CHEMISTRY A European Journal



Accepted Article Title: An Exceptionally Water Stable Metal-Organic Framework with Amide-Functionalized Cages: Selective CO2/CH4 Uptake, Removal of Antibiotics and Dyes from Water Authors: Wei-Guang Jin, Wei Chen, Pei-Hang Xu, Xin-Wen Lin, Xiao-Chun Huang, Guang-Hui Chen, Fushen Lu, and Xiao-Ming Chen This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article. To be cited as: Chem. Eur. J. 10.1002/chem.201701884 Link to VoR: http://dx.doi.org/10.1002/chem.201701884

Supported by ACES



An Exceptionally Water Stable Metal–Organic Framework with Amide-Functionalized Cages: Selective CO₂/CH₄ Uptake, Removal of Antibiotics and Dyes from Water

Wei-Guang Jin,^[a] Wei Chen,^[a] Pei-Hang Xu,^[a] Xin-Wen Lin,^[a] Xiao-Chun Huang,*^[a,b] Guang-Hui Chen,^[a] Fushen Lu,^[a] and Xiao-Ming Chen^[a,b]

Abstract: As the main organic pollutants in wastewater, antibiotics and organic dyes are harmful for environmental friendship and public health, and their removal is quite important but challenging. In this work, two three-dimensional high porous MOFs PCN-124-stu, namely $[M_2(PDBAD)(H_2O)]_n$ (M = Cu, Zn) has been synthesized and PCN-124-stu(Cu) is found to display excellent chemical and thermal stability. PCN-124-stu(Cu) was used as a host for efficient extraction of various organic dyes from water, especially the large size dye Coomassie brilliant blue, as well as fluoroquinolones in comparison with five chosen common MOFs and zeolite 13X as well as activated carbon. The result shown that PCN-124-stu(Cu) exhibits absolute predominance for fluoroquinolones adsorption among these microporous materials because of the H-bonds between fluoroguinolones molecules and the amide groups within the frameworks except for MIL-100(Cr), a mesoporous MOF. Moreover, PCN-124-stu(Cu) can release fluoroquinolones slowly physiological saline and retained its framework structure after four adsorption/desorption cycles. In addition, PCN-124-stu(Cu) can be a platform for selective adsorption of CO₂/CH₄.

Introduction

With the continuing economic development and urbanization, an ascending number of chemical products have been synthesized to meet the ever-increasing demands of various industrial products. Unfortunately, water pollution has also been produced simultaneously, and various kinds of organic pollutants have been detected recently in different water resource.¹⁻⁴ For example, antibiotics have been regarded as a hazardous category of pollutants for their high levels of residues in wastewater because of their continuous release without completely elimination during the current treatment process since they were abused in both medical treatment and animal

[a]	WG. Jin, W. Chen, PH. Xu, XW. Lin, Prof. Dr. GH. Chen,
	Prof.Dr. F. Lu, Prof. Dr. XC. Huang
	Department of Chemistry and Key Laboratory for Preparation and
	Application of Ordered Structural Materials of Guangdong Province,
	Shantou University, Guangdong 515063 (China)
	Fax: (+86) 754-82902767
	E-mail: <u>xchuang@stu.edu.cn</u>
[b]	Prof. Dr. XM. Chen
	MOE Key Laboratory of Bioinorganic and Synthetic Chemistry,
	Sun Yat-Sen University, Guangdong 510275 (China)
	Supporting information includes experimental and computational
	details, synthetic procedures, X-ray crystallographic file (CIF, CCDC
	1510445).

husbandry all around the world.^{5,6} It was reported that global antibiotic consumption has been increased by 30 % in the past ten years, and the total usage in China in 2013 reached approximately 162,000 tons and more than 50,000 tons were discharged into the water.⁷ Undoubtedly, antibiotics in water are harmful for the balance of the ecosystem as they can promote resistance formation on microbial populations.^{8,9} More seriously, public health would be damaged because of antibiotics polluted drinking water and their sustained accumulation in body.¹⁰⁻¹² Similarly, as raw materials, organic dyes have been extensively used in various industries, including medicine, printing, cosmetics and so on, which have been noticed as another class of significant organic pollutes in water. Organic dyes are chemically stable and highly toxic in water, which make them potentially harmful to the drinking water quality and ecoenvironment.13,14

Up to now, various technologies have been applied in wastewater purification, such as adsorption separation,¹⁵ photocatalytic degradation,¹⁶ hydroxylation,¹⁷ thermal decomposition,¹⁴ technical oxidation,18 as well as biodegradation.¹⁹ Among these methods, adsorption has been considered as the most effective one for pollutants removal because of its outstanding advantages: energy conservation, desired efficiency, low cost, easy operation and so on.²⁰ For instance, removing antibiotics from water has been performed with lots of traditional porous materials recently, such as carbon nanotubes, zeolites, activated carbons, etc. However, all of these materials' adsorption abilities are limited to some extent on account of their difficult modification and functionalization in the pores. Therefore, it is a great challenge to develop some promising porous materials to capture these water pollutants.

Metal-organic frameworks (MOFs), as a new type of porous materials, possess unique structural features: large functional surface area, high porosity, tunable pore size and shape.²¹⁻²⁶ All these features imply that MOFs exhibit great potential in applications of gas uptake and liquid phase adsorption, which attract more and more scientists' interest.^{27,28} Inspired by Zhou and co-workers' work on detection and removal of small-sized antibiotics and organic explosives in water,²⁹ we look forward to making effort on MOFs applied for water treatment as well. However, it is difficult to accomplish because only limited MOFs stable in water are known to date, especially those MOFs contain the cheap metal such as Cu, Zn, Fe, Co etc. (Table S3 in the Supporting Information). It is known that high surface area and high porosity are the necessary conditions for MOFs to capture larger organic species, 25, 26, 30-32 but the framework generally would be collapsed easily in water if they possess

