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# A Series of Robust Metal-Porphyrinic Frameworks Based on Rare Earth Clusters and Their Application in N-H Carbene Insertion

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Lei Xu,<sup>a</sup> Meng-Ke Zhai,<sup>a</sup> Fei Wang,<sup>a</sup> Lin Sun,<sup>a</sup> Hong-Bin Du<sup>a</sup>\*

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We herein report a series of microporous metal-porphyrinic frameworks (MPFs), denoted as NUPF-2M, based on rare earth (RE) clusters. NUPF-2M represent the first examples of RE clusterbased MPFs, possessing a rarely seen shp-a topology and exhibiting high thermal and thermal stabilities. After postmetallized with FeCl<sub>3</sub>, NUPF-2M is catalytically active as an efficient heterogeneous catalyst for intermolecular N-H carbene insertion.

(Metallo)porphyrins are a class of biologically relevant tetrapyrrole macrocycles,<sup>1</sup> which have attracted ever-growing research interests due to their unique electronic, catalytic properties.<sup>2</sup> Incorporating photochemical and into crystalline (metallo)porphyrins multidimensional assemblies linked by metal ions/clusters via coordination bond gives rise to metal-porphyrinic frameworks (MPFs),<sup>3</sup> a fascinating subclass of metal-organic frameworks (MOFs). Since the first report in 1990s,<sup>4</sup> MPFs have attracted escalating research interests due to their intriguing properties in heterogeneous catalysis, sensing, gas storage/separation, light-harvesting, etc.<sup>5</sup> Nowadays, much effort has been paid on constructing porous zirconium/hafnium based MPFs (Zr/Hf-MPFs) and exploring their underlying applications.<sup>6</sup> Adopting Zr/Hf clusters as nodes would not only impart the preeminent chemical/thermal stabilities to MPFs, but also render them remarkable catalytic properties,<sup>7</sup> diversifying the applications of MPFs. Nevertheless, compared with the fast developing MOFs or porphyrin chemistry, the chemistry of MPFs was still in its infancy. Considering the fascinating properties of (metallo)porphyrins, the construction of novel MPFs with diverse structures and the exploitation of their underlying applications are still highly desirable.

Compared with the *d*-block transition metals, rare-earth

(RE) metals exhibit unique electronic, optical, and magnetic properties and thus make RE-based materials multifunctional.<sup>8</sup> Recently, the incorporation of multinuclear RE clusters of particular geometry into MOFs has attracted much attention, resulting in unprecedented architectures and excellent properties. However, such multidimensional RE cluster based MOFs are scarce because of the difficulty in linking the highlyconnected RE cluster into crystalline extended frameworks. By using a modulated synthesis strategy, Eddaoudi and coworkers have successfully synthesized a series of MOFs that contain multinuclear clusters of RE metal ions.<sup>10-15</sup> Because of the high charge density and connectivity of the RE clusters, these RE-MOFs exhibit high chemical and thermal stabilities. Compared with the Zr/Hf clusters, the multinuclear RE clusters not only exhibit more abundant connectivities,<sup>11</sup> but also could coordinate to both carboxylate and pyrazol based ligands,<sup>10</sup> exhibiting more rich coordination chemistry. Moreover, the RE clusters present advantages over the Zr/Hf clusters as they offer opportunities to tune the properties of the resulting MOFs through use of different rare earth metals.<sup>14</sup> The combination of the RE clusters and porphyrinic ligands may produce RE-MPFs with unprecedented architectures and fascinating properties. Interestingly, such research has not been reported before this work.

One important motivation for pursuing MPFs is their excellent performance as heterogeneous catalysts. Generally, homogeneous catalyst (metallo)porphyrins were hard to synthesize, and catalyst recycling has long been an aspiration for chemists. Using MPFs as heterogeneous catalysts would overcome the issues of separation and re-utilization of porphyrin catalysts encountered in homogeneous catalysis. In the meanwhile, it could also make the catalytically-active porphyrinic units highly dispersed and accessible, enhancing the catalytic performance.<sup>16</sup> Transition-metal catalysts such as Re, Rh, Cu or Ru complexes for carbene insertion into N-H bonds have attracted significant attention,<sup>17</sup> although these catalysts may suffer from some limitations such as restricted reaction conditions, catalyst poisoning or low yield.<sup>18</sup> Recently, Fe-porphyrins were found to exhibit great efficiency in

<sup>&</sup>lt;sup>a</sup> State Key Laboratory of Coordination Chemistry, Collaborative Innovation Center of Chemistry for Life Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210023, China. E-mail: hbdu@nju.edu.cn

<sup>&</sup>lt;sup>+</sup>Electronic Supplementary Information (ESI) available: Materials and methods, synthesis, PXRD, FT-IR, TGA, UV-Vis, GC-MS, <sup>1</sup>H-NMR, and other characterization data, crystallographic data. See DOI: 10.1039/x0xx00000x

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catalyzing N-H insertion.<sup>19</sup> However, these reactions were all performed in homogeneous manner, which would cause issues in catalyst recycling and product purification. Till recently Son and co-workers reported a microporous Fe-porphyrin polymer as heterogeneous catalyst for N-H carbene insertion.<sup>20</sup> Herein, we report the synthesis of a series of stable RE clusters based MPFs  $M_9O_5(TCPP)_3 \cdot (solvents)_x$ (TCPP = tetrakis(4carboxyphenyl)porphyrin, M = Y, Gd, Tb, Dy, Er, Yb), denoted as NUPF-2M (NUPF: Nanjing University Porphyrinic Framework no. 2), which represent the first examples of MPFs assembled by highly-connected RE clusters. All the NUPF-2M frameworks exhibit not only large permanent porosity, but also high chemical and thermal stabilities, which facilitate their potential applications. As an exemplification, NUPF-2Y was chosen as a platform for post-metalized with FeCl<sub>3</sub>, the resulting NUPF-2Y-FeCl exhibit excellent catalytic property for N-H carbene insertion with high yield and good recyclability. To the best of our knowledge, no MPFs were reported for such an application.

