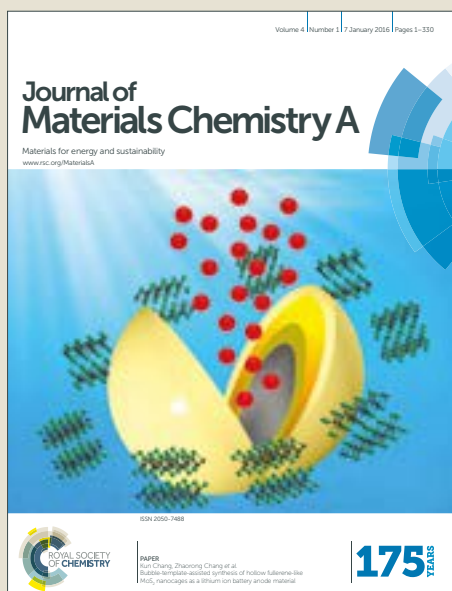


Journal of Materials Chemistry A

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: Z. Wang, J. Zhang, J. Jiang, H. Wang, Z. Wei, X. Zhu, M. Pan and C. Su, *J. Mater. Chem. A*, 2018, DOI: 10.1039/C8TA06249H.



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 [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), 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.



Journal Name

ARTICLE

A stable metal cluster-metalloporphyrin MOF with high capacity for cationic dye removal

Zheng Wang,^{a,b} Jian-Hua Zhang,^a Ji-Jun Jiang,^a Hai-Ping Wang,^a Zhang-Wen Wei,^a Xunjin Zhu,^{*b} Mei Pan,^{*a} and Cheng-Yong Su^a

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

A metalloporphyrin Cu₅-cluster based MOF (metal-organic framework), [Cu_{4.5}(H₄TZPP)(TZPP)Cl₂)(H₂O)_{0.5}]·CH₃NH₂CH₃·7EtOH·8H₂O (LIFM-WZ-3) was synthesized from the tetrapodal ligand {5,10,15,20-tetrakis[4-(2,3,4,5-tetrazolyl)phenyl]porphyrin (H₄TZPP) and copper chloride. LIFM-WZ-3 exhibits a rare 2D+3D→3D interpenetration topology, of which **frl**-type 3D MOF and layered 2D HOF (hydrogen bond organic framework) are intertwined, leading to an anionic framework with 1D spindle-like channels. Powder X-ray diffraction analysis reveals that the framework is stable in acid, base and various organic solvent environment. LIFM-WZ-3 exhibits moderately high separation performances for CO₂/CH₄, CO₂/N₂ and C₃H₆/CH₄, C₂H₆/CH₄, C₂H₄/CH₄ at room temperature. Specifically, the anionic framework in LIFM-WZ-3 containing dimethylamine cations can selectively adsorb cationic organic dyes from aqueous pollutants for recycle purpose. The high adsorption capacity for methylene-blue (MB⁺, 983 mg g⁻¹) and crystal violet (CV⁺, 713.5 mg g⁻¹) ranks the highest among those MOFs ever reported.

Introduction

Accompanying the rapid development of industries, organic dyes have been widely applied as eluent and colorant in different fields and enriched our lives.^{1,2} However, some dye molecules are toxic, carcinogenic, and very resistant to degradation under sunlight, heat, and oxidant in nature, which might cause serious water pollutions. Therefore, it is urgent to find efficient ways to remove dye pollutants from water before they are released for consumption. So far, various methods including physical, chemical and biological technologies have been developed. Among them, adsorption by porous materials is considered the most common technique to remove organic dyes from aqueous solution, characteristic of low cost and high efficiency.³ Currently, different kinds of porous adsorbents like zeolites, activated carbons, molecular sieves and polymeric materials have been used for removal of organic dyes.⁴ However, these materials encounter problems such as less selectivity and low capacity, which hinders the efficient removal, recovery and reuse of specific dyes.

As a new class of porous materials, metal-organic frameworks (MOFs) have aroused great attention in recent years, and widely applied in various fields including chemical sensing,⁵ light emitting,⁶ proton conductivity,⁷ catalysis,⁸ magnets,⁹ drug delivery and medical materials,¹⁰ energy storage,¹¹ and so on.¹² Compared with other porous materials such as activated carbons, zeolites and polymers, MOFs manifest controllable porosity (sometimes tunable by interpenetration), high surface areas, and ability to be functionalized for better interactions with certain kinds of guest molecules including organic dyes.¹³⁻¹⁷ Meanwhile, MOFs with charged frameworks may have unique advantages in adsorption, selection and separation by host-guest interactions.^{18,19} For example, cationic MOFs can selectively adsorb anionic dyes through ion-ion exchange processes, and vice versa. Besides electrostatic interactions, the driving forces might also include other kinds of intermolecular interactions between the active sites of host MOFs and guest dyes, such as hydrogen bonds, hydrophobic interactions, van der Waals interactions, and so on.²⁰

On the other hand, the application of MOFs in selective adsorption and separation of gases and hydrocarbons has been widely recognized in the past decades.²¹ If the confined channels of MOFs are with suitable sizes and specific interacting sites for certain guest molecules, effective adsorption and separation might be resulted for selective ingredients in mixed gases. For such purposes, abundant MOFs from carboxyl, pyridine, imidazole, pyrazole and

^a Lehn Institute of Functional materials, MOE Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, China.

^b Department of Chemistry, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong, China.

Electronic Supplementary Information (ESI) available: [Crystal structure, formula and size of dyes, TG, gas and dye adsorption, etc]. See DOI: 10.1039/x0xx00000x

ARTICLE

Journal Name

triazole ligands have been designed by researchers. Compared with these, 5-substituted tetrazolyl ligands are much less used for constructing MOFs, and 5-substituted tetrazolyl porphyrin ligands are even less developed.²² As a matter of fact, the multiple nitrogen atoms in 5-substituted tetrazolyl porphyrins will bring versatile coordination abilities and charged states by adopting different bridging or chelating modes, as well as unique framework stability with permanent channels due to the porphyrin core, and might find potential applications in MOF chemistry. In addition, more nitrogen sites within the frameworks can increase the specific adsorption capacity for gases, hydrocarbons or organic dyes.²³ Based on the above considerations, we designed herein an anionic MOF from 5,10,15,20-tetrakis[4-(2,3,4,5-tetrazolyl)phenyl]porphyrin ligand, which presents a rare example of 2D+3D→3D framework containing interpenetrated 2D metalloporphyrin HOF and 3D MOF elements simultaneously. The stable anionic framework with 1D spindle-like channels manifests rather good gas and hydrocarbon separation abilities, and can selectively adsorb cationic organic dyes from aqueous solution.