FULL PAPER

oversized pores that disperse and weaken integral binding energy.³³⁻³⁵ According to the previous work,³⁶ we found that selfinterpenetration should be an effective method to solve this problem. In 2012, a water-stable Cu(II)-MOFs, PCN-124 (PCN stands for "porous coordination network"), was constructed with V-shaped amide ligand by Zhou's group.³⁷ PCN-124 remains its structure as long as 3 days in water own to its selfinterpenetrated structure, and exhibits selective adsorption of CO₂/CH₄ because of its porosity and active sites (open metal sites and amide groups). It is well demonstrated that the open metal sites³⁸⁻⁴⁰ and amide groups⁴¹⁻⁴⁵ could serve as Lewis acids, Lewis bases, or hydrogen bond donors, ultimately increase the interaction between analytes and the pore surface. Motivated by topological design approach and special structural features of PCN-124, we speculated if it is possible to use a common spacer in ligand elongation to further expand the isostructural MOF. Recently, You and co-workers utilized amide groups to expand PCN-124 and produced two analogues: NJU-Bai22 and NJU-Bai23.46 Nevertheless, both of their water stabilities were enhanced slightly in comparison with PCN-124 because of their higher density of hydrophilic amide groups. Therefore, in order to strengthen overall framework's hydrophobicity simultaneously. we chose phenyl spacers as a basic spacer for the ligand elongation to give a new ligand, 5,5'-(pyridine-3,5dicarbonyl)bis(azanediyl)di-isophthalic acid (H₄PDAD) as shown in Scheme 1. As expected, three-dimensional isostructural MOFs, PCN-124-stu (stu stands for "Shantou University"), were successfully synthesized, maintaining the self-interpenetrated structure and active sites. Moreover, compared with the prototypical MOF of PCN-124, PCN-124-stu exhibits larger pore sizes and porosity, as well as higher surface area. Through metal salt alteration and partial metal ion exchange, PCN-124stu(Zn), and PCN-124-stu(Cu), as well as PCN-124stu(Cu_{0.81}Zn_{0.19}) were generated, and PCN-124-stu(Cu) and $PCN-124-stu(Cu_{0.81}Zn_{0.19}) \ \ were \ \ found \ \ to \ \ display \ \ excellent$ chemical and thermal stability, while PCN-124-stu(Zn) was destroyed easily when being exposed to air, which may be resulted from their different metal-oxygen coordination bond energy. Based on PCN-124-stu(Cu)'s high stability and considerable porosity, gas adsorption and removal of selected antibiotics and dyes were explored on it.

As expected, PCN-124-stu(Cu) shows selective adsorption of CO_2/CH_4 as same as PCN-124 due to the active sites inside the structure. In term of liquid phase adsorption, PCN-124-stu(Cu) can serve as a platform for efficient encapsulating fluoroquinolones (FQs),45 a typical antibiotic with extensive usage, as well as a variety of dyes, especially the large size dye Coomassie brilliant blue (R-250). To the best of our knowledge, there is few and far between work concerning FQs' capturing for MOFs has been reported so far. Then we studied and compared PCN-124-stu(Cu)'s FQs adsorption capacity with seven chosen materials with good water stability, five common MOFs and two traditional porous materials-zeolite 13 X and activated carbon. These MOFs allowed us to evaluate the influence of pore size, surface area, the presence of uncoordinated metal site and functional amide group on the FQs adsorption properties. In comparison with other microporous materials, PCN-124-stu(Cu) exhibits absolute predominance for FQs, following MIL-100(Cr), a mesoporous MOF, possesses the highest capacity for FQs among these materials. Furthermore, confirmed by calculation simulation, the amide groups within the frameworks of PCN-124stu strongly interact with FQs molecules via H-bonds. All these results confirm that relatively larger pore size and amide group of PCN-124-stu(Cu) contribute to its excellent adsorption abilities for FQs. Subsequently, PCN-124-stu(Cu) can release FQs slowly in physiological saline and retained its framework structure after four adsorption/desorption cycles. All of these results indicate that PCN-124-stu(Cu) is an excellent candidate material for the removal of specific antibiotics and organic dyes from water, being potentially useful in wastewater treatment.



Scheme 1. Schematic diagram of ligand design procedure.

Results and Discussion

Structural description.

PCN-124-stu(Zn) crystallizes in cubic space group Im3m with a = 42.153(1) Å and possesses a self-interpenetrated (3,36)connected prototypical pzh-type structure, which resembles the isostructural PCN-124 (Table S1 in the Supporting Information). There are two crystallographically independent metal ions in the asymmetric unit, and both are five-coordinated in a squarepyramidal geometry: the first one is occupied by five oxygen atoms (four equatorial atoms from four different carboxylates groups of ligand and one axial atom from water molecule); the second one is also surrounded by four oxygen atoms from ligand, but with a pyridyl N atom rather than an O atom on the axial position (Figure 1a). The total free volume of PCN-124stu(Zn) in fully desolvated close to the specific pore volume of 61.5 % as determined by PLATON based on single-crystal X-ray diffraction data. Similar to other MOFs consisting of isophthalate moieties, twenty-four isophthalate moieties and twelve paddlewheel like Zn₂(COO)₄ secondary building units (SBUs), generating by two five-coordinated metal atoms and bidentate bridging coordinated carboxyl groups, assemble into a metalorganic cuboctahedron (Figure 1b; namely cage 1). In cage 1, all the axial coordinated oxygen atoms on SBUs point to the center of cage, which can be removed by slight heating to generate open metal active sites. These cuboctahedral cages are connected by the ligands to form a three-dimensional cubic framework (Figure 1d), which further leads to the second cages (Figure 1c; namely cage 2). Through the Zn-N coordination bonds, one axial site of the Zn paddlewheel motif and pyridine N atom of the ligand from another identical framework to construct a self-interpenetrated framework, which result in a highlyconnected network. As expected, in addition to functional sites (open metal sites and amide moieties), PCN-124-stu exhibits larger porosity as well as higher surface area in comparison with PCN-124. Based on powder X-ray diffraction (PXRD) measurement (Figure S6 in the Supporting Information), the pattern of PCN-124-stu(Cu) is similar to that of PCN-124-stu(Zn),

FULL PAPER

demonstrating that PCN-124-stu(Cu) is an isostructural framework of PCN-124-stu(Zn).



Figure 1. (a) Coordination environment of the binuclear Zn(II) paddlewheel motifs and ligands. (b) Cuboctahedral cages (cage 1) in PCN-124-stu(Zn) assembled by two five-coordinated metal atoms and bidentate bridging coordinated carboxylate groups. (c) Cage 2 in the framework constructed by the connection of cages 1 and the ligands. (d) Network of PCN-124-stu(Zn) (Zn atoms are shown in cyan, O atoms in red, N atoms in blue, C atoms in gray). (e) Schematic **pzh** topological structure of PCN-124-stu(Zn).

Chemical and thermal stability.

