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De Novo Tailoring Pore Morphologies and Sizes for Different Substrates in a Urea-Containing MOFs Catalytic Platform

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Supporting Information Placeholder

ABSTRACT: To better understand the structure-catalytic property relationship, a platform of urea containing MOFs with diverse topologies as hydrogen bonding (H-bond) catalyst has been well established in the present work. During the construction of MOFs, we have proposed a new strategy called isoreticular functionalization approach, in which the desired topological net is firstly considered as blueprint, and then two pre-designed functionalized polydentate ligands link to four different metal clusters by *de novo* routes to achieve the MOFs with expected pore structure and catalytic sites. By means of this strategy, we have successfully synthesized four programmed MOFs (termed as **URMOF-1** through **URMOF-4**) with diverse topologies, pore morphologies and sizes and distribution of active sites. And subsequently, we have systematically investigated the Friedel–Crafts reactions of 1-methylpyrrole or 1-methylindole with nitroalkene derivatives with diverse sizes to assess the catalytic properties of the abovementioned URMOFs. These four URMOFs can act as reusable H-bond catalysts and show varied catalytic capacities and size-selectivity properties. Most significantly, the open morphologies of pores, large channels in the framework and effective distribution of active sites on the wall of channel are proved to facilitate the catalysis. This urea-containing MOF catalytic platform provides a new insight into on the catalytic properties of MOFs with same kind of active sites but diverse topologies, pore morphologies and sizes and distribution of active sites and sizes and distributions of catalytic sites.

INTRODUCTION

Metal-organic frameworks (MOFs), as a class of important nanoporous organic-inorganic hybrid materials, have attracted much attention owing to their diverse, porous and crystalline features, and the researches on MOFs have been one of the focuses and frontiers in the advanced materials field¹⁻⁴. Based on broad varieties and flexibilities of the constituents' geometry, size, and functionality, more than 20,000 MOFs have been reported and studied over the past decade.5, 6 However, the boundless of compositions, in some degree, lead to a bewildering variety of MOFs prepared, which has become one of the growing challenges for the current researchers on MOFs. Although stubbornly pursuing new MOFs possessing novel topologies may still be valuable work, researchers need to dial back on refining, modifying and functionalizing the reported MOFs whose properties are not fully explored or enhanced. Besides, much more effort should also be put on systematic and in-depth studies on the structure-properties relationships of the synthesized MOFs. And it might be hopefully to discover new prospects for potential industrial applications.

It has been well documented that numerous MOFs exhibit excellent feasibilities in many applications, such as gas storage⁷⁻¹³, molecule separation,¹⁴⁻²⁴ sensing and

recognition,25-29 catalysis,30-39 etc. And the catalysis in MOFs has become one of the most actively studied applications. In principle, MOFs as catalyst are superior to other porous materials due to the high versatility and crystalline nature.⁴⁰ On the one hand, the catalytic site and environment in MOFs can be rationally designed, which will help us to modulate their functionalities for desired catalysis. And on the other hand, the high order and uniformity of the porous network for size and shape selectivity in MOFs are favorable for catalysis.⁴¹ But, unfortunately, the systemic researches on the relationship between structures and catalytic properties of MOFs are still deficient. Up to now, only some catalytic platforms based on isoreticular MOFs have been built to study the relationship between pore size and catalytic activity.42, 43 And yet, more deep researches should be needed to gain insight into the influences of pore properties on catalysis in MOFs due to the fact of that the catalytic reaction rate is extremely related to the transport speed of substrates and products which are determined by kinds of pore properties of MOFs. Additionally, the relationships between diverse topological nets and catalytic properties in MOFs with same type of catalytic sites are still unexplored. Therefore, it is necessary to establish a platform in which MOFs can show different topologies, pore sizes and morphologies and metal clusters but possess same type of catalytic sites. This platform can help us to further grasp the relationships between MOFs' structures and their catalytic activities by systematic studies.

To establish this kind of catalytic platform, reticular chemistry is a good option,⁴⁴ which was first developed by Yaghi et al and has been well established nowadays. As is well-known, reticular chemistry can provide a unique opportunity for the rational design and synthesis of MOFs with predictable topology and property.^{7, 45} In view of this, we have proposed a new strategy as follows. Firstly, the expected topological net can be regarded as a blueprint which will be formulated from a diverse range of SBUs and ligands. Furthermore, the functionality can be preincorporated in the ligand which can be predesigned and synthesized. We call this proposed strategy "isoreticular functionalization approach" that will provide an opportunity for establishing a platform in which MOFs can possess not only the desired distinct topologies but also the same type of programmed functionality.

Scheme 1. Illustration of design of L_1 and L_2 , urea groups as catalytic sites were pre-incorporated into the backbone of selected hexatopic and tritopic carboxylate ligands while maintaining the initial linking geometries.



In the present work, we have establish a catalytic platform with tunable topologies, pore morphologies and sizes and distribution of active sites by means of this isoreticular functionalization strategy in order to explore the structure-catalytic property relationship in MOFs. Here, urea group has been chosen as the catalytic sites in MOFs due to the following major reasons. First of all, urea as an important functional group is well known in organocatalysis field and supramolecular chemistry. Its two-point Hbonding character makes it applied to hydrogen bond catalysis,⁴⁶⁻⁵³ cooperative catalysis,^{54, 55} molecular recogni-tion,⁵⁶⁻⁵⁸ ion transport⁵⁹ and anion coordination chemistry,⁶⁰⁻⁶³ and so on. Hence, the introduction of urea group into MOF might improve or generate novel catalytic performance in comparison with parent MOFs. Secondly, to our knowledge, currently reports on urea-containing MOFs (URMOFs) as catalysts are still not much. And there are only a handful of MOFs incorporating urea group as H-bond catalyst.^{64,65, 66,67} Farha, Hupp, and

Scheidt, et al. first reported seminal work on the synthesis of a novel urea-containing MOF as H-bond catalyst, which avoided self-quenching of urea unit and was more suitable to catalyze small substrate.⁶⁴ Thereafter, urea group was combined into Cr-MIL-101 and UiO-67 by post-synthesis and mixed dicarboxylic strut approach, respectively.^{65, 66} In these two cases, the functional groups stuck out from the wall of hole, which sacrificed porosity relative to their parent MOFs. Worse, the lack of the single crystal structure data in the aforementioned examples made the accurate distributions of active sites still unknown, which was not beneficial to understand the relationship between structure and catalytic activity.

Herein, we have reported four URMOFs according to the isoreticular functionalization strategy, and have discussed the relationship between catalytic activity and structure As shown in Scheme 1, the functional urea groups have been pre-incorporated into the hexatopic and tritopic ligands (labeled as L_1 and L_2), whereas the initial linking geometries remain unchanged. During the construction of MOFs, the *rht* and *gom* topology are regarded as blueprint, and then L_1 and L_2 are combined the well-known with $[Cu_2(sol)_2(O_2CR)_4],$ $[Zn_2(sol)_2(O_2CR)_4]$ and $[Zn_4(\mu_4-O)(O_2CR)_6]$ SBUs respectively to generate three programmed urea-containing MOFs by de novo routes, termed as URMOF-1 through URMOF-3. URMOF-4 are formed by combining L₂ with the reported $[In_3(OH)(\mu_3-O)(O_2CR)_6]$ SBUs,^{68, 69} which possesses a special *flu-3,6-P3121* topological net that has previously been generated theoretically⁷⁰ but never been observed in crystals. By using this isoreticular functionalization approach, URMOF-1-4 present both desired pore structures and catalytic capabilities within the MOFs. And subsequently, based on this established catalytic platform composed of these four URMOFs, we have systemically studied for the first time the Friedel-Crafts reactions of 1-methylpyrrole or 1-methylindole with nitroalkene derivatives with diverse sizes in order to give a deep insight into the influences of the distinct topologies, pore morphologies and sizes, and distribution of active sites of MOFs.

RESULTS AND DISCUSSION

Design and synthesis of ligands

MOFs as heterogeneous catalysts must possess large open channels in order to transport organic substrates and products which are typically very large.⁴² Therefore, to design and synthesize MOFs with large pore is crucial. For the sake of obtaining MOFs with non-interpenetrated nets and large pores, the reported *rht*⁷¹⁻⁸⁰ and *qom* topological nets^{81, 82} are considered as the blueprint. Meanwhile, as expected by the topological symmetry rules, tritopic linker combining with 6-connected trigonal-prismatic cluster [M₃O(CO₂)₆] can present huge channel. Thus, we chose the hexatopic and tritopic carboxylate ligands as organic struts to obtain the programmed MOFs with desired topological nets. 3,3',3",5,5',5"-benzene-1,3,5-triyl-hexabenzoate (bhb), 4,4',4"-benzene-1,3,5-triyl-

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59 60 benzoate (**btb**) and their elongated derivatives are the common-used hexatopic and tritopic carboxylate linkers, which can link diverse SBUs to form plenty of MOFs with different topologies, large pore size and high surface area due to their special geometries.⁷⁷ As shown in Scheme 1, urea groups were incorporated into the backbone of **bhb** and **btb** to form the pre-designed ligand L1 and L2, which are both elongated and functionalized with urea groups while maintaining the primary linking geometries. Owing to the fact that the active sites are all lying in the backbones of ligands, this kind of incorporation for urea groups not only brings the functionality to the subsequent construction but also gives the best possibility to avoid sacrifice of the porosity. In experimental procedure, the ligands were synthesized via the reactions of 1,3,5triisocyanatobenzene that was prepared according to the published method^{83, 84} with dimethyl 5-aminoisophthalate for H_6-L_1 and with benzocaine for H_3-L_2 . More detailed synthetic routes are shown in Scheme 2.