Experimental

Materials and Physical Measurements

All reagents of analytical grades were purchased from the Dieckmann company and used without further purification process. IR spectrum was recorded from KBr pellet on a FTS-40 spectrophotometer in the range of 4000-400 cm^{-1} . Elementary analysis was performed on a Vario EL element analyzer. NMR spectra were recorded on a JEOL EX270 spectrometer. Chemical shifts of ^1H NMR spectra were referenced to internal deuterated solvents and then recalculated to SiMe_4 . Powder X-ray diffraction (PXRD) was carried out with a Rigaku Smart Lab diffractometer (Bragg-Brentano geometry, $\text{Cu K}\alpha 1$ radiation, $\lambda = 1.54056 \text{ \AA}$). Thermogravimetric analyses (TGA) were performed on a NETZSCH TG209 system in nitrogen and under 1 atm of pressure at a heating rate of 10°C per min. Brunauer–Emmett–Teller (BET) surface area was measured using Quadrasorb SI-MP instrument. Gas adsorption isotherms with the pressures in the range of 0-1.0 bar were obtained by a volumetric method using a quantachrome autosorb-iQ2-MP gas adsorption analyzer. Gas adsorption measurements were performed using ultra-high purity N_2 , CH_4 , CO_2 and hydrocarbon gases.

X-ray single crystal structural analysis

The X-ray diffraction intensity data for LIFM-WZ-3 were performed on a Bruker Apex II CCD diffractometer graphite-monochromatic enhanced ultra Cu -radiation ($\lambda = 1.54178 \text{ \AA}$) at 100 K. The structure was solved by direct methods, and refined by full-matrix least-square methods with the SHELXL-1997 program package. All hydrogen atoms were located in calculated positions and refined anisotropically. The solvent molecules in LIFM-WZ-3 are disordered. The SQUEEZE routine of PLATON was applied to remove the highly disorder solvent molecules, and the final molecular formulas of LIFM-WZ-3 was determined by the combination of TGA (Fig. S1) and elemental analysis data. The 2D HOF layers within LIFM-WZ-3 are all disordered over two sites which form a rotate disorder angles by two occupied components

and were anisotropically dealt with occupancy of part 10.5. The crystal for LIFM-WZ-3 has no diffraction point at high angles, so we only collect half a degree to 52.99° . The LIFM-WZ-3 crystallographic data were listed in Table S1. The selected bonds distance and bonds angles are displayed in Table S2. The single crystal data have been deposited in the Cambridge Crystallographic Data Center (CCDC No: 1812995).

Synthesis of ligand

5,10,15,20-tetrakis(4-cyanophenyl)porphyrin (H_2TCNPP). H_2TCNPP was synthesized according to a modified literature method. 4-formyl benzonitrile (6.55 g, 50.00 mmol) and propionic acid (200 ml) were added to the flask and heated to 110°C , then pyrrole (3.35 g, 50.00 mmol) was added dropwisely to the mixture solvent through a period of one hour and heated to reflux for overnight. After the reaction, the propionic acid was removed under reduced pressure. The resulting dark residue was washed with cold ethanol and acetone until the purple solid appeared. And then, it was dried in vacuum to obtain H_2TCNPP (1.71 g) as a pure violet solid with 20 % yield. ^1H NMR (CDCl_3) δ 8.85 (s, 8H), 8.38 (d, 8H), 8.12 (d, 8H) ppm.

5,10,15,20-tetrakis[4-(2,3,4,5-tetrazolyl)phenyl]porphyrin (H_6TZPP). H_2TCNPP (3.00 g, 4.20 mmol), NH_4Cl (3.60 g, 33.71 mmol), NaN_3 (4.81 g, 36.72 mmol), and DMF (200 ml) were mixed and heated to reflux for 3 days. Additional NaN_3 (1.71 g, 25.92 mmol) and NH_4Cl (1.11 g, 20.52 mmol) were added to the mixture and continued to react for 2 days. After the reaction, a small part of DMF was removed under reduced pressure and cold water (500 ml), 6 mol l^{-1} HCl were added with quickly stirring. The precipitate was filtered and washed several times with cool water and cool ethanol, and dried in vacuum to get H_6TZPP as a green solid with 92 % yield. ^1H NMR ($\text{DMSO}-d_6$) δ 8.98 (s, 8H), 8.52 (d, 8H), 8.46 (d, 8H) ppm. IR (KBr, cm^{-1}): 3420 (b), 2926 (w), 2857 (w), 1654 (s), 1615 (m), 1574 (w), 1563 (w), 1496 (w), 1472 (w), 1435 (w), 1415 (m), 1385 (m), 1348 (w), 1270 (w), 1253 (w), 1224 (w), 1187 (w), 1151 (w), 1100 (w), 1061 (w), 1021 (w), 1012 (w), 993 (w), 981 (w), 966 (m), 858 (m), 800 (m), 751 (w), 729 (m), 663 (w), 633 (w), 561 (w), 474 (w), 456 (w).

Synthesis of MOF

$[\text{Cu}_{4.5}(\text{H}_6\text{TZPP})(\text{TZPP})\text{Cl}_2(\text{H}_2\text{O})_{0.5}] \cdot \text{CH}_3\text{NH}_2\text{CH}_3 \cdot 7\text{EtOH} \cdot 8\text{H}_2\text{O}$ (LIFM-WZ-3). A mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (5.30 mg, 0.03 mmol), HCl (4 ml, 1 mol l^{-1}) and H_6TZPP (8.86 mg, 0.01 mmol) dissolved in 2 ml of H_2O , 2 ml of DMF and 2 ml of ethanol were sealed in a Teflon vessel in a steel autoclave, and heated at 110°C for three days and then slowly cooled a period of 48 hours to room temperature. Purple red flake single crystal of LIFM-WZ-3 were collected. The yield is 90% based on the ligand. Analysis calcd. for $\text{C}_{112}\text{H}_{114}\text{N}_{41}\text{Cl}_2\text{O}_{15.5}\text{Cu}_{4.5}$: C 53.33, H 4.42, N 22.78%; found: C, 53.76, H, 4.97, N, 23.22%. IR (KBr, cm^{-1}): 3356 (b), 1615 (s), 1537 (w), 1495 (w), 1447 (w), 1421 (w), 1378 (s), 1345 (m), 1270 (w), 1247 (w), 1207 (w), 1157 (w), 1126 (w), 1100 (w), 1076 (w), 999 (s), 886 (w), 860 (w), 818 (w), 802 (w), 761 (w), 751 (w), 718 (w), 561 (w), 498 (w). The MOF samples were activated by soaking in MeOH and CH_2Cl_2 for 7 days and then heated at 120°C for 10 hours.

Results and discussion

Crystal structure

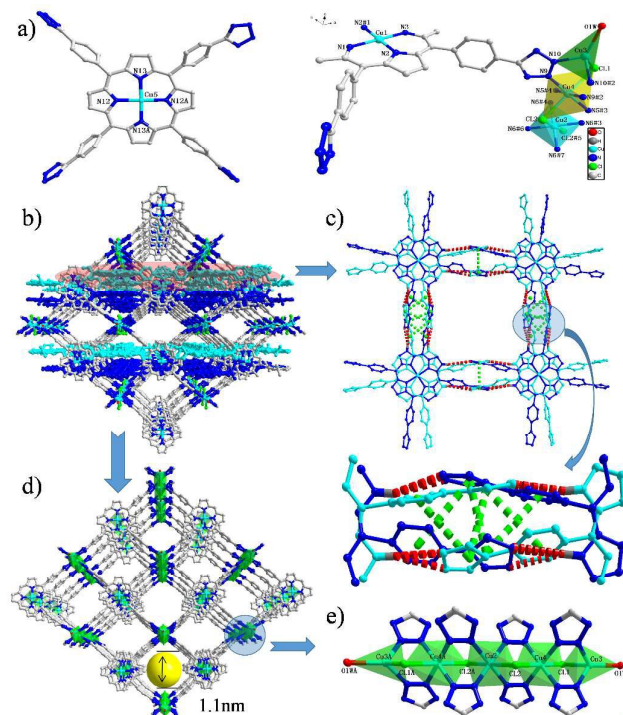


Fig. 1 Crystal structure of LIFM-WZ-3. a) Coordination environment of copper ions and porphyrin ligands. b) Self-assembly formation of 2D+3D→3D nets; c) 2D metalloporphyrin HOF layers formed via C-H...N and π - π stacking interactions; d) 3D metal cluster-metalloporphyrin MOF nets with 1D square channels; e) $\{Cu_5\}$ metal cluster.