For water stability determination of PCN-124-stu, the freshly prepared crystals of PCN-124-stu(Cu) and PCN-124-stu(Zn) were checked in water (pH = 7) at room temperature. After immersion in water for 24 h, the measured PXRD patterns (Figure 2) show that PCN-124-stu(Cu) retained the initial framework while PCN-124-stu(Zn) lost its crystallinity easily. More interestingly, PCN-124-stu(Cu) maintains its framework in water solution with different pH values (pH = $2 \sim 12$) for at least 1 week monitored by PXRD (Figure 2b). It should be mentioned that only limited MOFs can have excellent stability in such a wide pH range of aqueous solutions so far, including those constructed with relative expensive metals such as Zr, which possess higher metal-oxygen coordination bond energy (Table S3 in the Supporting Information).

Considering that the compounds are only different in the metal ions, we presumed that the outstanding chemical stability of PCN-124-stu(Cu) should be attributed to this difference. For further investigation, PCN-124-stu(Cu_{0.81}Zn_{0.19}) was generated by partial-metal exchanged from PCN-124-stu(Zn) (see the Experimental Section) and used for water stability test. The performance of PCN-124-stu(Cu_{0.81}Zn_{0.19}) was similar to that of PCN-124-stu(Cu) (Figure S12 in the Supporting Information). In addition, N₂ adsorption capacity of PCN-124-stu(Cu_{0.81}Zn_{0.19}) was dramatically higher than that of PCN-124-stu(Zn) under the same test conditions (Figure S13a in the Supporting Information). The above experiments prove that metal ions are the key factor for the structural stability and Cu(II) centers are more stable than Zn(II) ones in PCN-124-stu, because the former, with higher charge density and suitable coordination geometry in a paddlewheel substructure, can form stronger Cu-O coordination bonds with O atoms from carboxylate groups, which makes the MOF highly resistant to the attack of water, acid, and base.33,48,49 Besides the stable Cu(II) cluster, the excellent chemical stabilities of PCN-124-stu(Cu) may also be attributed to the

overall structural interpenetration as same as its isostructural MOF. $^{\rm 37,46}$

The thermal gravimetric analysis (TGA) indicates that PCN-124-stu(Cu) is thermally stable up to ca. 320 °C, after a step of guest lost from room temperature to 100 °C (Figure S8 in the Supporting Information). Generally, the thermal stability of MOFs is related to the strength of the metal coordination bonds as well as the nature of ligands. Inspired with the outstanding chemical and thermal stability of PCN-124-stu(Cu), PCN-124-stu(Cu) was been then chosen for the studies of adsorption and separation in this work.



Figure 2. (a) PXRD of PCN-124-stu(Zn) after immersion in water for 24 h and simulated PCN-124-stu(Zn) and (b) PXRD of as synthesized PCN-124-stu(Cu) and PCN-124-stu(Cu) after immersion in water (pH = 7), aqueous NaOH (pH = $10 \sim 14$), and HCl solutions (pH = $1 \sim 5$) for 7 days.

Gas adsorption.

In order to analyze the surface and porosity of PCN-124-stu(Cu), $N_{\rm 2}$ adsorption isotherm of the activated sample was conducted at 77 K (Figure 3a). The maximal adsorption capacity of N₂ was 604 cm³·g⁻¹ and the sorption isotherms are typical of type I, revealing the microporous nature of PCN-124-stu(Cu). The poresize distribution (insert) obtained from the isotherm indicates that there are two different kinds of pores with diameters of about 7.6 Å for cage 1 and 13.5~15.5 Å for cage 2 in PCN-124-stu(Cu). The Brunauer-Emmett-Teller (BET) and Langmuir surface areas of the sample were calculated as much as 2153 m²·g⁻¹ and 2438 m²·g⁻¹, respectively. The total pore volumes of PCN-124-stu(Cu) obtained from N_2 isotherms (P/P₀ = 0.99) is 0.94 cm³·g⁻¹, which is higher than that of PCN-124 (0.63 cm³·g⁻¹). The TGA data (Figure S8 in the Supporting Information) reveals that the weight percentage of the lost guest molecules was about 40 %, which agree well with the high porosity of PCN-124stu(Cu). Compared with the prototypical PCN-124, PCN-124stu(Cu) possesses a higher surface area, and bigger pore size,

FULL PAPER

as well as larger pore volume, as being expected (Table S2 in the Supporting Information).

It is known that excellent selective adsorption of CO₂ over CH₄ has attracted extensive attention for the purification of natural gas.^{25,29} CO₂ and CH₄ adsorption isotherms of the desolvated PCN-124-stu(Cu) were monitored at 273 K and 298 K under low pressure. As shown in the gas adsorption isotherms (Figure 3b), the uptakes of CO₂ are as high as 85.8 cm³ g⁻¹ at 298 K and 160 cm³·g⁻¹ at 273 K and 760 mmHg, both of which are much higher than the amount of CH₄. Ideal adsorbed solution theory (IAST) was employed to predict CO₂/CH₄ (50 / 50) mixture selective adsorption behaviour from the experimental pure-gas isotherms at 273 K (Figure S33 in the Supporting Information). The adsorption selectivity increases constantly as the pressure increases, which from 11.6 at 15 mmHg to 37.8 at 760 mmHg. Through Grand Canonical Monte Carlo (GCMC) simulation at 273 K and 1 bar, the zero-loading heats of adsorption were found to be 26 kJ·mol⁻¹ for CO₂ and 15 kJ·mol⁻¹ for CH₄, showing significant selective adsorption of CO2 over CH4 for PCN-124-stu(Cu) (Figure S31 in the Supporting Information).



Figure 3. (a) N₂ sorption isotherm of PCN-124-stu(Cu) at 77 K and its pore size distribution (inset). (b) CO₂ and CH₄ adsorption isotherms of PCN-124-stu(Cu) (blue dot, CO₂ at 273 K; red dot, CO₂ at 298 K; blue square, CH₄ at 273 K; red square, CH₄ at 298 K).

To further understand the relevant adsorption mechanism at a molecular level in PCN-124-stu(Cu), GCMC simulations were employed to investigate the positive effect of decorated amide groups and open metal sites on CO₂ uptake in the framework. As shown in density distribution of the center-of-mass of CO2 molecules (Figure S30 in the Supporting Information), we can see clearly that both open Cu(II) metal sites and the amide groups within the framework are the main adsorption sites of CO2 molecules, and the CO2 molecules prefer to locate inside the small cages 1 rather than the larger cages 2. Hydrogen bondings and van der Waals forces are main interaction between CO₂ molecules and amide groups based on the lowest energy frame by GCMC simulation (Figure S29 in the Supporting Information). However, compared with the CO₂ capacities of PCN-124 under the same conditions, those of PCN-124-stu(Cu) are reduced to some extent (Figure S14 in the Supporting Information). This fact may be attributed to larger surface area and porosity in PCN-124-stu(Cu).50-53

Adsorption of R-250.

