into framework not only access distinct network as well as modified pore structure, but also serve as special interaction sites for dyes adsorption, which have been demonstrated in a thoroughly experiments towards seven types of dyes with different charge and size.

The adsorption experimental data indicate that the electrostatic interactions between two anionic frameworks of **1** and **2** and dyes are the major driving force, and additional hydrogen-bonding interactions of amide group and dye molecules are also responsible for dye adsorption. Thus, both frameworks, especially **1**, demonstrate the outstanding size-selective adsorption towards cationic organic dye MB, and can potentially serve as column-chromatographic filler for separating dye molecule. This work not only highlights the promise of these two MOF materials for the practical removal of organic dyes, but more importantly uncovers the combined or collaborative effect of electrostatic affinity and hydrogenbonding interactions in dyes adsorption. The synergic effect of strong electrostatic affinity as well as hydrogen bond will promoted the potential application in highly efficient dyes

removal. Then, it is expected that this work will offer valuable guidance in designing ideal porous MOFsothat/cofferoniagh performance for dyes removal in the real practice.

Acknowledgements

This work was supported by the Natural Science Foundation of Jiangsu Normal University, China (No.17XLR044), PAPD of Jiangsu Higher Education Institution and Postgraduate Research & Practice Innovation Program of Jiangsu Province (KYCX18_2109).

Notes and references

- (a) X. Zhao, X. Bu, T. Wu, S.-T. Zheng, L. Wang and P. Feng, *Nat. Commun.*, 2013, **4**, 2344; (b) M. Cao, J. Lin, J. Lü, Y. You, T. Liu and R. Cao, *J. Hazard. Mater.*, 2011, **186**, 948; (c) Z. Hasan and S. H. Jhung, *J. Hazard. Mater.*, 2015, **283**, 329; (d) Y. Li, Z. Yang, Y. Wang, Z. Bai, T. Zheng, X. Dai, S. Liu, D. Gui, W. Liu, M. Chen, L. Chen, J. Diwu, L. Zhu, R. Zhou, Z. Chai, T. E. Albrecht-Schmitt and S. Wang, *Nat. Commun.*, 2017, **8**, 1354; (e) G. Martinez-Ariza, M. Ayaz, F. Medda and C. Hulme, *J. Org. Chem.*, 2014, **79**, 5153; (f) C.-Y. Sun, X.-L. Wang, C. Qin, J.-L. Jin, Z.-M. Su, P. Huang and K.-Z. Shao, *Chem. Eur. J.*, 2013, **19**, 3639; (g) Y.-Y. Jia, Y.-H. Zhang, J. Xu, R. Feng, M.-S. Zhang and X.-H. Bu, *Chem. Commun.*, 2015, **51**, 17439.
