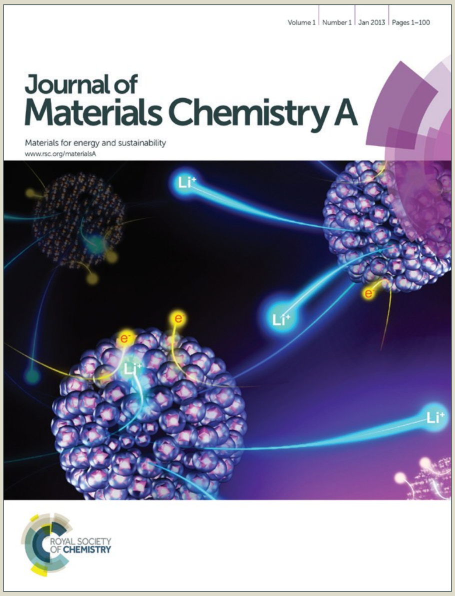
Journal of
Materials Chemistry A

Accepted Manuscript



ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/materialsA

Journal Name

ARTICLE

A multifunctional microporous anionic metal–organic framework for column-chromatographic dye separation and selective detection and adsorption of Cr^{3+}

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

Shu-Ran Zhang,[a] Jing Li,[a] Dong-Ying Du,*[a] Jun-Sheng Qin,[a] Shun-Li Li,[b] Wen-Wen He,[a] Zhong-Min Su*[a] and Ya-Qian Lan*[a,b]

In this work, a novel microporous anionic metal–organic framework (MOF), $[Zn(ABTC)_{0.5}(NO_3)][(CH_3)_2NH_2]\cdot DMA\cdot 3H_2O$ (**NENU-505**; NENU = Northeast Normal University; H_4ABTC = 3,3′,5,5′-azobenzenetetracarboxylic acid; DMA = *N,N*-dimethylacetamide), has been rationally synthesized under solvothermal conditions. Single-crystal X-ray analysis reveals that **NENU-505** is a (4,4)-connected 3D network with **pts** topology. Charge neutrality is achieved by $[(CH_3)_2NH_2]^+$ ion. It is noteworthy that **NENU-505** displays high stability in the air for more than two months. Particularly, the absorption ability of **NENU-505** toward ionic dyes has been also investigated. According to the UV/Vis spectroscopy analysis and the colour variance of **NENU-505**, we found that the cationic dyes could be efficiently absorbed over a period of time, while the neutral and anionic dyes could not be absorbed. Therefore, **NENU-505** exhibits selective absorption toward cationic dyes and can potentially serve as a column-chromatographic filler for the separation of dye molecules. Furthermore, the cationic dyes can be gradually released in the presence of NaCl. More interestingly, when **NENU-505** was immersed in the different metal ions DMA solutions, it performs as a rare example of a highly selective and sensitive sensing for Cr^{3+} ions. In connection to this, the probable sensing mechanism was also further investigated in detail in this paper. Remarkably, this is the first MOF can exhibit an excellent ability for the detection and adsorption of Cr^{3+} ions in a convenient, economical, and environmental-friendly manner.

Introduction

Metal–organic frameworks (MOFs), also known as porous coordination polymers (PCPs), which have attracted tremendous attention for their emerging energy- and environment-related applications in numerous areas,[1] including but not limited to, gas storage and separation,[2] luminescence,[3] heterogeneous catalysis[4] and chemical sensing.[5] In general, MOFs, as indicated by the name, are crystalline materials constructed in "one-pot" solvothermal or hydrothermal syntheses by judicious selection of the two main interacting components: single metal cations (primary building unit or PBU) or metal clusters (secondary building unit or SBU) and organic ligands.[6] MOFs are in possession of diverse topologies with aesthetic beauty through the formation of one, two, or three dimensional extended coordination networks by multiple binding sites of components. Numerous research efforts have mainly been aimed at preparing novel MOFs with structural fascinating and functional diversification,[7] and some MOFs are now commercialized. It should be noted that charged MOFs have been widely explored as an appealing subclass due to the framework charge (i.e., cationic, neutral, or anionic) of MOF materials have a profound effect on their functionalities.[8] Generally speaking, the charge-balancing cationics/anionics usually occupy the void space, potentially allowing the capture and separation of other anionics/cationics through ion exchange.[9]

It has been extensively recognized that dyes have found an increasingly wide utilization in many industry fields, including paper, printing, plastics, textiles, cosmetics, pharmaceuticals and so on.[10] However, the toxicities of several dyes have brought about a significant threat to the aqueous environment and caused serious consequences, such as aesthetic pollution, even carcinogenicity and perturbation to aquatic life.[11] Therefore, in daily life, technologies with high efficiency and low consumption to reduce the harmful pollutant contents of printing and dyeing are urgently required concerning a clean environment and human health. Nevertheless, most dyestuffs are difficult to degrade because their stability to light and oxidants.[12] Recently, MOFs have been also used for absorbing or separating dye molecules, and in most cases, dye removal depends on the size-exclusion effect.[13] Lan and co-workers have reported a series of mesoporous MOFs with rare corundum topology and tunable cage sizes which was employed as a column-chromatographic filler for the separation of bulk dye molecules by the existence of large cages.[14] To the best of our knowledge, a majority of dyes is charged and could prefer to accommodate in the channels of

---

[a] Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, Jilin, People's Republic of China. E-mail: zmsu@nenu.edu.cn

[b] Jiangsu Key Laboratory of Biofunctional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, Jiangsu, People's Republic of China. E-mail: yqlan@njnu.edu.cn

† Electronic Supplementary Information (ESI) available: TGA, XPRD patterns, IR, UV, EDS and XPS data and additional figures for **NENU-505**. CCDC 1412229. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

MOFs with opposite charge. Bearing this in mind, our group has constructed a novel anionic framework with primitive centered cubic (**pcu**) topology, which exhibited selectively absorption ability towards cationic dyes.[15] Nowadays, it remains a labor-intensive endeavor to synthesize new families of charged MOF materials used to absorb/separate dyes by virtue of ionic selectivity.[16]

Chromium is far and wide used in a large amount of industrial processes such as tanning, paint manufacturing, metal processing, electroplating, leather, steel fabrication and agricultural runoff.[17] Chromium is also a trace element necessary for humans and animals. Chromium deficiency can cause atherosclerosis and significantly increase the risk of diabetes and cardiovascular diseases associated with other complications.[18] However, one of its cationic forms, trivalent chromium (Cr^{3+}), has great influences on the human body and biological environment. An excess of Cr^{3+} can be harmful to human health, leading to deformity. Besides, Cr^{3+} in water body can be adsorbed on the solid substance and present in the sediments.[19] If there is too much chromium in the soil, it will inhibit nitrification of organic matter and make chromium accumulate in plants. The main source of anthropogenic pollution is the discharge of industrial waste gas and waste water containing chromium.[20] Chromium residue (chromium-containing solid waste) has become an important environmental issue of chromium pollution. The inappropriate treatment of industrial effluents containing chromium can result in the contamination of natural water sources, eventually threatening human health.[21] Therefore, there is an urgent need to develop an effective solution that is capable of detection of Cr^{3+}. As far as we know, considerable efforts have been focused on the detection of Zn^{2+}, Mg^{2+}, Cu^{2+}, Fe^{3+}, Ag^{+} and other ions based on MOFs[22], nevertheless, rarely reports have been devoted to the development of sensing and adsorption of Cr^{3+}. In this regard, a fast and efficient sensing approach to probe Cr^{3+} is very promising and significant, particularly with the realization of human health and environment beautification.

