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## Quest for highly porous metal–metalloporphyrin framework based upon a custom-designed octatopic porphyrin ligand†

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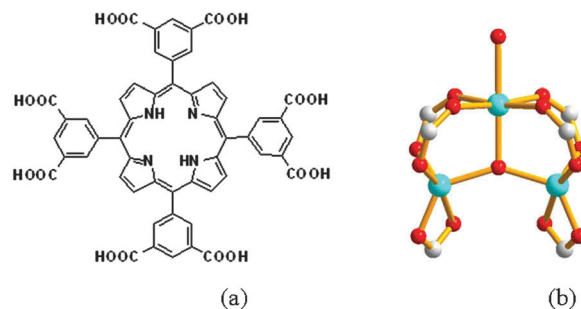
A porous metal–metalloporphyrin framework, MMPF-2, has been constructed from a custom-designed octatopic porphyrin ligand, tetrakis(3,5-dicarboxyphenyl)porphine, that links a distorted cobalt trigonal prism secondary building unit. MMPF-2 possesses permanent microporosity with the highest surface area of 2037 m<sup>2</sup> g<sup>-1</sup> among reported porphyrin-based MOFs, and demonstrates a high uptake capacity of 170 cm<sup>3</sup> g<sup>-1</sup> CO<sub>2</sub> at 273 K and 1 bar.

As an important type of biologically-relevant macrocycle, porphyrins and metalloporphyrins have been of intense research interests in the past decades.<sup>1</sup> One of their important features lies in the characteristic diversity which can be obtained through the addition of a variety of central metal entities, or *via* the introduction of functional peripheral substituents.<sup>2</sup> This has afforded them as a class of versatile materials for a range of applications,<sup>3</sup> as particularly witnessed by the rapid progress in the development of porphyrin/metalloporphyrin supramolecular materials.<sup>4</sup>

Concurrently, there has also been an escalating interest in constructing porphyrin/metalloporphyrin-based metal–organic framework (MOF) materials due to their potential applications for gas storage, artificial light harvesting system, heterogeneous catalysis, *etc.*<sup>5</sup> The first porphyrin-based MOF dates back to as early as 1991 as reported by Robson *et al.*,<sup>6</sup> and since then 94 two- or three-dimensional porphyrin-based MOF structures have been reported (see ESI† for complete references). Although the development of porphyrin-based MOFs as functional materials particularly as zeolite analogues for size and/or shape-selective heterogeneous catalysis as well as gas storage/separation,<sup>5,7</sup> has been pursued over two decades, limited progress has thus far been made in this research area. It has been recognized that porphyrin-based MOFs are notoriously prone to collapse upon the removal of guest solvent

molecules,<sup>8</sup> and that the low surface areas together with framework fragility have afforded them poor capability for gas storage<sup>9</sup> as well as moderate heterogeneous catalysis performance with either exterior surface catalysis<sup>5c,10</sup> or lack of recyclability.<sup>8</sup> Indeed, only 13 of those 94 porphyrin-based MOF structures have been reported to possess porosity as evidenced by gas sorption studies (Table S1†);<sup>5b,8,9,11</sup> and the highest surface area (Langmuir or NLDFT surface area) value reported thus far is merely ~1000 m<sup>2</sup> g<sup>-1</sup>,<sup>8b,11b</sup> which is much less than its predicted value, indicating the possible collapse of the majority of the framework. Hence, the construction of robust high-surface-area porphyrin-based MOFs and to develop them as functional materials for various applications particularly for gas storage and catalysis remains a grand challenge.

