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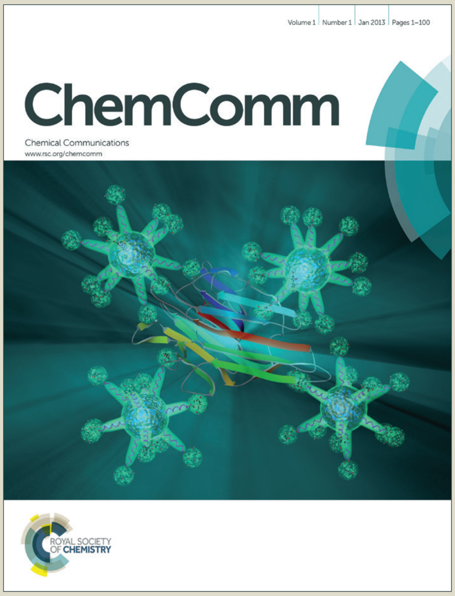

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High-performance "sweeper" for toxic cationic herbicides: an anionic metal–organic framework with tetrapodal cage

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Abstract: This paper reports a novel metal-organic framework exhibiting an excellent performance in adsorbing small toxic cationic herbicides, i.e. methyl viologen and diquat, with large adsorption capacities and ultratrace residue level. To the best of our knowledge, this is the first example of high-performance MOFs in trapping toxic cationic herbicides.

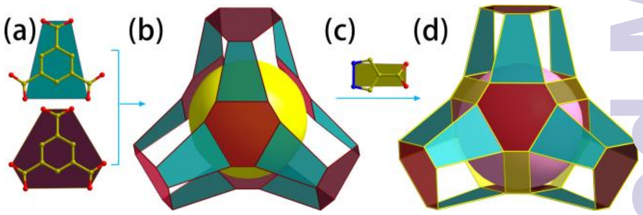

Fig. 1 The rational design of the tetrapodal cage in NKU-**101**. (a) The configuration of BTC-1 and BTC-2, (b) the cage built from BTC, (c) the coordination role of PyC and (d) the tetrapodal cage with large volume and small aperture.

Organic cationic pesticides, such as herbicides, insecticides, fungicides and sprout inhibitors, have been widely used in modern agriculture to raise the output. However, their long-termed residual accumulation in ecosystem has brought about serious environmental problems and food safety issues due to their intrinsic high toxicity and non-degradability,[1] which has become one key obstacle to modern green living and inspires scientists to seek for effective technical method to overcome it. Compared with distillation, membrane extraction and electrolysis, adsorption is a simple but feasible technique to treat and recover organic cationic herbicides-containing waste water,[2] relying closely on the adsorbent nature. The traditional adsorbents, e.g. activated carbon and zeolites, though have been widely applied in the recovery of herbicides pollutants, expose many deficiencies in their active site loadings, adsorption capacities, selectivity, and so on, which however is difficult to be improved because of their poor modifiability and therefore inspires the development of new adsorbent materials.[3] Presently, it still remains a great challenge to develop a high-performance adsorbent for collecting herbicides pollutants.

Metal–organic frameworks (MOFs) are a class of crystalline open structures constructed by metal ions (or clusters) as nodes and organic ligands as linkers.[4] It has been well established in literatures that MOFs generally exhibit superior performance over conventional adsorbents in selectively adsorbing targeted pollutants, including gas, metal ions, dyes, metal-containing species, organic explosive substance, and so on,[5] due to their intrinsic traits such as tunable porosities, exposed active sites and heterogeneous surface.[6] However, this class of materials has been surprisingly less explored in removing herbicides, especially in consideration of many reported public health and food safety events caused by herbicides spill and residue. A good herbicides adsorbent should possess some crucial characteristics, including large treatment capability, high selectivity and low residue level. The advantages of MOFs mentioned above enable them to be promising candidate of herbicides adsorbents *via* rational design of assembly composition and structure to meet the strict requirements of herbicides adsorption, which has been suggested by some successful utilizations of methyl viologen as structure-directing agents to construct porous MOFs.[7] Motivated by these considerations, we try to extend our experienced construction of functional MOFs to the field of herbicides adsorption.