Herein, we report a new microporous anionic MOF $[Zn(ABTC)_{0.5}(NO_3)][(CH_3)_2NH_2]\cdot DMA\cdot 3H_2O$ (**NENU-505**), synthesized by the solvothermal reaction of $Zn(NO_3)_2\cdot 6H_2O$ and H_4ABTC. It should be noted that **NENU-505** can still maintain integrate framework in the air for more than two months. Meanwhile, **NENU-505** can selectively absorb cationic dye molecules relative to neutral and anionic molecules because of its anionic framework so that make it be a column-chromatographic filler for adsorption and separation of dyes. Furthermore, **NENU-505** can be utilized as a probe for selectively sensing and adsorbing high toxic heavy metal Cr^{3+}. This is the first report on an anionic MOF that exhibits handy, saving, and environmental-friendly properties in the detection and adsorption of Cr^{3+}. However, it is still a long and tortuous procedure to synthesize innovative species of MOF materials for highly selective detection of heavy metal ions.

Results and discussion

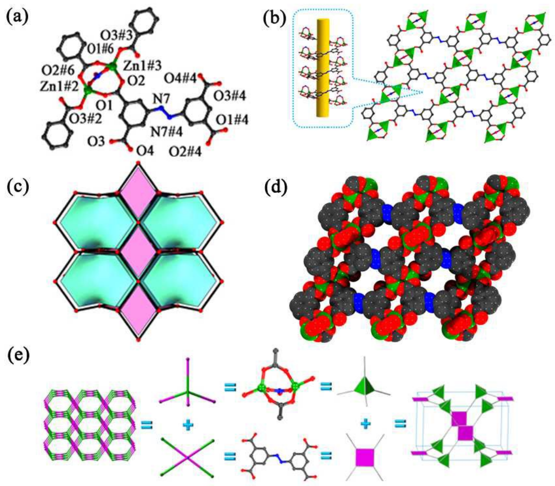


Fig. 1 (a) Coordination environments of Zn(II) in **NENU-505**. Symmetry code: #1 *x*, -*y*, *z*+1/2; #2 -*x*, -*y*, -*z*; #3 *x*, -*y*, *z*-1/2; #4 -*x*+1/2, -*y*+1/2, -*z*; #5 -*x*, *y*, -*z*+1/2; #6 -*x*, *y*, -*z*-1/2. (b) Representations of the helice in channel. (c) The (4,4)-connected augmented net as a natural tiling. (d) Ball-and-stick and space-filling representations of its packing arrangement of the 3D structure in **NENU-505**. (e) Ball-and-stick and polyhedral view of the (4,4)-connected topology network in **NENU-505**. All the hydrogen atoms are omitted for clarity.

A solvothermal reaction of $Zn(NO_3)_2\cdot 6H_2O$ and H_4ABTC in DMA yields yellow rhombus block crystals **NENU-505**. The formula of **NENU-505** $[Zn(ABTC)_{0.5}(NO_3)][(CH_3)_2NH_2]\cdot DMA\cdot 3H_2O$ was elucidated by taking single-crystal X-ray diffraction studies, thermogravimetric analysis (TGA; Fig. S1†), elemental analysis, and charge-balance into considerations. Single-crystal X-ray analysis reveals that **NENU-505** crystallizes in the monoclinic space group *C*2/*c* (Table S1†). The asymmetric unit of **NENU-505** contains a Zn^{2+}, a type of ligand fragment, a coordinated NO_3^- and a isolated $[(CH_3)_2NH_2]^+$. The Zn atom is four coordinated by three carboxylate oxygen atoms from three ligands and an oxygen atom from coordinated NO_3^- and exhibits a distorted-tetrahedral geometry (Fig. 1a). The Zn-O bond lengths are all within the normal ranges (Table S2†). The adjacent two Zn atoms are connected to each other by one NO_3^- and one H_4ABTC ligand to give rise to binuclear zinc cluster $[Zn_2(CO_2)_4(NO_3)]$. The ligand unit links the $[Zn_2(CO_2)_4(NO_3)]$ cluster to form an infinite 3D framework. Simultaneously, one binuclear zinc cluster connects four H_4ABTC ligands (Fig. S2a†), in turn, one H_4ABTC ligand coordinates to four binuclear zinc clusters (Fig. S2b†) to form a pore with an approximate size of 10 × 9.8 Å^2 along the *b* axis (Fig. 1b and 1d), thus suggesting a microporous characteristic of **NENU-505**. A more interesting feature here is that these channels are spiral (Fig. 1b). Then from the topological analysis, each $[Zn_2(CO_2)_4(NO_3)]$ cluster acts as a 4-connected node and each metalloligand unit is considered as a 4-connected node (Fig. 1c and 1e), which generates a (4,4)-connected 3D network with **pts** topology (Schläfli symbol of $(4^2\cdot 8^4)$).[23] Overall, the framework of **NENU-505** is anionic, $[(CH_3)_2NH_2]^+$ ions located in the channel help to balance the charge (Fig. S3†). The protonated $[(CH_3)_2NH_2]^+$ ions in **NENU-505** originate from the decarbonylation of dimethylamine.[24] Given single-crystal X-ray diffraction studies and the charge-balance consideration, there are one $[(CH_3)_2NH_2]^+$ ion per formula unit. The experimental X-ray powder diffraction (XRPD) patterns of both simulated and as-synthesized **NENU-505** match well in key positions, thus indicating its phase purity (Fig. S4†). **NENU-505** can just maintain its stability in water for several hours as demonstrated by XRPD (Fig. S4†), and then turn into amorphous. Notably, under ambient conditions, that is to say, exposure to air for more than two months, no major changes to either the external appearance or to the XRPD patterns of **NENU-505** were observed, confirming the extreme stability of the framework (Fig. S5†). To ensure structural integrity and stability of **NENU-505** exposed in the air after two months, we have presented its optical image taken by using a fluorescence microscope equipped with a CCD camera (Fig. S5†).

