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# Multivariable Sieving and Hierarchical Recognition for Organic Toxics in Nonhomogeneous Channel of MOFs

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## SUMMARY

Developing optimal molecular sieves, able to perform multivariable aqueous sieving of diverse harmful organics, is of practical significance in chemistry and environmental protection. Current porous sieves however can only recognize organics based on two variables (charge and size), which is far from enough due to the multi-complexity of the toxics. Herein, we report a series of isostructural metal-organic frameworks, MIL-140s [ZrO(O<sub>2</sub>C-R-CO<sub>2</sub>)], with triangular hydrophobic channels for the separation of dyes and practical toxics such as high carcinogenic pesticides and persistent organic pollutants (POPs). Theoretical calculations demonstrate the key role of nonhomogeneous electron distribution within channels for recognition of various guest molecules. Multivariable sieving for both dyes and practical toxics has been validated by both separation experiments and DFT calculation. The sieving mechanisms are revealed through presenting an outside-in theoretical model, hierarchical recognition, by the regulation of surface charge, pore size and potential energy surface of MIL-140s.

Multivariable sieving, hierarchical recognition, heterogeneous channels, metal-organic frameworks

## INTRODUCTION

Separation and purification are distinctly important in analytical chemistry and in diverse industrial processes.<sup>1</sup> Large quantities of artificial organic compounds such as persistent organic pollutants (POPs), pesticides, medicines, and dyes are produced annually, which are significant threats to global water resources. Therefore both green chemistry and environmental protection call for isolation and/or reuse of toxic organic compounds in liquid phase based on separation processes.<sup>2</sup> The most commonly used separation technologies at the industrial level such as liquid-liquid extraction and distillation lead to increased cost and vast energy consumption, raising toxicity issues due to the employment of organic solvents in large volumes.<sup>3</sup> Porous adsorbents are promising for the isolation of various toxics via adsorbent/membrane-based sieving and purification.<sup>4</sup> Active charcoal, zeolites and resins are commercial benchmark materials currently used for molecular sieving. However, these adsorbents are far from recognizing different organic molecules efficiently due to their lack of contrivable opening pore size, the existence of pore size gaps and shortage in well-designed pore chemistry.

Tremendous varieties of organics lead to multiple physical and chemical variates such as charge, size, shape, polarity and aromaticity, and this complex scenario increases the difficulty to separate specific substrates. Designing porous materials with refined tunable porosity,<sup>5-11</sup> appropriate surface charge properties,<sup>12, 13</sup> specific functionalization<sup>14-20</sup> and excellent water stability<sup>21-23</sup> is envisioned to realize multivariate sieving of a wide variety of organics. New advanced porous materials such as Metal-Organic Frameworks (MOFs), covalent organic polymers (COPs), porous organic cages and porous polymers have been considered recently as affordable alternatives in this direction. Zhao *et al.* and Li *et al.* reported size- and/or charge-selective capture of dyes by the use of MOFs with distinct pore sizes.<sup>24, 25</sup> However, the corresponding experiments were performed in organic solvent, which hampers the practical use of these MOFs in aqueous solution. Very recently, Ghosh *et al.* reported a base-resistant ionic MOF as an ion-exchange sorbent for dyes in water.<sup>26</sup> Porous polymers such as P-CDP and PFCMP-o have been shown to only remove contaminants rather than their isolation owing to the large size gaps of pores.<sup>27, 28</sup> These cases are limited in terms of ultrafine tuning of sieving "gates" at the Angström level, which lowers the precision of size separation. Nevertheless, COP-99, a porous network polymer, has been shown recently to realize charge- and size- based aqueous separation of water-soluble organics.<sup>29</sup>

Moreover, several studies reported the separation of organics by different MOFs involving a thermodynamic conformational or kinetics-driven separation and/or size exclusion.<sup>30</sup> However, these adsorptive separations can only recognize organics based on two variates (charge and size) in aqueous phase and other recognition is rarely realized as the weak interaction can be affected by water in channel.<sup>31-34</sup> Therefore there is a need to expand the list of adsorbents to achieve multivariable sieving of organics besides the charge and size-like mechanisms achieved so far. Furthermore, most of the previous studies have been devoted to explore charged dyes while toxic molecules encountered in real conditions such as high carcinogenic multivariable toxics, e.g. persistent organic pollutants (POPs) and pesticides, have not been investigated so far.