Scheme 2. Synthesis route of H₆-L₁ and H₃-L₂.



Construction and structures of MOFs

As mentioned in introduction, the design and synthesis of MOFs with large pores and open channels are crucial to transport organic substrates and products in the catalytic process. Some cases of topological nets with inherent capacity of forbidding framework interpenetration have been utilized in the practice of isoreticular chemistry that can produce MOFs with large pore size in high possibility. Hexatopic linker with 1,3-benzenecarboxylate unit combining with dicopper paddle-wheel unit is often used to construct 3D MOFs with a (3,24)-network topology.74-77 The *rht* topology has been utilized progressively in the practice of isoreticular chemistry. Moreover, the higher surface areas and larger free pore volumes can be achieved through the expansion of the organic linker for the reason that the formation of isophthalate-sustain cuboctahedra prohibits framework from interpenetration. Therefore, we choose this (3,24)-connected *rht* topology

as blueprint. Reaction of H_6-L_1 with $Cu(NO_3)_2 \cdot 6H_2O$ in dimethylformamide (DMF) at 75 °C for 24 h afforded dark green single crystals of URMOF-1. Single-crystal X-ray crystallography reveals that URMOF-1 crystallizes in the tetragonal I4/m space group. As expected, linking 24 isophthalate moieties with 12 dinuclear paddle-wheel units created a cuboctahedron, which and then connected to each other though coordination bonds to form 3D MOFs with (3,24)-connected *rht* topology (Figure 1).

As calculated by PLATON,⁸⁵ URMOF-1 present void volumes of 75.2% or 72.2% of the crystal volume for removing the coordinated H_2O or not. Although precise solvent content cannot be determined by X-ray crystal-lography resulting from their disordered nature, by means of the SQUEEZE routine of PLATON⁸⁵ and quantitative element analysis, it is found that the void space is filled by the DMF and water molecules. When H_6 - L_1 reacting with $Zn(NO_3)_2$ · GH_2O in DMF at 80 °C for 30 h, isostructural orange crystals of URMOF-2 were formed. URMOF-1 and -2 are isoreticular with reported (3,24)-connected MOFs while functionalized by the pre-incorporated urea groups. And the desired (3,24)-connected *rht* topological nets and programmed functionalities of MOFs have been successfully duplicated.



Figure 1. Crystal structure of URMOF-1 showing a (3,24)connected *rht* network. H atoms are omitted for clarity. Carbon, gray; oxygen, red; nitrogen, blue; copper, green. The largest spheres that the cavity of each cage can accommodate are represented in yellow.



Figure 2. (a) Crystal structure of URMOF-3 is formed by linking the Zn_4O clusters with a trigonal ligand L2. H atoms are omitted for clarity. Zinc, blue. The largest sphere that the channel can accommodate is represented in yellow. (b) (3,6)-connected *pyr* net in URMOF-3.

6-Connected octahedral $Zn_4O(CO_2)_6$ clusters as SBUs combining with tritopic linkers can produce an isoreticular series of structures featuring *qom* topology, such as MOF-177, MOF-180 and MOF-200. These MOFs are all

non-interpenetrated due to the *qom* topological inherent nature, while they show extra-large pores, high porosity and ultra-high BET surface areas. This huge enhancement of accessible internal volume and open channel size in non-interpenetrated structures are crucial to improve the catalytic performance by facilitating the diffusion of reactants and products. With this inspiriting *qom* topology as blueprint, reaction of tritopic L₂ with Zn(NO₃)₂·6H₂O in DMF/N-methyl-pyrrolidinone (NMP) at 100 °C for 36 h gave colorless crystal of URMOF-3. Single crystal analysis showed URMOF-3 crystallized in cubic Pa-3 space group. The asymmetric unit contains one-third ligand, two-third Zn atom and one-sixth O atom. Surprisingly, though a (3,6)-connected net was constructed (Figure 2) by the centre of the octahedral $Zn_4O(CO_2)_6$ cluster as the site of 6-connection and the centre of L₂ linker as the site of 3connection, the type of topology was not the expected *qom* but *pyr*. In despite of it, the (3,6)-connected *pyr* net looks very like *gom* net and URMOF-3 also possesses high void volumes of 88.5% of the crystal volume as calculated by PLATON. The treatment of solvent content in the void space is same with that of URMOF-1 and -2. Remarkably, (3,6)-connected pyr net in MOFs have been reported, most of the case afforded interpenetrated structure.^{86, 87} However, the pyr net in URMOF-3 is noninterpenetrated that is a rare occurrence and same as the PCN-101.⁸⁸ PCN-100 and The reported noninterpenetrated nature is essential to the application in catalysis.

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Assembly of benzene tricarbonic acid (btc) with trigonal-prismatic cluster $[M_2O(CO_2)_6]$ (M=Cr, Fe, Al, V) can afford classic MOFs MIL-100.89-92 Within this type of isostructural MOFs, the unique supertetrahedra and the mesoporous cages are fascinating for construction of MOFs catalyst. Unfortunately, no any extent frameworks have been reported. Nevertheless, in terms of the topological symmetry rules, there is a high possibility that the assembly of the elongated tritopic linker combining with 6-connected trigonal-prismatic cluster might form the MOFs with huge channel. Since the single crystal of MIL-100(M) (M=Cr, Fe, Al, V) is hard to obtain, our approach is to extend this $[M_2O(CO_2)_6]$ to contain In element. As is well known, In₃O(CO₂)₃ cluster is a commonly used SBUs that presents 6-connected trigonal-prismatic.^{68, 69} Reaction of L_2 with $In(NO_3) \cdot 4H_2O$ in DMF/NMP at 75 °C for 36 h gave colorless crystal of URMOF-4. Single crystal analysis shows URMOF-4 crystalized in trigonal P3,21 space group. The asymmetric unit contains one ligand, a half of $In_{2}O(CO_{2})_{2}$ cluster, a half of OH and one coordinated H₂O. Tritopic L₂ linking with 6-connected trigonalprismatic cluster affords a special *flu-3,6-P3121* topological net (Figure 3) which just has been predicted theoretically but never been observed in crystals before. URMOF-4 also has high void volumes of 88.1% or 87.5% of the crystal volume with removing the coordinated water or not. More significantly, URMOF-4 is the first framework constructed by unmixed $In_2O(CO_2)_2$ cluster with tritopic linker, which would promote the research on the assembly of $[M_2O(CO_2)_6]$ with tritopic linker.

To sum up, utilizing the isoreticular functionalization approach, the well-known *rht* and *qom* topological net have been regarded as blueprints and the programmed URMOF-1–3 can be successfully obtained. In comparison with the classic reported MOFs, URMOF-1–3 are isoreticular or close to isoreticular while possessing the desired active sites. And, both the desired pore structure and catalytic capability within the MOFs have been achieved. As for URMOF-4, it presents a unique topological net and can be readily formed by combining $[In_3O(CO_2)_6]$ with tritopic L₂ ligand, in which the desired large open channels have been obtained as well. The four functionalized MOFs containing urea groups provide an idea catalytic platform for systematic research on the relationship between catalytic activity and structure.



Figure 3. (a) Crystal structure of URMOF-4 is formed by linking the In_3O clusters with a trigonal ligand L2. Indium, pink or green. H atoms are omitted for clarity. (b) (3,6)-connected *flu-3,6-P3121* net in URMOF-4.

Theoretical characterization of pore structure

On the basis of the crystal structure of URMOF-1-4, high porosity and open channel are all obtained which are needed to efficiently transport substrate and product molecule to facilitate catalysis. However, nitrogen adsorption measurements are unsuccessful to give the expected experimental area despite various of activated methods such as solvent exchange, solution freeze-drying^{93, 94} and even supercritical CO₂ exchange have been adopted. It might be attributed to framework distortion upon solvent removal, which is a common phenomenon observed for MOFs with large open channels.^{42, 95-98} Furthermore, the organic struts are all semi-rigid in these four MOFs which could accelerate the framework distortion. Despite of that, powder X-ray diffraction patterns of fresh wet sample for URMOF-1-4, as shown in Figure S1-S8, indicate that the frameworks are stable in the solution. As we all know, high stability for catalyst in air is conductive to catalytic application especially in industry, and intentionally demanding high stability out of the reaction environment for catalyst is irrational. H-bond catalytic reactions are usually performed in solution, URMOF-1-4 are all stable in solution which is sufficient for store and application in the field of H-bond catalysis.

Chemistry of Materials



Figure 4. Accessible surfaces (denoted in green) of URMOF-1, -3 and -4 with probe radius of 1.8 Å.