Purple red flake crystals of LIFM-WZ-3 with sizes of $0.1 \times 0.5 \times 0.5 \text{ mm}^3$ were obtained under solvothermal reaction by heating the mixture of $CuCl_2 \cdot 2H_2O$ and H_6TZPP at $110^\circ C$ for 3 days. Single crystal X-ray diffraction reveals that LIFM-WZ-3 is crystallized in the monoclinic $P2_1/m$ space group. In the asymmetric unit of LIFM-WZ-3, there are a half of H_4TZPP^{2-} porphyrin ligand, a half of $TZPP^{6-}$, one chloride ion, two and one quarter of Cu^{2+} ions, one quarter of water molecules, a half of dimethylamine cation, and solvent molecules. There are altogether five kinds of Cu^{2+} coordination centers (Fig. 1a). Cu1 and Cu5 are located in respective porphyrin core and exhibit square planar geometry. To prove the occupancy of Cu at porphyrin center, LIFM-WZ-3 and H_6TZPP ligand were dissolved in NaOH aqueous solution ($1 \times 10^{-5} \text{ mol L}^{-1}$) for UV-Vis test. As can be seen in Fig. S2, the UV absorption of LIFM-WZ-3 is obviously different from that of the pure ligand, in which the Q band changes from four peaks to two peaks, proving that the porphyrin center is completely occupied by Cu ions. Cu2 and Cu4 display octahedral coordination environment, which are coordinated with four nitrogen atoms derived from four tetrazolyl rings of different $TZPP^{6-}$ ligands and two chloride ions coming from metallic salt. Cu3 forms a tetrahedral coordination surrounding and coordinated with two nitrogen atoms coming from tetrazolyl rings of

two $TZPP^{6-}$ ligands, one chloride ion and one water molecule. The Cu-N bond lengths change from 1.938(16) to 2.049(17) Å, and the Cu-Cl and Cu-O bond lengths vary in a reasonable range from 2.590(13) to 2.343(5) Å, which are in accordance with typical Cu complexes.^{24, 25}

It is interesting that in the framework of LIFM-WZ-3, there are two discrete elements, a 2D hydrogen bonded framework (HOF), and a 3D MOF (Fig. 1b). The 2D HOF is formed by intermolecular hydrogen bonding and π - π stacking linked CuH_4TZPP moieties (Fig. 1c), in which Cu5 ions are located in the porphyrin cores, and the tetrazolyl ends are not coordinated. In comparison, the 3D MOF is composed of $\{Cu_5\}$ clusters and Cu1-resided metalloporphyrins, showing an aperture of $\sim 1.1 \times 1.1 \text{ nm}$ (Fig. 1d). The porphyrin ligands containing Cu1 centers are extended via coordination of tetrazolyl ends with other Cu^{2+} ions (Cu2, Cu3, and Cu4). Further analysis reveals that, in the 3D MOF structure, Cu2, Cu3, Cu3A, Cu4 and Cu4A are connected by eight tetrazolyl groups and four Cl⁻ ions into a five-nuclear $\{Cu_5\}$ cluster with Cu...Cu distance of 3.448 and 3.526 Å (Fig. 1e). The $\{Cu_5\}$ clusters are further linked by the bridge of water molecules to form 1D zigzag metal ladders, as termed by Yaghi et al. to be rod-shaped secondary building units,²⁶ and are connected by $[CuTZPP]^{4-}$ ligands to produce a 3D anionic framework.

Topologically, simplifying $[CuTZPP]^{4-}$ metalloporphyrin as 4-connected points to link the zigzag ladders composed of $\{Cu_5\}$ clusters, a rare 3D **fri** structure with the Schläfli symbol of $(4^2 \cdot 6^4)_4(6^4 \cdot 8^2)$ is formed, presenting the first **fri** network in porphyrin-based MOFs, as far as we know. Furthermore, the 3D MOF is interpenetrated by the 2D HOF via H...Cl interactions and the whole LIFM-WZ-3 can be seen as an interpenetrated 2D+3D→3D network. Although the interpenetration of 2D HOF blocks half of the pores in the original 3D **fri** framework, the remaining 1D spindle-like channels along *c* axis (Fig. S3) afford LIFM-WZ-3 with selective adsorption abilities for certain gases and dyes. Meanwhile, the whole frameworks are anionic in nature and charge balanced by dimethylamine cations originated from the decomposition of DMF under hydrothermal conditions, leading to further adsorption selectivity.

The purity of LIFM-WZ-3 bulk samples were confirmed by PXRD tests (Fig. 2a). The diffraction patterns for as-synthesized sample are slightly shifted comparing with the simulated one, which might be due to small difference of the solvent inclusion states between the as-obtained bulk samples and single crystals. After activation, all of the measured peaks are closely matched with the simulated pattern.^{27, 28} The PXRD peaks keep almost the same after N_2 and dye adsorption experiment, manifesting the permanent pore structure. Furthermore, the chemical stability of LIFM-WZ-3 was tested by treating its samples in HCl, HNO_3 , H_2SO_4 , glacial acetic acid and NaOH aqueous solutions with variant pH values, and different organic solvents (CH_3CN , MeOH, deionized water and DMF) for 72 h at room temperature, respectively. The PXRD peaks of the treated samples remained unchanged, indicating the original crystal phase was maintained after the treatments (Fig. 2b). The

ARTICLE

Journal Name

super stability of the LIFM-WZ-3 framework warrants its application in gas and dye adsorption purposes.

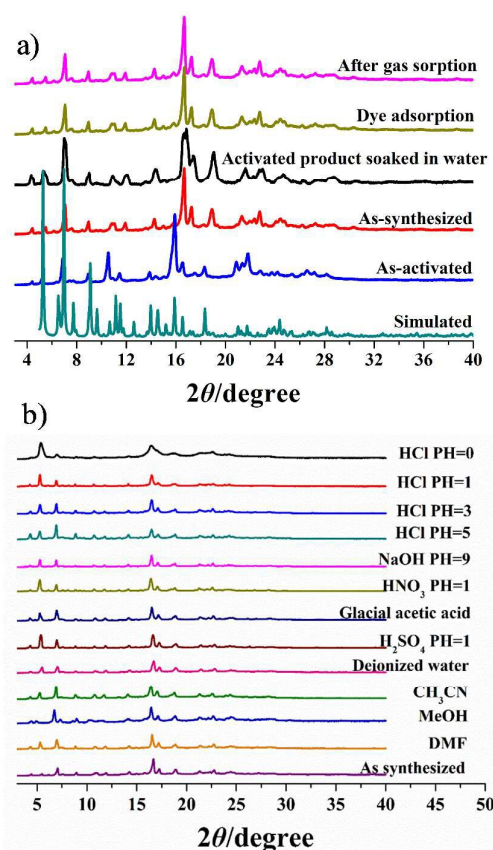


Fig. 2 PXRD patterns of LIFM-WZ-3. a) Simulated, as-activated, as-synthesized, activated product soaked in water again, after dye (RB⁺) adsorption, and after gas sorption; b) As-synthesized, soaked in aqueous solutions with different pH, acids, and different solvents for 72 h.