Herein, we report a novel three-dimensional (3D) Zn-MOF $[(CH_3CH_2)_2NH_2]_{1/2}[Zn(BTC)_{2/3}(PyC)_{1/4}]\cdot$solvent (denoted as NKU-**101**, NKU = Nankai University; H_2PyC = 4-pyrazolecarboxylic acid; H_3BTC = 1,3,5-benzenetricarboxylic acid, see Fig. 1 and Scheme S1), which performs excellent in adsorbing toxic herbicides, i.e. methyl viologen (MV) and diquat (DQ), with

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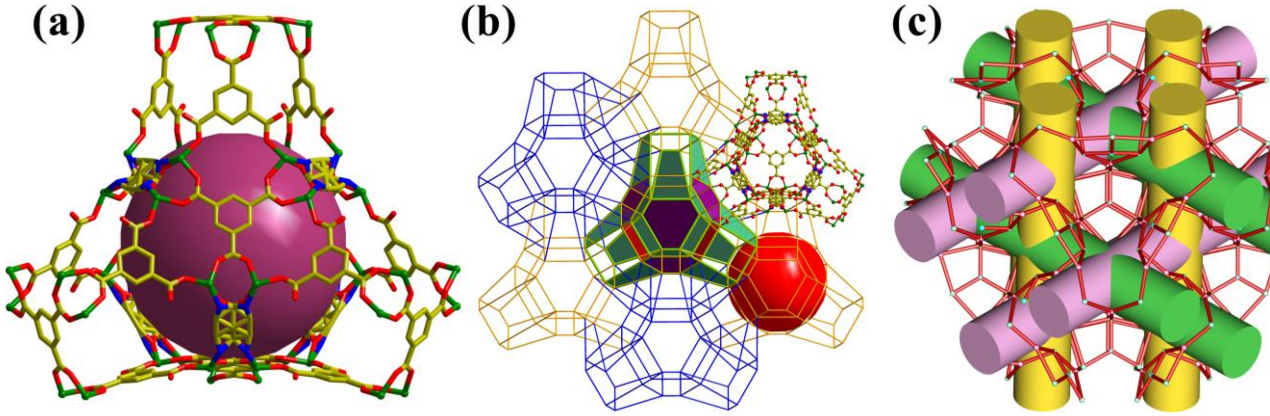

Fig. 2 The crystal structure of NKU-**101**. (a) The tetrapodal cage Zn$_{48}$(BTC-1)$_{12}$(BTC-2)$_8$(PyC)$_6$, (b) the packing of tetrapodal cages and (c) the 3D channels net running along *a*, *b*, and *c* directions.

large adsorption capacity (160 ± 5 and 200 ± 5 mg·g^{-1} for MV and DQ in alcohol solution, respectively) and an ultratrace residue (about 20 ppb and 10 ppb for MV and DQ, respectively) To the best of our knowledge, it is the first example of MOFs reported for efficient adsorption of toxic cationic herbicides, providing a potetinally useful material for dealing with pesticide pollutions and food safety issues.

X-Ray crystallographic analysis reveals that NKU-**101** crystallizes in the cubic space group I-43m and its asymmetric unit consists of one Zn(II) ion, a quarter of PyC^{2-} ligand, one-half μ$_4$-BTC^{3-} ligand (BTC-1) and one-sixth of another crystallographically independent μ$_6$-BTC^{3-} ligand (BTC-2). Each Zn(II) ion is located inside a tetrahedron geometry completed by three oxygen atoms from three BTC^{3-} ligands, and one nitrogen adjacent BTC-1 links up through six Zn(II) ions to form an inward face. Four such inward faces are further connected by six PyC^{2-} ligands and truncated by other four BTC-2 ligands to form a tetrapodal cage Zn$_{48}$(BTC-1)$_{12}$(BTC-2)$_8$(PyC)$_6$, featuring twelve rectangles apertures of 7 Å × 9 Å and large free void with an inner diameter of∼16 Å (D$_{max}$ = 24 Å) (Fig. 1d and Fig. 2a). As for the polyhedral packing of NKU-**101**, each tetrapodal cage was surrounded by eight neighbouring ones each by sharing one BTC-2 to generate a 3D extended open framework (Fig. 2b and Fig. S3) of a *bcu* network when considering the cage as one 8-connected node (Fig. S4). Besides the inner cavities of the cages, the extended network embraces a 3D intersecting channel system with a cross section of approximately 8 Å (Fig. 2c). Notably, all the uncoordinated oxygen atoms of BTC-1 are exposed toward the channel (Fig. S2), which facilitate its interaction with polar guests to be trapped. The framework of NKU-**101** is anionic, which is occupied by [(CH$_3$CH$_2$)$_2$NH$_2$]$^+$ ions and solvent molecules. The [(CH$_3$CH$_2$)$_2$NH$_2$]$^+$ ions in NKU-**101** originate from the decarbonylation of N,N-diethylformamide. However, the highly disorder nature of the guest molecules cannot be mapped by single crystal XRD.[8] The effective free volume is 65.9 % of the crystal volume (14663.6 Å^3 of the 22241.0 Å^3 unit /cell volume) calculated by the PLATON analysis after removing all of the guest molecules.[9] The gas adsorption experiments were performed to examine the permanent porosity of NKU-**101** (ESI S4, Fig. S8-S14). Topological analysis was carried out to get insight of the structure of NKU-**101**. By simplifying dinuclear Zn (II) as a 5-connected node and BTC-1 and BTC-2 ligands both as 3-connected nodes, the 3D framework of NKU-**101** can be viewed as a trinodal (3,3,5)-connected topology with a Schläfli symbol of (4·7^2)$_3$(4^2·6·7^5·9^2)$_3$(4^3) (Fig. S5).