It is well known that organic dyes are widely used for industrial dyeing and cell biological imaging, and often cause pollution to water even at low concentrations. Inspired by the existing large cages of PCN-124-stu(Cu), we explored its potential applications

in dyes-capture from wastewater. For the convenience of tracking of the dyes adsorption by the naked eye, the colorless zinc crystals were chosen as the absorbent to examine various organic dyes with different molecular sizes. After non-activated PCN-124-stu(Zn) was soaked in different dye ethanol solutions for several minutes, color changes were clearly observed with all crystals (Figure S16 in the Supporting Information), including the large molecule-Coomassie brilliant blue (R-250).

Taking into account that there are limited specific adsorption studies of R-250 for MOFs, we further investigated the adsorption property on R-250 of activated PCN-124-stu(Cu) in water and traced the dynamical concentration changes of the dye solutions by UV-vis absorption spectroscopy. The UV-vis absorbance of the R-250 solution with PCN-124-stu(Cu) was reduced gradually from an initial concentration of 3×10^{-5} mol·L⁻¹ and maintained stable after 48 h, accompanying with noticeable color change of the solution (Figure 4a). In order to better understand the adsorption performance, adsorption isotherms of R-250 were measured versus the equilibrium concentration over a period of 48 h and calculated the concentration in accordance to standard concentration curve (Figure 4b), and the corresponding experimental process were described in the Experimental Section. According to the isotherms absorption curve, the adsorption capacities sharply increase with the increasing concentration, then reach a plateau when the dye concentration reaches certain limits after 48 h (Figure 4c). Adsorption equilibrium curve (Figure 4d) obeys Langmuir isotherm model with a R^2 of ca. 0.97, and the maximum adsorption capacity (Q_m) was calculated to be 78.7 mg·g⁻¹.



Figure 4. (a) Time-dependent UV-vis spectra of R-250 ($C_0 = 3 \times 10^{-5} \text{ mol·}L^{-1}$) adsorbed into PCN-124-stu(Cu) (insert: the color change of R-250 solution). (b) UV-vis spectra of R-250 solution in the certain concentration range (1 × 10⁻⁶ mol·L⁻¹ to 6 × 10⁻⁵ mol·L⁻¹) and standard curve fitting (insert). (c) Adsorption isotherms of R-250 for PCN-124-stu(Cu). (d) Langmuir plots of the isotherms of R-250 for PCN-124-stu(Cu).

Moreover, compared with the N₂ sorption isotherm of activated PCN-124-stu(Cu) at 77 K, the N₂ capacity of R-250@PCN-124-stu(Cu) decrease dramatically, which directly affirms the adsorption of R-250 inside PCN-124-stu(Cu) (Figure S19 in the Supporting Information). The PXRD patterns of PCN-124-

FULL PAPER

stu(Cu) measured after adsorption matched well with its initial framework and be completely different with PXRD of R-250, which indicates good stability of crystalline sample of PCN-124-stu(Cu) during adsorption and even further demonstrates the adsorption happened inside the cages rather than surface of PCN-124-stu(Cu) (Figure S20 in the Supporting Information). FT-IR spectra confirms the characteristics peak (1042 cm⁻¹) of R-250 in PCN-124-stu(Cu) after immersion (Figure S21 in the Supporting Information).

Adsorption of Fluoroquinolones.

As third largest category of synthetic antibiotics accounting for 17% of the global market, fluoroquinolones (FQs) are widely used in hospitals, households, and veterinary applications, and their production and usage increase every year.^{54,55} However, when released into the environment, they can promote resistance formation on microbial populations and induce toxic effects on aquatic organisms.^{8,56} What's worse, they have long residence times and lots of residues in the environment result from their lack of biodegradation and high adsorption affinity.^{45,57}

Motivated by the high porosity and excellent water stability of PCN-124-stu(Cu), we studied its capacity in FQs removal from water. In consideration with the extensive usage and structure features (size and specific organic groups), norfloxacin (NOR), ofloxacin (OFL), and enrofloxacin (ENR) were chosen for the adsorption performance (Figure S22 in the Supporting Information). Freshly prepared PCN-124-stu(Cu) was activated to remove guest molecules and then immersed in these antibiotics solutions at room temperature. After soakage within 3 days (long time for equilibrium absorption), the residual concentrations were detected by HPLC-FLD (High Performance Liquid Chromatography equipped with Fluorescence Detector), and then the uptakes of these analytes in PCN-124-stu(Cu) were calculated according to Langmuir adsorption isotherm (details described in Experimental section). Adsorption isotherms were measured up to 1000 g·L⁻¹ in water in which PCN-124-stu(Cu) exhibited excellent capacities for these three antibiotics with maximum adsorption capacity (Qm) calculated as high as 198 mg·g⁻¹, 292 mg·g⁻¹ and 354 mg·g⁻¹ for ENR, OFL, and NOR, respectively. Their adsorption enthalpies were calculated as 36.61 kcal·mol⁻¹ (NOR), 43.41 kcal·mol⁻¹ (OFL), and 42.33 kcal·mol-1 (ENR), all of them agree with high adsorption capacities of three FQs for PCN-124-stu(Cu). The adsorption capacities of PCN-124-stu(Cu) for these antibiotics follow the order of NOR > OFL > ENR. The large capture capacity at relative low concentration (< 50 g·L⁻¹) is important for the application indicating high affinity between all analyzed FQs and PCN-124-stu(Cu) framework (Figure 5).



Figure 5. (a) Adsorption isotherms and (b) Langmuir plots of the isotherms of NOR (blue line), OFL (red line), and ENR (black line) for PCN-124-stu(Cu) in water.



Figure 6. Adsorption isotherms of NOR (a), OFL (b), and ENR (c) for studied materials in water.

For comparison, FQs adsorption performance was conducted with other seven chosen porous materials with good water stability, including five commom MOFs and zeolite 13 X as well as activated carbon. The BET and Langmuir surface areas, pore volume, crystal density, and pore diameter for each sample are summarized in Table S4 in the supporting information. According to the FQs isotherms (Figure 6), MIL-100(Cr), a mesoporous MOFs with highest surface area and pore size among these materials, possesses the highest capacity for three analytical FQs, which closely followed by PCN-124-stu(Cu). Besides, the isotherms for MIL-100(Cr) and PCN-124-stu(Cu) do not reach the saturation, implying their potential for even higher adsorption amounts. It is worth mentioning that PCN-124stu(Cu) exhibits absolute predominace for FQs adsorption among these analytical microporous materials, including

FULL PAPER

traditional porous materials—zeolite 13X and activated carbon. By contrast, other six samples' figures saw steady increase before 100 g·L⁻¹ and remain relative stable for higher detective concentrations except the NOR adsorption for PCN-124, reaching its peak at around 160 mg·g⁻¹ in 400 g·L⁻¹. The Q_e of NOR for PCN-124 is greater noticeably than those of HKUST-1 and MOF-74(Mg), which have as similar porous size and activated metal sites as PCN-124. Considering the similar pore structure properties of the HKUST-1 and MOF-74(Mg) as well as PCN-124, we speculate that the amide groups in PCN-124 contribute to its higher adsorption of NOR, though it encapsulates few OFL and ENR because of their relative larger molecular structure. As PCN-124-stu(Cu) is the expanded structure of PCN-124, we also think that amide groups display an key role for its antibiotics capture.