Gas adsorption

N₂ sorption measurements were carried out at 77 K for LIFM-WZ-3, which manifests a type I adsorption isotherm behavior with the maximal adsorption amount of 141 cm³ g⁻¹ (Figs. 3a, S4, S5). The Langmuir and Brunauer–Emmett–Teller (BET) surface area were estimated to be 457 and 509 m² g⁻¹, and the total pore volume and pore size are 0.143 cm³ g⁻¹ and 0.64 Å, respectively. Although the surface area of LIFM-WZ-3 is not large, the significant number of uncoordinated nitrogen sites in the framework might enhance selective adsorption of CO₂ and certain hydrocarbons (Figs. S6–16). First, the CO₂ sorption isotherms at different temperature were measured, which show an uptake of 103.6 cm³ g⁻¹ at 195 K and 29.5 cm³ g⁻¹ at 298 K (Fig. 3b). For comparison, the CH₄ and N₂ uptakes at 298 K are very low, accounting for 7.1 cm³ g⁻¹ and 1.7 cm³ g⁻¹ only (Fig. 3c), which leads to the calculated CO₂/CH₄ and CO₂/N₂ selectivity of 7.6 and 34.4 at 298 K and 1 bar, respectively. Meanwhile, the gas selectivity for CO₂/N₂ and CO₂/CH₄ at 273 K was calculated to be 17.9 and 7.3, respectively (Figs. 3c and S13). We deduce that the good selectivity for CO₂ over CH₄ and N₂ should be due to the strong interactions with uncoordinated/open nitrogen

sites and dimethylamine cations in the framework induced by the quadrupole moment of CO₂. Further analysis affords the isosteric heat of LIFM-WZ-3 for CO₂ adsorption to be 46.8 kJ·mol⁻¹ (Fig. S11).

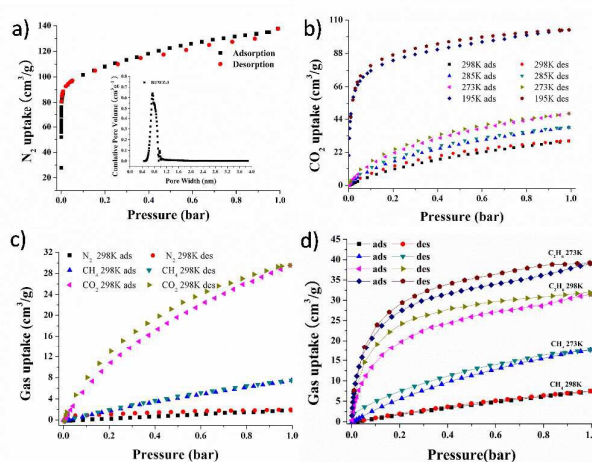


Fig. 3 Gas sorption for LIFM-WZ-3: a) N₂ sorption isotherm at 77 K (inset: pore size distribution analyzed with SF method); b) CO₂ sorption isotherms at different temperature; c) selective uptake of CO₂ over CH₄ and N₂ at 298 K; d) CH₄ and C₂H₆ sorption isotherms at 298 K and 273 K.

The application of LIFM-WZ-3 for potential separation of light hydrocarbons was also investigated through measuring the uptake of C₃H₆, C₂H₄, C₂H₆, and CH₄ at 273 and 298 K, respectively (Fig. 3d). We can clearly see the trend of adsorption ability with C₃>C₂>C₁ for LIFM-WZ-3. IAST calculation was applied to evaluate the multi-component selectivities. Under 1 atm, the selectivities of C₃H₆, C₂H₆, and C₂H₄ with respect to CH₄ are 202.1, 26.8 and 10.7 at 298 K, and 218.2, 17.3 and 9.8 at 273 K. Meanwhile, the selectivities of C₃H₆/C₂H₆ and C₃H₆/C₂H₄ are 9.7, 10.7 at 298 K, and 15.4, 13.1 at 273 K, respectively (Figs. S14–16). The above results suggest that LIFM-WZ-3 can be a potential candidate for the separation of C₃ with respect to C₂ hydrocarbons and C₃/C₂ hydrocarbons over CH₄.

Dye adsorption and desorption

As for the adsorption of organic dyes, in order to get high selectivity, the sizes, shapes and charges of dye molecules are several important factors to be considered. Thus, nine kinds of dyes, namely, cationic-type methylene blue (MB⁺), crystal violet (CV⁺), rhodamine B (RB⁺) and basic red (BR⁺), anionic-type methyl orange (MO⁻) and acid orange (AO⁻), and neutral-type dimethyl yellow (DY), Sudan I (SD-I), and Sudan II (SD-II) with different attributes (Table S2) were chosen as adsorbent target dyes. The fresh crystalline LIFM-WZ-3 were soaked in aqueous solution of MB⁺, CV⁺, RB⁺, BR⁺, MO⁻, AO⁻, DY, SD-I and SD-II, respectively. The concentration of dye molecules during the adsorption process can be viewed by direct color change and detected quantitatively by UV-Vis absorption spectroscopy. As a result, the color and concentration of MO⁻, AO⁻, DY, SD-I and SD-II solutions keep almost constant with the time shifting, while the changes are clear-cut for MB⁺, CV⁺, BR⁺ and RB⁺ solutions (Figs. 4 and S17–23). The above

phenomenon demonstrates that LIFM-WZ-3 only selectively adsorb cationic dyes.

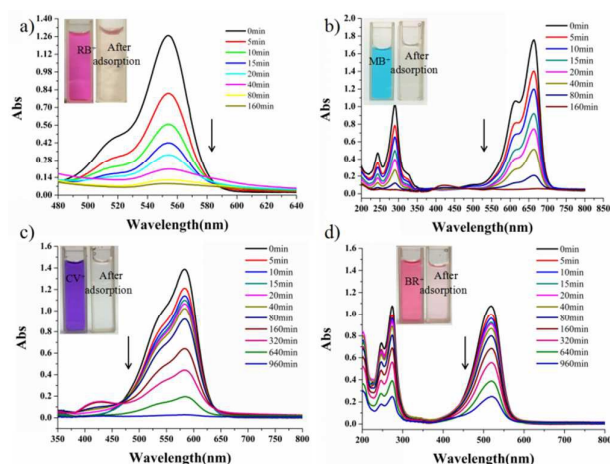


Fig. 4 Temporal evolution of UV-Vis absorption spectra of 20 ml aqueous solution containing a) RB^+ , b) MB^+ , c) CV^+ and d) BR^+ (10 mg l^{-1} for each kind of dye) by LIFM-WZ-3 (10 mg) adsorption. The photo-graphs show the colors of solution before and after 160 or 960 min of organic dye adsorption.