It is extremely important to remove dyes from effluents before discharge into natural bodies from an environmental point of view since dyes have been widely employed in several industries.[25] Up to now, a great deal of methods has been utilized in order to remove dyes from the environment. Significantly, this involves the adsorption approach without chemical degradation is extremely attractive in virtue of its effectiveness, efficiency and economy.[26] Owing to its simple preparation, ease acquisition of raw materials and its porous anionic framework nature, **NENU-505** was explored as a column-chromatographic filler for adsorption and separation of dyes based on ionic interaction between the cationic dyes and anionic framework. **NENU-505** does not require any activation process compared with other reported MOFs for dye sorption.[27] To evaluate whether **NENU-505** has the absorption ability to separate dye molecules, we selected freshly prepared **NENU-505** to capture dyes from solutions in DMA. We carefully select nine dye molecules in accordance with different shapes, sizes and charges, including cationic dyes (methylene blue (MB), basic red 2 (BR 2), and basic green 1 (BG 1)), anionic dyes (congo red (CR), methyl orange (MO), food green 3 (FG 3), and R-250), and neutral dyes (solvent yellow 2 (SY) and basic red 1 (BR 1)), in which some perhaps would be absorbed. Typically, when freshly prepared **NENU-505** (100 mg) was soaked in DMA solutions of different kinds of dyes (10 mL, 1.0 mmol), the cationic dyes (MB, BR 2, and BG

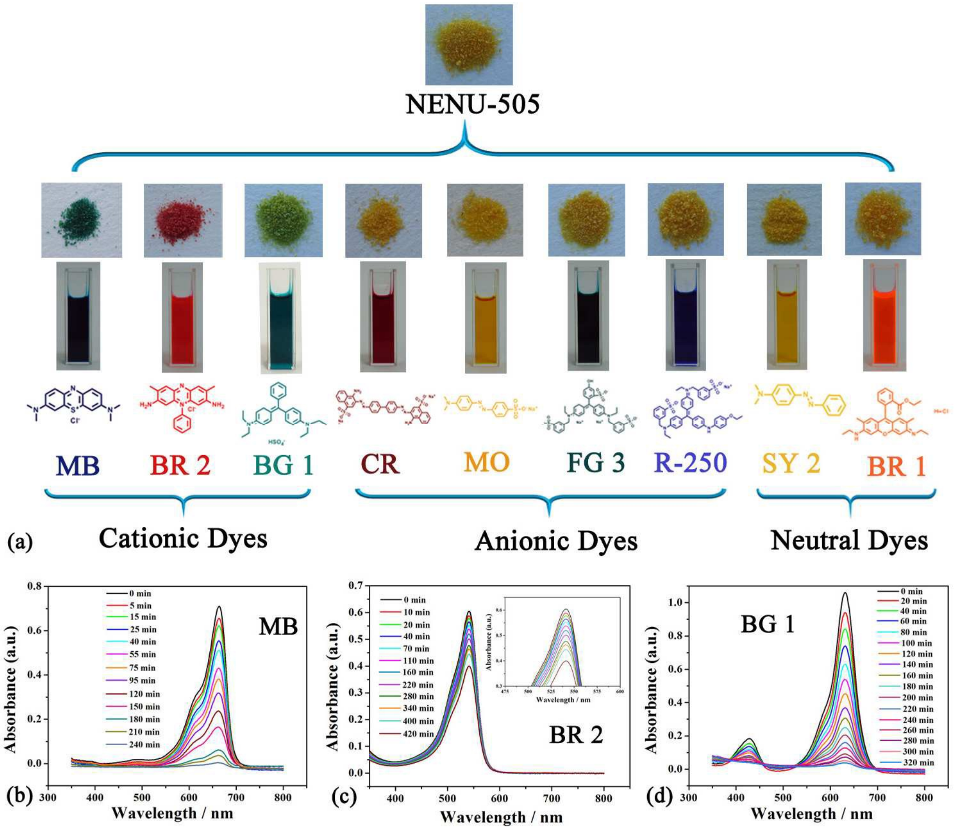


Fig. 2 (top a) Schematic illustration of the dye molecules employed in the dye-absorption experiments and photographs of the corresponding colour change of crystals after immersion into the solutions of the dyes for a period of time. (bottom) UV/Vis spectra of DMA solutions of (b) MB, (c) BR 2, and (d) BG 1 with freshly prepared **NENU-505**, respectively. Insets: the enlargements of corresponding UV/Vis absorption.

1) could be efficiently absorbed over a period of time and the yellow crystals gradually became coloured, while the neutral and anionic dyes could not be absorbed (Fig. 2a). Among these dyes, for MO and SY 2, the main reason for non-absorbing is that the charge does not match, as well as larger shapes and sizes for CR, FG 3, R-250 and BR 1. Meanwhile, the capability of **NENU-505** to absorb the three cationic dyes from solutions of DMA was quantitatively determined through UV/Vis spectroscopy analysis (Fig. 2b-d), which indicated that the concentration of cationic dyes in DMA significantly decreased with the passage of time. At the same instant, spectroscopic investigations of the supernatants also showed that **NENU-505** could completely and rapidly absorb MB. The adsorption capacity of **NENU-505** at room temperature was 33.5 mg g^{-1} for MB, 4.5 mg g^{-1} for BR 2, and 17.6 mg g^{-1} for BG 1. The adsorptivity of **NENU-505** for MB is higher than that of some other materials reported up to now (Table S3†). The shape and size of the three dyes may result in the difference of adsorption quantity to different types of cationic dyes. According to the structure, MB is linear and BR and BG 1 are planar, which make MB is relatively smaller than other two cationic dyes. In addition, no major changes to either the external appearance or to the XRPD and IR patterns of **NENU-505** were detected after the successful exchange of cationic dyes, as proved by the XRPD and IR profiles (Fig. S6 and S7†).

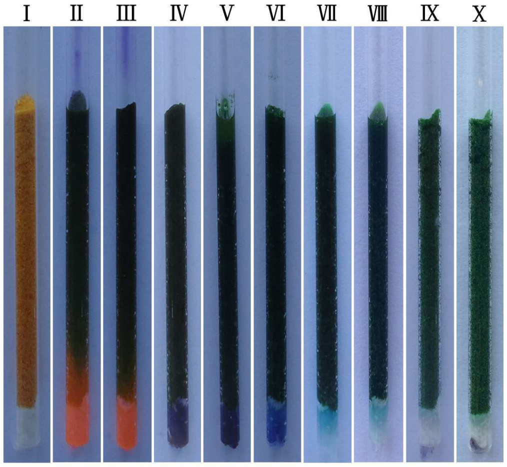


Fig. 3 Photograph records for **NENU-505**-filled column-chromatographic separation process for MB and BR 1 dyes, in which (I) **NENU-505**-filled column, (II-IX) separation process with gradually changed colour, and (X) complete separation with only MB absorbed.

The above results inspired us that **NENU-505** may be a potential absorbent for the removal of cationic dyes from effluents. Therefore, we have prepared a column-chromatographic filled with **NENU-505** and make DMA solutions of mixed two different types of dyes MB and BR 1 (1:1, 1.0 mmol) pass through the column-chromatographic filler. As displayed in Fig. 3, the colour of the column finally became blackish green, which indicated that cationic dye MB was absorbed inside **NENU-505** for longer time along with the DMA stream. In the meantime, neutral and unabsorbed dye BR 1 was rapidly transported through the column. Thus the two kinds of dyes MB and BR 1 can be successfully and quickly separated by passing them through the MOF-filled column, which was not only observed by the naked eye but also evaluated through UV/Vis spectroscopy of the effluent (Fig. 4). The continuing decrease of characteristic wavelength for MB reveals its successful absorbance, while unchanged peak of BR 1 suggests its exclusion by **NENU-505**. Additionally, we have also monitored UV/Vis spectroscopy of other dye mixtures in order to ensure the capability of **NENU-505** to adsorb cationic dyes from the effluent, which is indicative of its generality (Fig. S8 and S9†). Moreover, we also calculated the adsorption capacity of **NENU-505** for every dye in mixture dye (Table S4†). The adsorption capacity is almost the same as single component dye.