To target in the multivariate sieving of a broader variety of toxic molecules, the molecular sieves should combine different recognition mechanisms and specific sites are needed to interact with toxic molecules. Inspired by multivariable recognition of ligands in biology through multiple NCIs, involving dispersed variations of electromagnetic interactions, we hypothesized similar artificial channels within MOFs might interact with toxic molecules and separate different mixtures.<sup>35</sup> However, in the field of porous molecular sieves, only charge interactions are widely used for charge-based separation in charged frameworks,<sup>26</sup> and no one applied other NCIs such as various  $\pi$ -effects in the field of aqueous toxics sieving.<sup>36</sup> In this regard, we synthesized a series of isostructural MIL-140s and examined their sieving performance for both dye stuff and various practical toxics. We found that these MOFs can not only accomplish charge- and size-based separation of charged dye mixtures, but also realize isolation of a wider range of practical toxics such as POPs and pesticides with very high separation effect. To reveal the separation mechanisms, an

outside-in their theoretical model, hierarchical recognition, is presented: (i) the surface charge state, which acts as a first barrier for charged molecules through the external surface of the porous materials, (ii) the sieving “gate”, which works through the discrimination of organics of different dimensions via a size exclusion effect (**Scheme 1a**) and (iii) NClS (NClS stands for Non-Covalent Interactions) with attractive sites present at the pore wall, which is similar to ligand recognition in transporters and based on non-regular electronic distribution created by either a non-regular shape of the porosity or by the incorporation of functional groups (see **Scheme 1b** and **c**). Both the separation experiments and theoretical calculation demonstrate the key role of hierarchical recognition for multivariable sieving.

## RESULTS AND DISCUSSION

### Structural Design and Characterization

In order to design continuous water-stable triangular channels as well as control the potential energy surface of pores by regulating the length and chemistry of ligands, an isorecticular series of water stable microporous Zr dicarboxylate MOFs with triangular pores, namely MIL-140s or  $[\text{ZrO}(\text{O}_2\text{C-R-CO}_2)]$  (MIL stands for Materials from Institut Lavoisier; R=organic spacer) has been selected for the systematic sieving performances of complex toxic molecules through the combination of advanced experimental and computational approaches.<sup>37</sup> MIL-140s differ from the family of most versatile Zr-based UiO series MOFs (UiO stands for University of Oslo) in water stability, it is admitted that the extended analog of UiO-66, such as UiO-67 or  $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{O}_2\text{CC}_{12}\text{H}_8\text{CO}_2)_{12}]$ , was degradable under humidity.<sup>38</sup> The current set of MIL-140s solids was completed through the design of either first examples of functionalized analogues of MIL-140C (MIL-140C-2NO<sub>2</sub>, -2CO<sub>2</sub>H) or new larger pores candidates bearing longer organic linkers (MIL-140E and MIL-140F). The synthesis of MIL-140s is based on the solvothermal reaction of  $\text{ZrCl}_4$  and dicarboxylic linkers. This involves here 1,4-H<sub>2</sub>BDC (1,4-benzenedicarboxylic acid), 2,6-H<sub>2</sub>NDC (2,6-naphthalenedicarboxylic acid), 4,4'-H<sub>2</sub>BPDC (4,4'-biphenyldicarboxylic acid), previously used to produce MIL-140A, B and C, as well as new linkers such as H<sub>2</sub>BPDC-2NO<sub>2</sub> (2,2'-Dinitrophenyl-4,4'-dicarboxylic acid), H<sub>2</sub>BPDC-2CO<sub>2</sub>H (2,2'-Dicarboxylbiphenyl-4,4'-dicarboxylic acid), 4,4'-H<sub>2</sub>SDC (4,4'-Stilbenedicarboxylic acid) and 4,4'-H<sub>2</sub>EDC (4,4'-Ethyne-1,2-diylidibenzoic acid) that were employed for the first time to produce analogues of the MIL-140 structure type. The so-obtained MIL-140s with a formula  $[\text{ZrO}(\text{O}_2\text{C-R-CO}_2)]$  are denoted as MIL-140A (R=C<sub>6</sub>H<sub>4</sub>), B (R=C<sub>10</sub>H<sub>6</sub>), C (R=C<sub>12</sub>H<sub>8</sub>), C-2CO<sub>2</sub>H (R=(C<sub>14</sub>O<sub>4</sub>H<sub>8</sub>)<sub>x</sub>(C<sub>12</sub>H<sub>8</sub>)<sub>1-x</sub>), C-2NO<sub>2</sub> (R=(C<sub>12</sub>N<sub>2</sub>O<sub>4</sub>H<sub>6</sub>)<sub>x</sub>(C<sub>12</sub>H<sub>8</sub>)<sub>1-x</sub>), E (R=C<sub>14</sub>H<sub>10</sub>) and F (R=C<sub>14</sub>H<sub>8</sub>) (see **Figure 1D** and **Figure S11-S14**).

