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## A urea decorated (3,24)-connected *rht*-type metal-organic framework exhibiting high gas uptake capability and catalytic activity<sup>†</sup>

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A (3,24)-connected *rht*-type metal organic framework (MOF Cu-UBTA) containing urea group was readily prepared by the solvothermal reaction between a hexacarboxylate ligand and Cu(NO<sub>3</sub>)<sub>2</sub>. Gas sorption investigations demonstrated its high porosity and high uptake capacities for CO<sub>2</sub> and H<sub>2</sub>. Moreover, the MOF can act as an efficiently heterogeneous catalyst for Friedel-Craft alkylation of *N*-methyl pyrrole or indole with nitroalkenes.

Metal-organic frameworks (MOFs) are well-defined porous and crystalline solids consisting of metal ions or metal-containing clusters connected to multidentate organic linkers *via* metal coordination bonds.<sup>1-7</sup> Due to their hybrid inorganic-organic compositions, the structures and properties of MOFs can be easily tuned through judicious combination of metal centres and organic linkers toward specific applications,<sup>1-7</sup> such as gas storage and separation,<sup>8-14</sup> heterogeneous catalysis<sup>15-19</sup> and sensing.<sup>20-23</sup>

In comparison to the purely inorganic porous materials (for example activated porous carbons), the inherent modular nature of MOFs highly enables the rational design and preparation of these materials with pre-determined ordered structures and topologies via reticular synthesis.<sup>24-26</sup> Recently, it has been evidenced that a (3,24)-connected rht-topology could serve as an ideal blueprint for the development of MOFs,<sup>27</sup> in which a 24-connected paddlewheel-based supermolecular building block (SBB) with rhombicuboctahedral geometry linked through trigonal (3-connected) nodes.<sup>28-45</sup> These isoreticular MOFs are typically prepared by the solvothermal reaction between copper(II) ions and an over-all C3-symmetrical hexacarboxylate acid linker composed of three coplanar isophthalates.<sup>46-48</sup> Owing to the highly connected framework presented in these *rht*-MOFs, they possess several specific advantages, such as the robust framework with high surface area and high concentration of open-metal sites. Therefore,

most of research attention regarding *rht*-MOFs has mainly been devoted into the gas storage and separation.<sup>27-45</sup> However, only a few rare examples exploited their potential applications in the other areas except gas uptake has been reported so far.<sup>49,50</sup> To our knowledge, Shi's group reported the first example of luminescent *rht*-MOF Zn-TDPAT (TDPAT = 2,4,6-tris(3,5-dicarboxyl phenylamino)-1,3,5-triazine), which serve as a dual functional sensor for quantitatively detecting the concentration of nitrobenzene and temperature.<sup>50</sup>

One of possible reasons for limiting the applications of rht-MOFs should be ascribed to the slow development of novel ligands with functional groups. Recently, we reported a porous rht-MOF Cu-ABTA in which acylamide group was used to replace one of triazole units in parent MOF NTU-105, suggesting that (3,24)-connected rht-topological MOFs could be constructed from a suitable unsymmetrical hexacarboxylate acid ligand.<sup>51</sup> Along with this research line, herein, we designed and synthesized another unsymmetrical hexacarboxylate ligand H6-L having a urea group (Fig. 1), which can act as a hydrogen-bond-donating catalytic site<sup>52,53</sup>. Then, a copper(II) rht-type MOF Cu-UBTA was successfully prepared with this new ligand. As expected, MOF Cu-UBTA exhibited high porosity with high uptake capacities for CO<sub>2</sub> and H<sub>2</sub>. Moreover, it can efficiently catalyze Friedel-Craft alkylation of N-methyl pyrrole or indole with nitroalkenes.

The unsymmetrical hexacarboxylate linker 5,5'-(4,4'-(5-(3-(3,5-dicarboxyphenyl)ureido)-1,3-phenylene)bis(1*H*-1,2,3-

triazole-4,1-diyl))diisophthalic acid (**H6-L**)was synthesized as described in Scheme S1 (in ESI). Similar to the ligands constructed in our group,<sup>6,7,39,43,51</sup> herein, we still used the click reaction and condensation reaction to design and synthesize the target ligand **H6-L**. Specifically, 3,5-diiodophenyl isocyanate was reacted with di-*tert*-butyl 5-aminoisophthalate to get the urea-functionalized precursor compound di-*tert*-butyl 5-(3-(3,5-diiodophenyl)ureido)isophthalate (1), which was converted into

di-*tert*-butyl 5-(3-(3,5-diethynylphenyl)ureido)isophthalate (2) by Sonogashira reaction with (trimethylsilyl)acetylene and subsequent deprotection with *tetra*-n-butylammonium fluoride. Then, the click reaction of diethynyl 2 and di-*tert*-butyl 5-azidoisophthalate gave the *tert*-butyl ester <sup>t</sup>Bu6-L, which was deprotected with trifluoroacetic acid to get the ligand H6-L in a high yield.