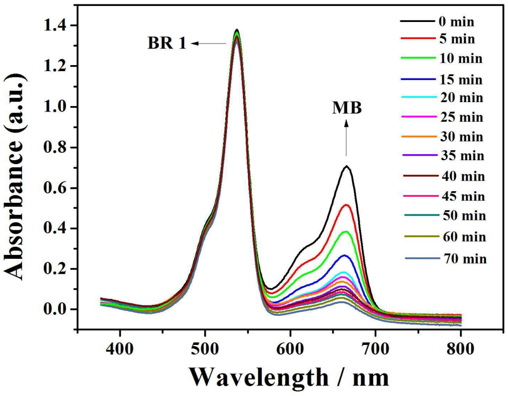


Fig. 4 UV/Vis spectra of DMA solution of mixed MB and BR 1 with **NENU-505**.

To authenticate the kinetic reason for selective absorption toward cationic dyes is ionic interaction between anionic framework and cationic dye, dye releasing experiments were also carried out in a saturated solution of NaCl in DMA and pure DMA, respectively. **NENU-505** was first soaked in a DMA solution of MB for a period of time to make them saturated. Then 15 mg of the saturated **MB@NENU-505** was added to a 3 mL saturated solution of NaCl in DMA and pure DMA, respectively.[28] UV/Vis spectra were monitored at different time intervals. The results indicate that MB in **MB@NENU-505** can be gradually released in the action of NaCl (Fig. 5a), whereas the dye molecules are scarcely released in DMA without NaCl (Fig. 5b). Moreover, it further strengthens the evidence that MB is released *via* the ion exchange process with NaCl acting as a trigger. UV/Vis spectra of **BR 2@NENU-505** and **BG 1@NENU-505** were also recorded both in saturated solution of NaCl in DMA and pure DMA (Fig. S10 and S11†). Owing to the shape and size of the three dyes, the release quantity and rate to different types of cationic dyes are different within 420 min. The release percentage is approximate 14.1% for MB, 6.2% for BR 2, and 9.4% for BG 1 within 420 min, respectively. In the circumstances, we can safely speculate that selective absorption is ascribed to the ionic interaction of the dyes with the anionic framework. The experimental results make it possible that **NENU-505** can be utilized to separate dyes with similar sizes but opposite charges. For the sake of confirming the regeneration and cyclicity of **NENU-505** toward MB, UV/Vis spectra analysis was carried out on a solution of MB in DMA after adsorption experiments with **NENU-505**, as well as the MB released (desorption) from **MB@NENU-505** by taking advantage of a saturated solution of NaCl in DMA after six adsorption–desorption cycles (Fig. S12a†). Apart from that, the corresponding removal and regeneration percentages were also calculated (Fig. S12b†). The XRPD patterns further verify that the framework is retained after cycle 6 (Fig. S13†). These results manifested that the dye adsorption and release is a reversible process and **NENU-505** is reusable as an excellent and effective adsorbent.

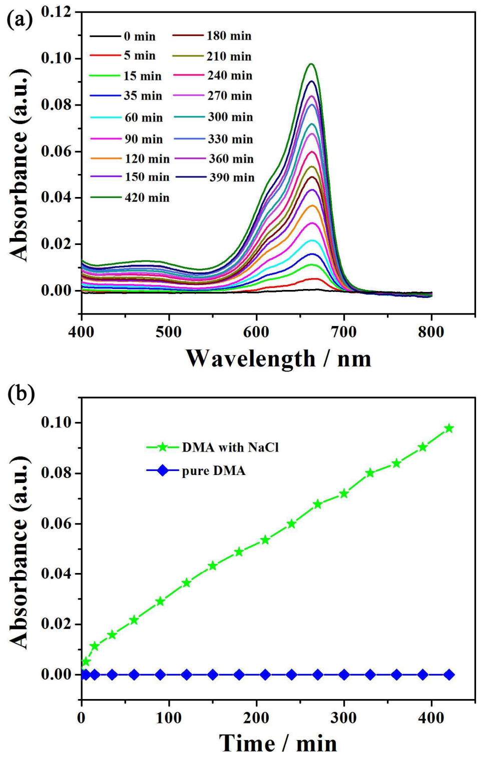


Fig. 5 (a) The MB released from **MB@NENU-505** in a saturated solution of NaCl in DMA monitored by UV absorption. (b) The release-rate comparison of MB from **MB@NENU-505** in a saturated solution of NaCl in DMA (green) and pure DMA (blue).

The existence of $[(CH_3)_2NH_2]^+$ cations and several carboxylate oxygen atoms on the pore surface prompted us to examine the potential of **NENU-505** for the sensing of metal ions by immersing **NENU-505** in DMA solutions containing single coloured metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+} and Cr^{3+}, 0.01 M), respectively. Owing to the peak positions of XRPD and IR curves for samples immersed in different metal ions essentially remain unchanged (Fig. S14† and S15†), we can speculate that the basic frameworks in the compounds remained intact after immersion different metal ions. Interestingly, the samples exhibit obvious change of solid colour compared to the original one (Fig. 6). It is noticeable that the colour has become bottle green after soaking in DMA solutions containing Cr^{3+} for 48 h (**Cr^{3+}@NENU-505**, 0.01 M), while the colours of other metal ions did not change. Inductively Coupled Plasma (ICP) analysis of resulting samples indicated that **NENU-505** has encapsulated 4.655% Cr^{3+}, which is much higher compared to the other metal ions (Fig. 7). Besides that, the corresponding energy dispersive spectroscopy (EDS) also verified the encapsulation of Cr^{3+} in **NENU-505** (Fig. S16†). To understand the mechanism of the selective capture of Cr^{3+}, we investigated the UV/Vis spectra of solid **NENU-505** and **Cr^{3+}@NENU-505** (Fig. S17†). There is a new band in the UV/Vis spectra of **Cr^{3+}@NENU-505** at 580 nm in addition to the band at 358 nm as observed in **NENU-505**. This may be ascribed to the coordination of Cr^{3+} with the carboxylate oxygen atoms of **NENU-505** through d–d transition. In other words, Cr^{3+} ions were adsorbed on the carboxylate groups. It is widely acknowledged that the flexible geometry of Cr^{3+} as a result of it can exist in a variety of coordination environments. As shown in the shadow parts (Fig. S14†), for instance, the diffraction intensities corresponding to (1 1 1), (2 0 2), $(3\ 1\ \bar{1})$, (4 0 2), (5 1 0), $(1\ 1\ \bar{4})$, (3 1 3) and (1, 1 4) crystallographic planes at 13.16°, 14.08°, 14.84° (shadow 1, Fig. S14†), 19.3°, 20.2° (shadow 2, Fig. S14†), 22.6°, 23.7° and 24.5° (shadow 3, Fig. S14†), respectively, in 2θ of **Cr^{3+}@NENU-505** are slightly different compared to simulated **NENU-505**. In addition, the peak intensities of IR curve for **Cr^{3+}@NENU-505** at 1018, 779 and 727 cm^{-1} (shadow 1 and 2, Fig. S15†) are relatively weaker than those of **NENU-505**. Generally speaking, the peak intensity changes of a few peaks in the XRPD and IR pattern of **Cr^{3+}@NENU-505** are primarily due to structural reorganization after encapsulation of Cr^{3+}. In order to further identify whether Cr^{3+} turn into more nocuous Cr^{6+} after encapsulation or not, X-ray photoelectron spectrometry (XPS) spectrum of **Cr^{3+}@NENU-505** was monitored (Fig. S18†). In the XPS spectrum, a pair of peaks at 587.1 and 577.4 eV, which can be ascribed to Cr^{3+} $2p_{1/2}$ and Cr^{3+} $2p_{3/2}$, respectively[29], which indicate that the valence state