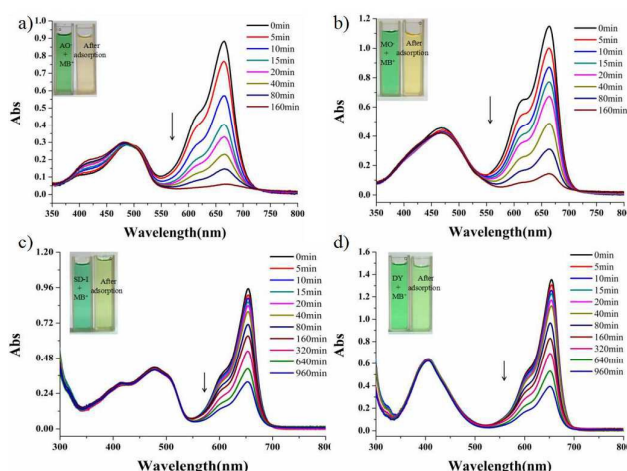


Fig. 5 Temporal evolution of UV-Vis absorption spectra of 40 ml aqueous solution containing a) AO/MB^+ , b) MO/MB^+ , c) SD-I/MB^+ and d) DY/MB^+ (10 mg l^{-1} for each kind of dye) by LIFM-WZ-3 (10 mg) adsorption. The photo-graphs show the colors of solution before and after 160 or 960 min of organic dyes adsorption.

In order to further verify this conclusion, crystalline LIFM-WZ-3 samples were immersed into the aqueous solutions containing mixed dyes of DY/MB^+ , SD-I/MB^+ , SD-II/MB^+ , MO/MB^+ and AO/MB^+ , respectively (Figs. 5 and S22). It can be observed that LIFM-WZ-3 only adsorb cationic dyes from the mixed solution, and therefore, the solution colors change from green to yellow for AO/MB^+ , MO/MB^+ and SD-II/MB^+ , from jade to shallow green for SD-I/MB^+ , and from green to shallow green for DY/MB^+ . The intensity changes of relative adsorption peaks are more obvious, in which those related with MB^+ are drastically dropped, while the peaks related with other

dyes remain unchanged. It can thus be inferred that dye adsorption can happen in facile via ion-exchange process between the dimethylamine cations in the 1D channels of LIFM-WZ-3 and the cations of MB^+ in aqueous solution, while exchange with neutral and negatively charged dyes are not allowed.

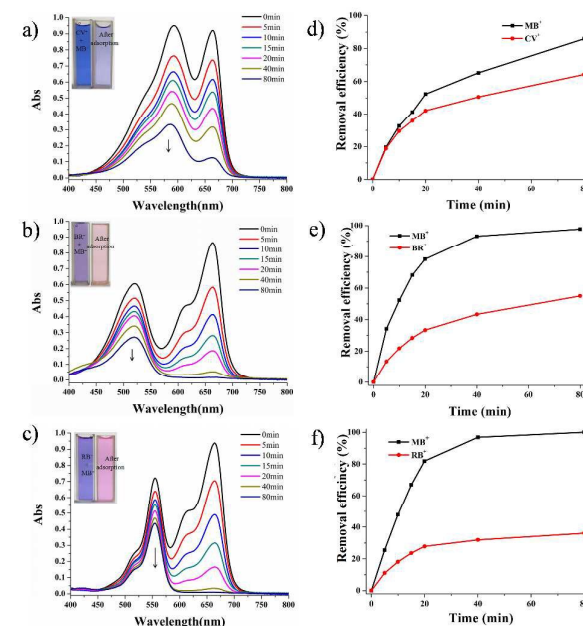


Fig. 6 Temporal evolution of UV-Vis absorption spectra of 40 ml aqueous solution containing a) CV^+/MB^+ , b) BR^+/MB^+ , and c) RB^+/MB^+ (10 mg l^{-1} for each kind of dye) by LIFM-WZ-3 (10 mg) adsorption. The photo-graphs show the colors of solution before and after 80 min of organic dyes adsorption. The removal efficiency of LIFM-WZ-3 with time for binary dye mixtures, d) MB^+/CV^+ , e) MB^+/BR^+ , and f) MB^+/RB^+ (Removal efficiency = $(c_0 - c_t) / c_0 \times 100\%$, c_0 represents the original concentration and c_t represents the instantaneous concentration of t moment).

We also studied the discriminative adsorption and separation of cationic dyes with variant sizes by LIFM-WZ-3. The four cationic dyes MB^+ , CV^+ , BR^+ and RB^+ possessing the same kind of positive charge but different molecular sizes were mixed into binary solutions with the same concentration and volume ratio. As shown in Table S3, the molecular sizes for the dyes are in order of $\text{MB}^+ < \text{CV}^+ < \text{BR}^+ < \text{RB}^+$ as calculated by software of material studio. Then samples of LIFM-WZ-3 were immersed in aqueous solutions of CV^+/MB^+ , BR^+/MB^+ and RB^+/MB^+ . Obviously, the homologous colors of the mixed CV^+/MB^+ , BR^+/MB^+ and RB^+/MB^+ aqueous solution changed from blue to purple, from purple to pink and from blue to pink, respectively (Figs. 6a-c). In UV-Vis spectra, the absorption peak intensity at 654 nm assigned for MB^+ is dropped more abruptly and almost faded away after 80 min. While the absorption peaks of CV^+ , BR^+ and RB^+ are decreased sluggishly, suggesting that the adsorption of these larger molecules are suppressed upon the co-existence of MB^+ , manifesting size and steric effects. Meanwhile, we can also notice that the outer contour of MB^+ is more suitable for the spindle-like channels of LIFM-WZ-3 and can easily get access into the channels by ion exchange process. This size and shape effect can be more evidenced by the selective

ARTICLE

Journal Name

removal efficiency curves for the binary dye mixtures (Figs. 6d-f). For comparison, the ground MOF powders were further used for dye adsorption and the removal efficiency is obvious increased than large crystals. This is due to the fact that the smaller size in powder samples leads to more surface contact with the dye molecules, and results in more fast adsorption. As we can see in Fig. S24, the adsorption rate for MB⁺ ion with MOF powders was several orders of magnitude higher than that of MOF crystals. Similarly, the adsorption rate for CV⁺, RB⁺ and BR⁺ are also increased by using the MOF powders.

For practical application of both the adsorbents and aimed dyes with recycle purpose in industry, release experiments were performed in pure CH₃CN and NaCl saturated solution of CH₃CN, for MB⁺/LIFM-WZ-3, CV⁺/LIFM-WZ-3, BR⁺/LIFM-WZ-3 and RB⁺/LIFM-WZ-3 samples after loading dyes. As shown in Fig. 7, MB⁺, CV⁺, BR⁺, and RB⁺ can be released into NaCl saturated CH₃CN solution from the loaded samples, and the release rate for MB⁺ is more sharply than CV⁺ and RB⁺ in the same time of 12 h. However, no dyes can be released from the loaded samples in pure CH₃CN solution. This confirms that the release of cationic dyes from the loaded MOFs is also via ion-ion exchange pathway in Na⁺ containing CH₃CN solution, and further illustrates the MOF with an anionic attribute. Furthermore, recycling adsorption experiments were done after dyes release. As can be seen from Fig. S25, the recovered MOF can be recycled and reused for further dyes absorption experiment for more than 8 runs without losing the uptake capacity. And PXRD tests also manifest the stability of the framework after repeating cycles of dye adsorption and release (Fig. S26).