A computational assisted strategy based on the interplay between density functional theory (DFT) geometry optimizations and X-Ray Powder Diffraction data (XRPD) were considered to propose structure models for the newly synthesized MOFs with the corresponding cell parameters reported in **Table S1**. As shown in **Figure 1**, all MIL-140s crystallize in the monoclinic space group  $C2/c$  ( $n^\circ 15$ ) (see **Table S1**, **Figure S8-S10** and **Data S1-S4**), and they are built from the infinite edge sharing Zr-oxide chains bridged by dicarboxylic ligands. The Zr atoms are seven-coordinated—three  $\mu_3$ -O oxygen atoms, and four oxygen atoms from the dicarboxylic ligands—all  $\text{Zr}^{4+}$  ions have the same coordinated environment (**Figure 1C**). This delimits one-dimensional triangular channels of free apertures, from 3.2 to 7.2 Å when standing from MIL-140A to MIL-140F along the *c* axis (see **Figure S1** and **Table S2**). Thus, these MOFs possess tunable pore sizes to sieve organics with a wide variety of dimensions. And on the other hand, the arrangement mode of ligand on pore wall indicates that these MOFs allow flipping of the benzene rings (see **Figure 1A** and **B**). The experimental BET areas for MIL-140 (A, B, C, E, F) range from 390 (20) to 1320 (20)  $\text{m}^2\cdot\text{g}^{-1}$  and these values are in good agreement with the theoretical N<sub>2</sub>-accessible area calculated from the crystal structures as summarized in **Table S2** and **Figure S15**. In the case of partially substituted MIL-140C-2CO<sub>2</sub>H (with BPDC-2CO<sub>2</sub>H of 16.7 % replacing BPDC in the framework) and MIL-140C-2NO<sub>2</sub> (with BPDC-2NO<sub>2</sub> of 22.2 % replacing BPDC in the framework, see **Figure S2** and **S3**), the lower experimental BET areas and pore volumes compared to MIL-140C are attributed to the steric hindrance created by the presence of the functional groups.



To investigate the chemical properties of the channels, we further analysed the electronic distribution of MIL-140s. We found that the channels of MIL-140s possess particular electronic distribution on its pore wall. As revealed in **Figure 1E** and **Figure S4**, in the sectional view, yellow-to-cyan colors indicate high-to-low electron densities, MIL-140s present two distinct electronic regions in the edges of the triangular channels: i.e. an electron-poor zone A and electron-rich zone B surrounding the ligands arranged perpendicular and parallel to the channel respectively. The introduction of  $-\text{CO}_2\text{H}$  and  $-\text{NO}_2$  groups in MIL-140C-2 $\text{CO}_2\text{H}$  and MIL-140C-2 $\text{NO}_2$  act as a subtle modifier of the electronic distribution in the pore wall and afford extra electron rich region (see **Figure 1E**). The electronic distribution calculation reveal that MIL-140s have heterogeneous potential energy surface owing to either the non-regular shape of the porosity and or the incorporation of functional groups.

### Charge and Size-based Separation of Dye Mixtures

It is known that hydrothermally stable MIL-101(Cr) or  $[\text{Cr}_3(\mu_3\text{-O})(\text{OH})(\text{H}_2\text{O})_2(\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2)_3]\cdot n\text{H}_2\text{O}$  was intensively studied for various organic adsorption due to its large surface areas and mesoporous cages accessible through large microporous windows (see **Figure S15** and **S16**). MIL-101(Cr)s were thus investigated here for the sake of comparison and understanding the importance of pore architecture for multivariable molecular sieving.<sup>39</sup> Experimental BET areas of MIL-101(Cr)s solids vary from 1520 to 3250  $\text{m}^2\cdot\text{g}^{-1}$  (see Table S4) and their pore sizes are over 2.5 nm, accessible through large microporous windows. In order to reveal the nature of the external surface chemistry, zeta potentials of MIL-140s and MIL-101(Cr)s were first examined as a function of pH. As shown in **Figure S6**, under neutral conditions,  $\text{pH}=6.8$ , which corresponds typically to the value of the solutions to be purified, MIL-140s solids all exhibit a negative zeta potential a priori in favor of repulsion of negatively charged organics out of the channel. MIL-101(Cr) exhibits on the contrary a positively charged zeta potential. Whereas, the functionalized MIL-101(Cr)s exhibit negatively charged surface at around pH 6.8, in the order of MIL-101(Cr)- $\text{NO}_2$  (only -10 mV)>MIL-101(Cr)- $\text{CO}_2\text{H}$ >MIL-101(Cr)- $\text{SO}_3\text{H}$ , which is consistent with decreasing  $\text{pK}_a$  values and thus increasing acidic character (see **table S3** and **Figure S5**). These results suggest that a fine-tuning of the nature of the functional groups allows a control of the surface charge properties.

