

# Clicked Isorecticular Metal–Organic Frameworks and Their High Performance in the Selective Capture and Separation of Large Organic Molecules

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**Abstract:** Three highly porous metal–organic frameworks (MOFs) with a uniform *rht*-type topological network but hierarchical pores were successfully constructed by the assembly of triazole-containing dendritic hexacarboxylate ligands with  $\text{Zn}^{\text{II}}$  ions. These transparent MOF crystals present gradually increasing pore sizes upon extension of the length of the organic backbone, as clearly identified by structural analysis and gas-adsorption experiments. The inherent accessibility of the pores to large molecules endows these materials with unique properties for the uptake of large guest molecules. The visible selective adsorption of dye molecules makes these MOFs highly promising porous materials for pore-size-dependent large-molecule capture and separation.

Owing to their intriguing structures, high porosity, and wide potential application, metal–organic frameworks (MOFs) have attracted tremendous attention over the past decade.<sup>[1,2]</sup> One inherent structural feature of MOFs that distinguishes them from other inorganic porous materials, such as zeolites, porous silica, and activated porous carbon materials, is that they are hybrid materials with inorganic units and organic moieties. This characteristic endows them

with chemical tunability and together with their diverse coordination geometries enables them to be tailored into various frameworks with different pore sizes for target applications.<sup>[1,2]</sup> Abundant MOF structures have been fabricated by the judicious combination of organic ligands and metal ions or metal–cluster secondary building units generated in situ, and great effort has been dedicated to the exploration of their application for gas or small-molecule capture and storage.<sup>[2]</sup> To extend their applicability to large-molecule-based applications, such as organic-pollutant removal, bioimaging, drug delivery, heterogeneous catalysis, and even selective molecular capture and separation, the development of efficient MOFs with pores accessible to large molecules is highly desired.<sup>[3,4]</sup>

Versatile click chemistry, that is, copper(I)-catalyzed azide–alkyne cycloaddition, has been utilized extensively in the fabrication of various functional materials.<sup>[5–7]</sup> Since the reactions can be carried out under mild conditions in high yield, click chemistry provides a straightforward and effective approach to the design and synthesis of organic ligands suitable for the assembly of MOFs.<sup>[7]</sup> Meanwhile, reticular chemistry, as exemplified in a series of reported MOFs, has been well documented as a reliable strategy for the construction of frameworks with predetermined porosity.<sup>[8,9]</sup> Desired structural analogues with tailored pore sizes can be fabricated from such frameworks by employing suitable ligands to replace initial ligands in a known ordered network. By taking advantage of convenient click reactions and the conceptual approach of reticular chemistry, the “click” extension of isorecticular frameworks should be a feasible strategy for developing MOFs with pores that are accessible to large molecules. Herein, we describe the successful application of this strategy for the fabrication of three isorecticular MOFs, **1–3**,<sup>[10]</sup> and demonstrate their remarkable capability for the selective capture and separation of large molecules.

The *rht*-type MOF framework usually shows a high surface area, large open pores, and the absence of framework interpenetration.<sup>[7b,11,12]</sup> These salient features make the *rht*-type network an ideal prototypical framework for the development of novel large-pore MOFs by the strategy of click extension. Thus, a dendritic hexacarboxylate ligand ( $\text{H}_6\text{L}$ ), 5,5',5''-(4,4',4''-(benzene-1,3,5-triyl)tris(1*H*-1,2,3-triazole-4,1-diyl))trisisophthalic acid (**H<sub>6</sub>L1**, Figure 1a), was first designed and successfully synthesized through click chemistry. Subsequently, colorless crystals of MOF **1** were obtained by treatment of the ligand with  $\text{Zn}^{\text{II}}$  ions. Motivated by this