- (a) Q. L. P. Yu, Y. Hu, N. Liu, L. Zhang, K. Su, J. Qian, S. Huang and M. Hong, *Chem. Commun.*, 2016, **52**, 7978; (b) Y. Li, Q. Du, T. Liu, X. Peng, J. Wang, J. Sun, Y. Wang, S. Wu, Z. Wang, Y. Xia and L. Xia, *Chem. Eng. Res. Des.*, 2013, **91**, 361; (c) H. Molavi, A. Shojaei and A. Pourghaderi, *J. Colloid Interface Sci.*, 2018, **524**, 52; (d) A. Yousaf, N. Xu, A. M. Arif, J. Zhou, C.-Y. Sun, X.-L. Wang and Z.-M. Su, *Dyes Pigments*, 2019, **163**, 159; (e) S.-N. Zhao, C. Krishnaraj, H. S. Jena, D. Poelman and P. Van Der Voort, *Dyes Pigments*, 2018, **156**, 332; (f) A. Buffa and D. Mandler, *Chem. Eng. J.*, 2019, 359, 130.
- (a) H. Li, K. Wang, Y. Sun, C. T. Lollar, J. Li and H.-C. Zhou, *Mater. Today*, 2018, **21**, 108; (b) Y. Li, A.-S. Xiao, B. Zou, H.-X. Zhang, K.-L. Yan and Y. Lin, *Polyhedron*, 2018, **154**, 83; (c) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724; (d) Y. Zhang, S. Yuan, G. Day, X. Wang, X. Yang and H.-C. Zhou, *Coord. Chem. Rev.*, 2018, **354**, 28; (e) M. Zhang, B. Li, Y. Li, Q. Wang, W. Zhang, B. Chen, S. Li, Y. Pan, X. You and J. Bai, *Chem. Commun.*, 2016, **52**, 7241.
- (a) Q. Gao, J. Xu and X.-H. Bu, *Coord. Chem. Rev.*, 2018, doi:10.1016/j.ccr.2018.03.015; (b) L. Sun, Q. Pan, Z. Liang and J. Yu, *Inorg. Chem. Front.*, 2014, **1**, 478; (c) S. Yao, T. Xu, N. Zhao, L. Zhang, Q. Huo and Y. Liu, *Dalton Trans.*, 2017, **46**, 3332.
- (a) A. Karmakar, A. V. Desai and S. K. Ghosh, *Coord. Chem. Rev.*, 2016, **307**, 313; (b) P. Kumar, A. Pournara, K.-H. Kim, V. Bansal, S. Rapti and M. J. Manos, *Prog. Mater. Sci.*, 2017, **86**, 25; (c) P. Li, N. A. Vermeulen, X. Gong, C. D. Malliakas, J. F. Stoddart, J. T. Hupp and O. K. Farha, *Angew. Chem. Int. Ed. Engl.*, 2016, **55**, 10358; (d) Q. Li, D.-X. Xue, Y.-F. Zhang, Z.-H. Zhang, Z. Gao and J. Bai, *J. Mater. Chem. A*, 2017, **5**, 14182; (e) Y.-X. Tan, Y.-P. He, M. Wang and J. Zhang, *RSC Adv.*, 2014, **4**, 1480; (f) S. T. Zheng, F. Zuo, T. Wu, B. Irfanoglu, C. Chou, R. A. Nieto, P. Feng and X. Bu, *Angew. Chem. Int. Ed. Engl.*, 2011, **50**, 1849; (g) M. Zhou, Z. Ju and D. Yuan, *Chem. Commun.*