Following the surface charge characterization, we investigated the relatively easy charge- and size-based separation in water. Four model organics were first selected including an anionic Methyl Orange (MO, 5.3 Å) and three cationic organics: methylene blue (MB, 4.7 Å), Nile blue (NB, 6.1 Å) and Rhodamine 6G (R6G, 10.1 Å) (see **Figure 2C**). We selected only the positively charged MIL-101(Cr) and the negatively charged MIL-101(Cr)- $\text{SO}_3\text{H}$  as representative candidates to study the separation performances. As shown in **Figure 2A**, MIL-101(Cr)s only realize charge-based separation. The positively charged MIL-101(Cr) adsorbs negative MO almost exclusively, as previously reported,<sup>40</sup> while the negatively charged MIL-101(Cr)- $\text{SO}_3\text{H}$  shows an opposite trend extracting almost only the MB from the solution. As shown in **Figure 2B**, size exclusion-based separation for NB and R6G was however not successful, the mesoporous MIL-101(Cr)- $\text{SO}_3\text{H}$  allows both small and large organics to pass through the pores, while MIL-101(Cr) shows weak adsorption for both NB and R6G. These results undoubtedly demonstrate the impact of chemical groups such as  $-\text{SO}_3\text{H}$  acidic groups attributed to the strong NCIs that occur between the ionized  $-\text{SO}_3^-$  moieties and the positively charged molecules, and size sieving calls for ultrafine regulation of channel size.

MIL-140s were then investigated for both charge- and size-based separation (see **Figure S17** and **S18**). As shown in **Figure 2A**, MIL-140s show a preferred adsorption for the positive MB over the negative MO as a result of their negative surface charge (see **Figure S6**). The separation results show that channel size affects the separation performance (see **Figure 1D** and **Figure S7**). MIL-140A (3.2 Å) precludes from the penetration of MB (4.7 Å) through its channels. When one considers MIL-140F with the largest pore size, the adsorption capacity of organics increased, with however a limited selectivity toward MO. Noteworthy, other MIL-140s can realize a selective adsorption of MB due to the charge barrier. Specifically, MIL-140C partially substituted with BPDC linker bearing  $-\text{CO}_2\text{H}$  and  $-\text{NO}_2$  groups allow a complete selective adsorption of MB due to the much higher electron

density of the pore walls, which is evidenced in **Figure 1E**. These results indicate that the electronic distribution in pores markedly influences the molecular separation of charged dyes. To further reveal the mechanism of MO/MB separation in MIL-140s, we conducted DFT calculations to evaluate the adsorption induced structural deformation of MOF ligands/guest molecules upon adsorption in the confined pores. DFT calculations showed that MB is arranged along the channel tightly and parallel to the confined pore wall with a lower degree of freedom and at the vicinity of the functional groups. The DFT calculations further evidence that the presence of guest molecules induce a significant reorientation of the phenyl rings, which emphasizes that the MOF adapts its geometry to accommodate the organics (see **Figure 2D** and **E**). The major structural changes of the MOF ligands we have observed can be characterized by either a twist of aromatic rings around the central C-C bond or by a ripple effects resulting locally to skewed ligands. As depicted in **Figure S19**, we can see that in the presence of MB: i) aromatic rings of the biphenyl ligands in MIL-140-C-2CO<sub>2</sub>H are mutually rotated leading to an ~55° dihedral angle change compared to their pristine state, and ii) the phenyl rings are skewed into convex or concave shapes to best accommodate the MB molecules within the pores. For size exclusion-based sieving, we investigated the sieving performance of NB/R6G in MIL-140s. As shown in **Figure 2B**, NB (6.1 Å) is easier to be adsorbed by MIL-140s than R6G (10.1 Å) due to its lower dimension and the limited channel size. Typically, MIL-140s, except for MIL-140A (smallest pore diameter) and MIL-140F (largest pore diameter), allow an efficient separation of the organics. The preferential DFT-optimized geometry of NB in MIL-140E is illustrated in **Figure 2F** and it emphasizes a significant guest-induced distortion of the MIL-140E framework caused by the  $\pi$ - $\pi$  interactions between NB and the MOF framework. The adsorption capacities MOFs for dye molecules are highly related to the channel size and pore environment, as analysed above (see **Figure S28-S31** and **Table S4-S5**). To further understand the importance of NCIs in these separation experiments, we conducted similar separation of MB/MO with MIL-140C and MIL-140-C-2NO<sub>2</sub> in ethanol. As shown in **Figure S20**, all of these MOFs become invalid for separation of MB/MO mixtures. This results indicate that organic solvents obstruct NCIs between guest molecules and pore wall.