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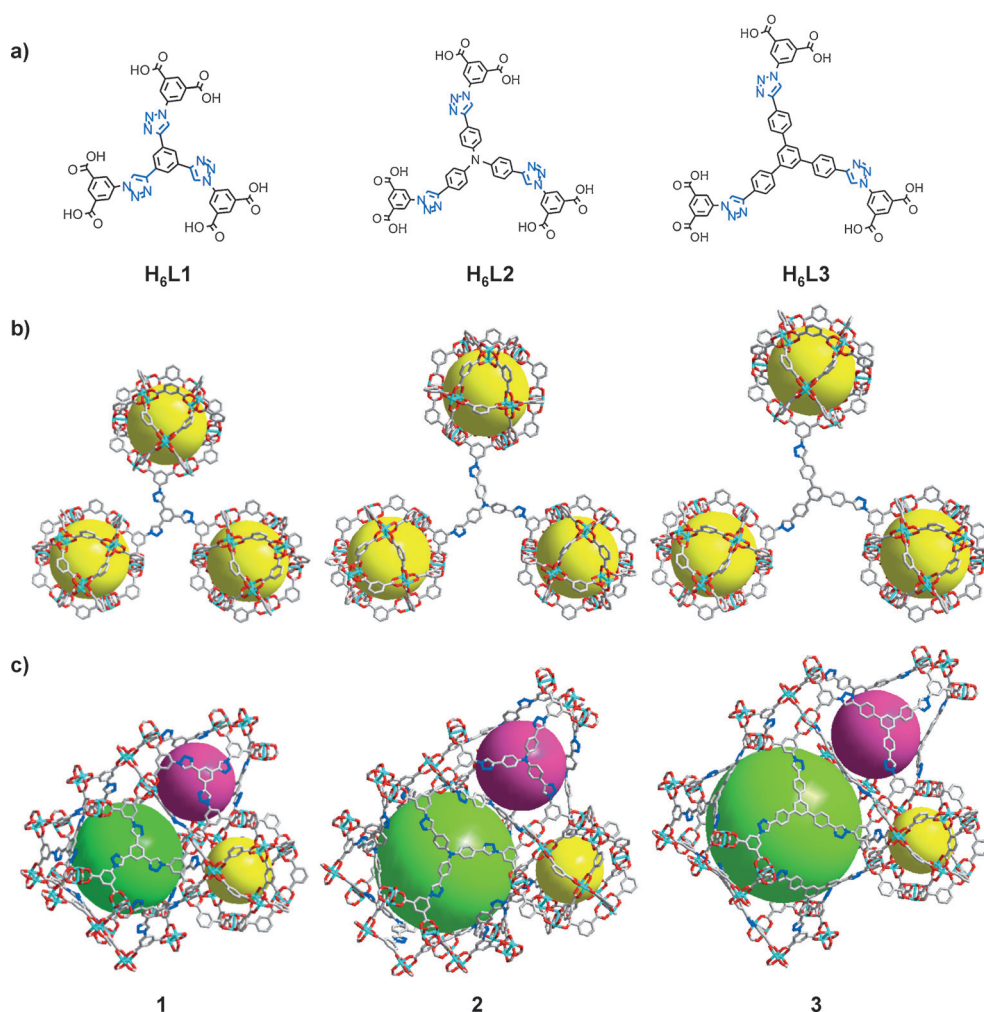
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**Figure 1.** a) Structure of the click-extended dendritic hexacarboxylate ligands **H<sub>6</sub>L1**, **H<sub>6</sub>L2**, and **H<sub>6</sub>L3**. b) (3,24)-Connected *rhf*-type frameworks of MOFs **1**, **2**, and **3**. c) Three types of metal-organic polyhedrons in MOFs **1**, **2**, and **3**: cub-*O<sub>h</sub>* (yellow), T-*T<sub>d</sub>* (violet), and T-*O<sub>h</sub>* (green).