Table 1 Theoretical pore structure information for URMOF-1-4

| - | Compound | Formula | Porosity (%) | Density (g/cm ³) | SA (m²/g) | V _p (cm ³ /g) | |
|---|----------------------|----------------------------------|-----------------|---------------------------------|-------------------|--|--|
| | URMOF-1 ^a | $Cu_3(L_1)(H_2O)_3$ | 72.2 | 0.63 | 2910 | 1.14 | |
| | URMOF-1 ^b | $Cu_3(L_1)$ | 75.2 | 0.60 | 3295 [°] | 1.25 | |
| | URMOF-2 ^a | $Zn_3(L_1)(H_2O)_3$ | 72.6 | 0.62 | 2980 | 1.17 | |
| | URMOF-2 ^b | $Zn_3(L_1)$ | 75.5 | 0.59 | 3431 [°] | 1.28 | |
| | URMOF-3 ^a | $Zn_4O(L_2)_2$ | 88.5 | 0.25 | 5843 | 3.50 | |
| | URMOF-3 ^b | $Zn_4O(L_2)_2$ | 88.5 | 0.25 | 6695 [°] | 3.50 | |
| | URMOF-4 ^a | $In_{3}O(OH)(L_{2})(H_{2}O)_{3}$ | 87.5 | 0.28 | 5194 | 3.09 | |
| | | | | | | | |

SA is the accessible surface area. V_p is the calculated pore volume. *a*, not removed the coordinated H₂O; *b*, removed the coordinated H₂O. *c*, the simulated BET surface area.



Figure 5. The simulated pore size distribution as seen by GCMC simulation for URMOF-1-4, coordinated H₂O in the MOFs were removed. a-d for URMOF-1-4, respectively.

The calculated pore volumes were calculated by *PLATON* with probe radius of 1.8 Å, the accessible surfaces were created and calculated using *Mercury* and *Poreblazer* (Figure 4).⁹⁹ In order to better understand the pore structures, the atomistic Grand canonical Monte Carlo (GCMC) simulations were performed to estimate the adsorption isotherms of N₂ at 77.35 K for URMOF-1-4 using *RASPA*,¹⁰⁰ which implements the latest state-of-theart algorithms for molecular dynamics. As show in the Figure S18, the GCMC N₂ sorption of URMOF-1-4 clearly

shows type-I isotherms, and the simulated BET surface areas for URMOF-1-4 are estimated as 3295, 3431, 6695 and 5061 m²/g, respectively (Figure S19 - S22). The caculated pore volume and the simulated BET surface areas of these URMOFs are listed in Table 1. The URMOF-1 and -2 have the almost same values of surface area and pore volume due to the nature of the isomorphism, while URMOF-3 and -4 show high theoretical surface areas which are up to 6695 and 5061 m^2/g respectively. Figure 5 plots the simulated pore size distributions (PSDs) by GCMC simulations for URMOF-1-4 without coordinated solvents. The PSD of URMOF-1 shows four peaks at 7.0, 10.9, 12.4 and 17.6 Å, which correspond to the four types of polyhedral cages in structure considering the curvature of the ligand. The maximum probe size of URMOF-1 is 17.6 Å. However, the pore limiting diameter is only about 7.0 Å, which will hamper the diffusion of larger substrate during catalytic reaction. The PSD of URMOF-2 shows the similar characteristic as URMOF-1. The PSDs of URMOF-3 and -4 are similar to each other and feature a main peak in 17.3 and 19.6 Å, respectively. Compared with URMOF-1 and -2, the pore limiting diameters of URMOF-3 and -4 are much larger than the former and exceed 12.4 Å. Analysis of the connectivity of the porous space shows that the pore systems in URMOF-3 and -4 are percolated in 3 dimensions (Figure 4). The 3D pores with large pore size in URMOF-3 and -4 make them good candidates for catalytic reaction.

Structure-catalytic performance relationship

At first, the catalytic activities of URMOF 1–4 as catalysts were assessed by the Friedel-Crafts alkylation reaction of trans- β -nitrostyrene with 1-methylpyrrole. Using 10 mol% (based on per urea unit) of URMOF-1–4 as catalyst, the reactions were carried out in CH₃CN at 60 °C for 24 h and 48 h, respectively. The yields of desired products are presented in Table 2 (entries 1–4), which indicated that the Friedel-Crafts reaction can be well catalyzed by these urea-containing MOFs. And then a series of control experiments without URMOFs catalysts were performed under the same condition in order to well understand the catalysis of these URMOFs. As shown in entries 5-11 of Table 2, only trace product were found even after 48 h, confirming that these URMOFs can effectively catalyze the Friedel-Crafts reaction. From the structure point of

view, it can be noted that there are four different metal clusters as SBUs existed in the four framework, which are $[Cu_2(H_2O)_2(O_2CR)_4], [Zn_2(H_2O)_2(O_2CR)_4], [Zn_4O(O_2CR)_6]$ and $[In_3O(CO_2)_6]$ for URMOF-1-4, respectively. Although it has been reported that the metal clusters as Lewis acids have low catalytic activities for Friedel-Crafts reaction,^{65,} ⁶⁷ it is still necessary to evaluate the catalytic activities of the metal clusters in these URMOFs. And therefore, other control experiment were designed and performed. With the aid of these control experiments, a further insight into the roles of urea units and SBUs of the URMOFs in catalytic reactions could be gained. Since it is hard to synthesize MOFs with same structures and pore sizes whereas without urea units related to the corresponding URMOFs, we choose some similar reported MOFs without urea groups as catalysts, whose SBUs were same with that of URMOFs. According to the literatures, Cu₃(BTC)₂,¹⁰¹ MOF-14,¹⁰² MOF-177⁸¹ and $[In_{3}O(C_{8}O_{4}H_{4})_{3}(H_{2}O)_{1.5}(C_{3}N_{2}H_{3})(C_{3}N_{2}H_{4})_{0.5}]$ ·DMF·0.5(CH₃ CN)⁶⁸ were prepared to carry out the Friedel–Crafts reactions under the same conditions as described above, respectively. It is should demonstrated that these MOFs have different structures and molecular formulas comparing with those of the URMOFs. Thus, crudely utilizing 10 mol% of these MOFs as catalyst is not rational, and the used mole equivalents of metal clusters in the MOFs should be equal to that of URMOFs base on per urea unit. The product yields of these control experiments are given in entries 6-9 of Table 2, which reveal that these MOFs have lower catalytic activities in comparison with URMOFs under same condition. In addition, these results also demonstrated that the high catalytic activities of URMOF-1-4 arise mainly from urea groups, and that the metal clusters can be only seen as some added active sites on the wall of pore besides urea groups in some degree. Actually, the low catalytic contribution of metal clusters in the framework cannot interfere with the expected research on the relationship between pore morphologies, sizes and the catalytic properties. Finally, the control experiments by using L₁ methyl ester and L₂ ethyl ester as catalysts were also carried out under the same condition, and still low yields (Table 2, entries 10, 11) were found due to the poor solubility of the two esters in CH₃CN. In fact, these esters present very poor solubility in most of general organic solvents. So that, under such condition, these esters can be actually considered as heterogeneous catalysts due to their insolubility. The strong intermolecular H-bond maybe exist in the solid state for these esters, which lead to low catalytic reactivity in comparison with URMOF-1-4.

With these results in hand, we set out to change the substrates diverse in sizes to explore the relationship between catalytic activities and pore properties for URMOF-1–4. The four MOFs present different topologies, pore morphologies and sizes and diverse clusters while possessing same kind of urea groups as active sites, which can provide a rational catalytic platform to investigate the relationship between catalytic activities and above structural features. Thus, Friedel-Crafts reactions of 1methylpyrrole or 1-methylindole with nitroalkene derivatives were performed to evaluate the catalytic activities for these URMOFs, in which four kinds of nitroalkene derivatives with different sizes and shapes (Table 3, and 4) were employed.

| Table 2. | URMOFs c | atalyzed Fı | riedel- | -Craft a | alkylation |
|----------|-------------|-------------------|---------|----------|------------|
| between | trans-β-ni | trostyrene | and | 1-meth | nylpyrrole |
| and cont | rol experim | ents ^a | | | |

| | +NO2 | catalyst (10%) CH ₃ CN, 60°C | R NO2 |
|-------|------------------------------------|--|---------------------------|
| entry | catalyst | 24h yield(%) ^b | 48h yield(%) ^b |
| 1 | URMOF-1 | 56 | 72 |
| 2 | URMOF-2 | 55 | 73 |
| 3 | URMOF-3 | 91 | 94 |
| 4 | URMOF-4 | 93 | 95 |
| 5 | No catalyst | _ ^c | - |
| 6 | $Cu_3(BTC)_2$ | 22 | 27 |
| 7 | MOF-14 | 18 | 30 |
| 8 | MOF-177 | 25 | 34 |
| 9 | In ₃ O-MOF ^d | 7 | 14 |
| 10 | L1 methyl ester | 9 | 15 |
| 11 | L ₂ ethyl ester | 15 | 23 |

^{*a*} Reactions were carried out with 1-methylindole (1.5 mmol), nitroalkene (0.5 mmol), catalysts (10 mol%, based on per urea unit for URMOFs and ligand esters, or mole equivalents of metal clusters equal to those of URMOF for other MOFs), CH₃CN (0.75 mL). ^{*b*} the yield is based on nitrostyrene. ^{*c*} Trace, ^{*d*} $[In_3O(C_8O_4H_4)_3(H_2O)_{1.5}(C_3N_2H_3)(C_3N_2H_4) _{0.5}]$ ·DMF·0.5(CH₃CN).