### Multivariable Sieving of Pesticides and POPs

The above mentioned dyes are model molecules. On the other hand, charge and size are the two most common variates, which cannot satisfy the molecular sieving of a broader range of organics. The more frequent representative toxics such as pesticides and polycyclic aromatic hydrocarbons (PAHs), which have potential carcinogenicity and mutagenicity, call for a careful separation and recovery. The excellent separation results for charge and size encouraged us to further evaluate the sieving performance of these practical toxics in water. We therefore studied the isolation performance for pesticides in water of MIL-140s, and compared their performances with representative water-stable MIL-101(Cr) and MIL-101(Cr)-SO<sub>3</sub>H (3-D pores), as well as benchmark porous solids such as MCM-41 and activated charcoals. As shown in **Figure 3A**, three representative pesticides: paraquat (5.5 Å), difenzoquat (6.6 Å) and clopyralid (7.4 Å) were selected. As shown in their molecular structure and electrostatic potentials, these organics have similar sizes but differ in chemical properties, thus allowing to explore the influence of the NCIs-based recognition besides size sieving.

Separation experiments of paraquat/difenzoquat are firstly performed. As shown in **Figure 3B**, the separation of paraquat and difenzoquat is hardly achieved using MCM-41 and porous activated charcoal. These results indicates that MCM-41 and porous activated charcoal have equivalent affinities toward both paraquat and difenzoquat. Positively charged MIL-101(Cr) rejecting cationic paraquat and difenzoquat, while negatively charged MIL-101(Cr)-SO<sub>3</sub>H adsorbing both paraquat and difenzoquat. All above-mentioned porous materials thus fail in multivariable sieving toward new variables. MIL-140s on the contrary exhibit multivariable recognition based on the preferential NCIs. As the two positive pesticides exhibit almost similar dimensions (5.5 Å and 6.6 Å respectively), the former two levels of recognition, namely surface charge barrier and "sieving gate", are not applicable. We even found that difenzoquat was preferentially extracted although it possesses 1 Å larger size than paraquat (**Figure 3B**). At equilibrium, separation factor between a preferred toxic A and a lesser adsorbed toxic B is defined as  $(y_A/y_B)/(x_A/x_B)$ , in

which  $y$  and  $x$  are the mole fractions in the adsorbed phase and the solution respectively. A former study revealed that MIL-140C exhibited only a low separation factor around 2.5 for isolation of hydroquinone and catechol from water.<sup>41</sup> In the present study, MIL-140C-2CO<sub>2</sub>H and MIL-140C-2NO<sub>2</sub> exhibit on the contrary extremely high separation factors for paraquat and difenzoquat (**Figure 3C**).

We further selected MIL-140C-2CO<sub>2</sub>H as a representative adsorbent to investigate the origin of the NCIs-based recognition by molecular simulations. Typically, the DFT-optimized geometries for both the empty and the guest loaded MIL-140C-2CO<sub>2</sub>H were then considered to evaluate the electronic density fluctuations ( $\Delta n_{\text{int}}$ ) upon adsorption using the formula:  $\Delta n_{\text{int}} = n_{\text{molecule@MOF}} - (n_{\text{MOF}} + n_{\text{molecule}})$ . From the analysis of such a 3-D electron density map of MIL-140C-2CO<sub>2</sub>H loaded with difenzoquat, we noticed a significant charge transfer between the MOF and the guest that occurs mainly in the vicinity of the cations (see **Figure 3D**). These calculations reveal that the channel undergoes a higher deformation upon adsorption of difenzoquat resulting from a reorientation of the phenyl rings that tends to optimize the interactions between difenzoquat and the pore wall. The DFT simulation also reveal that the aromatic rings of the confined difenzoquat molecule freely rotates with respect to the central pyrazol node (see **Figure S21**). As shown in **Figure 3E**, the phenyl rings of the difenzoquat and the MOF pore wall interact in a displaced-face-to-face or edge-to-face configurations, which is an optimal configuration for  $\pi$ - $\pi$  interaction. DFT simulation also reveals that electron-deficient -CH<sub>3</sub> of difenzoquat points to electron-rich -CO<sub>2</sub>H of the pore wall after interaction. The difenzoquat can also interact with phenyl rings via the cation- $\pi$  interaction when there is no -CO<sub>2</sub>H in the pores according to previous research in chemical recognitions.<sup>42</sup> On the other hand, the simulation results did not show obvious configuration change for MIL-140C-2CO<sub>2</sub>H enclosed with linear paraquat, which indicates the interaction between heterocyclic and pore wall is weak.