**Fig. 1** Molecular structure of the ligand hexacarboxylate acid **H6-L** (left) and single crystal structure of (3,24)-connected *rht*-topological framework in MOF **Cu-UBTA** (right).

A typical solvothermal reaction of H6-L with Cu(NO<sub>3</sub>)<sub>2</sub> in *N*,*N*-dimethylformamide (DMF) at 75 °C for 3 days afforded MOF Cu-UBTA (Cu<sub>3</sub>(L)(H<sub>2</sub>O)<sub>3</sub>·10DMF·9H<sub>2</sub>O) as block green-blue crystals. Powder X-ray diffraction (PXRD) measurements confirmed the phase purity of its bulk sample. Single-crystal X-ray diffraction studies revealed that MOF Cu-UBTA was crystallized in the tetragonal space group *I4/m* with unit-cell dimensions a = b = 31.4206 Å and c = 44.8239 Å (Table S1 in ESI). In the crystal structure of MOF Cu-UBTA, as anticipated, each 3-connected organic linker L connects with three 24-connected rhombicuboctahedral SBBs, thus generating a (3,24)-connected *rht*-topological framework (Fig. 1).



**Fig. 2** Nitrogen sorption isotherm for MOF **Cu-UBTA** at 77 K (STP = standard temperature and pressure; filled symbols, absorption; open symbols, desorption. Inset shows the BET specific surface area plot).

The total accessible volume of MOF **Cu-UBTA** after the removal of the guest solvents and coordinated water molecules was estimated to be 76% using the PLATON/VOID routine.<sup>54</sup>

The desolvated samples were prepared by exchanging the solvent in the fresh MOF **Cu-UBTA** with dichloromethane, followed by evacuation under high vacuum at 60 and 120 °C, respectively. PXRD patterns of the activated samples exhibited a good agreement with the simulated one from its crystal data (Fig. S3 in ESI), indicating the retention of the framework during the activation process. To confirm the permanent porosity of MOF **Cu-UBTA**, nitrogen sorption at 77 K was performed as shown in Fig. 2. It was found that the N<sub>2</sub> sorption isotherm exhibits a reversible pseudo-type I with a small step before the plateau appears, suggesting the presence of both micro- and mesopores within the framework. The Brunauer–Emmett–Teller (BET) surface area was calculated to be 3134 m<sup>2</sup> g<sup>-1</sup>, which is very close to our reported MOF **NTU-105** and comparable with some *rht*-MOFs (Table S2 in ESI).



Fig. 3 Gas sorption isotherms of MOF Cu-UBTA for CO<sub>2</sub> and N<sub>2</sub> measured at 273 K, and H<sub>2</sub> measured at 77 K.

In order to evaluate the potential application of MOF Cu-UBTA in gas storage and separation, we further investigated its gas uptake capacities towards  $CO_2$  and  $H_2$ . As shown in Fig. 3, the CO<sub>2</sub> sorption isotherm was measured at 273 K, revealing an uptake of 165 cm<sup>3</sup> g<sup>-1</sup> (32.4 wt%) at 1 bar. This value is still among the high CO<sub>2</sub> uptake ability reported for MOFs,<sup>55,56</sup> and even higher than some of its isoreticular rht-MOFs, such as rht-MOF-9<sup>45</sup> (Table S2 in ESI). As for nitrogen, the N<sub>2</sub> uptake of MOF Cu-UBTA was only 2.6 cm<sup>3</sup> g<sup>-1</sup> at 273 K and 1 bar, suggesting its high selectivity towards CO<sub>2</sub> over N<sub>2</sub>. Besides, the H<sub>2</sub> sorption isotherm of MOF Cu-UBTA demonstrates a H<sub>2</sub> uptake capacity as high as 281 cm<sup>3</sup> g<sup>-1</sup> (2.51wt%) at 77 K and 1 bar (Fig. 3), which is greater than MOFs PCN-6X series under the same conditions (Table S2 in ESI). Then, the isosteric heat of adsorption  $(Q_{st})$  for H<sub>2</sub> was calculated from the isotherms at 77 and 87 K by using the Clausius-Clapeyron equation, providing that the  $Q_{st}$  value for MOF Cu-UBTA decreased from 6.23 to 5.13 kJ mol<sup>-1</sup> in the uptake range of 6-164 cm<sup>3</sup> g<sup>-1</sup>. Similarly, the high performance of MOF Cu-UBTA for CO<sub>2</sub> and H<sub>2</sub> sorption should also be attributed to the high density of open copper sites and coordination-free nitrogen-rich triazole moieties within the robust rht-framework.<sup>27-45</sup>