Still under the same conditions described above, the Friedel-Crafts reactions of 1-methylpyrrole with diverse nitroalkene derivatives $(S_1 - A)$ were carried. As shown in Table 3, desired products are all obtained but with different yields. It can be note that URMOF-1 and URMOF-2 have not high catalytic activities due to their structural features. Furthermore, because of isostructure for URMOF-1 and -2, reactions catalyzed by them show little difference in yields, which also in part proves that the reaction are mainly catalyzed by urea sites and that Cu and Zn in the SBUs hardly influence the yield. Based on URMOF-3, the reactions give desired products with high yields except for S_4 , implying that URMOF-3 possesses high activity towards the reaction. As compared with URMOF-1-3, URMOF-4 shows the highest catalytic activity for these reactions. As shown in Tables 3, one can note that the size of nitroalkene derivatives has an important influence on the reaction yields. Figure 6a clearly shows the relationship between the yields for 1-methylpyrrole corresponding to different URMOFs catalysts and the nitroalkene derivatives with different sizes. It can be seen that for the same reaction, URMOF-4 and -3 present better reactivity. This plot also reveals that the catalytic reactions for 1-methylpyrrole and 1-methylindole show similar tendencies of yields of the desired products for diverse nitroalkene derivatives upon URMOF-1-4. The catalytic activities can be demonstrated in the order of URMOF-4>URMOF-3>URMOF-2~URMOF-1. To confirm this tendency, reactions of 1-methylindole with nitroalkene were also carried out under the same condition, the yields of

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reactions of 1-methylindoleare all slightly higher than those of 1-methylpyrrole, indicating that the inherent reactivity of 1-methylindole is superior to that of 1methylpyrrole. As shown in Table 4 and Figure 6b, the tendency of yields for the desired products for diverse nitroalkene derivatives upon URMOF-1-4 are according with those of 1-methylpyrrole.

Table 3. URMOFs catalyzed Friedel-Craft alkylate for 1-methylpyrrole^α

| $ \begin{array}{rcl} & & & \\ & & $ | | | | | | | 02 | | | |
|--|-----------------------|----------------|---------------|------|------|------|------|------|------|--|
| | | | $Yield(\%)^b$ | | | | | | | |
| nitroalkene | product | URM | IOF-1 | URM | OF-2 | URM | OF-3 | URM | OF-4 | |
| | | 24 h | 48 h | 24 h | 48 h | 24 h | 48 h | 24 h | 48 h | |
| S ₁ | -N NO ₂ | 56 | 72 | 55 | 73 | 91 | 94 | 93 | 95 | |
| Br NO ₂ | Br NO ₂ | 54 | 74 | 50 | 71 | 93 | 95 | 94 | 96 | |
| S ₃ NO ₂ | | _ ^c | 5 | - | 7 | 65 | 83 | 89 | 94 | |
| S4 | NO2 | - | - | - | - | 10 | 20 | 69 | 77 | |

^{*a*} Reactions were carried out with 1-methylpyrrole (1.5 mmol), nitroalkene (0.5 mmol), URMOFs (10 mol%, based on per urea unit), CH₃CN (0.75 mL). ^{*b*} The yield is based on nitroalkene. ^c Trace.



Figure 6. URMOF-1-4 catalyzed Friedel-Craft alkylate for 1methylpyrrole (a) and 1-methylindole (b). The reaction were carried out with 1-methylpyrrole or 1-methylindole (1.5 mmol), nitroalkene (0.5 mmol), URMOFs (10 mol%), CH₃CN (0.75 mL) for 48 h, relationship of the yields based on nitroalkene derivatives diverse in size (S_{1-4}) upon URMOF-1-4 catalyst were illustrated. In which, the sizes of S_{1-4} are gradually increasing.

As mentioned above, the four URMOFs show different catalytic performances, which can be attributed to their structure features. As shown in Figure 7a, four two-third of L_1 linking two SBUs forms an irregular *paddle wheel* unit, and the H atoms of urea groups are pointing to the inner of *paddle wheel* unit. The short distances of O–O and H–H imply that the channels are narrow, and cannot facilitate transportation of the substrates and products, and that urea groups are not accessible to interaction with the substrate. Meanwhile, according to the 3D coordination framework of URMOF-1, one can note that there

are two kinds of channels along c-direction while urea groups distribute in the windows of smaller channel (Figure 4a). Therefore, URMOF-1 and -2 show lower catalytic activities for all the reactions despite of the fact that they possess high porosity.

Table 4. URMOFs catalyzed Friedel-Craft alkylate for1-methylindole^a

| | .N + R∕∖ | -NO ₂ | URM CH ₃ C | OF (10 N, 60° | 0%) C | R | NO | 2 | |
|----------------|----------|------------------|--------------------------|------------------|----------|-----------|------|------|------|
| | | | | | Yield | $l(\%)^b$ | | | |
| nitroalkene | product | URM | IOF-1 | URM | IOF-2 | URM | OF-3 | URM | OF-4 |
| | | 24 h | 48 h | 24 h | 48 h | 24 h | 48 h | 24 h | 48 h |
| S ₁ | | 69 | 81 | 65 | 82 | 96 | 98 | 95 | 98 |
| Br NO2 S2 | Br NO2 | 72 | 80 | 69 | 78 | 94 | 95 | 96 | 98 |
| S ₃ | | 12 | 21 | 10 | 24 | 77 | 94 | 92 | 96 |
| S4 | | _c | 5 | - | 4 | 14 | 23 | 72 | 83 |

^{*a*} Reactions were carried out with 1-methylindole (1.5 mmol), nitroalkene (0.5 mmol), URMOFs (10 mol%, based on per urea unit), CH_3CN (0.75 mL). ^{*b*} the yield is based on nitroalkene. ^{*c*} Trace.

For URMOF-3, high porosity and large pore make it become an excellent catalyst for nearly all substrates except S_4 . As shown in Figure 2, L_2 linking with SBUs affords a (3,6)-connected **pyr** net with the center of the octahedral $Zn_4O(CO_2)_6$ cluster as the site of 6-connection and with the center of the L2 linker as the site of 3-connection. The structure of this non-interpenetrated net determines large pore size. As a result, URMOF-3 has extra-large pores capable of transporting the substrate and product rapidly. Furthermore, each one-third of L_2 is equitably allocated to the vertex of octahedral $Zn_4O(CO_2)_6$ cluster (Figure 7b), which can maximize the distance of urea groups. Thus the urea groups as accessible active sites are exposed in the large pores (Figure 4b). **Chemistry of Materials**



Figure 7. The positions, surroundings and distances of urea groups in subunits of the sturctures. (a) for URMOF-1, (b) for URMOF-3 and (c) for URMOF-4. H atoms are omitted for clarity except for urea groups. Carbon, gray; oxygen, red; nitrogen, blue; metal ion, green.

(3,6)-connected *flu-3,6-P3121* net of URMOF-4 provides three kinds of rings in the structure, as shown in Figure 7c, these two-, three- and four-membered rings are formed by sharing one-third of ligand. The distances of urea group are diverse in different rings, and most of them are long. It is more important that the packed structure can afford large open channels along the same direction (Figure 4c), and that parts of urea groups are fixed on the wall of these large channels. Thus, all of the selected substrates can be well catalyzed by URMOF-4 due to the huge channels and accessible urea groups. It should be noted that the substrate S_4 is one of the largest nitroalkene derivatives in size in comparison with those utilized in the MOFs catalyses based on urea group. Moreover, all of the reported urea containing MOFs^{64, 65, 67} along with URMOF-1-3 in this article show lower activities as encountering the large substrates. In other word, URMOF-4 is a unique and excellent catalyst that can provide high catalytic activities even for large substrate.

Obviously, pore morphologies and sizes and effective distribution of the urea groups are all play crucial roles in catalytic reaction. In such reaction environments defined by these factors, URMOF-1-4, thus, present distinct catalytic activities and show size selectivities. It is also indicated that these catalytic reactions mainly occur in the pores of the MOFs. The open shape of pores, large channel in the framework and effective distribution of active sites on the wall of channel also make contribution to catalyzing the reaction. Furthermore, distinct clusters maybe influence the transportation of organic molecules which have been proved by the separation application of MOFs. Due to the fact that the catalytic reaction rate is extremely related to the transport speed of substrates and products, the distinct cluster in URMOF-1-4 might affect catalytic reaction rate in some degree. As testing the recyclability of the urea-containing MOF heterogeneous catalyst, as shown in Figure S13, one can note that the URMOF-3 and -4 can be easily isolated from the reaction suspension by centrifugation and can be reused at least five times with little or no loss of activity, whereas they still retain their crystallinity as verified by PXRD. On the contrary, the catalytic activities of URMOF-1 and -2 are lost in some degree, which might be ascribed to their narrow windows of cuboctahedron. After catalysis, the product or the byproduct could stoppage the channels and the transfer of the substrate and product could be stopped. However, their frameworks are still stable as verified by PXRD. Overall, these MOFs with different topologies and precise structural feature provide an excellent platform for investigating the relationship between catalysis and structure. Despite the fact that some MOFs possessing the same topologies and the relationship of pore size and catalytic activity have been reported, 42, 43 to our best of knowledge, the catalytic MOFs platform with same type of functional group but possessing diverse topological nets, pore morphologies and sizes and distinct distribution of activity sites has never been reported. This work has investigated the relationship of these features and catalytic activity for the first time.