We further conducted the separation experiments of heterocyclic toxics such as paraquat and clopyralid. Clopyralid possesses indeed an electron-rich -CO<sub>2</sub>H group, and a "σ-hole" near the Cl moieties (**Figure 3A**).<sup>43</sup> Thus these two molecules not only differ in terms of dimensions (paraquat; 5.5 Å and clopyralid; 7.4 Å) but also in electronic density distribution due to the presence of different functional groups. As shown in **Figure 4A**, the blue and red blocks represent paraquat and clopyralid are preferentially adsorbed respectively. Clopyralid is 2 Å larger than paraquat, which leads to its lower uptake when the pore size is small. The sieving results show that MIL-140A (3.2 Å) repulses both clopyralid and paraquat. MIL-140B and MIL-140C capture more paraquat, with a separation factor of 17.6 and 11.4 respectively (**Figure 4B**). These results show very high correlation with the molecule sizes, small paraquat is preferentially extracted. When the channel size increases, more clopyralid can be extracted in MIL-140E and MIL-140F, with a separation factor of 2.2 and 6.9 respectively (**Figure 4B**). We also observed that -CO<sub>2</sub>H and -NO<sub>2</sub> decorated MOFs show opposite separation results with MIL-140C. To evaluate the interaction mechanism, DFT calculation is conducted with MIL-140C-2CO<sub>2</sub>H containing clopyralid. DFT calculation reveals that the adsorption of clopyralid in the MIL-140C-2CO<sub>2</sub>H induces a shift of electron density distributions near -CO<sub>2</sub>H and -Cl, and we can also observe a rotation of the phenyl ring and a slight deformation of the framework (**Figure 4C**). The formation of hydrogen-bonds between -CO<sub>2</sub>H groups from the pore wall and the -CO<sub>2</sub>H function of the clopyralid illustrates the strong host/guest interactions resulting into a significant charge transfer as depicted in **Figure 4D**. All above-mentioned separation results show that MIL-140s can accomplish the multivariable sieving of two heterocyclic organics based on the competition between size effect and NCIs, which means that we can selectively extract one organic from the mixture according to our requirements. As a contrast, porous activated charcoal shows a high but non selective uptake for these heterocyclic organics while MCM-41 can only extract paraquat from the mixture. Positively surface charged MIL-101(Cr) extracts very few of these two heterocyclic molecules, while MIL-101(Cr)-SO<sub>3</sub>H adsorbed both the paraquat and clopyralid.

We then extended the study to the sieving of nonpolar PAH, such as pyrene. Their separation from charged organics in water is topical, however none of the commercial

sieves such as porous activated charcoal are able to make it. According to the former results and dimensions of the toxics, MIL-140B is selected to conduct the separation of pyrene/MO and pyrene/R6G. As shown in **Figure S22**, the separation results show that MIL-140B can extract pyrene from the aqueous solution of both MO and R6G with high separation factor (147 and 231 respectively). To intuitively observe the adsorption of pyrene with MIL-140B, powder of MIL-140B was directly added in the cloudy mixture of pyrene and water. As shown in **Figure S23**, the mixture becomes clear and few pyrene can be detected in water. These experiments show that hydrophobic MIL-140B congenitally adsorb pyrene owing to the  $\pi$ - $\pi$  interactions as we discussed in former examples. In the case of dye molecules, the reason MIL-140B excludes MO and R6G is the same as we verified in former dye experiments, which is surface-charge repulsion for MO and size exclusion for R6G.

### Recycling Performance and Interference Experiment

MIL-140C-2CO<sub>2</sub>H and MIL-101(Cr)-SO<sub>3</sub>H were finally investigated to assess the sustainability and reusability of MOF sieves through multiple cycled sieving-desorption tests over MB/MO. Remarkably, these MOFs were shown to be still efficient for the separation of MB/MO after five cycles (see **Figure S24**). Moreover, the integrity of their frameworks was kept as demonstrated by PXRD (see **Figure S25** and **S26**) carried out after sieving, which is consistent with the excellent water stability of MIL-140s and MIL-101(Cr)s. These results are of great interest in a view of potential applications. To highlight the superiority of these solids, various functionalized UiO-67s bearing a same initial ratio of functional groups as for the preparation of MIL-140C-2CO<sub>2</sub>H and MIL-140C-2NO<sub>2</sub> were also synthesised. However, the PXRD patterns of UiO-67s after sieving demonstrated their poor water stability (see **Figure S27**). This result highlights that MIL-140s can not only serve as multivariable sieves but also possess adequate water-stability, comparable here to the MIL-101(Cr)s, mainly due to the more hydrophobic character of MIL-140s as well as their infinite metal oxide building units. Interference experiment is then conducted to evaluate the influence of disturbing ions for separation. Sodium chloride is selected as the interfering ions. As shown in **Figure S32**, the separation performance of MIL-140C-2CO<sub>2</sub>H is not affected with the existence of tenfold moles of sodium chloride in water.