To address this challenge, herein we report the approach of combined use of a custom-designed multitopic porphyrin ligand and a robust secondary building unit (SBU), which is expected to stabilize the MOF structure and preserve its permanent porosity upon removal of guest solvent molecules thus affording superior gas storage performances compared to existing porphyrin-based MOFs. To achieve this goal, we designed a novel octatopic porphyrin ligand, tetrakis(3,5-dicarboxyphenyl)porphine (H<sub>10</sub>tdcpp) (Scheme 1a), and linked it to a distorted cobalt trigonal prism SBU (Scheme 1b) generated *in situ* to afford a robust (6, 8, 8)-connected MOF with a new topology of *msq*,<sup>12</sup> which we denote MMPF-2 (MMPF represents metal–metalloporphyrin framework). MMPF-2 possesses a surface area of 2037 m<sup>2</sup> g<sup>-1</sup>, the highest among reported porphyrin-based MOFs. The high surface area in combination with the



**Scheme 1** (a) tetrakis(3,5-dicarboxyphenyl)porphine (H<sub>10</sub>tdcpp) ligand; (b) the distorted cobalt trigonal prism SBU (turquoise, Co; grey, C; red, O; hydrogen atoms omitted for clarity).

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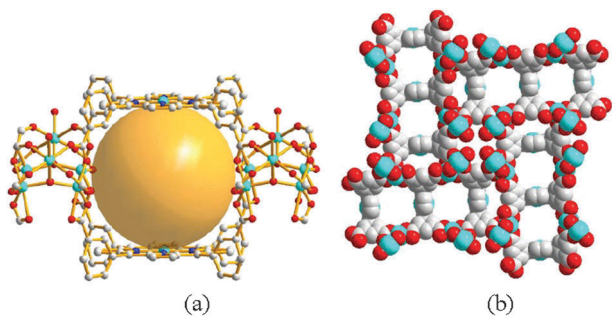
† Electronic supplementary information (ESI) available: Experimental procedures for the synthesis MMPF-2, single crystal X-ray diffraction experiment, structural topology picture, TGA plot, and procedures for gas adsorption experiments. CCDC 840130. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc33118g

high density of open cobalt centers of the porphyrin macrocycles, that are rigidly located in a “face-to-face” configuration to form the channel walls, also affords it interesting CO<sub>2</sub> capture performances.

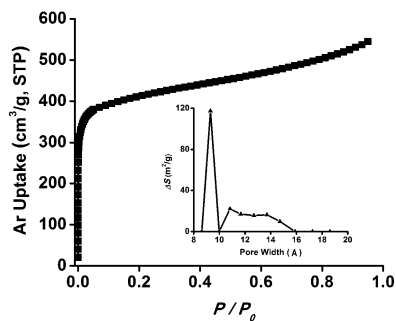
Crystals of MMPF-2 were formed *via* solvothermal reaction of the H<sub>10</sub>tdcpp and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in dimethylacetamide (DMA) at 115 °C. The product was isolated as dark red block crystals of {[Co(II)<sub>3</sub>(OH)(H<sub>2</sub>O)<sub>4</sub>(Co(II)tdcpp)<sub>3</sub>·(H<sub>2</sub>O)<sub>20</sub>·(CH<sub>3</sub>OH)<sub>22</sub>·(DMA)<sub>25</sub>} at 60% yield. The overall formula was determined by X-ray crystallography, elemental analysis, and thermogravimetric analysis (TGA) (Fig. S1†).

Single-crystal X-ray studies conducted using synchrotron micro-crystal diffraction at the Advanced Photon Source, Argonne National Laboratory, revealed that MMPF-2 crystallizes in the tetragonal space group *P*<sub>4</sub>/*mbm*. It adopts a rare distorted cobalt trigonal prism SBU,<sup>13</sup> in which three cobalt atoms bridged by the μ<sub>3</sub>-OH group connect with six carboxylate groups from six different tdcpp ligands (Scheme 1b). The distorted cobalt trigonal prism SBU<sup>14</sup> of MMPF-2 exhibits four carboxylate groups that are bi-dentate and two that are mono-dentate; only one cobalt atom is six coordinate while the other two cobalt atoms are five coordinate. Each SBU links six tdcpp ligands which are divided into two types according to the mono/bi-chelation modes of the carboxylate groups, and every tdcpp ligand connects with eight SBUs. If one assumes the SBU to be a six connected node and the tdcpp ligand to be an eight connected vertex, topologically MMPF-2 possesses an unprecedented (6, 8, 8)-connected trinodal net with a new topology of *msq* (vertex symbol: (4<sup>13</sup>·6<sup>2</sup>)<sub>4</sub>(4<sup>20</sup>·6<sup>8</sup>)<sub>2</sub>-(4<sup>24</sup>·6<sup>4</sup>)<sub>4</sub>) (Fig. S2†).<sup>15</sup>