Conclusion

In summary, a catalytic MOFs platform with tunable topologies, pore morphologies and sizes and accessible active sites has been established for the first time. By reviewing the library of MOFs, a new isoreticular functionality approach has been developed. With the desired topological nets as blueprints, by means of pre-incorporating urea groups into the selected polytopic ligand with fixed linking geometry and choosing rational SBUs, four programmed urea-containing MOFs as H-bond catalysts with distinct topological nets have been constructed by de novo synthesis. Base on this platform, the relationship between the catalytic activity and the features of distinct topologies, pore shapes and sizes and distribution of active sites in the framework have been investigated systematically. The morphology of pores, open large channel in the framework and effective distribution of active sites on the wall of channel play key roles in the catalysis, and the better reactivity mainly originates from these features. Meanwhile, isoreticular functionality approach provides an opportunity to obtain MOFs with same type of functional group but possessing tunable topologies. We anticipate that the number of urea containing MOFs could be explosively increased and abounding of desired topological nets with urea units could be duplicated by using this facile approach. The present study might pave a new way

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59 60 of research on interdiscipline for MOFs and supramolecule chemistry based on urea, and other application of these MOFs such as molecule recognition, ions transfer may be realized.

EXPERIMENTAL SECTION

General experimental section and detailed procedures for the reported MOFs, catalytic substrates and products synthesis and characterization are provided in the Supporting Information. Only experimental procedures for the ligands and MOFs are shown below.

Synthesis of L₁ methyl ester: A solution of 1,3,5benzenetriisocyanate (2.0 g, 10 mmol) in dry toluene (100 mL) was added dropwise to a solution of dimethyl-5aminoisophthalate (10.46 g, 50 mmol) in dry toluene (200 mL) at 80 °C. After stirring the mixture for 12 h, the precipitation was filtered and washed by toluene and CH₂Cl₂, respectively. The white solid of L₁ methyl ester was obtained and dried in air (Yied: 88% based on 1,3,5benzenetriisocyanate). IR (KBr pellet, cm⁻¹): 3395, 3376, 3110, 2956, 1708, 1609, 1547, 1438, 1352, 1259, 1214, 1006, 756, 721, 675. ¹H NMR (400MHz, DMSO-d₆): δ 9.05 (s, 3H, N-H), 8.92 (s, 3H, N-H), 8.36 (s, 6H, Ph-H), 8.10 (s, 3H, Ph-H), 7.49 (s, 3H, Ph-H), 3.92(s, 18H, C-H). ¹³C NMR (100 MHz, DMSO-d₆): δ 165.9, 152.8, 141.3, 140.5, 131.1, 123.1, 123.0, 102.9, 53.0. Anal. Calcd for $C_{39}H_{40}N_6O_{17}$ (Me₆-L₁·2H₂O): C 54.17, H4.66, N 9.72%. Found: C 54.30, H 4.59, N 9.87%.

Synthesis of H₆-L₁: L₁ methyl ester was dispersed in 40 mL CH₃OH / 40 mL H₂O, excessive LiOH was added, the mixture was stirred for 8 h at 65 °C, then cooled to room temperature and 100 mL H₂O was added, finally, 5% hydrochloric acid (HCl) aqueous solution was added to the solution until the pH value is adjusted to 2. White desired powdered H_6-L_1 was obtained by filtration, washed by water and acetone and dried in air (Yield: 81% based on 1,3,5-benzenetriisocyanate). IR (KBr pellet, cm⁻¹):3099, 2562, 1713, 1564, 1447, 1262, 1227, 899, 759, 675. ¹H NMR (400MHz, DMSO-d₆): δ 13.17 (s, 6H, -COO-H), 9.21 (s, 3H, N-H), 9.05 (s, 3H, N-H), 8.31 (s, 6H, Ph-H), 8.09 (s, 3H, Ph-H), 7.41 (s, 3H, Ph-H). ¹³C NMR (100 MHz, DMSO-d₆): δ 167.1, 153.0, 141.0, 140.6, 132.2, 123.6, 122.9, 102.9. Anal. Calcd for $C_{33}H_{51}Cl_5N_6O_{26}$ (H₆-L₁·5HCl·11H₂O): C 35.23, H4.57, N 7.47%. Found: C 35.43, H 4.28, N 7.52%.

Synthesis of L_2 ethyl ester: A solution of benzocaine (8.26 g, 50 mmol) in dry toluene (200 mL) was added dropwise to a solution of 1,3,5-benzenetriisocyanate (2.0 g, 10 mmol) in 70 mL toluene at 80 °C. After stirring the mixture for 12 h, the precipitation was filtered and washed by toluene and acetone, respectively. L_2 ethyl ester was obtained as white solid and dried in air (Yield: 80% based on 1,3,5-benzenetriisocyanate). IR (KBr pellet, cm⁻¹): 3383, 3290, 3120, 2982, 1715, 1679, 1596, 1535, 1454, 1368, 1282, 1210, 1172, 1105, 1019, 854, 768, 694. ¹H NMR (400MHz, DMSO d_6): δ 8.92 (d, 6H, N-H), 7.90 (m, 6H, Ph-H), 7.59 (m, 6H, Ph-H), 7.38 (s, 3H, Ph-H), 4.29(d, 6H, C-H), 1.32(t, 9H, C-H). ¹³C NMR (100MHz, DMSO-d₆): δ 165.5, 152.0, 144.3, 140.1, 130.4, 122.8, 117.3, 102.1, 60.3, 14.3. Anal. Calcd for $C_{36}H_{38}N_6O_{10}$ (Et_3-L2·H2O): C 60.61, H5.30, N 11.96%. Found: C 60.50, H 5.36, N 11.76%.

Synthesis of H₂-L₂: L₂ ethyl ester was dispersed in 40 mL CH₃CH₂OH / 40 mL H₂O, excessive LiOH was added, the mixture was stirred for 8 h at 65 °C, then cooled to room temperature and 100mL H₂O was added, finally, 5% hydrochloric acid (HCl) aqueous solution was added to the solution until the pH value is adjusted to 2. White desired powdered H₃-L₂ was obtained by filtration, washed by water and acetone and dried in air (Yield: 74% based on 1,3,5-benzenetriisocyanate). IR (KBr pellet, cm⁻¹): 3113, 2541, 1698, 1541, 1419, 1313, 1220, 1172, 765, 665. ¹H NMR (400MHz, DMSO-*d*₆): δ 12.58 (s, 3H, -COO-H), 8.91 (d, 6H, N-H), 7.88 (m, 6H, Ph-H), 7.58 (t, 6H, Ph-H), 7.38 (d, 3H, Ph-H). ¹³C NMR (100MHz, DMSO-d₆): δ 167.9, 152.9, 144.7, 140.9, 131.4, 124.5, 118.1, 103.0. Anal. Calcd for $C_{30}H_{32}N_6O_{13}(H_3-L_2\cdot 4H_2O)$: C 52.63, H4.71, N 12.28%. Found: C 52.24, H 4.69, N 12.35%.

Synthesis of URMOF-1: 5 mg H_6 - L_1 and 15 mg $Cu(NO_3)_2$ · $6H_2O$ were dissolved in 1.5mL DMF, 4 drops of HBF4 (40% in water) were added to the solution. The mixture was sealed in a glass vial and heated at 75[°]C for 24 h. After cooling to room temperature, dark green crystals of **URMOF-1** were obtained in a yield 65% base on H_6 - L_1 . IR (KBr pellet, cm⁻¹): 1657, 1557, 1420, 1380, 1218, 1105, 777, 668.

Synthesis of URMOF-2: 5 mg H_6-L_1 and 15 mg $Zn(NO_3)_2 \cdot 6H_2O$ were dissolved in 1.5 mL DMF, 2 drops of HBF4 (40% in water) were added to the solution. The mixture was sealed in a glass vial and heated at 75 °C for 36 h. After cooling to room temperature, brown crystals of **URMOF-2** were obtained in a yield 57% base on H_6-L_1 . IR (KBr pellet, cm⁻¹): 1654, 1561, 1419, 1387, 1210, 1105, 775, 665.

Synthesis of URMOF-3: 10 mg H_3 - L_2 , 40 mg $Zn(NO_3)_2$ · $6H_2O$, 1.5 mL DMF and 1.5mL NMP were sealed in a glass vial and heated at 100 °C for 32 h, then cooled to room temperature, colorless crystals of **URMOF-3** were obtained in a yield 72% base on H_3 - L_2 . IR (KBr pellet, cm⁻¹): 1620, 1554, 1400, 1320, 1224, 1178, 1019, 954, 777, 694.

Synthesis of URMOF-4: 10 mg H_3 - L_2 , 15 mg In(NO₃)₃·4H₂O, 1.5 mL DMF and 0.5 mL NMP were sealed in a glass vial and heated at 75 °C for 36 h, cooled to room temperature afford colorless crystal of URMOF-4 in a yield 41% base on H_3 - L_2 . IR (KBr pellet, cm⁻¹): 1657, 1605, 1415, 1387, 1317, 1217, 1175, 1101, 784, 668.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental section and procedures for the reported MOFs, catalytic substrates and products synthesis and characterization, simulated adsorption isotherms of N₂ for URMOFs, single crystal data, PXRD, TGA and NMR spectra. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

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Notes

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REFERENCES

(1) O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M. The Reticular Chemistry Structure Resource (RCSR) Database of, and Symbols for, Crystal Nets. Acc. Chem. Res. 2008, 41, 1782-1789.

(2) Ferey, G. Hybrid porous solids: past, present, future. Chem. Soc. Rev. 2008, 37, 191-214.

(3) Zhou, H. C.; Long, J. R.; Yaghi, O. M. Introduction to metalorganic frameworks. Chem. Rev. 2012, 112, 673-674.