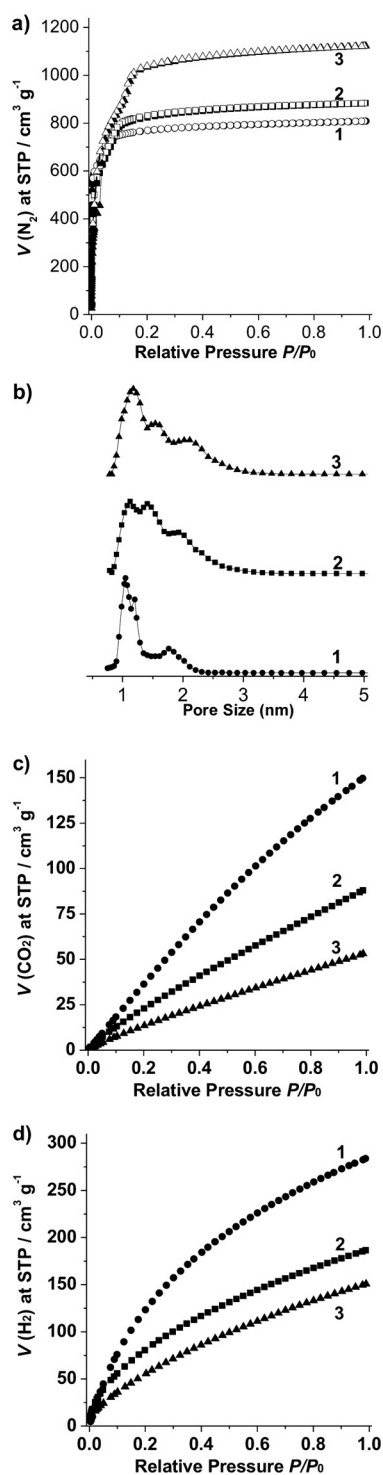
success, we also synthesized two larger **H<sub>6</sub>L** ligands, 5,5',5''-(4,4',4''-((triphenylamine)-4,4',4''-triyl)tris(1*H*-1,2,3-triazole-4,1-diyl))triisophthalic acid (**H<sub>6</sub>L2**) and 5,5',5''-(4,4',4''-((1,3,5-triphenylbenzene)-4,4',4''-triyl)tris(1*H*-1,2,3-triazole-4,1-diyl))triisophthalic acid (**H<sub>6</sub>L3**, Figure 1a). Thus, two new MOFs, **2** (light yellow) and **3** (colorless), were fabricated by a similar process (see the experimental section and Figure S1 in the Supporting Information).

Crystal-structure analysis of MOFs **1**, **2**, and **3** confirmed that all three MOFs possess the same framework and share a similar framework formula described by  $[\text{Zn}_3(\text{L})(\text{H}_2\text{O})_3]_n$ . In the crystal structures, 24 isophthalate moieties from organic ligands connect 12  $\{\text{Zn}_2(\text{OOC}-)_4\}$  paddlewheel units to form a metal-organic cuboctahedron (cub-*O<sub>h</sub>*),<sup>[11–13]</sup> three of which are connected by an organic linker to afford a (3,24)-connected isoreticular *rhf*-type framework (Figure 1b; see also Figures S2–S4). The cuboctahedrons can be interconnected through clicked hexacarboxylate ligands to form two other types of metal-organic polyhedrons, that is, truncated tetrahedrons (T-*T<sub>d</sub>*) and truncated octahedrons (T-*O<sub>h</sub>*; Figure 1c).<sup>[7b,11,12]</sup> The pore diameters of the cub-*O<sub>h</sub>* polyhedrons

are predefined by the geometry of the dimetal paddlewheel units and the span of the dicarboxylate groups of the isophthalate moieties on each terminus of the hexacarboxylate ligands. Thus, the inner sphere diameter of the cub-*O<sub>h</sub>* polyhedrons is the same in all three MOFs: approximately 11.0 Å if the van der Waals radii are taken into consideration. Because of the variation in the length of the triazole-containing hexacarboxylate ligands, however, the size of the inner sphere diameters for both the T-*T<sub>d</sub>* and T-*O<sub>h</sub>* polyhedrons increases from 13.0 and 20.0 Å in **1** to 14.0 and 23.0 Å in **2**, and to 15.0 and 25.0 Å in **3** (Figure 1c). Structural analysis clearly showed that these isoreticular MOFs, especially **3**, possess pores that are accessible to large molecules.