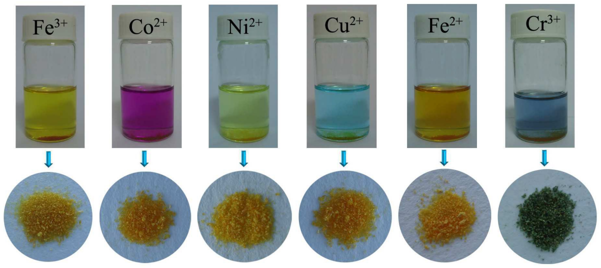


Fig. 6 The photographs of **NENU-505** in 10 mL DMA solutions containing single coloured metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Cr^{3+}, 0.01 M), respectively.

of chromium does not change. The XPS spectrum also further confirmed that the interaction between Cr^{3+} and the uncoordinated carboxylate oxygen atoms. Subsequently, in order to further explore its extraction capacity in multi-element solutions, 50 mg of **NENU-505** is immersed in 10 mL DMA solutions containing three equal concentration of each metal ion (1: Fe^{2+}, Cu^{2+} and Cr^{3+}; 2: Cu^{2+}, Ni^{2+} and Cr^{3+}; 3: Cu^{2+}, Co^{2+} and Cr^{3+}; 4: Ni^{2+}, Co^{2+} and Cr^{3+}, 0.01 M) for 48 h at the room temperature. The colour of **NENU-505** has still become bottle green because of adsorbing Cr^{3+} (Fig. S19†). The ICP percentage of Cr^{3+} encapsulated by **NENU-505** has been listed in Table S5†. The ICP percentage of Cr^{3+} encapsulated by **NENU-505** in multi-element solutions is relatively smaller than that of in single metal solutions (4.655%). We speculate the possible factor that affects separation is the interaction between other metal ions and uncoordinated carboxylate oxygen atoms of **NENU-505**, giving rise to a competition with Cr^{3+}. Therefore, **NENU-505** could be applied as a chemical sensor for Cr^{3+} with high sensitivity in the systems with complicated components in a convenient, economical, and environmental-friendly manner.

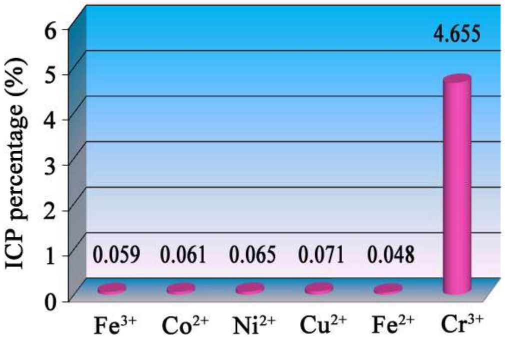


Fig. 7 The ICP percentage of different metal ions encapsulated by **NENU-505**.

Conclusions

In summary, we have successfully constructed a microporous anionic MOF **NENU-505** with a (4,4)-connected **pts** topology. **NENU-505** is extremely stable in the air for more than two months. Owing to its anionic framework, **NENU-505** not only can be used for selective adsorption and separation of cationic dye molecules but also demonstrates that **NENU-505** can be a column-chromatographic filler for separating dye molecules. Moreover, the cationic dyes could be gradually released in the presence of NaCl, illustrating that the absorption perhaps results from the ionic interaction between the anionic framework and the cationic dyes. And the process of the dye uptake and release is reversible, which suggested that **NENU-505** is reusable as a prominent and effective adsorbent. Especially, for the first time, an anionic MOF **NENU-505** has been exploited for selectively sensing and adsorbing Cr^{3+} in a high efficiency and low consumption mode due to its presence of $[(CH_3)_2NH_2]^+$ cations and carboxyl groups. The present research has opened up a promising approach to design and prepare MOF-based multifunctional materials, which will probably be useful under more realistic conditions in the future. Considering the charming specific anionic groups in MOF could facilitate targeted fabrication of smart materials with versatile properties, many look forward to synthesizing and exploring novel charged MOF are currently underway.

Experimental

Materials and measurements

Chemicals were obtained from commercial sources and were used without further purification. X-Ray powder diffraction (XRPD) were performed on a Siemens D5005 diffractometer with Cu-Kα (λ = 1.5418 Å) radiation in the range of 3–60° at 293 K. Elemental microanalyses (C, H and N) were performed on a Perkin-Elmer 240C elemental analyzer. Cr and other cations were determined with a Plasma-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 4000–400 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer heated from 50 °C to 1000 °C at a ramp rate of 10 °C min^{-1} under nitrogen. The UV/Vis absorption spectra were examined on a Shimadzu UV-2550 spectrophotometer in the wavelength range of 300-800 nm. Energy dispersive X-ray spectroscopy (EDS) was obtained with a XL30 ESEM FEG microscope. X-ray photoelectron spectrometry (XPS) spectrum was performed on a thermo ECSALAB 250 spectrometer with an Al *Kα* (1486.6 eV) achromatic X-ray source running at 15 kV. The XPS binding energy (BE) was internally referenced to the aliphatic C(1s) peak (BE, 284.6 eV).

Synthesis of $[Zn(ABTC)_{0.5}(NO_3)][(CH_3)_2NH_2]\cdot DMA\cdot 3H_2O$ (NENU-505)

A mixture of H_4ABTC (0.01 g, 0.03 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (0.19 g, 0.64 mmol), DMA (5 mL), H_2O (3 mL) and three drops of HCl (6 mol L^{-1}) was sealed in a Teflon-lined stainless steel container and heated in an autoclave at 110 °C for 4 days. After the autoclave was cooled to room temperature, yellow crystals were obtained and isolated by washing with DMA and dried at room temperature. Yield: 58% based on H_4ABTC. Elemental microanalysis: Anal. calc. for $C_{14}H_{26}N_{3.5}O_{9.5}Zn$ (460.18): C, 36.54; H, 5.65; N, 10.66. Found: C, 36.96; H, 5.74; N, 11.21%. IR (KBr, cm^{-1}, Fig. S7†): 3079 (m), 2937 (m), 2487 (w), 1634 (s), 1448 (s), 1357 (s), 1244 (s), 1188 (m), 1018 (m), 961 (w), 928 (w), 779 (s), 672 (w), 593 (w), 473 (m).

X-Ray crystallography

Single crystal X-ray diffraction data in this work were recorded on a Bruker APEXII CCD diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71069 Å) at 293 K. Absorption corrections were applied using multi-scan technique. All the structures were solved by Direct Method of SHELXS-97[30a] and refined by full-matrix least-squares techniques using the SHELXL-97 program[30b] within WINGX[30c]. Non-hydrogen atoms were refined with anisotropic temperature parameters. The SQUEEZE program implemented in PLATON[30d] was used to remove these electron densities for the compounds. Thus, all of electron densities from free solvent molecules have been “squeezed” out. The detailed crystallographic data and structure refinement parameters are summarized in Table S1†.