(4) Horike, S.; Shimomura, S.; Kitagawa, S. Soft porous crystals. Nat. Chem. 2009, 1, 695-704.

(5) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The chemistry and applications of metal-organic frameworks. Science **2013,** *341*, 1230444.

(6) Morris, R. E.; Bu, X. Induction of chiral porous solids containing only achiral building blocks. Nat. Chem. 2010, 2, 353-361.

(7) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. Science 2002, 295, 469-472.

(8) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. Hydrogen storage in microporous metal-organic frameworks. Science 2003, 300, 1127-1129.

31 (9) Murray, L. J.; Dinca, M.; Long, J. R. Hydrogen storage in metal-organic frameworks. Chem. Soc. Rev. 2009, 38, 1294-1314. 32

(10) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D. W. Hydrogen 33 Storage in Metal-Organic Frameworks. Chem. Rev. 2012, 112, 782-34 835. 35

(11) He, Y. B.; Zhou, W.; Yildirim, T.; Chen, B. L. A series of metal-organic frameworks with high methane uptake and an empirical equation for predicting methane storage capacity. Energy Environ. Sci. 2013, 6, 2735-2744.

39 (12) Deshmukh, M. M.; Ohba, M.; Kitagawa, S.; Sakaki, S. Absorption of CO_2 and CS_2 into the Hofmann-type porous 40 coordination polymer: electrostatic versus dispersion 41 interactions. J. Am. Chem. Soc. 2013, 135, 4840-4849. 42

(13) Lin, Q.; Wu, T.; Zheng, S.-T.; Bu, X.; Feng, P. Single-Walled 43 Polytetrazolate Metal-Organic Channels with High Density of 44 Open Nitrogen-Donor Sites and Gas Uptake. J. Am. Chem. Soc. 45 2012, 134, 784-787.

46 (14) Li, J. R.; Sculley, J.; Zhou, H. C. Metal-Organic Frameworks 47 for Separations. Chem. Rev. 2012, 112, 869-932.

(15) Matsuda, R. MATERIALS CHEMISTRY Selectivity from 48 flexibility. Nature 2014, 509, 434-435. 49

(16) Zhang, Z.; Yao, Z.-Z.; Xiang, S.; Chen, B. Perspective of 50 microporous metal-organic frameworks for CO₂ capture and 51 separation. Energy Environ. Sci. 2014, 7, 2868-2899.

52 (17) Xiang, S.; He, Y.; Zhang, Z.; Wu, H.; Zhou, W.; Krishna, R.; 53 Chen, B. Microporous metal-organic framework with potential 54 for carbon dioxide capture at ambient conditions. Nat. Commun. 55 2012, 3, 954.

(18) Xiang, S. C.; Zhang, Z.; Zhao, C. G.; Hong, K.; Zhao, X.; Ding, 56 D. R.; Xie, M. H.; Wu, C. D.; Das, M. C.; Gill, R.; Thomas, K. M.; Chen, B. Rationally tuned micropores within enantiopure metal-58

organic frameworks for highly selective separation of acetylene and ethylene. Nat. Commun. 2011, 2, 204.

(19) Liao, P. Q.; Zhou, D. D.; Zhu, A. X.; Jiang, L.; Lin, R. B.; Zhang, J. P.; Chen, X. M. Strong and dynamic CO₂ sorption in a flexible porous framework possessing guest chelating claws. J. Am. Chem. Soc. 2012, 134, 17380-17383.

(20) Lin, J.-B.; Zhang, J.-P.; Chen, X.-M. Nonclassical Active Site for Enhanced Gas Sorption in Porous Coordination Polymer. J. Am. Chem. Soc. 2010, 132, 6654-6656.

(21) Duan, J.; Higuchi, M.; Horike, S.; Foo, M. L.; Rao, K. P.; Inubushi, Y.; Fukushima, T.; Kitagawa, S. High CO₂/CH₄ and C₂ Hydrocarbons/CH₄ Selectivity in a Chemically Robust Porous Coordination Polymer. Adv. Funct. Mater. 2013, 23, 3525-3530.

(22) Horike, S.; Kishida, K.; Watanabe, Y.; Inubushi, Y.; Umeyama, D.; Sugimoto, M.; Fukushima, T.; Inukai, M.; Kitagawa, S. Dense Coordination Network Capable of Selective CO₂ Capture from C1 and C2 Hydrocarbons. J. Am. Chem. Soc. 2012, 134, 9852-9855.

(23) Du, M.; Li, C. P.; Chen, M.; Ge, Z. W.; Wang, X.; Wang, L.; Liu, C. S. Divergent Kinetic and Thermodynamic Hydration of a Porous Cu(II) Coordination Polymer with Exclusive CO₂ Sorption Selectivity. J. Am. Chem. Soc. 2014, 136, 10906-10909.

(24) Chen, S.; Zhang, J.; Wu, T.; Feng, P.; Bu, X. Multiroute Synthesis of Porous Anionic Frameworks and Size-Tunable Extraframework Organic Cation-Controlled Gas Sorption Properties. J. Am. Chem. Soc. 2009, 131, 16027-16029.

(25) Cui, Y. J.; Yue, Y. F.; Qian, G. D.; Chen, B. L. Luminescent Functional Metal-Organic Frameworks. Chem. Rev. 2012, 112, 1126-1162.

(26) Hu, Z. C.; Deibert, B. J.; Li, J. Luminescent metal-organic frameworks for chemical sensing and explosive detection. Chem. Soc. Rev. 2014, 43, 5815-5840.

(27) Chen, B.; Xiang, S.; Qian, G. Metal-Organic Frameworks with Functional Pores for Recognition of Small Molecules. Acc. Chem. Res. 2010, 43, 1115-1124.

(28) Doherty, C. M.; Buso, D.; Hill, A. J.; Furukawa, S.; Kitagawa, S.; Falcaro, P. Using functional nano- and microparticles for the preparation of metal-organic framework composites with novel properties. Acc. Chem. Res. 2014, 47, 396-405.

(29) Wang, H.; Xu, J.; Zhang, D. S.; Chen, Q.; Wen, R. M.; Chang, Z.; Bu, X. H. Crystalline capsules: metal-organic frameworks locked by size-matching ligand bolts. Angew. Chem. Int. Ed. 2015, 54, 5966-5970.

(30) Yoon, M.; Srirambalaji, R.; Kim, K. Homochiral Metal-Organic Frameworks for Asymmetric Heterogeneous Catalysis. Chem. Rev. 2012, 112, 1196-1231.

(31) Dhakshinamoorthy, A.; Garcia, H. Metal-organic frameworks as solid catalysts for the synthesis of nitrogen-containing heterocycles. Chem. Soc. Rev. 2014, 43, 5750-5765.

(32) Liu, J. W.; Chen, L. F.; Cui, H.; Zhang, J. Y.; Zhang, L.; Su, C. Y. Applications of metal-organic frameworks in heterogeneous supramolecular catalysis. Chem. Soc. Rev. 2014, 43, 6011-6061.

(33) Wang, C.; Zheng, M.; Lin, W. Asymmetric Catalysis with Chiral Porous Metal-Organic Frameworks: Critical Issues. J. Phys. Chem. Lett. 2011, 2, 1701-1709.

(34) Wang, C.; Wang, J. L.; Lin, W. Elucidating molecular iridium water oxidation catalysts using metal-organic frameworks: a comprehensive structural, catalytic, spectroscopic, and kinetic study. J. Am. Chem. Soc. 2012, 134, 19895-19908.

(35) Ma, L.; Abney, C.; Lin, W. Enantioselective catalysis with homochiral metal-organic frameworks. Chem. Soc. Rev. 2009, 38, 1248-1256.

(36) Kong, G.-Q.; Ou, S.; Zou, C.; Wu, C.-D. Assembly and Post-Modification of a Metal-Organic Nanotube for Highly Efficient Catalysis. J. Am. Chem. Soc. 2012, 134, 19851-19857.

(37) Sawano, T.; Thacker, N. C.; Lin, Z.; McIsaac, A. R.; Lin, W. Robust, chiral, and porous BINAP-based metal-organic

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36

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59 60

frameworks for highly enantioselective cyclization reactions. J. Am. Chem. Soc. 2015, 137, 12241-12248.