To confirm the porosity of the MOFs, we carried out  $\text{N}_2$ -adsorption/desorption measurements at 77 K after the activation process. All three MOFs exhibited reversible quasi-type-IV sorption isotherms (Figure 2a),<sup>[14]</sup> thus demonstrating that all

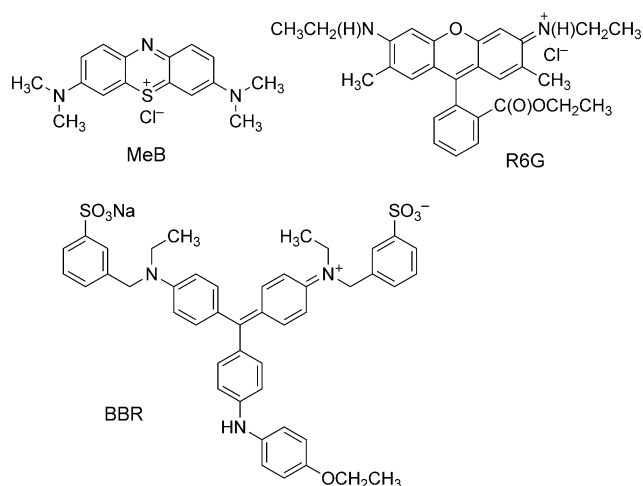
of them possess the feature that micropores dominate, with a modicum of mesopores.<sup>[7b,11,12,14]</sup> The overall  $\text{N}_2$  uptake of MOF **1** was 809  $\text{cm}^3 \text{g}^{-1}$  at 1 atm and 77 K. Its Brunauer–Emmett–Teller (BET) surface area was calculated to be 3157  $\text{m}^2 \text{g}^{-1}$ , which is comparable to that of reported MOFs with a similar framework, such as NTU-105, NOTT-122, and NU-125.<sup>[7b,11,12]</sup> MOF **2** showed higher  $\text{N}_2$  uptake of 884  $\text{cm}^3 \text{g}^{-1}$  at 1 atm and 77 K, and a BET surface area of 3529  $\text{m}^2 \text{g}^{-1}$ . MOF **3** showed the highest  $\text{N}_2$  uptake of 1123  $\text{cm}^3 \text{g}^{-1}$  under the same conditions and the largest BET surface area of 4814  $\text{m}^2 \text{g}^{-1}$ , which is comparable to that of reported MOFs with a similar framework, such as NOTT-119, NU-140, and PCN-68.<sup>[11,12]</sup> The pore-size distributions were calculated from the  $\text{N}_2$ -sorption isotherms at 77 K on the basis of nonlocal density functional theory. The pore-size distributions showed two sharp peaks focused at 10.5 and 12 Å and a broad peak ranging from 16 to 21 Å for MOF **1**, two peaks at 11 and 14 Å with a broad peak ranging from 18 to 23 for MOF **2**, and two peaks at 11 and 15.5 Å with a broad peak ranging from 20 to 25 Å for MOF **3** (Figure 2b). These results are consistent with the observations from the corresponding



**Figure 2.** a)  $\text{N}_2$ -adsorption/desorption isotherms at 77 K, b) pore-size distributions, c)  $\text{CO}_2$ -adsorption isotherms at 273 K, and d)  $\text{H}_2$ -adsorption isotherms at 77 K of activated MOFs 1–3. STP = standard temperature and pressure.

crystal structures. Furthermore, all three MOFs showed good  $\text{CO}_2$ - and  $\text{H}_2$ -adsorption capabilities (Figure 2c,d; see also Figures S11–S15). Gas-adsorption analysis further confirmed that these isorecticular MOFs have high porosity with large pore sizes.