Based on above structural analysis, three potential advantages of NKU-**101** used as adsorbent are summarized: 1) the mesoporous cage-based framework of NKU-**101** is restricted with small aperture, which not only endows the framework size-exclusion effect, but also delays the escaping of adsorbate from the cage;[10] 2) the countless uncoordinated oxygen atoms populating on the wall of channel provide sufficient adsorption active sites to interact with guests;[11] 3) the anionic framework endows NKU-**101** with a superior adsorption affinity toward positive pollutant.[12]

The MOFs performing well in dye adsorption usually feature large accessible cavity to accommodate dye molecules through channels or apertures.[13] Along this line of thought, the porous NKU-**101** should be capable of trapping certain guest molecule. Just as the most of reported MOFs, NKU-**101** is not stable in water and its crystal PXRD signals will vanish after 12 hours dipping in water (Fig. S15), due to the decomposition of crystal framework. Therefore, the sorption behaviors of NKU-**101** was investigated by soaking into the ethanol solution containing a variety of cationic, neutral and anionic dyes including Coumarin (CM), Sudan I (SD I), Rhodamine 6G (R6G), Methyl Orange (MO), Methylene Blue trihydrate (MB), Leucocrystal Violet (LV), Rhodamine B (RB), and Victoria Blue (VB) (Fig. S16). After 24 h at room temperature, the NKU-**101** crystal underwent observable colour change only in the solution of smaller cationic dyes MB, which unveils the preferred adsorption of NKU-**101** toward MB (Fig. 3a and Fig. S17-18). For precise comparison, the competitive adsorption of MB in the presence of other dyes was also monitored in methanol through UV-Vis spectroscopy. As shown in Fig. S19, after 24 h adsorption the absorption peak of MB around 655 nm is eliminated completely, while that of the other dyes remain unchanged. It is worth noting that the adsorption of MB occurs not only on the surface, but also inside the crystal, verified by the uniform dyeing throughout the whole crystal.

Evidently, the adsorption affinity toward MB lies on two structural traits of NKU-**101**: firstly, the anionic framework of NKU-**101** has strong electrostatic affinity toward cationic dyes; secondly, the cabined channel and aperture of NKU-**101** (8 Å) exclude the diffusion of larger cationic dyes into the inner cavity. Thus, as a result of the synergic effect of these two factors, only cationic dyes of smaller size, e.g. MB can be effectively collected from the solution of NKU-**101**.

Motivated by the selective adsorption of MB, we proceed to investigate the adsorption behaviors of NKU-**101** toward other small cationic organic compounds, e.g. some herbicides that persist as toxic pollutant in ecological environment. At present, the bioaccumulation of organic cationic methyl viologen (MV), diquat (DQ) (Fig. S20-S21) and many other related toxic herbicides widely used in modern agriculture have raised great hazards to the health of human beings.[14] Therefore, it is urgent to develop new adsorbents to sweep these toxic herbicides efficiently. Despite some studies on the adsorption of MV by MOFs were applied to construct functional supramolecular systems, less attention was paid on the adsorption behaviors of MOFs toward herbicides, especially from the environment protection point of view.[15] In light of the intrinsic adsorption properties of NKU-**101** solution (40 ppm)) and monitored through UV-Vis absorption spectra. Just as expected, both MV and DQ were effectively adsorbed by NKU-**101**, verified by the nearly complete elimination of their characteristic electron absorption peaks in the UV-Vis spectra of methanol solution after 48 h (Fig. 4 and Fig. S22).

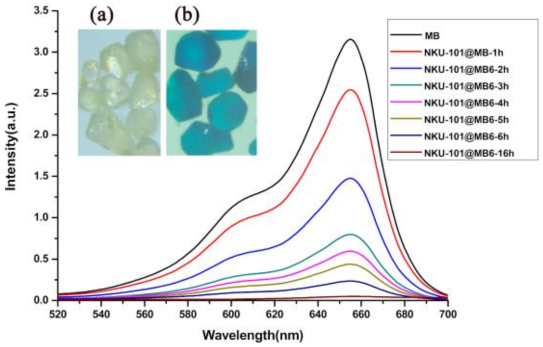

Fig. 3 Sequential UV/Vis spectral change of MB solutions upon adsorption by NKU-**101**. The inset photos represent the NKU-**101** before (a) and after (b) adsorption.