- 2 (38) Thacker, N. C.; Lin, Z.; Zhang, T.; Gilhula, J. C.; Abney, C. W.; Lin, W. Robust and Porous beta-Diketiminate-3 Functionalized Metal-Organic Frameworks for Earth-Abundant-4 Metal-Catalyzed C-H Amination and Hydrogenation. J. Am. 5 Chem. Soc. 2016, doi: 10.1021/jacs.1025b13394. 6
- (39) Zhang, T.; Manna, K.; Lin, W. Metal-Organic Frameworks 7 Stabilize Solution-Inaccessible Cobalt Catalysts for Highly 8 Efficient Broad-Scope Organic Transformations. J. Am. Chem. 9 Soc. 2016, doi: 10.1021/jacs.1026b00849.
- 10 (40) Gascon, J.; Corma, A.; Kapteijn, F.; Llabrés i Xamena, F. X. Metal Organic Framework Catalysis: Quo vadis? ACS Catal. 2014, 11 4, 361-378. 12
- (41) Dhakshinamoorthy, A.; Alvaro, M.; Corma, A.; Garcia, H. 13 Delineating similarities and dissimilarities in the use of metal 14 organic frameworks and zeolites as heterogeneous catalysts for 15 organic reactions. Dalton Trans. 2011, 40, 6344-6360.
- 16 (42) Song, F. J.; Wang, C.; Falkowski, J. M.; Ma, L. Q.; Lin, W. B. 17 Isoreticular Chiral Metal-Organic Frameworks for Asymmetric Alkene Epoxidation: Tuning Catalytic Activity by Controlling 18 Framework Catenation and Varying Open Channel Sizes. J. Am. 19 Chem. Soc. 2010, 132, 15390-15398. 20
- (43) Ma, L.; Falkowski, J. M.; Abney, C.; Lin, W. A series of 21 isoreticular chiral metal-organic frameworks as a tunable 22 platform for asymmetric catalysis. Nat. Chem. 2010, 2, 838-846.
- 23 (44) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; 24 Eddaoudi, M.; Kim, J. Reticular synthesis and the design of new 25 materials. *Nature* **2003**, *423*, 705-714.
- (45) Zhang, Y. B.; Zhou, H. L.; Lin, R. B.; Zhang, C.; Lin, J. B.; 26 Zhang, J. P.; Chen, X. M. Geometry analysis and systematic 27 synthesis of highly porous isoreticular frameworks with a unique 28 topology. Nat. Commun. 2012, 3, 642. 29
- (46) Zhang, Z.; Schreiner, P. R. (Thio)urea organocatalysis--what 30 can be learnt from anion recognition? Chem. Soc. Rev. 2009, 38, 31 1187-1198. 32
 - (47) Veitch, G. E.; Jacobsen, E. N. Tertiary aminourea-catalyzed enantioselective iodolactonization. Angew. Chem. Int. Ed. 2010, 49, 7332-7335.
 - (48) Gu, Q.; You, S. L. Desymmetrization of Cyclohexadienones via Asymmetric Michael Reaction Catalyzed by Cinchonine-Derived Urea. Org. Lett. 2011, 13, 5192-5195.
- 37 (49) Brindle, C. S.; Yeung, C. S.; Jacobsen, E. N. Chiral beta-38 Urea-Catalyzed Iodoamines by Iodocyclization of 39 Trichloroacetimidates. Chem. Sci. 2013, 4.
- 40 (50) Auvil, T. J.; So, S. S.; Mattson, A. E. Arylation of diazoesters 41 by a transient N-H insertion organocascade. Angew. Chem. Int. 42 *Ed.* **2013**, *52*, 11317-11320.
- (51) Odagi, M.; Furukori, K.; Watanabe, T.; Nagasawa, K. 43 Asymmetric alpha-hydroxylation of tetralone-derived beta-44 ketoesters by using a guanidine-urea bifunctional organocatalyst 45 in the presence of cumene hydroperoxide. Chem. Eur. J. 2013, 19, 46 16740-16745.
- 47 (52) McGuirk, C. M.; Stern, C. L.; Mirkin, C. A. Small molecule 48 regulation of self-association and catalytic activity in a 49 supramolecular coordination complex. J. Am. Chem. Soc. 2014, 50 136, 4689-4696.
- (53) So, S. S.; Oottikkal, S.; Badjic, J. D.; Hadad, C. M.; Mattson, A. E. Urea-Catalyzed N-H Insertion-Arylation Reactions of 52 Nitrodiazoesters. J. Org. Chem. 2014, 79, 4832-4842.
- 53 (54) Xu, H.; Zuend, S. J.; Woll, M. G.; Tao, Y.; Jacobsen, E. N. 54 Asymmetric cooperative catalysis of strong Bronsted acid-55 promoted reactions using chiral ureas. Science 2010, 327, 986-56 990. 57
 - (55) Schreiner, P. R. Chemistry. Cooperativity tames reactive catalysts. Science 2010, 327, 965-966.

(56) Sambrook, M. R.; Hiscock, J. R.; Cook, A.; Green, A. C.; Holden, I.; Vincent, J. C.; Gale, P. A. Hydrogen bond-mediated recognition of the chemical warfare agent soman (GD). Chem. Commun. 2012, 48, 5605-5607.

(57) Tresca, B. W.; Zakharov, L. N.; Carroll, C. N.; Johnson, D. W.; Haley, M. M. Aryl C-H…Cl hydrogen bonding in a fluorescent anion sensor. Chem. Commun. 2013, 49, 7240-7242.

(58) Custelcean, R. Urea-functionalized crystalline capsules for recognition and separation of tetrahedral oxoanions. Chem. Commun. 2013, 49, 2173-2182.

(59) Valkenier, H.; Judd, L. W.; Li, H.; Hussain, S.; Sheppard, D. N.; Davis, A. P. Preorganized Bis-Thioureas as Powerful Anion Carriers: Chloride Transport by Single Molecules in Large Unilamellar Vesicles. J. Am. Chem. Soc. 2014, 136, 12507-12512.

(60) Custelcean, R.; Bonnesen, P. V.; Duncan, N. C.; Zhang, X.; Watson, L. A.; Van Berkel, G.; Parson, W. B.; Hay, B. P. Ureafunctionalized M4L6 cage receptors: anion-templated selfassembly and selective guest exchange in aqueous solutions. J. Am. Chem. Soc. 2012, 134, 8525-8534.

(61) Pramanik, A.; Khansari, M. E.; Powell, D. R.; Fronczek, F. R.; Hossain, M. A. Absorption of atmospheric CO₂ as carbonate inside the molecular cavity of a new tripodal hexaurea receptor. Org. Lett. 2014, 16, 366-369.

(62) Wu, B.; Li, S. G.; Lei, Y. B.; Hu, H. M.; Amadeu, N. D.; Janiak, C.; Mathieson, J. S.; Long, D. L.; Cronin, L.; Yang, X. J. The Effect of the Spacer of Bis(biurea) Ligands on the Structure of A_2L_3 -type (A = anion) Phosphate Complexes. Chem. Eur. J. 2015, 21, 2588-2593.

(63) Wu, B.; Cui, F. J.; Lei, Y. B.; Li, S. G.; Amadeu, N. D.; Janiak, C.; Lin, Y. J.; Weng, L. H.; Wang, Y. Y.; Yang, X. J. Tetrahedral Anion Cage: Self-Assembly of a (PO₄)₄L₄ Complex from a Tris(bisurea) Ligand. Angew. Chem. Int. Ed. 2013, 52, 5096-5100.

(64) Roberts, J. M.; Fini, B. M.; Sarjeant, A. A.; Farha, O. K.; Hupp, J. T.; Scheidt, K. A. Urea metal-organic frameworks as effective and size-selective hydrogen-bond catalysts. J. Am. Chem. Soc. 2012, 134, 3334-3337.

(65) Dong, X. W.; Liu, T.; Hu, Y. Z.; Liu, X. Y.; Che, C. M. Urea postmodified in a metal-organic framework as a catalytically active hydrogen-bond-donating heterogeneous catalyst. Chem. Commun. 2013, 49, 7681-7683.

(66) Siu, P. W.; Brown, Z. J.; Farha, O. K.; Hupp, J. T.; Scheidt, K. A. A mixed dicarboxylate strut approach to enhancing catalytic activity of a de novo urea derivative of metal-organic framework UiO-67. Chem. Commun. 2013, 49, 10920-10922.

(67) Wang, X.-J.; Li, J.; Li, Q.-Y.; Li, P.-Z.; Lu, H.; Lao, Q.; Ni, R.; Shi, Y.; Zhao, Y. A urea decorated (3,24)-connected rht-type metal-organic framework exhibiting high gas uptake capability and catalytic activity. CrystEngComm 2015, 17, 4632-4636.

(68) Liu, Y.; Eubank, J. F.; Cairns, A. J.; Eckert, J.; Kravtsov, V.; Luebke, R.; Eddaoudi, M. Assembly of metal-organic frameworks (MOFs) based on indium-trimer building blocks: a porous MOF with soc topology and high hydrogen storage. Angew. Chem. Int. Ed. 2007, 46, 3278-3283.

(69) Zheng, S. T.; Zhao, X.; Lau, S.; Fuhr, A.; Feng, P.; Bu, X. Entrapment of metal clusters in metal-organic framework channels by extended hooks anchored at open metal sites. J. Am. Chem. Soc. 2013, 135, 10270-10273.

(70) Blatov, V. A.; Proserpio, D. M. Topological relations between three-periodic nets. II. Binodal nets. Acta Crystallogr. Sect. A 2009, 65, 202-212.

(71) Nouar, F.; Eubank, J. F.; Bousquet, T.; Wojtas, L.; Zaworotko, M. J.; Eddaoudi, M. Supermolecular building blocks (SBBs) for the design and synthesis of highly porous metal-organic frameworks. J. Am. Chem. Soc. 2008, 130, 1833-1835.

(72) Farha, O. K.; Özgür Yazaydın, A.; Eryazici, I.; Malliakas, C. D.; Hauser, B. G.; Kanatzidis, M. G.; Nguyen, S. T.; Snurr, R. Q.; Hupp, J. T. De novo synthesis of a metal-organic framework material featuring ultrahigh surface area and gas storage capacities. Nat. Chem. 2010, 2, 944-948.

(73) Zheng, B.; Bai, J.; Duan, J.; Wojtas, L.; Zaworotko, M. J. Enhanced CO₂ binding affinity of a high-uptake rht-type metalorganic framework decorated with acylamide groups. J. Am. Chem. Soc. 2011, 133, 748-751.