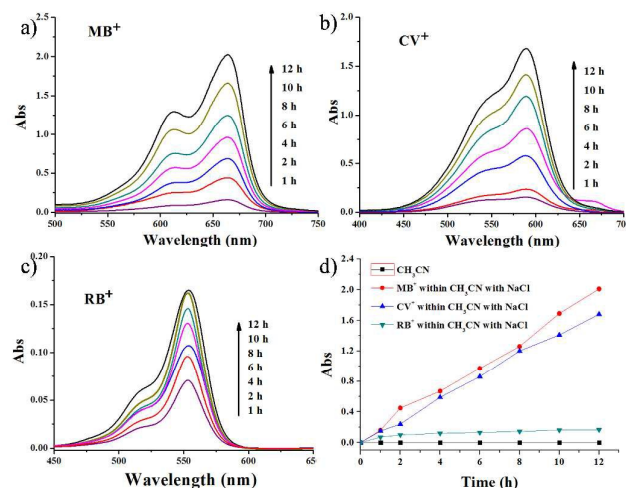


Fig. 7 a) MB⁺, b) CV⁺ and c) RB⁺ release experiment from the corresponding LIFM-WZ-3 adsorbed samples in NaCl saturated solution of CH₃CN; d) the dye release rate in CH₃CN and NaCl saturated solution of CH₃CN (black line for MB⁺/LIFM-WZ-3 in CH₃CN, green, blue and red line for MB⁺/LIFM-WZ-3, CV⁺/LIFM-WZ-3 and RB⁺/LIFM-WZ-3 in NaCl saturated solution of CH₃CN, respectively).

To further quantify the dye uptake capacities of LIFM-WZ-3, amounts of adsorbents from 1 to 5 mg were added into five different centrifuge plastic tubes containing 20 ml (20 mg l⁻¹) aqueous

solution of organic dyes of MB⁺, CV⁺, RB⁺, respectively. The temporal UV-Vis spectra evolution relating to the decrease of MB⁺, CV⁺ or RB⁺ was monitored to determine the uptake capacity of LIFM-WZ-3 (Figs. S27-29). And the dye adsorption amount was calculated using the equation $q_e = V(c_0 - c_e)/M$, where q_e (mg/g) is the equilibrium removal capacity; c_0 (ppm) and c_e (ppm) represent the initial and equilibrium concentrations of ST solution, respectively; V (L) is the volume of adsorbate solution; M (g) is the mass of adsorbents. As a result, the maximum uptake capacities of LIFM-WZ-3 is determined to be 983 mg g⁻¹ for MB⁺, 713.5 mg g⁻¹ for CV⁺, and 141.5 mg g⁻¹ for RB⁺, respectively (Table S4). The MB⁺ and CV⁺ uptake capacities rank the toppest compared with those reported adsorbents including MOFs, graphene, activated carbon, SiO₂ complex, zero-valent iron, etc (Table 1), as far as we know.

Table 1 Comparison of MB⁺ and CV⁺ adsorption capacity in various materials.

Materials	Adsorption capacity (mg/g)	Ref
Fe ₃ O ₄ @Ag/SiO ₂	128.5 (MB ⁺)	29a
magnesium silicate	602 (MB ⁺)	29b
Graphene	397 (MB ⁺)	30
Activated carbon	135 (MB ⁺)	31
zero-valent iron	151.5 (MB ⁺), 172.4 (CV ⁺)	32
In-MOF	724 (MB ⁺)	33
Amino-MIL-101(Al)	762 (MB ⁺)	34
ErCu-POM (Er-3)	391.3 (MB ⁺)	35
ZJU-24-0.89	902 (MB ⁺)	36
Ce(III)-doped UiO-66	145.3 (MB ⁺)	37
Cd-MOF	221 (CV ⁺)	38
BTTC	270 (MB ⁺), 184 (CV ⁺)	4
LIFM-WZ-3	713.5 (CV ⁺)	This work
LIFM-WZ-3	983 (MB ⁺)	This work

Conclusions

In summary, a unique tetrazolyl porphyrin-based microporous 2D+3D→3D anionic MOF (LIFM-WZ-3) has been successfully synthesized, showing good thermal and chemical stabilities. The spindle-like 1D pores and abundant nitrogen vacant sites in the framework afford selective adsorption and separation abilities for CO₂/N₂, CO₂/CH₄, and C₃/C₂ hydrocarbons over CH₄ gases. Meanwhile, LIFM-WZ-3 can selectively adsorb cationic dyes with appropriate sizes and shapes in aqueous solutions through an ion-ion exchange process and manifests record-high adsorption capacities for MB⁺ and CV⁺, respectively. Furthermore, the adsorbed dyes can be released again from the framework in saturated NaCl solution of CH₃CN, qualifying the recycle of both MOF adsorbents and aimed

dyes. This work provides more direct evidence of MOFs in the application of selective adsorption and separation of gases, hydrocarbons and dyes, and paves the way for the design of MOFs with specific functionalities in sustainable production and environmental protection fields.

Acknowledgements

This work was supported by NSFC (21771197, 21720102007), STP Project of Guangzhou (201504010031), NSF of Guangdong Province (S2013030013474), Local Innovative and Research Teams Project of Guangdong Pearl River Talents Program (2017BT01C161), and FRF for the Central Universities. Zhu thanks Hong Kong Research Grants Council (HKBU 22304115-ECS), Areas of Excellence Scheme ([AoE/P-03/08]) for support.