Experimental details for dye adsorption, release and separation

Dye adsorption

Freshly prepared **NENU-505** (100 mg) was soaked in DMA solutions of cationic dyes (methylene blue (MB), basic red 2 (BR 2), and basic green 1 (BG 1)), anionic dyes (congo red (CR), methyl orange (MO), food green 3 (FG 3), and R-250), and neutral dyes (solvent yellow 2 (SY) and basic red 1 (BR 1)), respectively. After two days of soakage, the samples were washed with DMA.

Dye release

The **NENU-505** samples loaded with MB, BR 2, and BG 1 (15 mg) were transferred into pure DMA and a saturated solution of NaCl in DMA (3 mL) in cuvettes (4 mL), respectively. UV/Vis spectra were employed to monitor the absorption ability and release process of **NENU-505** after certain time intervals.

Column-chromatographic dye separation

The sealed bottom of NMR sample tube (Ø5 mm, 180 mm) was cut off from middle and **NENU-505** was filled in the NMR sample tube (80 mm) as a chromatographic column. **NENU-505** does not need any activation procedure. First, the DMA solutions of mixed MB / BR 1 (1:1, 1.0 mmol) were passed through the chromatographic column at the room temperature. Then pure DMA were traversed the chromatographic column. The time of completing the whole separation is probably 30 min. The UV-Vis spectra of effluents were examined to confirm the separation capability.

Experimental details for sensing of Cr^{3+}

Firstly, 50 mg of **NENU-505** is immersed in 10 mL DMA solutions containing single coloured metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+} and Cr^{3+}, 0.01 M) for 48 h at the room temperature. Then so as to further investigate its extraction capacity in multi-element solutions, 50 mg of **NENU-505** is immersed in 10 mL DMA solutions containing three equal concentration of each metal ion (1: Fe^{2+}, Cu^{2+} and Cr^{3+}; 2: Cu^{2+}, Ni^{2+} and Cr^{3+}; 3: Cu^{2+}, Co^{2+} and Cr^{3+}; 4: Ni^{2+}, Co^{2+} and Cr^{3+}, 0.01 M) for 48 h at the room temperature. The samples were washed with DMA after soakage.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21371099 and 21401021), China Postdoctoral Science Foundation (No. 2014M551154 and 2015T80284), the Science and Technology Development Planning of Jilin Province (No. 20140520089JH and 20140203006GX), the Jiangsu Specially-Appointed Professor, the NSF of Jiangsu Province of China (No. BK20130043), the Priority Academic Program Development of Jiangsu Higher Education Institutions, the Foundation of Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, and the Fundamental Research Funds for the Central Universities (No. 14QNJJ013).

Notes and references

1 (*a*) H. Furukawa, K. E. Cordova, M. O’Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 1230444; (*b*) A. G. Slater and A. I. Cooper, *Science*, 2015, **348**, 8075; (*c*) Q.-L. Zhu and Q. Xu, *Chem. Soc. Rev.*, 2014, **43**, 5468; (*d*) W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle III, M. Bosch and H.-C. Zhou, *Chem. Soc. Rev.*, 2014, **43**, 5561; (*e*) R. J. Kuppler, D. J. Timmons, Q.-R. Fang, J.-R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang and H.-C. Zhou, *Coord. Chem. Rev.*, 2009, **253**, 3042; (*f*) J. R. Long and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 121; (*g*) S.-L. Li and Q. Xu, *Energy Environ. Sci.*, 2013, **6**, 1656.

2 (*a*) L. J. Murray, M. Dincă and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294; (*b*) T. A. Makal, J.-R. Li, W. Lu and H.-C. Zhou, *Chem. Soc. Rev.*, 2012, **41**, 7761; (*c*) M. P. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.*, 2012, **112**, 782; (*d*) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724; (*e*) J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869; (*f*) H. Wu, Q. Gong, D. H. Olson and J. Li, *Chem. Rev.*, 2012, **112**, 836; (*g*) P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, **495**, 80; (*h*) T. Grancha, J. Ferrando-Soria, H.-C. Zhou, J. Gascon, B. Seoane, J. Pasán, O. Fabelo, M. Julve and E. Pardo, *Angew. Chem. Int. Ed.*, 2015, **54**, 6521; (*i*) J.-S. Qin, D.-Y. Du, W.-L. Li, J.-P. Zhang, S.-L. Li, Z.-M. Su, X.-L. Wang, Q. Xu, K.-Z. Shao and Y.-Q. Lan, *Chem. Sci.*, 2012, **3**, 2114; (*j*) P. Shen, W.-W. He, D.-Y. Du, H.-L. Jiang, S.-L. Li, Z.-L. Lang, Z.-M. Su, Q. Fu and Y.-Q. Lan, *Chem. Sci.*, 2014, **5**, 1368.

3 (*a*) Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2012, **112**, 1126; (*b*) Y. Cui, B. Chen and G. Qian, *Coord. Chem. Rev.*, 2014, **273**, 76; (*c*) Y. Cui, T. Song, J. Yu, Y. Yang, Z. Wang and G. Qian, *Adv. Funct. Mater.*, 2015, **25**, 4796; (*d*) M.-J. Dong, M. Zhao, S. Ou, C. Zou and C.-D. Wu, *Angew. Chem. Int. Ed.*, 2014, **53**, 1575; (*e*) S.-R. Zhang, D.-Y. Du, J.-S. Qin, S.-L. Li, W.-W. He, Y.-Q. Lan and Z.-M. Su, *Inorg. Chem.*, 2014, **53**, 8105; (*f*) S.-R. Zhang, D.-Y. Du, K. Tan, J.-S. Qin, H.-Q. Dong, S.-L. Li, W.-W. He, Y.-Q. Lan, P. Shen and Z.-M. Su, *Chem. Eur. J.*, 2013, **19**, 11279; (*g*) L.-H. Cao, F. Shi, W.-M. Zhang, S.-Q. Zang and T. C. W. Mak, *Chem. Eur. J.*, 2015, DOI: 10.1002/chem.201501162.

4 (*a*) M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, 2012, **112**, 1196; (*b*) H. R. Moon, D.-W. Lim and M. P. Suh, *Chem. Soc. Rev.*, 2013, **42**, 1807; (*c*) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450; (*d*) J.-P. Ma, S.-Q. Wang, C.-W. Zhao, Y. Yu and Y.-B. Dong, *Chem. Mater.*, 2015, **27**, 3805.

5 (*a*) Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815; (*b*) B. Chen, S. Xiang and G. Qian, *Acc. Chem. Res.*, 2010, **43**, 1115; (*c*) Y. Cui, F. Zhu, B. Chen and G. Qian, *Chem. Commun.*, 2015, **51**, 7420; (*d*) Y. Cui, H. Xu, Y. Yue, Z. Guo, J. Yu, Z. Chen, J. Gao, Y. Yang, G. Qian and B. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 3979; (*e*) A. Lan, K. Li, Haohan Wu, D. H. Olson, T. J. Emge, W. Ki, M. Hong and J. Li, *Angew. Chem. Int. Ed.*, 2009, **48**, 2334; (*f*) S. Pramanik, C. Zheng, X.