In the tdcpp ligand, four isophthalate moieties are almost perpendicular to the porphyrin plane so that four carboxylate groups point upwards and the other four point downwards. This allows the tdcpp ligand featuring the mono-chelated carboxylate groups to rigidly bridge two other tdcpp ligands *via* eight distorted cobalt trigonal prism SBUs, resulting in porphyrin macrocycles located in a “face-to-face” configuration with the distance between two cobalt centers within a porphyrin rings of 10.262 Å (atom to atom distance) (Fig. 1a). Every fourth SBU is bridged by four isophthalate moieties and propagates along the *c* direction to form a small hydrophilic square channel with all the terminal aqua ligands from SBUs pointing toward the channel center (Fig. 1b); the distance between two opposite water molecules in the channel is 5.388 Å and that between two neighboring ones is 3.810 Å. The square hydrophilic channel is surrounded by four sets of three cofacial metalloporphyrin rings, which extend along *c* direction to form



**Fig. 1** (a) Three cobalt porphyrins located in the “face-to-face” configuration in MMPF-2; (b) space filling model of three types of channels in MMPF-2 viewed from the *c* direction.



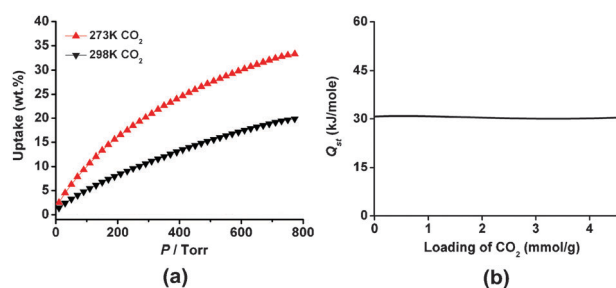
**Fig. 2** Ar adsorption isotherm of MMPF-2 at 87 K (insert DFT pore size distribution).

two rectangular channels with a size of 10.046 Å × 10.099 Å. A third channel surrounding it is enclosed by two SBUs, one tdcpp ligand, and one isophthalate moiety and exhibits dimensions of 6.204 Å × 7.798 Å (Fig. 1b). Both the distal and proximal positions of the cobalt atoms within the porphyrin macrocycles are open toward the channels, allowing substrate or guest molecules to bind. The solvent accessible volume of MMPF-2 calculated using PLATON is 60.1%.<sup>16</sup>

TGA studies of the fresh MMPF-2 sample (Fig. S1†) reveals almost a continuous weight loss of ~30% from 30 to ~360 °C corresponding to loss of guest solvent molecules and terminal aqua ligands liberated from distorted cobalt trigonal prism SBUs, which is closely followed by the loss of tdcpp ligands till ~450 °C leading to complete collapse of the MMPF-2 framework.

One of the most challenging issues for porphyrin-based MOFs lies in the preservation of porosity upon removal of guest solvent molecules.<sup>8</sup> To assess the permanent porosity of MMPF-2, we performed gas sorption measurements on the activated MMPF-2 sample. As shown in Fig. 2, the Ar adsorption isotherm at 87 K reveals that MMPF-2 exhibits an uptake capacity of 545 cm<sup>3</sup> g<sup>-1</sup> at the saturation pressure with typical type-I sorption behavior, as expected for microporous materials. Derived from the Ar adsorption data, MMPF-2 has a Langmuir surface area (*P*/*P*<sub>0</sub> = 0.9) of 2037 m<sup>2</sup> g<sup>-1</sup> (BET surface area (*P*/*P*<sub>0</sub> = 0.02–0.2), 1410 m<sup>2</sup> g<sup>-1</sup>), which is the highest among reported porphyrin-based MOFs (Table S1†).<sup>5b,8,9,11</sup> The measured pore volume of MMPF-2 is 0.61 cm<sup>3</sup> g<sup>-1</sup>, which is consistent with the solvent accessible volume of 60.1% and also matches the calculated value of 0.63 cm<sup>3</sup> g<sup>-1</sup>,<sup>16</sup> highlighting the robustness of its framework. The high surface area of MMPF-2 was further confirmed by N<sub>2</sub> adsorption at 77 K (Fig. S4†) and O<sub>2</sub> adsorption at 87 K (Fig. S5†), both of which reveal similar surface area values. Density functional theory (DFT) pore size distribution analysis based on the Ar adsorption data at 87 K revealed that the pore size of MMPF-2 is predominantly around 9.5 Å (Fig. 2 insert), which is close to the cofacial metalloporphyrin channel size of ~10 Å observed crystallographically.