Notes and references

- P. Woodtli, S. Giger, P. Müller, L. Sägger, N. Zucchetto, M. J. Reber, A. Ecker and D. Brühwiler, *Dyes Pigments*, 2018, **149**, 456-461.
- S. Karimi, J. Feizy, F. Mehrjo and M. Farrokhnia, *RSC Adv.*, 2016, **6**, 23085-23093.
- Y.-C. He, J. Yang, W.-Q. Kan, H.-M. Zhang, Y.-Y. Liu and J.-F. Ma, *J. Mater. Chem. A*, 2015, **3**, 1675-1681.
- Y. Shen, C. C. Fan, Y. Z. Wei, J. Du, H. B. Zhu and Y. Zhao, *Dalton Trans.*, 2016, **45**, 10909-10915.
- (a) Z. Hu, B. J. Deibert, J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815-5840; (b) L. Chen, J.-W. Ye, H.-P. Wang, M. Pan, S.-Y. Yin, Z.-W. Wei, L.-Y. Zhang, K. Wu, Y.-N. Fan, C.-Y. Su, *Nat. Commun.*, 2017, **8**, 15985; (c) S. Rapti, D. Sarma, S. A. Diamantis, E. Skliri, G. S. Armatas, A. C. Tsipis, Y. S. Hassan, M. Alkordi, C. D. Malliakas, M. G. Kanatzidis, T. Lazarides, J. C. Plakatouras and M. J. Manos, *J. Mater. Chem. A*, 2017, **5**, 14707-14719.
- (a) Y. Cui, B. Chen, G. Qian, *Coord. Chem. Rev.*, 2014, **273-274**, 76-86; (b) M. Pan, Y.-X. Zhu, K. Wu, L. Chen, Y.-J. Hou, S.-Y. Yin, H.-P. Wang, Y.-N. Fan, C.-Y. Su, *Angew. Chem. Int. Ed.*, 2017, **56**, 14582-14586; (c) Z. Wang, Z. Wang, B. Lin, X. Hu, Y. Wei, C. Zhang, B. An, C. Wang and W. Lin, *ACS Appl. Mater. Interface*, 2017, **9**, 35253-35259.
- (a) B. Joarder, J. B. Lin, Z. Romero, G. K. H. Shimizu, *J. Am. Chem. Soc.*, 2017, **139**, 7176-7179; (b) W. Chen, S. Horike, D. Umeyama, N. Ogiwara, T. Itakura, C. Tassel, Y. Goto, H. Kageyama and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2016, **55**, 5195-5200; (c) F. M. Zhang, L. Z. Dong, J. S. Qin, W. Guan, J. Liu, S. L. Li, M. Lu, Y. Q. Lan, Z. M. Su, H. C. Zhou, *J. Am. Chem. Soc.*, 2017, **139**, 6183-6189.
- (a) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.-Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011-6061; (b) A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkov, F. Verpoort, *Chem. Soc. Rev.*, 2015, **44**, 6804-6849; (c) Y.-B. Huang, J. Liang, X.-S. Wang, R. Cao, *Chem. Soc. Rev.*, 2017, **46**, 126-157; (d) B. An, L. Zeng, M. Jia, Z. Li, Z. Lin, Y. Song, Y. Zhou, J. Cheng, C. Wang and W. Lin, *J. Am. Chem. Soc.*, 2017, **139**, 17747-17750; (e) H. Jiang, Q. Wang, H. Wang, Y. Chen and M. Zhang, *ACS Appl. Mater. Interface*, 2016, **8**, 26817-26826.
- (a) J. Zhou, Y. Liang, X. He, L. Chen and Y. Zhang, *ACS Sus. Chem. Engineer.*, 2017, **5**, 11413-11421; (b) C.-M. Liu, D.-Q. Zhang and D.-B. Zhu, *Chem. Commun.*, 2016, **52**, 4804-4807.
- (a) Y. Yang, Q. Hu, Q. Zhang, K. Jiang, W. Lin, Y. Yang, Y. Cui and G. Qian, *Mol. Pharmaceut.*, 2016, **13**, 2782-2786; (b) M. H. Teplensky, M. Fantham, P. Li, T. C. Wang, J. P. Mehta, L. J. Young, P. Z. Moghadam, J. T. Hupp, O. K. Farha, C. F. Kaminski and D. Fairen-Jimenez, *J. Am. Chem. Soc.*, 2017, **139**, 7522-7532; (c) S. Rojas, F. J. Carmona, C. R. Maldonado, P. Horcajada, T. Hidalgo, C. Serre, J. A. Navarro and E. Barea, *Inorg. Chem.*, 2016, **55**, 2650-2663; (d) P. Horcajada, C. Serre, G. Maurin, N. A. Ramsahye, F. Balas, M. Vallet-Regí, M. Sebban, F. Taulelle and G. Férey, *J. Am. Chem. Soc.*, 2008, **130**, 6774-6780; (e) J. Liu, L. Zhang, J. Lei, H. Shen and H. Ju, *ACS Appl. Mater. Interface*, 2017, **9**, 2150-2158.
- (a) D. Alezi, Y. Belmabkhout, M. Suyetin, P. M. Bhatt, L. J. Weselinski, V. Solovyeva, K. Adil, I. Spanopoulos, P. N. Trikalitis, A. H. Emwas and M. Eddaoudi, *J. Am. Chem. Soc.*, 2015, **137**, 13308-13318; (b) B. Zheng, R. Yun, J. Bai, Z. Lu, L. Du and Y. Li, *Inorg. Chem.*, 2013, **52**, 2823-2829; (c) S. J. Yang, T. Kim, J. H. Im, Y. S. Kim, K. Lee, H. Jung and C. R. Park, *Chem. Mater.*, 2012, **24**, 464-470; (d) E. Tsivion and M. Head-Gordon, *J. Phys. Chem. C*, 2017, **121**, 12091-12100; (e) S. J. Yang, J. Y. Choi, H. K. Chae, J. H. Cho, K. S. Nahm and C. R. Park, *Chem. Mater.*, 2009, **21**, 1893-1897.
- (a) H. Fei and S. M. Cohen, *J. Am. Chem. Soc.*, 2015, **137**, 2191-2194; (b) A. J. Cairns, J. Eckert, L. Wojtas, M. Thommes, D. Wallacher, P. A. Georgiev, P. M. Forster, Y. Belmabkhout, J. Ollivier and M. Eddaoudi, *Chem. Mater.*, 2016, **28**, 7353-7361; (c) W. Q. Zhang, Q. Y. Li, Q. Zhang, Y. Lu, H. Lu, W. Wang, X. Zhao and X. J. Wang, *Inorg. Chem.*, 2016, **55**, 1005-1007; (d) L. Fu, Y. Liu, M. Pan, X.-J. Kuang, C. Yan, K. Li, S.-C. Wei, C.-Y. Su, *J. Mater. Chem. A*, 2013, **1**, 8575-8580; (e) K. Wang, X. L. Lv, D. Feng, J. Li, S. Chen, J. Sun, L. Song, Y. Xie, J. R. Li and H. C. Zhou, *J. Am. Chem. Soc.*, 2016, **138**, 914-919.
- (a) J. T. Hughes and A. Navrotsky, *J. Am. Chem. Soc.*, 2011, **133**, 9184-9187; (b) M. Klimakow, P. Klobes, A. F. Thünemann, K. Rademann and F. Emmerling, *Chem. Mater.*, 2010, **22**, 5216-5221; (c) D. A. Gomez-Gualdrón, P. Z. Moghadam, J. T. Hupp, O. K. Farha and R. Q. Snurr, *J. Am. Chem. Soc.*, 2016, **138**, 215-224.
- (a) Chen, R. Liu, Y. Guo, L. Chen and H. Gao, *ACS Catal.*, 2014, **5**, 722-733; (b) D. T. Lee, J. Zhao, C. J. Oldham, G. W. Peterson and G. N. Parsons, *ACS Appl. Mater. Interface*, 2017, **9**, 44847-44855; (c) V. Stavila, R. K. Bhakta, T. M. Alam, E. H. Majzoub and M. D. Allendorf, *ACS Nano*, 2012, **6**, 9807-9817.
- (a) S. Kitagawa and K. Uemura, *Chem. Soc. Rev.*, 2005, **34**, 109-119; (b) L. Hou, J.-P. Zhang and X.-M. Chen, *Cryst. Growth Des.*, 2009, **9**, 2415-2419; (c) S. R. Batten, *CrystEngComm*, 2001, **3**, 67-72.
- (a) S. Ma, X.-S. Wang, D. Yuan and H.-C. Zhou, *Angew. Chem. Int. Ed.*, 2008, **120**, 4198-4201; (b) J. Y. Kim, L. Zhang, R. Balderas-Xicohtencatl, J. Park, M. Hirscher, H. R. Moon and H. Oh, *J. Am. Chem. Soc.*, 2017, **139**, 17743-17746; (c) E. J. Carrington, C. A. McAnally, A. J. Fletcher, S. P. Thompson, M. Warren and L. Brammer, *Nat. Chem.*, 2017, **9**, 882-889.
- (a) C. X. Chen, Z. Wei, J. J. Jiang, Y. Z. Fan, S. P. Zheng, C. C. Cao, Y. H. Li, D. Fenske and C. Y. Su, *Angew. Chem. Int. Ed.*, 2016, **55**, 9932-9936; (b) J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304-1315; (c) S. Ma, D. Sun, M. Ambrogio, J. A.