For practical application, the desirable adsorbent should meet two strict requirements: large adsorption capability and trace residue level, the data of which were accessible from the UV-Vis spectra and LC-MS/MS.

The adsorption capacity of NKU-**101** toward herbicides can be deduced from the dependence of saturate adsorption amount (q_e) on the initial concentration of adsorbate (c_0) according to Eqs. (S1).[16]

As shown in Fig. S23a and Fig. S24a, q_e approaches a plateau with increasing c_0 in the q_e-c_0 profile both for MV and DQ, which gives adsorption capacities of ca. 160 and 200 mg·g^{-1} for MV (c_0 = 0.8 mg·ml^{-1}) and DQ (c_0 = 1.0 mg·ml^{-1}), respectively. The residue concentration of adsorbate is of practical significance, which is often evaluated by the adsorption performance of adsorbent in low concentration adsorbate solution. Codex Alimentarius Commission has set the maximum level of MV and DQ contamination in food (200 ppb).[17] Here, the residue concentration of MV and DQ upon sorption was measured by LC-MS/MS analysis. In detail, 5 mg NKU-**101** was added in 5 ml ethanol solution of MV and DQ (10 ppm) respectively. After 48 h, the residual concentration of MV and DQ, deduced from the standard curve of concentration-peak area of LC-MS/MS, can be about 20 ppb and 10 ppb, respectively (Fig. S25 and Fig. S26), far lower than the criterion of 200 ppb requested by the Codex Alimentarius Commission. [17]

Furthermore, the adsorption efficiency and capacities of NKU-**101** were compared with those of activated carbon and 10X molecular sieve of a similar porosity size. These data were recorded in Fig. S27-S28 and Table S1. The experimental results showed that NKU-**101** is one promising adsorption material for MV and DQ in ethanol solution.

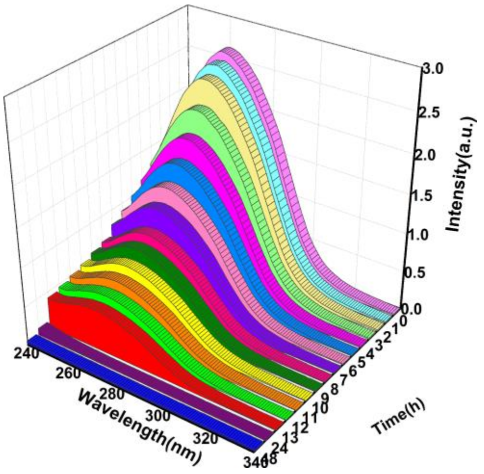

Fig. 4 Sequential UV/Vis spectral change of MV solutions upon adsorption by NKU-**101**.

In order to characterize the adsorption behaviors of NKU-**101**, the kinetic relationship between the concentration of adsorbent (c_t) and adsorption time (t) was investigated based on UV-Vis absorption data. The theoretical fitting on the profile of c_t-t was performed both in pseudo-first-order kinetic model (Eqs. (S2a)) and the pseudo-second-order model (Eqs. (S2b)).[16] Evidently, as indicated in Fig. S23b and Fig. S24b, S29-30, the fitting based on pseudo-second-order kinetic model agrees much better with experimental data than that on first-order model, evaluated by comparing the fitting coefficient as well as predicted q_e collected in Table S2.

The recyclability of NKU-**101** is also vital for its practical application. It is revealed that the herbicide molecules adsorbed by NKU-**101** can be gradually released by exchanging with other inorganic or organic cations in DMF. Here, as an example, the release of herbicides from NKU-**101** was carried out in the presence of NaCl in DMF solution. After exchanged for 24 h, the adsorbent sample was collected and reused directly for guest adsorption. Five times repeat of such adsorption–release cycle finds minimal increasing of herbicides residue (Fig. S31), which could be abated by prolonging exchange time, indicative of good recyclability of NKU-**101** in herbicides adsorption.

In summary, a novel cage-based MOF, NKU-**101**, has been rationally synthesized. Single crystal structure analysis reveals a cabined 3D channel net and aperture (7 Å × 9 Å) to the large cage ($D_{\max}$ = 24 Å), which in combination with its positive framework, accounts for its selective adsorption of small cationic herbicides, such as MV and DQ. The excellent adsorption property of NKU-**101** was manifested by its higher adsorption capacity toward MV (160 ± 5 mg·g^{-1}) and DQ (200 ± 5 mg·g^{-1}) than that of zeolite and activated carbon, as well as the trace residual level of MV (< 20 ppb) and DQ (< 10 ppb). Furthermore, the toxic herbicides uptake is reversible by being exchanged with metal cationic ions and the recollected NKU-**101** exhibits good adsorption recyclability, which extends the application range of MOF materials to the field of toxic herbicides-treatment.

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