We investigated CO<sub>2</sub> uptake performances of MMPF-2. The CO<sub>2</sub> adsorption isotherm measured at 273 K indicates that MMPF-2 has an uptake capacity of 33.4 wt% (or 170 cm<sup>3</sup> g<sup>-1</sup>, or 7.59 mmol g<sup>-1</sup>) (Fig. 3a) at 760 torr, which is comparable to the highest value of 38.5 wt% for the porous MOF, SNU-5 under the same condition despite its much lower surface area (2037 m<sup>2</sup> g<sup>-1</sup> vs. 2850 m<sup>2</sup> g<sup>-1</sup>).<sup>17</sup> The CO<sub>2</sub> uptake capacity of



**Fig. 3** (a) CO<sub>2</sub> and N<sub>2</sub> adsorption isotherms of MMPF-2 at 273 K and 298 K; (b) isosteric heats of adsorption of MMPF-2 for CO<sub>2</sub>.

MMPF-2 at 298 K and 760 torr is 19.8 wt% (or 101 cm<sup>3</sup> g<sup>-1</sup>, or 4.51 mmol g<sup>-1</sup>), which is also among the highest yet reported for porous MOFs under the same conditions.<sup>18</sup> The isosteric heats of adsorption ( $Q_{st}$ ) for CO<sub>2</sub> were calculated based on the CO<sub>2</sub> gas adsorption isotherms at 273 K and 298 K using the virial method (Fig. S6†).<sup>19</sup> As shown in Fig. 2c, MMPF-2 exhibits a constant  $Q_{st}$  of ~31 kJ mol<sup>-1</sup> at all loadings, distinguishing it from other MOFs with open metal sites, whose  $Q_{st}$  usually decreases abruptly to 20–25 kJ mol<sup>-1</sup> with the increase of CO<sub>2</sub> loading despite their high initial  $Q_{st}$ .<sup>18b</sup> We tentatively attribute this to the high density of open metal sites (~5 open cobalt sites nm<sup>-3</sup>) in MMPF-2, since open metal sites have been well-known to contribute to interactions between CO<sub>2</sub> and MOF frameworks.<sup>18a,b</sup>

In summary, by self-assembling the custom designed octatopic porphyrin ligand, tdcpp with the distorted cobalt trigonal prism SBU, we constructed a novel (6, 8, 8)-connected porphyrin-based MOF, MMPF-2, which features cobalt(II) metallated porphyrin macrocycles rigidly arranged in a “face-to-face” configuration. The linkage between the multitopic porphyrin ligand and the robust SBU together with the rigid cofacial arrangement of the metalloporphyrin macrocycles affords MMPF-2 by far the highest surface area of 2037 m<sup>2</sup> g<sup>-1</sup> among reported porphyrin-based MOFs and interesting CO<sub>2</sub> capture performances. Considering the versatility of metalloporphyrins, this work lays a solid foundation for developing porphyrin-based MOFs as a type of functional materials for applications in gas storage, CO<sub>2</sub> capture, heterogeneous catalysis, sensing, *etc.* Ongoing work in our laboratories includes investigation on the catalysis performances of MMPF-2 and construction of porous porphyrin-based MOFs with new variants of functional porphyrin ligands for various applications.

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