Zhang, T. J. Emge and J. Li, *J. Am. Chem. Soc.*, 2011, **133**, 4153; (*g*) Y.-S. Xue, Y. He, L. Zhou, F.-J. Chen, Y. Xu, H.-B. Du, X.-Z. You and B. Chen, *J. Mater. Chem. A*, 2013, **1**, 4525; (*h*) Y. Cui, R. Song, J. Yu, M. Liu, Z. Wang, C. Wu, Y. Yang, Z. Wang, B. Chen and G. Qian, *Adv. Mater.*, 2015, **27**, 1420; (*i*) S. Bhattacharyya, A. Chakraborty, K. Jayaramulu, A. Hazra and T. K. Maji, *Chem. Commun.*, 2014, **50**, 13567; (*j*) S.-R. Zhang, D.-Y. Du, J.-S. Qin, S.-J. Bao, S.-L. Li, W.-W. He, Y.-Q. Lan, P. Shen and Z.-M. Su, *Chem. Eur. J.*, 2014, **20**, 3589.

6 F. A. A. Paz, J. Klinowski, S. M. F. Vilela, J. P. C. Tomé, J. A. S. Cavaleiroc and J. Rocha, *Chem. Soc. Rev.*, 2012, **41**, 1088.

7 (*a*) G. Férey, C. Serre, T. Devic, G. Maurin, H. Jobic, P. L. Llewellyn, G. De Weireld, A. Vimont, M. Daturi and J.-S. Chang, *Chem. Soc. Rev.*, 2011, **40**, 550; (*b*) M. Kurmoo, *Chem. Soc. Rev.*, 2009, **38**, 1353; (*c*) N. Stock and S. Biswas, *Chem. Rev.*, 2011, **112**, 933; (*d*) S. Horike, D. Umeyama and S. Kitagawa, *Acc. Chem. Res.*, 2013, **46**, 2376; (*e*) A. Karmakar, A. V. Desai, B. Manna, B. Joarder and S. K. Ghosh, *Chem. Eur. J.*, 2015, **21**, 7071; (*f*) X. Lian, D. Feng, Y.-P. Chen, T.-F. Liu, X. Wang, H.-C. Zhou, *Chem. Sci.*, 2015, DOI: 10.1039/C5SC02587G.

8 (*a*) S.-N. Zhao, X.-Z. Song, M. Zhu, X. Meng, L.-L. Wu, J. Feng, S.-Y. Song and H.-J. Zhang, *Chem. Eur. J.*, 2015, **21**, 9748; (*b*) A. Schoedel, L. Wojtas, S. P. Kelley, R. D. Rogers, M. Eddaoudi and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2011, **50**, 11421; (*c*) J. An, C. M. Shade, D. A. Chengelis-Czegan, S. Petoud and N. L. Rosi, *J. Am. Chem. Soc.*, 2011, **133**, 122; (*d*) D. Chen, W. Shi and P. Cheng, *Chem. Commun.*, 2015, **51**, 370; (*e*) Z.-J. Zhang, W. Shi, Z. Niu, H.-H. Li, B. Zhao, P. Cheng, D.-Z. Liao and S.-P. Yan, *Chem. Commun.*, 2011, **47**, 6425.

9 (*a*) P.-F. Shi, B. Zhao, G. Xiong, Y.-L. Hou and P. Cheng, *Chem. Commun.*, 2012, **48**, 8231; (*b*) L. Shi, T. Wang, H. Zhang, K. Chang, X. Meng, H. Liu and J. Ye, *Adv. Sci.*, 2015, **2**, 1500006; (*c*) T. H. Noh, H. Lee, J. Jang, and O.-S. Jung, *Angew. Chem. Int. Ed.*, 2015, **54**, 9284; (*d*) H. Fei, D. L. Rogow and S. R. J. Oliver, *J. Am. Chem. Soc.*, 2010, **132**, 7202; (*e*) J. Yu, Y. Cui, H. Xu, Y. Yang, Z Wang, B Chen and G. Qian, *Nat. Commun.*, 2013, **4**, 2719.

10 (*a*) L.-H. Cao, Y.-L. Wei, C. Ji, M.-Li Ma, S.-Q. Zang and T. C. W. Mak, *Chem. Asian J.*, 2014, **9**, 3094; (*b*) Y. Zhu, Y.-M. Wang, S.-Y. Zhao, P. Liu, C. Wei, Y.-L. Wu, C.-K. Xia and J.-M. Xie, *Inorg. Chem.*, 2014, **53**, 7692; (*c*) Y.-X. Tan, Y. Zhang, Y.-P. He, Y.-J. Zheng and J. Zhang, *Inorg. Chem.*, 2014, **53**, 12973.

11 *(a)* F.-Y. Yi, W. Zhu, S. Dang, J.-P. Li, D. Wu, Y.-h. Li and Z.-M. Sun, *Chem. Commun.*, 2015, **51**, 3336; *(b)* S. Lin, Z. Song, G. Che, A. Ren, P. Li, C. Liu and J. Zhang, *Microporous Mesoporous Mater.*, 2014, **193**, 27; *(c)* C.-F. Zhang, L.-G. Qiu, F. Ke, Y.-J. Zhu, Y.-P. Yuan, G.-S. Xu and X. Jiang, *J. Mater. Chem. A*, 2013, **1**, 14329; *(d)* W. Fan, W. Gao, C. Zhang, W. W. Tjiu, J. S. Pan and T. X. Liu, *J. Mater. Chem.*, 2012, **22**, 25108.

12 S. H. Chen, J. Zhang, C. L. Zhang, Q. Y. Yue, Y. Li and C. Li, *Desalination*, 2010, **252**, 149.

13 (*a*) H.-L. Jiang, Y. Tatsu, Z.-H. Lu and Q. Xu, *J. Am. Chem. Soc.*, 2010, **132**, 5586; (*b*) F. Pu, X. Liu, B. Xu, J. Ren and X. Qu, *Chem. Eur. J.*, 2012, **18**, 4322.

14 Y.-Q. Lan, H.-L. Jiang, S.-L. Li and Q. Xu, *Adv. Mater.*, 2011, **23**, 5015.

15 J.-S. Qin, S.-R. Zhang, D.-Y. Du, P. Shen, S.-J. Bao, Y.-Q Lan and Z.-M. Su, *Chem. Eur. J.*, 2014, **20**, 5625.

16 C.-Y. Sun, X.-L. Wang, C. Qin, J.-L. Jin, Z.-M. Su, P. Huang and K.-Z. Shao, *Chem. Eur. J.*, 2013, **19**, 3639.

17 K. Selvi, S. Pattabhi and K. Kadirvelu, *Bioresour. Technol.*, 2001, **80**, 87.

18 (*a*) S. Paul, S.Goswami and A. Manna, *Dalton Trans.*, 2015, **44**, 11805; (*b*) Z. Zhou, M. Yu, H. Yang, K. Huang, F. Li, T. Yi and C. Huang, *Chem. Commun.*, 2008, 3387.

19 (*a*) X. Wang, T. M. Johnson and A. S. Ellis, *Geochim. Cosmochim. Acta*, 2015, **153**, 72; (*b*) T. A. Saleh, S. A. Haladu and S. A. Ali, *Chem. Eng. J.*, 2015, **269**, 9; (*c*) Y. Li, C. Liu and C. Chiou, *J. Colloid Interface Sci.*, 2004, **273**, 95.