ARTICLE

Journal Name

- Fillinger, S. Parkin and H.-C. Zhou, *J. Am. Chem. Soc.*, 2007, **129**, 1858-1859; (d) P. Lama, H. Aggarwal, C. X. Bezuidenhout and L. J. Barbour, *Angew. Chem. Int. Ed.*, 2016, **55**, 13271-13275.
- 18 (a) X. S. Wang, J. Liang, L. Li, Z. J. Lin, P. P. Bag, S. Y. Gao, Y. B. Huang and R. Cao, *Inorg. Chem.*, 2016, **55**, 2641-2649; (b) Y.-Y. Jia, G.-J. Ren, A.-L. Li, L.-Z. Zhang, R. Feng, Y.-H. Zhang and X.-H. Bu, *Cryst. Growth Des.*, 2016, **16**, 5593-5597; (c) S.-R. Zhang, J. Li, D.-Y. Du, J.-S. Qin, S.-L. Li, W.-W. He, Z.-M. Su and Y.-Q. Lan, *J. Mater. Chem. A*, 2015, **3**, 23426-23434.
- 19 (a) X. Zhao, X. H. Bu, T. Wu, S. T. Zheng, L. Wang, P. Y. Feng, *Nat. Commun.*, 2013, **4**, 2344; (b) H. Fei, D. L. Rogow, S. R. J. Oliver, *J. Am. Chem. Soc.*, 2010, **132**, 7202-7209; (c) A. V. Desai, B. Manna, A. Karmakar, A. Sahu, S. K. Ghosh, *Angew. Chem. Int. Ed.*, 2016, **128**, 7942-7946.
- 20 (a) B. Q. Song, X. L. Wang, Y. T. Zhang, X. S. Wu, H. S. Liu, K. Z. Shao, Z. M. Su, *Chem. Commun.*, 2015, **51**, 9515-9518; (b) 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, S. Wang, *Nat. Commun.*, 2017, **8**, 1354.
- 21 (a) Q. Lin, T. Wu, S. T. Zheng, X. Bu and P. Feng, *J. Am. Chem. Soc.*, 2012, **134**, 784-787; (b) P.-Q. Liao, N.-Y. Huang, W.-X. Zhang, J.-P. Zhang, X.-M. Chen, *Science*, 2017, **356**, 1193-1196.
- 22 (a) Z. Guo, D. Yan, H. Wang, D. Tesfagaber, X. Li, Y. Chen, W. Huang and B. Chen, *Inorg. Chem.*, 2015, **54**, 200-204. (b) D. Liu, T. F. Liu, Y. P. Chen, L. Zou, D. Feng, K. Wang, Q. Zhang, S. Yuan, C. Zhong and H. C. Zhou, *J. Am. Chem. Soc.*, 2015, **137**, 7740-7746.
- 23 (a) X. Liu, W. Fan, M. Zhang, G. Li, H. Liu, D. Sun, L. Zhao, H. Zhu and W. Guo, *Mater. Chem. Front.*, 2018, **2**, 1146-1154; (b) Z. Hasan, S. H. Jhung, *J. Hazard. Mater.*, 2015, **283**, 329-339.
- 24 (a) A. Karmakar, L. M. D. R. S. Martins, S. Hazra, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Cryst. Growth Des.*, 2016, **16**, 1837-1849; (b) J. Chun, H. S. Lee, I. G. Jung, S. W. Lee, H. J. Kim and S. U. Son, *Organometallics*, 2010, **29**, 1518-1521.
- 25 H. K. Kim, W. S. Yun, M. B. Kim, J. Y. Kim, Y. S. Bae, J. Lee and N. C. Jeong, *J. Am. Chem. Soc.*, 2015, **137**, 10009-10015.
- 26 N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 1504-1518.
- 27 L. R. Parent, C. H. Pham, J. P. Patterson, M. S. Denny, Jr., S. M. Cohen, N. C. Gianneschi and F. Paesani, *J. Am. Chem. Soc.*, 2017, **139**, 13973-13976.
- 28 J. Arinez-Soriano, J. Albalad, C. Vila-Parrondo, J. Perez-Carvajal, S. Rodriguez-Hermida, A. Cabeza, J. Juanhuix, I. Imaz and D. MasPOCH, *Chem. Commun.*, 2016, **52**, 7229-7232.
- 29 (a) J. Saini, V. K. Garg, R. K. Gupta, *J. Mol. Liq.*, 2018, **250**, 413-422; (b) C. Zhao, J. Yang and B. Jiang, *RSC Adv.*, 2017, **7**, 47225-47234.
- 30 J.-D. Xiao, L.-G. Qiu, X. Jiang, Y.-J. Zhu, S. Ye and X. Jiang, *Carbon*, 2013, **59**, 372-382.
- 31 X. Liu, H. Ao, X. Xiong, J. Xiao and J. Liu, *Water Air Soil Pollution*, 2011, **223**, 1033-1044.
- 32 J. Liu, Y. Wang, Y. Fang, T. Mwamulima, S. Song and C. Peng, *J. Mol. Liq.*, 2018, **250**, 468-476.
- 33 Q. Li, D.-X. Xue, Y.-F. Zhang, Z.-H. Zhang, Z. Gao and J. Bai, *J. Mater. Chem. A*, 2017, **5**, 14182-14189.
- 34 E. Haque, V. Lo, A. I. Minett, A. T. Harris and T. L. Church, *J. Mater. Chem. A*, 2014, **2**, 193-203.
- 35 F.-Y. Yi, W. Zhu, S. Dang, J.-P. Li, D. Wu, Y.-h. Li and Z.-M. Sun, *Chem. Commun.*, 2015, **51**, 3336-3339.
- 36 Q. Zhang, J. Yu, J. Cai, R. Song, Y. Cui, Y. Yang, B. Chen and G. Qian, *Chem. Commun.*, 2014, **50**, 14455-14458.
- 37 J.-M. Yang, R.-J. Ying, C.-X. Han, Q.-T. Hu, H.-M. Xu, J.-H. Li, Q. Wang and W. Zhang, *Dalton Trans.*, 2018, **47**, 3913-3920.
- 38 S. Chand, S. M. Elahi, A. Pal and M. C. Das, *Dalton Trans.*, 2017, **46**, 9901-9911.
- 39 C.-X. Chen, Z.-W. Wei, Q.-F. Qiu, Y.-Z. Fan, C.-C. Cao, H.-P. Wang, J.-J. Jiang, D. Fenske and C.-Y. Su, *Cryst. Growth Des.*, 2017, **17**, 1476-1479.

Journal Name

ARTICLE

TOC