To further study the relevant adsorption mechanism at a molecular level, CBMC simulations were performed to understand the positive effect between FQs' molecular and PCN-124-stu(Cu)'s functional pore surface. As shown in density distribution simulated of the absorbed FQs molecules in the framework (Figure S34 in the Supporting Information). NOR. OFL, and ENR molecules prefer to locate at both the open Cu(II) metal sites and the amide groups within the framework. It is demonstrated that the main interaction between the host and guest are hydrogen bonds between the amide groups, carboxylate groups in the pores, with the F atoms, carboxylate groups and terminal amine N atom (for NOR only) from three analytes (Figure S35 in the Supporting Information), which contributes to its excellent adsorption performance for FQs. In addition, the size matching between absorbate and absorbent is the dominating factor for adsorption performace,58,59 and it is consistent with the largest capacity of NOR, the smallest molecular size one among these three analytes. Therefore, for these three fluoroquinolones, we conclude that the active sites (open Cu(II) site and amide groups) in the framework play a pivotal role on their excellent adsorption performance, and FQs' molecular sizes and amounts of corresponding active groups determine their different adsorption quantities, thus leading the adsorption capacities order of NOR > OFL > ENR.

Considering releasing of loaded FQs from PCN-124-stu(Cu) is significant for their recycling. Then, NRO, the largest adsorption capacity among three FQs, has been chosen for further investigation. Activated PCN-124-stu(Cu) was soaked in NRO aqueous solution (1.0 M) for 1 week (high concentration and long time in order to ensure a maximal loading), and then NROloaded PCN-124-stu(Cu) (referred to as NRO@PCN-124stu(Cu)) was obtained. The loaded weight percentage is around 30 %, closing to the Q_m (354 mg·g⁻¹) according to TGA curves of PCN-124-stu(Cu) (Figure S24 in the Supporting Information). Drug release experiments were conducted by dialyzing the NRO@PCN-124-stu(Cu) against PBS buffer solution (pH = 7.4) at 37 °C. The release rate was markedly increase in PBS, more than 55 % of NRO released in ca. 3 h, and the release reached a plateau and NRO was released at all within 6 h (Figure S25 in the Supporting Information). We presume this fast release was ascribed to the destruction of PCN-124-stu(Cu) in PBS buffer solution as phosphate in PBS solution may compete with the organic ligand and coordinate with Cu(II) centers in structure. A high-angle peak (32 °) appeared in PXRD (Figure S26 in the Supporting Information) implying the generation of metal salt. Then, in order to protect the adsorbent from destruction during delivery process, other solution system-physiological saline solution (pH = 7) was used to replace PBS buffer solution (Figure 7a). As expected, the entire release time was extended to 3 days and around 30 % of loaded NRO released during the initial burst release (1 h). Similar results were observed for ENR delivery in physiological saline solution (Figure 7b). Confirmed by PXRD patterns (Figure S27 in the Supporting Information), PCN-124-stu(Cu) retained its porous structure after the process of FQs release while N₂ sorption isotherm (Figure S28 in the Supporting Information) indicates some FQs stayed in the pore. It may because FQs have strong interaction with framework, then it is difficult to release total adsorptive FQs. Such an adsorption and release process was tested for 4 continuous cycles, and the process is reversible with a little drop in the adsorption capacity (Figure 8). This result suggests the possibility for recovery of FQs from wastewater by PCN-124stu(Cu).



Figure 7. Kinetics of delivery of (a) NOR and (b) ENR from PCN-124-stu(Cu) in physiological saline solution at 37 °C. (Two parallel experiments for each FQs release, red line is the first run, black line is the second run)



Figure 8. The amounts of FQs adsorbed at equilibrium for 4 adsorption-release cycles.

Conclusions

A new pzh-type topological frameworks, PCN-124-stu, has been designed and synthesized. In contrast with prototypical PCN-124 PCN-124-stu exhibits higher surface area, bigger pore size, and larger porosity. PCN-124-stu(Cu) exhibits very high chemical and thermal stabilities like its prototype because of its self-interpenetrated network and strong coordination energy of Cu-O bonds while PCN-124-stu(Zn) loses its crystallinity easily. Similar to PCN-124, PCN-124-stu(Cu) displays CO_2/CH_4 selective adsorption for the interaction between CO_2 and the active sites—the coordinative unsaturated metal sites and amide groups. Interestingly, PCN-124-stu(Cu) showed excellent performances for removal of fluoroquinolone antibiotics in water, and its maximum adsorption capacity calculated as high as 198

FULL PAPER

mg·g⁻¹, 292 mg·g⁻¹ and 354 mg·g⁻¹ for ENR, OFL, and NOR, respectively. In addition, we have studied and compared its FQs adsorption capacity with five common MOFs and two traditional porous materials-zeolite 13X and activated carbon, the results have shown that PCN-124-stu(Cu) exhibits absolute predominance for FQs adsorption among these materials except the mesoporous MOF-MIL-100(Cr). Confirmed by CBMC simulations, the amide groups and open metal site within the framework strongly interact with analytes molecules and result in a favorable influence on the high adsorption behaviors, along with the size effect of antibiotics, which lead to the adsorption sequence of these adsorbates: NOR > OFL > ENR. Moreover, the fluoroquinolones release experiments were conducted successful in physiological saline. PCN-124-stu(Cu) retained their structure after the process, suggesting possible recycling of MOFs and fluoroquinolones. In addition, PCN-124-stu(Cu) can also capture a number of organic dyes in aqueous solution, especially the large size dye Coomassie brilliant blue (R-250). In short, these results indicate that PCN-124-stu(Cu) is a promising porous material for removal of both antibiotics and organic dyes from water.

Experimental Section

Physical Measurements.