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Since a functional urea group was introduced into MOF **Cu-UBTA** *via* ligand pre-design, in order to validate its catalytic activity, we also employed a simple Friedel–Crafts alkylation of *N*-methylpyrrole and *trans*- $\beta$ -nitrostyrene (2 :1 molar ratio) as a model reaction.<sup>53</sup> As shown in Fig. 4, the reaction with 5% molar MOF **Cu-UBTA** as catalyst was performed in CH<sub>3</sub>CN at 60 °C and monitored by <sup>1</sup>H NMR spectroscopy. The desired product was obtained in 85% yield after 48 h. No significant increase was observed with further extension of reaction time. Whereas only a trace of product was found in the control experiment without catalyst, this indicates that MOF **Cu-UBTA** can effectively catalyze the Friedel–Crafts reaction.



Fig. 4 Catalytic activities of MOF Cu-UBTA, NTU-105 and a control.

Next, to understand the role of urea unit played in the catalytic reaction, we utilized the similar MOF **NTU-105** without urea to repeat this reaction under the same conditions. It was found that MOF **NTU-105** exhibited a lower catalytic activity in relative to **Cu-UBTA** (Fig. 4). This confirms that the urea group in *rht*-MOF **Cu-UBTA** can also work as hydrogenbond-donating site to catalyze Friedel–Crafts reaction. On the other hand, the yield of product catalyzed by MOF **NTU-105** is medium 48% after 48 h, which should be attributed the Lewis acidic open copper sites in the framework. Thus, we believe that the high catalytic activity of MOF **Cu-UBTA** should originate from the synergistic effect of open metal site and urea group within the framework.

Meanwhile, the recyclability of MOF **Cu-UBTA** heterogeneous catalyst for the reaction was also investigated, which can be easily isolated from the reaction system by a simple centrifugation. It was reused for three times without obvious loss of the catalytic activity (81% for  $2^{nd}$  run, 75% for  $3^{rd}$  run). PXRD patterns for recycled catalyst revealed that MOF **Cu-UBTA** maintained its crystalline structure and framework after catalysis (Fig. S3 in ESI). Besides, the low concentration (by mass%) of Cu<sup>2+</sup> in reaction solution after catalysis and removal of MOF, was determined by inductively

coupled plasma (ICP) analysis to be  $0.5\% 1^{st}$  run,  $1.1\% 2^{nd}$  run, and  $1.8\% 3^{rd}$  run, respectively. These results confirmed the high stability of MOF **Cu-UBTA** in the catalytic reaction. Finally, we preliminarily extended the scope of the substrate including *N*-methyl indole and other nitroalkenes, giving the desired products with good to excellent yields (Table S3 in ESI).

#### Conclusions

In summary, we have successfully constructed a novel ureacontaining *rht*-type MOF **Cu-UBTA** *via* the rational ligand predesign. The *rht*-MOF demonstrated a large porosity as well as high CO<sub>2</sub> and H<sub>2</sub> uptake capacities. More importantly, the ureafunctionalized *rht*-MOF **Cu-UBTA** can act as a highly efficient heterogeneous catalyst for Friedel-Crafts reactions, due to the synergistic effect of urea groups and open metal sites within the robust framework. To the best of our knowledge, this is the first example of *rht*-type MOFs based catalyst. Furthermore, it is expected that more multi-functional *rht*-MOFs with novel properties will be constructed by the sophisticated ligand design with functional groups. Such research efforts are currently underway in our group.

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#### Notes and references

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\*Electronic Supplementary Information (ESI) available: Detailed experimental procedure, IR spectra, PXRD patterns, TGA, table of X-ray data of Cu-UBTA, gas adsorption data. CCDC 1056256. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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### TOC

## A urea decorated (3,24)-connected *rht*-type metal-organic framework exhibiting high gas

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Xiao-Jun Wang, Jian Li, Qiu-Yan Li, Pei-Zhou Li, Han Lu, Qianying Lao, Rui Ni, Yanhui Shi, and Yanli Zhao



A urea decorated *rht*-MOF exhibited high gas uptake for  $CO_2$  and  $H_2$  as well as worked as a heterogeneous catalyst for Friedel-Craft reactions.