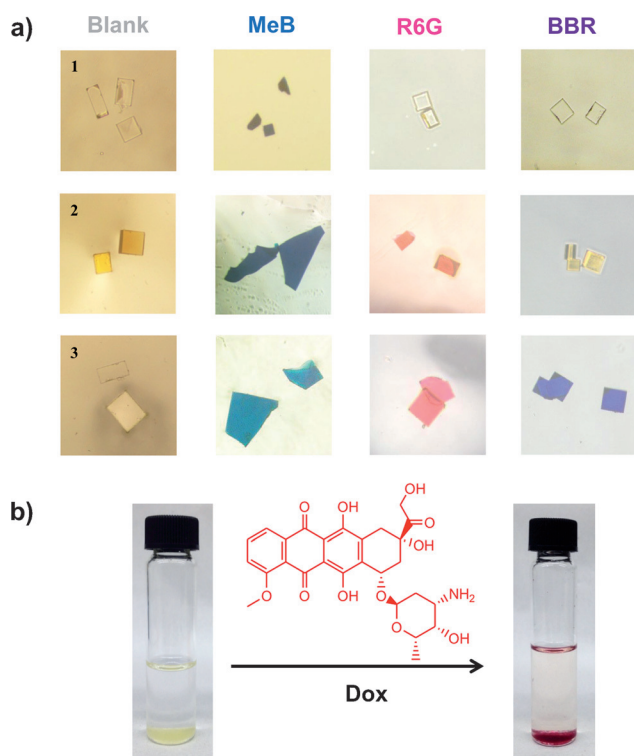
The high porosity and large accessible pores of these triazole-containing MOFs inspired us to investigate their potential for large-molecule applications. Organic dyes are large molecules that form a big group of organic pollutants that often cause aesthetic and environmental problems, even at low concentrations,<sup>[15]</sup> and are also frequently used as biological markers for bioimaging.<sup>[16]</sup> Thus, we took advantage of the visible color of these large organic molecules and the colorless nature/light-yellow color of the MOF crystals and examined a range of organic dyes with different molecular sizes in large-molecule capture and separation by MOFs 1–3. When activated crystals of all three MOFs were immersed in solutions of methylene blue (MeB, blue), rhodamine 6G (R6G, red), and brilliant blue R (BBR, blue)



in *N,N*-dimethylformamide (DMF), color changes were clearly observed by the naked eye (Figure 3a). With the relatively small molecule MeB, color changes were observed in all MOF crystals, thus indicating that the adsorption of relatively small molecules occurred in these frameworks. With the larger molecule R6G, color changes only occurred in the crystals of 2 and 3, and with the largest molecule BBR, a color change only occurred in the crystals of 3. The results clearly show that these triazole-containing MOFs could potentially be used as size-dependent adsorbents for pollutant removal through large-molecule uptake, as well as probe carriers for bioimaging. To further investigate large-molecule uptake by the MOFs, we examined their adsorption of other dye molecules (toluylene red, rhodamine B, and fast green FCF; see Figure S16) as well as a large anticancer drug molecule, doxorubicin (Dox). After immersing activated crystals of 3 in a solution of Dox in DMF (Figure 3b; see also Figure S17), we clearly observed a color change of the crystals from colorless to dark-red by the naked eye, thus indicating that the “clicked” MOFs with large pores could also potentially be used for drug-delivery applications.