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20

21

22

23

24

25

26

27

28

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58

59 60

- (74) Zhao, D.; Yuan, D. Q.; Sun, D. F.; Zhou, H. C. Stabilization of Metal-Organic Frameworks with High Surface Areas by the Incorporation of Mesocavities with Microwindows. J. Am. Chem. Soc. 2009, 131, 9186-9188.
- 9 (75) Yuan, D. Q.; Zhao, D.; Sun, D. F.; Zhou, H. C. An Isoreticular 10 Series of Metal-Organic Frameworks with Dendritic Hexacarboxylate Ligands and Exceptionally High Gas-Uptake 11 Capacity. Angew. Chem. Int. Ed. 2010, 49, 5357-5361. 12
- (76) Yuan, D. Q.; Zhao, D.; Zhou, H. C. Pressure-Responsive 13 Curvature Change of a "Rigid" Geodesic Ligand in a (3,24)-14 Connected Mesoporous Metal-Organic Framework. Inorg. Chem. 15 **2011**, 50, 10528-10530. 16
 - (77) Lu, W. G.; Wei, Z. W.; Gu, Z. Y.; Liu, T. F.; Park, J.; Park, J.; Tian, J.; Zhang, M. W.; Zhang, Q.; Gentle, T.; Bosch, M.; Zhou, H. C. Tuning the structure and function of metal-organic
- frameworks via linker design. Chem. Soc. Rev. 2014, 43, 5561-19 5593.
 - (78) Yan, Y.; Yang, S.; Blake, A. J.; Schroder, M. Studies on metalorganic frameworks of Cu(II) with isophthalate linkers for hydrogen storage. Acc. Chem. Res. 2014, 47, 296-307.
 - (79) Yan, Y.; Telepeni, I.; Yang, S.; Lin, X.; Kockelmann, W.; Dailly, A.; Blake, A. J.; Lewis, W.; Walker, G. S.; Allan, D. R.; Barnett, S. A.; Champness, N. R.; Schroder, M. Metal-organic polyhedral frameworks: high H₂ adsorption capacities and neutron powder diffraction studies. J. Am. Chem. Soc. 2010, 132, 4092-4094.
 - (80) Eubank, J. F.; Nouar, F.; Luebke, R.; Cairns, A. J.; Wojtas, L.; Alkordi, M.; Bousquet, T.; Hight, M. R.; Eckert, J.; Embs, J. P.; Georgiev, P. A.; Eddaoudi, M. On demand: the singular rht net, an ideal blueprint for the construction of a metal-organic framework (MOF) platform. Angew. Chem. Int. Ed. 2012, 51, 10099-10103.
 - (81) Chae, H. K.; Siberio-Perez, D. Y.; Kim, J.; Go, Y.; Eddaoudi, M.; Matzger, A. J.; O'Keeffe, M.; Yaghi, O. M. A route to high surface area, porosity and inclusion of large molecules in crystals. Nature 2004, 427, 523-527.
- 37 (82) Furukawa, H.; Ko, N.; Go, Y. B.; Aratani, N.; Choi, S. B.; 38 Choi, E.; Yazaydin, A. O.; Snurr, R. Q.; O'Keeffe, M.; Kim, J.; 39 Yaghi, O. M. Ultrahigh Porosity in Metal-Organic Frameworks. 40 Science 2010, 329, 424-428.
- 41 (83) van Gorp, J. J.; Vekemans, J. A. J. M.; Meijer, E. W. C₃-42 symmetrical supramolecular architectures: Fibers and organic gels from discotic trisamides and trisureas. J. Am. Chem. Soc. 43 2002, 124, 14759-14769. 44
- (84) Li, L. Y.; Chen, Z. L.; Zhong, H.; Wang, R. H. Urea-Based 45 Porous Organic Frameworks: Effective Supports for Catalysis in 46 Neat Water. Chem. Eur. J. 2014, 20, 3050-3060.
- 47 (85) Spek, A. L. Single-crystal structure validation with the 48 program PLATON. J. Appl. Crystallogr. 2003, 36, 7-13.
- 49 (86) Choi, M. H.; Park, H. J.; Hong, D. H.; Suh, M. P. Comparison 50 of Gas Sorption Properties of Neutral and Anionic Metal-Organic Frameworks Prepared from the Same Building Blocks but in 51 Different Solvent Systems. Chem. Eur. J. 2013, 19, 17432-17438. 52
- (87) Zhang, Y. B.; Furukawa, H.; Ko, N.; Nie, W.; Park, H. J.; 53 Okajima, S.; Cordova, K. E.; Deng, H.; Kim, J.; Yaghi, O. M. 54 Introduction of functionality, selection of topology, and 55 enhancement of gas adsorption in multivariate metal-organic 56 framework-177. J. Am. Chem. Soc. 2015, 137, 2641-2650. 57
 - (88) Fang, Q. R.; Yuan, D. Q.; Sculley, J.; Li, J. R.; Han, Z. B.; Zhou, H. C. Functional mesoporous metal-organic frameworks

for the capture of heavy metal ions and size-selective catalysis. Inorg. Chem. 2010, 49, 11637-11642.

(89) Serre, C.; Millange, F.; Surble, S.; Ferey, G. A route to the synthesis of trivalent transition-metal porous carboxylates with trimeric secondary building units. Angew. Chem. Int. Ed. 2004, 43, 6286-6289.

(90) Horcajada, P.; Surble, S.; Serre, C.; Hong, D. Y.; Seo, Y. K.; Chang, J. S.; Greneche, J. M.; Margiolaki, I.; Ferey, G. Synthesis and catalytic properties of MIL-100(Fe), an iron(III) carboxylate with large pores. Chem. Commun. 2007, 2820-2822.

(91) Volkringer, C.; Popov, D.; Loiseau, T.; Ferey, G.; Burghammer, M.; Riekel, C.; Haouas, M.; Taulclle, F. Synthesis, Single-Crystal X-ray Microdiffraction, and NMR Characterizations of the Giant Pore Metal-Organic Framework Aluminum Trimesate MIL-100. Chem. Mater. 2009, 21, 5695-5697.

(92) Lieb, A.; Leclerc, H.; Devic, T.; Serre, C.; Margiolaki, I.; Mahjoubi, F.; Lee, J. S.; Vimont, A.; Daturi, M.; Chang, J. S. MIL-100(V) - A mesoporous vanadium metal organic framework with accessible metal sites. *Microporous Mesoporous Mater.* 2012, 157, 18-23.

(93) Lohe, M. R.; Rose, M.; Kaskel, S. Metal-organic framework (MOF) aerogels with high micro- and macroporosity. Chem. Commun. 2009, 6056-6058.

(94) Mondloch, J. E.; Karagiaridi, O.; Farha, O. K.; Hupp, J. T. Activation of metal-organic framework materials. CrystEngComm 2013, 15, 9258-9264.

(95) Serre, C.; Millange, F.; Thouvenot, C.; Nogues, M.; Marsolier, G.; Louer, D.; Ferey, G. Very large breathing effect in the first nanoporous chromium(III)-based solids: MIL-53 or $Cr^{III}(OH) \cdot \{O_2C - C_6H_4 - CO_2\} \cdot \{HO_2C - C_6H_4 - CO_2H\}_x \cdot H_2O_y.$ J. Am. Chem. Soc. 2002, 124, 13519-13526.

(96) Ghoufi, A.; Maurin, G. Hybrid Monte Carlo Simulations Combined with a Phase Mixture Model to Predict the Structural Transitions of a Porous Metal-Organic Framework Material upon Adsorption of Guest Molecules. J. Phys. Chem. C 2010, 114, 6496-6502.

(97) Llewellyn, P. L.; Maurin, G.; Devic, T.; Loera-Serna, S.; Rosenbach, N.; Serre, C.; Bourrelly, S.; Horcajada, P.; Filinchuk, Y.; Ferey, G. Prediction of the conditions for breathing of metal organic framework materials using a combination of X-ray powder diffraction, microcalorimetry, and molecular simulation. J. Am. Chem. Soc. 2008, 130, 12808-12814.

(98) Barin, G.; Krungleviciute, V.; Gomez-Gualdron, D. A.; Sarjeant, A. A.; Snurr, R. Q.; Hupp, J. T.; Yildirim, T.; Farha, O. K. Isoreticular Series of (3,24)-Connected Metal-Organic Frameworks: Facile Synthesis and High Methane Uptake Properties. Chem. Mater. 2014, 26, 1912-1917.

(99) Sarkisov, L.; Harrison, A. Computational structure characterisation tools in application to ordered and disordered porous materials. Mol. Simulat. 2011, 37, 1248-1257.

(100) Dubbeldam, D.; Calero, S.; Ellis, D. E.; Snurr, R. O. RASPA: molecular simulation software for adsorption and diffusion in flexible nanoporous materials. Mol. Simulat. 2015, 42, 81-101.

(101) Xiang, S. C.; Zhou, W.; Gallegos, J. M.; Liu, Y.; Chen, B. L. Exceptionally High Acetylene Uptake in a Microporous Metal-Organic Framework with Open Metal Sites. J. Am. Chem. Soc. 2009, 131, 12415-12419.

(102) Chen, B. L.; Eddaoudi, M.; Hyde, S. T.; O'Keeffe, M.; Yaghi, O. M. Interwoven metal-organic framework on a periodic minimal surface with extra-large pores. Science 2001, 291, 1021-1023.

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