## DISCUSSION

In summary, we discovered that a series of distinctive MOF (MIL-140s) with nonhomogeneous electronic distribution in channels can induce various NCIs with guest molecules, leading to the high performance separation of both dyes and practical organic toxics. The fundamental sieving mechanism of MIL-140s for the sieving of organics has been demonstrated through separation experiments and DFT theoretical calculations, indicating that the separation results match well with a presented outside-in theoretical model (hierarchical recognition). The sieving mechanisms follow several chemical and/or physical patterns: (i) surface charge-based barrier at the external surface of MIL-140s as primary recognition, (ii) a sieving "gate" at the Angström level within the pores as a secondary recognition and finally (iii) NCIs-based mechanism within the channels to obtain a third-level recognition. The strategy we presented in this work is expected to expand the applications of aqueous molecular sieving by targeting more variables in the way similar to translocator in organisms. This further discerns the design of new generations of host-guest systems particularly in the area of porous sieves, and promisingly this strategy could be extended to other related areas such as functional membranes, chemical sensors and biomimetic molecular devices.

## EXPERIMENTAL PROCEDURES

### Synthesis of [ZrO(O<sub>2</sub>C-R-CO<sub>2</sub>)](MIL-140s)

MIL-140C was obtained by reflux for 24 h with a mixture of ZrCl<sub>4</sub> (116.5 mg, 0.5 mmol) in 2 mL DMF, 4,4'-H<sub>2</sub>BPDC (4,4'-biphenyldicarboxylic acid) (121 mg, 0.5 mmol) in DMF (20 mL) and acidic acid (2.29 mL, 40 equivalent of ZrCl<sub>4</sub>). The white powder was collected by filtration and washed with DMF and methanol. MIL-140C-2NO<sub>2</sub> was achieved with similar method, but using the mixture of H<sub>2</sub>BPDC-2NO<sub>2</sub>/H<sub>2</sub>BPDC (H<sub>2</sub>BPDC-2NO<sub>2</sub>:H<sub>2</sub>BPDC=1:3, 1:2, 1:1) and acidic acid (1.65 mL) in 9 mL DMF. MIL-140C-2CO<sub>2</sub>H was achieved with similar method, but using the mixture of the H<sub>2</sub>BPDC-2CO<sub>2</sub>H/H<sub>2</sub>BPDC (H<sub>2</sub>BPDC-2CO<sub>2</sub>H:H<sub>2</sub>BPDC=1:3, 1:2, 1:1) and acidic acid (1.4 mL) in 10 mL DEF. MIL-140E was

achieved with similar method, but using acidic acid (1.145 mL) in 16 mL DMF. MIL-140F was achieved with similar method, but using acidic acid (1.65 mL) in 11 mL DMF. MIL-140A and MIL-140B were synthesized as the reported method.<sup>44</sup>

#### Synthesis of MIL-101(Cr)s

MIL-101(Cr)s were synthesized with the published methods,<sup>39, 45</sup> except for MIL-101(Cr)-SO<sub>3</sub>H for which a new protocol was used. For MIL-101(Cr), Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (400 mg, 1 mmol (Aldrich, 99%)), fluorhydric acid (1mmol), 1,4-benzene dicarboxylic acid (164 mg, 1 mmol (Aldrich 99%)) were added in 4.8 mL H<sub>2</sub>O, the mixture was put in a hydrothermal bomb which was heated for 8h at 220°C; For MIL-101(Cr)-CO<sub>2</sub>H, the starting materials CrCl<sub>3</sub> (198 mg, 1.25 mmol) and 1.25 mmol of ligand (equimolar mixture of the two derivatives) were introduced into a 20 mL Teflon reactor, after the addition of 5 mL of deionized water, the reactor was heated to 180 °C within 1 h and held for 96 h; MIL-101(Cr)-NO<sub>2</sub> was achieved by a hydrothermal reaction of CrCl<sub>3</sub> and H<sub>2</sub>BDC-NO<sub>2</sub> (molar ratio CrCl<sub>3</sub> : H<sub>2</sub>BDC-NO<sub>2</sub> : H<sub>2</sub>O = 1.6 : 1 : 278) at 180 °C for 96 hours. MIL-101(Cr)-SO<sub>3</sub>H was achieved with a new method without HF and Cr(VI), adapted from a reported synthesis of MIL-101(Cr) using tetramethylammonium (TMAOH) solutions,<sup>46</sup> Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (400 mg, 1 mmol), aqueous solution of TMAOH (5 mL, 0.025 M), H<sub>2</sub>BDC-SO<sub>3</sub>Na (536 mg, 2 mmol) were added into a 23 mL Teflon reactor, the bomb was put in the oven for 24 h at 190°C. The powder of MIL-101(Cr)s was washed with water and ethanol for three times and dried at 150°C overnight before the test.