Since the soaking experiments suggested that these porous MOFs could also be used for the size-dependent separation of mixtures of large molecules, we soaked crystals of 1 and 2 in solutions in DMF of MeB/R6G and R6G/BBR

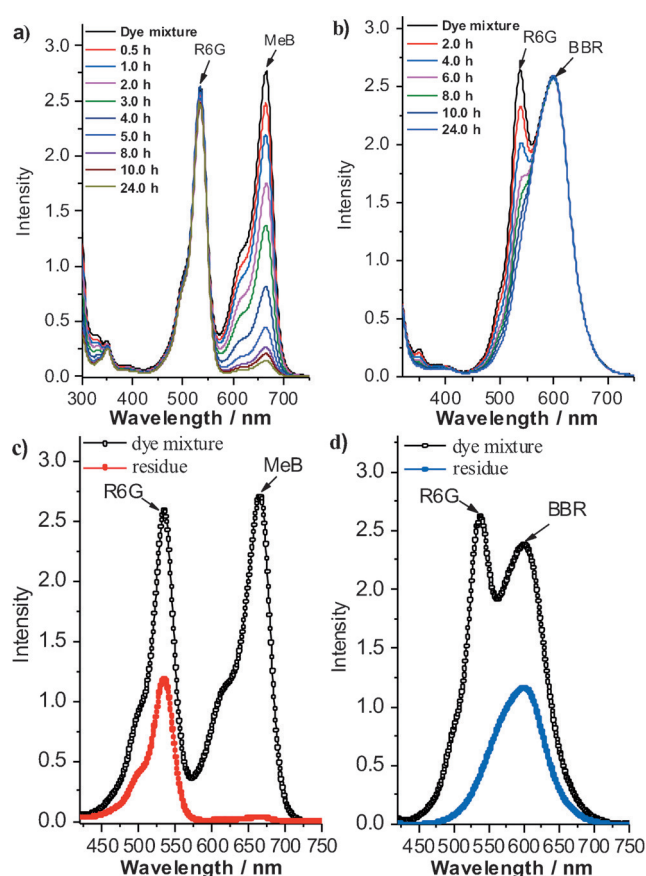




**Figure 3.** a) Comparison of the color of crystals of MOFs 1–3 before and after dye soaking. b) Change in the color of crystals of MOF 3 upon soaking in a solution of Dox in DMF.

mixtures, respectively, and detected concentration changes of the dye mixtures by UV/Vis spectroscopy (Figure 4a,b). The results clearly show that the smaller dye molecules could be incorporated into the MOF crystals, whereas the larger dye molecules remained in solution, thus confirming our hypothesis that these triazole-containing MOFs could serve as highly effective materials for size-dependent large-molecule separation. We then prepared columns packed with crystals of **1** and **2** to investigate their performance in column-based large-molecule separation. When the MeB/R6G dye mixture was passed several times slowly through the column packed with **1**, a sharp decrease in the ratio of MeB to R6G was detected in the residue of the dye mixture by UV/Vis spectroscopy, thus indicating effective separation by pore-size-dependent molecule-selective capture (Figure 4c). The same phenomenon was also observed when the R6G/BBR dye mixture was passed through the column packed with **2** (Figure 4d). Since the capacity of porous materials for molecule capture is always highly influenced by the pore diameters, the demonstrated strategy of isorecticular extension through versatile click chemistry to engineer MOFs with suitable pore sizes would be an ideal approach for large-molecule applications.

In summary, by subtly varying the length of known hexacarboxylate ligands by click chemistry, three highly porous isorecticular MOFs with hierarchical large pores were successfully assembled. The investigations on size-dependent large-molecule capture and separation clearly indicate that these triazole-containing MOFs are promising porous materials for pollutant removal, bioimaging, and drug delivery. On



**Figure 4.** UV/Vis spectra of solutions of MeB/R6G and R6G/BBR dye mixtures during the soaking of a) **1** or b) **2** in the solution as well as before and after being passed several times through a column packed with c) **1** or d) **2**.

account of the straightforward and efficient generation of diverse frameworks with different pore sizes appropriate for certain large guest molecules, the present method of isorecticular extension through click chemistry could serve as a general protocol for the development of more delicate MOFs with desired functionalities.

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