View Article Online DOI: 10.1039/C9CE00065H

Published on 08 March 2019. Downloaded by University of Texas at Dallas on 3/8/2019 12:31:43 PM

2018, **54**, 2998; (h) J. Xia, J. Xu, Y. Fan, T. Song, L. Wang and J. Zheng, *Inorg. Chem.*, 2014, **53**, 10024; (i) J. Qian, F. Jiang, K. Su, Q. Li, D. Yuan and M. Hong, *Inorg. Chem.*, 2014, **53**, 12228; (j) H. He, Y. Song, C. Zhang, F. Sun, R. Yuan, Z. Bian, L. Gao and G. Zhu, *Chem. Commun.*, 2015, **51**, 9463.

- (a) C. Li, Z. Xiong, J. Zhang and C. Wu, J. Chem. Eng. Data, 2015, 60, 3414; (b) T.-T. Li, Y.-M. Liu, T. Wang, Y.-L. Wu, Y.-L. He, R. Yang and S.-R. Zheng, *Micropor. Mesopor. Mat.*, 2018, 272, 101; (c) X.-P. Luo, S.-Y. Fu, Y.-M. Du, J.-Z. Guo and B. Li, *Micropor. Mesopor. Mat.*, 2017, 237, 268; (d) Q. Zhang, J. Yu, J. Cai, R. Song, Y. Cui, Y. Yang, B. Chen and G. Qian, *Chem. Commun.*, 2014, 50, 14455.
- (a) N. A. Khan, Z. Hasan and S. H. Jhung, J. Hazard. Mater., 2013, 244-245, 444; (b) Y. Y. Pan, Y. N. Wu, Z. Z. Chen, W. J. Hao, G. Li, S. J. Tu and B. Jiang, J. Org. Chem., 2015, 80, 5764; (c) L. Dai, W. Zhu, L. He, F. Tan, N. Zhu, Q. Zhou, M. He and G. Hu, Bioresour. Technol., 2018, 267, 510.
- (a) H. Y. Liu, J. Liu, G. M. Gao and H. Y. Wang, *Inorg. Chem.*, 2018, **57**, 10401; (b) H. Liu, F. Meng, Z. Lu and J. Bai, *CrystEngComm*, 2016, **18**, 9003; (c) H. Liu, Q. Wang, M. Zhang and J. Jiang, *CrystEngComm*, 2015, **17**, 4793; (d) M. Zhang, Q. Wang, Z. Lu, H. Liu, W. Liu and J. Bai, *CrystEngComm*, 2014, **16**, 6287; (e) H.-Y. Liu, L.-F. Chen, H.-Y. Wang, Y. Wan and H. Wu, *RSC Adv.*, 2016, **6**, 94833; (f) K. Tang, R. Yun, Z. Lu, L. Du, M. Zhang, Q. Wang and H. Liu, *Cryst. Growth. Des.*, 2013, **13**, 1382; (g) H.-Y. Liu, G.-M. Gao, J. Liu and H.-Y. Wang, *Polyhedron*, 2018, **152**, 11; (h) H. Y. Wang and H. Y. Liu, *Transit. Met. Chem.*, 2017, **42**, 165.
- (a) G. M. Sheldrick, Acta Crystallogr. A, 2008, 64, 112; (b) P. Van Der Sluis and A. L. Spek, Acta Crystallogr. A, 1990, 46, 194.
- (a) B. H. Hameed and A. A. Rahman, *J. Hazard. Mater.*, 2008, 160, 576; (b) Q. Chen, Q. He, M. Lv, Y. Xu, H. Yang, X. Liu and F. Wei, *Appl. Surf. Sci.*, 2015, 327, 77.
- (a) B. Zheng, J. Bai, J. Duan, L. Wojtas, and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2011, **133**, 748; (b) B.u Zheng, X. Luo, Z. Wang, S. Zhang, R. Yun, L. Huang, W. Zeng and W. Liu, *Inorg. Chem. Front.*, 2018, **5**, 2355; (c) X.-Y. Li, L.-N. Ma, Y. Liu, L. Hou, Y.-Y. Wang and Z. Zhu, *ACS Appl. Mater. Inter.*, 2018, **10**, 10965; (d) M. Zhang, W. Zhou, T. Pham, K. A. Forrest, W. Liu, Y. He, H. Wu, T. Yildirim, B. Chen, B. Space, Y. Pan, M. J. Zaworotko and J. Bai, *Angew. Chem. Int. Ed. Engl.*, 2017, **56**, 11426.
- (a) H. Molavi, A. Shojaei and A. Pourghaderi, J. Colloid Interface Sci., 2018, 524, 52; (b) E. Haque, J. W. Jun and S. H. Jhung, J. Hazard. Mater., 2011, 185, 507; (c) T. X. S. Yao, N. and L. Z. Zhao, Q. Huo and Y. Liu, Dalton Trans., 2017,46, 3332-3337 46, 3332; (d) W.-J. Ji, R.-Q. Hao, W.-W. Pei, L. Feng and Q.-G. Zhai, Dalton Trans., 2018, 47, 700; (e) Z. Cui, X. Zhang, S. Liu, L. Zhou, W. Li and J. Zhang, Inorg. Chem., 2018, 57, 11463.

Published on 08 March 2019. Downloaded by University of Texas at Dallas on 3/8/2019 12:31:43 PM

Graphical Abstract

Amide-functionalized ionic indium-organic frameworks for efficient separation of organic dyes based on diverse adsorption interactions

Huiyan Liu,* Guimei Gao, Jie Liu, Fenlin Bao, Yuhui Wei and Haiying Wang*



Based on varying solvents, two anionic indium-organic frameworks were synthesized. Both MOFs feature amide group functionalized anionic frameworks and different channel of size and shape, which consequently afford diverse interactions during adsorption towards dyes of different charge and size, and thus different adsorption potential. Especially, **1** demonstrated outstanding adsorption toward small cationic organic dye methylene blue, and be applicable in column-chromatographic separation of dyes.