#### Computational exploration of the MIL-140s structure and their interactions with the organics

DFT-based geometry optimizations of the empty and organics-loaded MOFs were performed at the general gradient approximation (GGA) level with the functional and basis sets as specified in the SI. The organic molecule was inserted in each pore of a 1x1x3 supercell model of the respective MOFs. This supercell approach ensures translational movements of the organic molecules within the pores. MB loaded in MIL-140C-2CO<sub>2</sub>H and MIL-140C-2NO<sub>2</sub>, NB loaded in MIL-140E and toxics loaded in MIL-140C-2CO<sub>2</sub>H were considered as typical cases to investigate the preferential location of these confined molecules and the guest-induced deformation of the MOFs.

#### SUPPLEMENTAL INFORMATION

Supplemental Information includes Supplemental Experimental Procedures, 32 figures, 5 tables, and 4 data files and can be found with this article online.

Data S1. Crystal Structure of MIL-140C-2CO<sub>2</sub>H

Data S2. Crystal Structure of MIL-140C-2NO<sub>2</sub>

Data S2. Crystal Structure of MIL-140E

Data S2. Crystal Structure of MIL-140F

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#### AUTHOR CONTRIBUTIONS

Q.Z. and M.W. contributed equally. Q.Z., G.Q. and C.S. conceived and designed the experiments. Q.Z. synthesized the materials and performed the molecular recognition experiments. F.N., M.W. and G.M. analyzed the structure. M.W. and G.M. performed the computational simulation of both the structure and host-guest interactions. S.W., S.H., N. A., E.G., F.N., C.Si. and C.M. assisted with the syntheses and characterization of the

material. Q.Z., M.W., E.G., F.N., Y.C., G.M., G.O. and C.S. analyzed the data and co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

## DECLARATION OF INTERESTS

The authors declare no competing interests.

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**Scheme 1. Theoretical model of outside in hierarchical recognition of ideal molecular sieves**

- (A) Charge-specific recognition (the left part) and size recognition (the right part).  
(B) The electronic distribution at the pore wall, the protrusions represent functional groups.  
(C) NCIs between parts with inverse electronic distributions on guest molecules and pore wall.

**Figure 1. Chemical structures and pore chemistry of MIL-140s**

- (A) Simplified construction of MIL-140s, pink, red, and gray represent Zr, O, and ligand, respectively.  
(B) Connolly surface of the fluctuant triangular channels running through the structure.  
(C) Perpendicular views of the one-dimensional chains of Zr-O clusters.  
(D) Depiction of the bridging ligand precursors.  
(E) A sectional view of the electronic distribution perpendicular to the channel.

**Figure 2. Charge- and size-based molecular separation in MOFs**

- (A) Performance of charge-based molecular separation.  
(B) Performance of size-based molecular separation.  
(C) Illustration of the organics and their sizes/charges.  
(D) DFT optimized geometry of MB loaded MIL-140C-2CO<sub>2</sub>H.  
(E) DFT optimized geometry of MB loaded MIL-140C-2NO<sub>2</sub>.  
(F) DFT optimized geometry of NB loaded MIL-140E.

**Figure 3. Multivariable molecular sieving of paraquat/difenzoquat**

- (A) Molecular representation of the investigated pesticides and their electrostatic potentials.  
(B) Paraquat/difenzoquat uptakes using the different porous materials.  
(C) Separation factors of MIL-140s for molecular separation of paraquat/difenzoquat.  
(D) Electronic density difference ( $\Delta n_{int}$ ) map for difenzoquat loaded MIL-140C-2CO<sub>2</sub>H.  
(E) The restrained electrostatic potential (RESP) map on the electronic density on regular grid for the same host-guest system.

**Figure 4. Molecular sieving of heterocyclic paraquat/clopyralid**

- (A) Performance of molecular separation with different porous materials for paraquat/clopyralid.  
(B) Separation factors of MIL-140s for the molecular separation of paraquat/clopyralid.  
(C) Electronic density difference ( $\Delta n_{int}$ ) for clopyralid loaded MIL-140C-2CO<sub>2</sub>H.  
(D) The formation of hydrogen bonds between the -CO<sub>2</sub>H of the framework and that of clopyralid.