¹H-NMR spectra were measured on Bruker Advance 400 MHz with tetramethylsilane as the internal standard. Elemental analyses of C, H and N were tested using an Elementary Vario EL cube CHNS analyzer. Inductively coupled plasma_atomic emission spectrometry (ICP-AES) detection was performed on a Shimadzu ICPE-9000. Scanning electron microscope (SEM) was performed on QUANTA 450 FEG and energy dispersive Xray spectroscopy (EDS) was carried out by X-Max20 with Oxford EDS system equipped with X-ray mapping. FT-IR spectra were recorded by a Nicolet Avatar 360 FTIR spectrometer in the range of 4000-400 cm⁻¹. Thermogravimetric analysis (TGA) were measured on TA Instruments Q50 thermogravimetric instrument under N₂ flow (40 mL·min⁻¹) and heated from room temperature to 800 °C at rate of 10 °C·min⁻¹. Powder X-ray diffraction (PXRD) patterns of the bulk samples were carried out on a Bruker D8 Advance diffractometer with a Cu sealed tube (λ = 1.54178 Å) at room temperature. Single-Crystal X-ray Crystallography measurement was performed on a Rigaku XtaLAB P300DS single-crystal diffractometer equipped with a low temperature device and a fine focus sealed-tube X-ray source (CuK α radiation, λ = 1.54178 Å). Gas adsorption isotherms (Low pressure: up to 1 bar) were reported by a volumetric method using a Micromeritics ASAP2020 surface area and porosity analyzer. UV-vis spectra were tracked by an Agilent 8453 UV-vis spectrometer at room temperature. Concentration of FQs in solution were checked using High performance liquid chromatography equipped with fluorescence detector (HPLC-FLD). Details are provided in the Supporting Information.

Synthesis, characterization of PCN-124-stu(Zn).

 $Zn(NO_3)_2{}^{\circ}6H_2O$ (15.0 mg), H_4PDBAI (12.0 mg), DMAc (2.0 mL) and deionized water (0.50 mL) containing HBF4 (0.1 mL) were

ultrasonically mixed in grass vial for 30 mins. The mixture was heated in 90 °C for 3 days and cooled down slowly to room temperature, then octahedral colorless crystals were harvested by filtration (*ca.* 10 mg). The FT-IR spectrum, PXRD pattern and N₂ adsorption measurement at 77 K of the compound were conducted (Figure S5-6 and S13a in the Supporting Information). Single crystals of PCN-124-stu(Zn) with suitable sizes for single-crystal X-ray diffraction were obtained in this procedure (Figure S2-4 and Table S1 in the Supporting Information).

Synthesis, characterization of PCN-124-stu(Cu).

Cu(NO₃)₂·3H₂O (12.0 mg), H₄PDBAI (12 mg), DMAc (2.0 mL) and deionized water (0.50 mL) containing HBF₄ (0.1 mL) were ultrasonically mixed in grass vial for 30 mins. The mixture was heated in 90 °C for 3 days and cooled down slowly to room temperature, then octahedral green crystals were harvested by filtration (ca. 10 mg).

Synthesis, characterization of PCN-124-stu(Cu_{0.81}Zn_{0.19}).

PCN-124-stu(Zn) soaked in saturated cupric nitrate ethanol solution (20 mL) for one day until the color of crystals were turned to be green implying exchange of metal ions. Through ICP-AES detection of the product, the concentration ratio of Cu : Zn was confirmed to be 0.81 : 0.19, further demonstrated by with SEM and EDS (Figure S10-11 in the Supporting Information). The PXRD and water stability of this product were also determined (Figure S12 in the Supporting Information). N₂ adsorption determination was conducted at 77 K (Figure S13 in the Supporting Information). The synthesized process detail is provided in the Section 3 of Supporting Information.

Sample Activation.

Before gaseous/liquid phase adsorption experiment, assynthesized PCN-124-stu(Cu) sample was soaked in MeOH for 24 h to exchange the guest. Subsequently, the sample were filtrated and activated by drying under vacuum at 100 °C for 24 h

Stability Test.

As-synthesized PCN-124-stu(Cu) (75.0 mg) was collected from mother liquor, and washed with EtOH, then distributed equally into 15 vials containing different pH solutions (5 mL, adjusted by HCl or NaOH) and pure water. After immersion for several time, the sample were filtrated and dried under vacuum at 100 °C for 24 h and then a small amount of the solid was transferred to mineral oil and analyzed using PXRD (Figure 2b). Similarly, PCN-124-stu(Zn) (Figure 2a) and PCN-124-stu(Cu_{0.81}Zn_{0.19}) (Figure S13b in the Supporting Information) were tested by PXRD after 24 h pure water immersion.

Gas Adsorption.

After the process of sample activation, PCN-124-stu(Cu) (100 mg) were further dried by "degas" function of the gas adsorption analyzer at 100 °C for 10 h, and CO_2 and CH_4 isothermal adsorption carried out at 273 K and 298 K with activated PCN-124-stu(Cu), respectively (Figure 3b).

Adsorption of Dyes.

FULL PAPER

WILEY-VCH

To examine capture and separation of organic dyes with different molecular sizes by PCN-124-stu based on visible color of dyes and the colorless nature of the crystal, PCN-124-stu(Zn) (5 mg) was soaked in EtOH solution containing dyes of large molecules and test their PXRD respectively (Figure S16 and S17 in the Supporting Information). For R-250 adsorption, an aqueous stock solution of R-250 (C_0) was prepared by dissolving R-250 in water. The activated adsorbents (5 mg) were added into vials filled with R-250 solutions (5 mL) of different concentrations (5–200 × 10⁻⁴ mol·L⁻¹), which were prepared by successive dilution of the stock solution. After quiescence at room temperature for 2 days, the solutions were separated from the adsorbents, and monitored with a UV-vis spectrophotometer at 588 nm. The adsorbed amount Q_e (mg·g⁻¹) of R-250 was calculated using the mass balance with eq. 1.

$$Q_e = (C_0 - C_e) V/M \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of solutions on centration of R-250 (mg·L⁻¹); *V* is the volume of solution (L); and *M* is the mass of adsorbent (g). And the resulting adsorption isotherms are fitted by Langmuir mode.

$$C_{e}/Q_{e} = 1/(K_{L} \cdot Q_{m}) + C_{e}/Q_{m}$$
(2)

where C_e is the equilibrium concentration of R-250 (mg·L⁻¹); Q_e and Q_m are the equilibrium and maximum monolayer adsorbed amount (mg·g⁻¹); K_L (L·g⁻¹) is the Langmuir constant related to the free energy of adsorption.

Adsorption of FQs.