20 (*a*) J. Dui, G. Zhu and S. Zhou, *ACS Appl. Mater. Interfaces*, 2013, **5**, 10081; (*b*) D. Park, Y.-S. Yun and J. M. Park, *Environ. Sci. Technol.*, 2004, **38**, 4860; (*c*) M. Bhaumik, H. J. Choi, M. P. Seopela, R. I. McCrindle and A. Maity, *Ind. Eng. Chem. Res.*, 2014, **53**, 1214.

21 (*a*) D. Kratochvil, P. Pimentel and B. Volesky, *Environ. Sci. Technol.*, 1998, **32**, 2693; (*b*) N. Shevchenko, V. Zaitsev and A. Walcarius, *Environ. Sci. Technol.*, 2008, **42**, 6922; (*c*) B. Li, D. Pan, J. Zheng, Y. Cheng, X. Ma, F. Huang and Z. Lin, *Langmuir*, 2008, **24**, 9630.

22 (*a*) B. Zhao, X.-Y. Chen, P. Cheng, D.-Z. Liao, S.-P. Yan and Z.-H. Jiang, *J. Am. Chem. Soc.*, 2004, **126**, 15394; (*b*) W. Liu, T. Jiao, Y. Li, Q. Liu, M. Tan, H. Wang and L. Wang, *J. Am. Chem. Soc.*, 2004, **126**, 2280; (*c*) Z. Hao, X. Song, M. Zhu, X. Meng, S. Zhao, S. Su, W. Yang, S. Song and H. Zhang, *J. Mater. Chem. A*, 2013, **1**, 11043; (*d*) X.-Z. Song, S.-Y. Song, S.-N. Zhao, Z.-M. Hao, M. Zhu, X. Meng, L.-L. Wu and H.-J. Zhang, *Adv. Funct. Mater.*, 2014, **24**, 4034; (*e*) Z. Hao, G. Yang, X. Song, M. Zhu, X. Meng, S. Zhao, S. Song and H. Zhang, *J. Mater. Chem. A*, 2014, **2**, 237; (*f*) B. Zhao, H.-L. Gao, X.-Y. Chen, P. Cheng, W. Shi, D.-Z. Liao, S.-P. Yan and Z.-H. Jiang, *Chem. Eur. J.*, 2006, **12**, 149; (*g*) B. Zhao, X.-Y. Chen, Z. Chen, W. Shi, P. Cheng, S.-P. Yan and D.-Z. Liao, *Chem. Commun.*, 2009, 3113; (*h*) D. K. Singha and P. Mahata, *Inorg. Chem.*, 2015, **54**, 6373; (*i*) Z. Chen, Y. Sun, L. Zhang, D. Sun, F. Liu, Q. Meng, R. Wang and D. Sun, *Chem. Commun.*, 2013, **49**, 11557; (*j*) B. Liu, W.-P. Wu, L. Hou and Y.-Y. Wang, *Chem. Commun.*, 2014, **50**, 8731; (*k*) L. Wen, X. Zheng, K. Lv, C. Wang and X. Xu, *Inorg. Chem.*, 2015, **54**, 7133; (*l*) R.-M. Wen, S.-D. Han, G.-J. Ren, Z. Chang, Y.-W. Li and X.-H. Bu, *Dalton Trans.*, 2015, **44**, 10914.

23 V. A. Blatov, A. P. Shevchenko and D. M. Proserpio, *Cryst. Growth Des.*, 2014, **14**, 3576.

24 G.-S. Yang, Y.-Q. Lan, H.-Y. Zang, K.-Z. Shao, X.-L. Wang, Z.-M. Su and C.-J. Jiang, *CrystEngComm*, 2009, **11**, 274.

25 B. Adhikari, G. Palui and A. Banerjee, *Soft Matter*, 2009, **5**, 3452.

26 (*a*) G. Crini, *Bioresour. Technol.*, 2006, **97**, 1061; (*b*) Q.-R. Fang, G.-S. Zhu, Z. Jin, Y.-Y. Ji, J.-W. Ye, M. Xue, H. Yang, Y. Wang and S.-L. Qiu, *Angew. Chem., Int. Ed.*, 2007, **46**, 6638.

27 (*a*) A. A. Adeyemo, I. O. Adeoye and O. S. Bello, *Toxicol. Environ. Chem.*, 2012, **94**, 1846; (*b*) E. Haque, V. Lo, A. I. Minett, A. T. Harris and T. L. Church, *J. Mater. Chem. A*, 2014, **2**, 193; (*c*) M. Du, X. Wang, M. Chen, C.-P. Li, J.-Y. Tian, Z.-W. Wang and C.-S. Liu, *Chem. Eur. J.*, 2015, **21**, 9713.

28 (*a*) J. Jia, F. Sun, T. Borjigin, H. Ren, T. Zhang, Z. Bian, L. Gao and G. Zhu, *Chem. Commun.*, 2012, **48**, 6010; (*b*) J. A. Greathouse, N. W. Ockwig, L. J. Criscenti, T. R. Guilinger, P. Pohl and M. D. Allendorf, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12621; (*c*) F.-Y. Yi, J.-P. Li, D. Wu and Z.-M. Sun, *Chem. Eur. J.*, 2015, **21**, 11475.

29 (*a*) S. Deng and Y. P. Ting, *Environ. Sci. Technol.*, 2005, **39**, 8490; (*b*) B. A. Manning, J. R. Kiser, H. Kwon and S. R. Kanel, *Environ. Sci. Technol.*, 2007, **41**, 586; (*c*) H.-K. Zhang, H. Lu, J. Wang, J.-T. Zhou and M. Sui, *Environ. Sci. Technol.*, 2014, **48**, 12876.

30 (*a*) G. M. Sheldrick, SHELXS-97, *Programs for X-ray Crystal Structure Solution*, University of Göttingen, Germany, 1997; (*b*) G. M. Sheldrick, SHELXL-97, *Programs for X-ray Crystal Structure Refinement*, University of Göttingen, Germany, 1997; (*c*) L. J. Farrugia, WINGX, *A Windows Program for*

Crystal Structure Analysis, University of Glasgow, UK, 1988;
(*d*) A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

A multifunctional microporous anionic metal–organic framework for column-chromatographic dye separation and selective detection and adsorption of Cr^{3+}

Shu-Ran Zhang,[a] Jing Li,[a] Dong-Ying Du,*[a] Jun-Sheng Qin,[a] Shun-Li Li,[b] Wen-Wen He,[a] Zhong-Min Su*[a] and Ya-Qian Lan* [a,b]

[a] Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, Jilin, People's Republic of China. E-mail: zmsu@nenu.edu.cn

[b] Jiangsu Key Laboratory of Biofunctional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, Jiangsu, People's Republic of China. E-mail: yqlan@njnu.edu.cn

NENU-505 exhibits selective absorption toward cationic dyes and can potentially serve as a column-chromatographic filler for the separation of dye molecules. For the first time, an anionic MOF **NENU-505** has been exploited for selectively sensing and adsorbing Cr^{3+} in a high efficiency and low consumption mode due to the presence of $[(CH_3)_2NH_2]^+$ cations and carboxyl groups.