At room temperature, activated PCN-124-stu(Cu) (5 mg) was transtransferred to water solutions (10 mL) containing given concentrations of ENR (enrofloxacin), NOR (norfloxacin) and OFL (ofloxacin), respectively. After three days of soakage (for adsorption balance), HPLC-FLD of the solutions were recorded to characterize the adsorption performances of PCN-124-stu(Cu) at specific condition (exciting wavelength: 280 nm, emission wavelength: 450 nm; injection volume: 2 L; flowing phase: acetonitrile-0.067 moL·L⁻¹ H₃PO₄ solution in volume ratio of 15 : 85; flow rate: 1.0mL·min⁻¹; detection temperature: 30 °C). The adsorbed amount Q_e of each different concentration FQs was calculated using the mass balance with eq. 1 shown above, and the adsorption isotherms are also fitted by Langmuir mode as eq. 2.

Release of FQs.

PCN-124-stu(Cu)@ENR (30 mg) and PCN-124-stu(Cu)@NOR (30 mg) were loaded in 30 mL physiological saline at room temperature for 5 days, respectively. During each time interval, 0.5 mL of supernatant was taken out to track the concentration by HPLC-FLD before adding another fresh solution (0.5 mL) (Figure 7). To ensure the accuracy of measurements, all samples were carried out with parallel experiments. For study of solvent effect, PBS buffer solution (30 mL, pH = 7.4) was used for ENR release (Figure S25 in the Supporting Information). After all these experiments, adsorbents were filtrated, dried, and tested using PXRD and N₂ adsorb test (Figure S27-28 in the Supporting Information).

Computational Methods.

In order to evaluate the adsorption mechanism of CO₂, ENR, NOR, and OFL molecules in adsorbent at molecular level, the non-covalent interactions between adsorbates and Framework are described using Dreiding force field, and the atomic charges calculated by charge equilibration method were used to describe electrostatic interaction by spherical Lennard-Jones (LJ) 12⁻⁶ potentials. In this work, Grand canonical Monte Carlo (GCMC) were performed to obtain the density distribution of CO2 within PCN-124-stu at 1 bar and 273 K, and Configurational bias Monte Carlo (CBMC) simulations were performed to FQs molecules at 1 bar and 303 K. In Monte Carlo simulation, a total of 4×107 steps were used; the first 50 % of these moves were used for equilibration, and the remaining 107 steps were used for calculating the ensemble averages. Above all, three antibiotics' optimal structures were simulated via B3LYP/6-311+G* in Gaussian 09. Process detail is provided in the Section 7 of Supporting Information

Acknowledgements

We gratefully acknowledge financial support from the National Basic Research Program of China (973 Program. 2013CB834803), NSFC (No. 21571122 , 21171113), and Department of Education in Guangdong Province (2014KCXTDO12).

Keywords: amide functionalization • Metal-organic frameworks • chemical stability• antibiotics removal • dyes adsorption

- [1] J. Pastor, A. J. Hernandez, J. Environ. Manage. 2012, 95, S42-S49.
- [2] X. N. Zhang, Q. P. Guo, X. X. Shen, S.W. Yu, G. Y. Qiu, J. Integ. Agri. 2015, 14, 2365-2379.
- [3] E. D. Ongle, L. Z. Xiao, Y. Tao, Environ. Pollut. 2010, 158, 1159-1168.
- [4] Z. Hasan, S. H. Jhung, J. Hazard. Mater. 2015, 283, 329-339.
- [5] K. Bondarczuk, A. Markowicz, Z. Piotrowska-Seget, Environ. Int. 2016, 87, 49-55.
- [6] R. Gothwal, T. Shashidhar, Clean Soil, *Air. Water* **2015**, *43*, 479-489.
- [7] Q. Q. Zhang, G. G. Ying, C. G. Pan, Y. S. Liu, J. L. Zhao, *Environ. Sci. Technol.* 2015, 49, 6772-6782.
- [8] J. L. Martinez, *Environ. Pollut.* **2009**, *157*, 2893-2902.
- [9] R. APRIL A, B. JASON B, Environ. Toxicol. Chem. 2005, 24, 423-430.
- [10] B. Petrie, R. Barden, B. Kasprzyk-Hordern, Water. Res. 2015, 72, 3-27.
- [11] A.Passuello, M. Mari, M. Nadal, M. Schuhmacher, J. L. Domingo, *Environ. Int.* **2010**, *36*, 577-583.
- [12] P. Collignon, J. H. Powers, T. M. Chiller, A. Aidara-Kane, F. M. Aarestrup, *Clin. Infect. Dis.* **2009**, *49*, 132-141.
- [13] P. A. Carneiro, G. A. Umbuzeiro, D. P. Oliveira, M. V. Zanoni, J. Hazard. Mater. 2010, 174, 694-699.
- [14] W. T. Tsai, H. C. Hsu, T. Y. Su, K. Y. Lin, C. M. Lin, T. H. Dai, J. Hazard. Mater. 2007, 147, 1056-1062.
- [15] X. Zhang, W. Guo, H. H. Ngo, H. Wen, N. Li, W. J. Wu, J. Environ. Manage. 2016, 172, 193-200.
- [16] C. C. Wang, J.R. Li, X. L. Lv, Y.-Q. Zhang, G. Guo, *Energy. Environ. Sci.* 2014, 7, 2831-2867.
- [17] H. Peng, B. Pan, M. Wu, Y. Liu, D. Zhang, B. Xing, J. Hazard. Mater. 2012, 233-234, 89-96.
- [18] A. Gulkowska, H. W. Leung, M. K. So, S. Taniyasu, N. Yama-shita, L.
 W. Yeung, B. J. Richardson, A. P. Lei, J. P. Giesy, P. K. Lam, *Water. Res.* 2008, *42*, 395-403.
- [19] V. Homem, L. Santos, J. Environ. Manage. 2011, 92, 2304-2347.
- [20] Z. Zhou, M. Hartmann, Chem. Soc. Rev. 2013, 42, 3894-3912.
- [21] H.-C. Zhou, S. Kitagawab, Chem. Soc. Rev. 2014, 43, 5415-5418.
- [22] X.-C. Huang, Y. Y. Lin, J.-P. Zhang, X.-M. Chen, Angew. Chem. 2006, 118, 1587-1589; Angew. Chem. Int. Ed. 2006, 45, 1557-1559.

- FULL PAPER
- [23] X.-C. Huang, J.-P. Zhang, X.-M. Chen, J. Am. Chem. Soc. 2004, 126, 13218-13219.
- [24] T. R. Cook, Y. R. Zheng, P. J. Stang, Chem. Rev. 2013, 113, 734-777.
- [25] J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown, J. Liu, *Chem. Soc. Rev.* 2012, 41, 2308-2322.
- [26] B. Van de Voorde, B. Bueken, J. Denayer, D. De Vos, *Chem. Soc. Rev.* 2014, 43, 5766-5788.
- [27] Q. L. Zhu, Q. Xu, Chem. Soc. Rev. 2014, 43, 5468-5512.
- [28] J.-R. Li, J. Sculley, H. C. Zhou, Chem. Rev. 2012, 112, 869-932.
- [29] B. Wang, X. L. Lv, D. Feng, L. H. Xie, J. Zhang, M. Li, Y. Xie, J. R. Li, H. C. Zhou, J. Am. Chem. Soc. 2016, 138, 6204-6216.
- [30] S. Chaemchuen, N. A. Kabir, K. Zhou, F. Verpoort, *Chem. Soc. Rev.* 2013, 42, 9304-9332.
- [31] D. Feng, T. F. Liu, J. Su, M. Bosch, Z. Wei, W. Wan, D. Yuan, Y. P. Chen, X. Wang, K. Wang, X. Lian, Z. Y. Gu, J. Park, X. Zou, H. C. Zhou, *Nat. commun.* **2015**, *6*, 5979-5986.
- [32] J. Yu, Y. Cui, H. Xu, Y. Yang, Z. Wang, B. Chen, G. Qian, *Nat. commun.* 2013, 4, 2719-2725.
- [33] P. Guo, D. Dutta, A. G. Wong-Foy, D. W. Gidley, A. J. Matzger, J. Am. Chem. Soc. 2015, 137, 2651-2657.
- [34] J. M. Taylor, R.Vaidhyanathan, S. S. Iremonger, G. K. Shimizu, J. Am. Chem. Soc. 2012, 134, 14338-14340.
- [35] J. M. Taylor, K. W. Dawson, G. K. Shimizu, J. Am. Chem. Soc. 2013, 135, 1193-1196.
- [36] Burtch, N. C.; Walton, K. S. Acc. Chem. Res. 2015, 48, 2850-2857.
- [37] J. Park, J. R. Li, Y. P. Chen, J. Yu, A. A. Yakovenko, Z. U. Wang, L. B. Sun, P. B. Balbuena, H. C. Zhou, *Chem. Commun.* **2012**, *48*, 9995-9997.
- [38] Y. W. Li, J. R. Li, L. F. Wang, B. Y. Zhou, Q. Chen, X. H. Bu, J. Mater. Chem. A. 2013, 1, 495-499.
- [39] B. Van de Voorde, M. Boulhout, F. Vermoortele, P. Horcajada, D. Cunha, J. S. Lee, J. S. Chang, E. Gibson, M. Daturi, J. C. La-valley, A. Vimont, I. Beurroies, D. E. De Vos, *J. Am. Chem. Soc.* **2013**, *135*, 9849-9856.
- [40] S. C. Xiang, W. Zhou, J. M. Gallegos, Y. Liu, B. L. Chen, J. Am. Chem. Soc. 2009, 131, 12415-12419.
- [41] B. Zheng, J. Bai, J. Duan, L. Wojtas, M. J. Zaworotko, J. Am. Chem. Soc. 2011, 133, 748-751.
- [42] B. Zheng, Z. Yang, J. Bai, Y. Li, S. Li, Chem. Commun. 2012, 48, 7025-7027.
- [43] J. Duan, Z. Yang, J. Bai, B. Zheng, Y. Li, S. Li, *Chem. Commun.* 2012, 48, 3058-3060.
- [44] B. S. Zheng, H. T. Liu, Z. X. Wang, X. Y. Yu, P. G. Yi, J. F. Bai, *Cryst. Eng. Comm.* 2013, *15*, 3517-3520.
- [45] S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa,K. Mochizu-ki, Y. Kinoshita, S. Kitagawa, J. Am. Chem. Soc. 2007, 129, 2607-2614.
- [46] Z. Y. Lu, J. F. Bai, C. Hang, F. Meng, X. Z. You, Chem. Eur. J. 2016, 22, 6277-6285.
- [47] X. Van Doorslaer, J. Dewulf, H. Van Langenhove, K. Sci. Demeestere, *Total. Environ.* 2014, 500-501, 250-269.
- [48] K. A. Cychosz, A. J. Matzger, *Langmuir.* **2010**, *26*, 17198-17202.
- [49] J. J. Low, A. I. Benin, P. Jakubozak, J. F. Abrahamian, S. A. Faheem, R. R. Willis, *J. Am. Chem. Soc.* 2009, *131*, 15834-15842.
- [50] M. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2009**, *131*, 3875-3877.
- [51] J. Kim, S.-T. Yang, S. B. Choi, J. Kim, W.-S. Ahn, J. Mater. Chem. 2011, 21, 3070-3076.
- [52] P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi, M. J. Zaworotko, *Nature*. 2013, 495, 80-84.
- [53] J. An, N. L. Rosi, J. Am. Chem. Soc. 2010, 132, 5578-5579.
- [54] B. Hamad, Nat. Rev. Drug. Discov. 2010, 9, 675-676.
- [55] Y. Cabeza, L. Candela, D. Ronen, G. Teijon, J. Hazard. Mater. 2012, 239-240, 32-39.
- [56] K. Kummerer, *Chemosphere*. **2009**, *75*, 435-441.
- [57] A. Roberto, R. Marotta, Chemosphere. 2003, 50, 1319-1330.
- [58] W. G. Lu, Z. W. Wei, Z. Y. Gu, T. F. Liu, J. Park, T. Gentle, M. Boscha, H. C. Zhou, *Chem. Soc. Rev.* **2014**, *43*, 5561-5593.



Layout:

FULL PAPER

FULL PAPER

An exceptionally water stable Metal– Organic Framework with amidefunctionalized cages, namely PCN-124-stu(Cu) has been synthesized and it displays CO_2/CH_4 selective adsorption for its porous structure. What is more, PCN-124-stu(Cu) can severs as an ideal platform for removal of antibiotics and dyes from water to purify it.



Wei-Guang Jin, Wei Chen, Pei-Hang Xu, Xin-Wen Lin, Xiao-Chun Huang,* Guang-Hui Chen, Fushen Lu, and Xiao-Ming Chen

Page No. – Page No.

An Exceptionally Water Stable Metal–Organic Framework with Amide-Functionalized Cages: Selective CO₂/CH₄ Uptake, Removal of Antibiotics and Dyes from Water