Dark purple hexagonal prism-shaped single crystals of NUPF-2M were obtained via solvothermal reactions of porphyrinic ligand TCPP with rare earth metal nitrates in DMF and H<sub>2</sub>O at 120 °C for 72 h by using 2-fuorobenzoic acid as a modulator (S2<sup>+</sup> and Fig. S1<sup>+</sup>). The synthesis process could also be achieved by using microwave-assisted reactions in a relatively faster manner (S3<sup>+</sup> and Fig. S3<sup>+</sup>). Single-crystal X-ray diffraction studies disclosed that all the NUPF-2M frameworks are isostructural; thus only NUPF-2Y was described in detail. The structure of NUPF-2Y crystallized in a primitive hexagonal space group, P6/mmm, composed of 4-connected TCPP linker and 12-connected Y nonanuclear cluster (Fig. 1). The porphyrin macrocycle of TCPP was core-free and nearly planar without obvious out-of-plane deformation. Each benzoate arm of TCPP were almost perpendicular to the porphyrin plane with a dihedral angle of 88.7° (Fig. 1a). The 12-connected Y<sub>9</sub> cluster possessed a truncated hexagonal bipyramid geometry containing the disordered Y<sub>9</sub> atoms, which can be simplified as 12-connected structural nod with hexagonal-prism coordination geometry (Fig. 1b and Fig. S4<sup>+</sup>).

In NUPF-2Y, each TCPP ligand links four Y<sub>9</sub> clusters through its four benzoate arms, while each Y<sub>9</sub> cluster is connected by 12 porphyrinic ligands. The combination of Y<sub>9</sub> cluster and quadrangular porphyrin ligand TCPP gives NUPF-2Y a rare **shpa** topology that is similar to its Zr<sub>6</sub>-based analogue PCN-223 (Fig. 1c).<sup>16</sup> NUPF-2Y possesses a highly opened 3D framework (Fig. 1d). Uniform one-dimensional triangular channels of ~1.2 nm in opening sizes were propagated along the c-axis, while smaller rhombus channels of ~0.9 nm were parallel to *a*- and *b*-axes. The solvent accessible volume of NUPF-2Y was estimated to be 59.8% by using PLATON.<sup>21</sup> Notably, the 12connected RE<sub>9</sub> clusters in NUPF-2M were rarely seen among the reported poly-nuclear RE clusters, which was only once recorded in hybrid clusters of Y-**pek**-MOF-2 reported in the literature.<sup>12</sup>

To assess the permanent porosity of NUPF-2M, N<sub>2</sub> adsorption was performed on the activated samples (S10<sup>+</sup>). As shown in Fig. 2a, all the adsorption isotherms of NUPF-2M exhibit a fully reversible type I behavior with high gas uptakes, indicating their microporous nature. The BET surface area of NUPF-2Y derived from the adsorption data was 1948  $m^2/g$ , slight higher than its Zr-analogue PCN-223 (~1600 m<sup>2</sup>/g).<sup>16</sup> As the molecular weights of NUPF-2M increase from Yttrium to Ytterbium, the surface areas decrease from 1948 m<sup>2</sup>/g (NUPF-2Y) to 1219  $m^2/g$  (NUPF-2(Yb)) (Table S1<sup>+</sup>). The pore size distributions for NUPF-2M assessed using the N2 sorption curves revealed two types of pores with average sizes centered around ~0.8 nm and ~0.6 nm (Fig. S8<sup>+</sup>), which is consistent with the crystallographic data. It is noted that RE-MPFs were rarely explored in areas related to gas sorption because of the difficulty in obtain these materials with permanent porosity.<sup>22</sup> To the best of our knowledge, NUPF-2M may represent the most porous RE-based MPFs to date. Notably, all the NUPF-2M samples preserved their crystallinity and framework integrity before and after adsorption experiments as evidenced by PXRD patterns (Fig. S9<sup>+</sup>).



(b) (a) NUPF-2Yb NUPF-2Er NUPF-2Dy NUPF-2Th NUPF-2G NUPF-2G NUPF-2Dy NUPF-2Dy NUPF-2Er NUPF-2Gd NUPF-2Y Simulated 0.2 0.6 0.8 1.0 40 45 5 15 20 25 30 35 10 P/P 20 / deg. (c) (d) NUPF-2Y NUPF-2Yb NUPF-2Er NUPF-2Er NUPF-2Dy NUPF-2Dy NUPF-2Th NUPF-2Gd NUPF-2Y NUPF-2Y Simulated Simulated 15 20 25 30 35 40 45 15 20 25 30 35 40 10 10 20 / Deg. 20 / Deg

**Fig. 1** (a) the 4-connected TCPP linker used in NUPF-2Y. (b) the disordered 12connected  $Y_9$  cluster observed in NUPF-2Y. (c) the highly opened 3D networks with **shpa** topology found in NUPF-2Y. (d) one dimensional channels propagated along the c-axis. The connolly surfaces were calculated using a 1.7 Å probe radius.

Fig. 2 (a)  $N_2$  adsorption (solid symbols) and desorption (open symbols) isotherms of NUPF-2M at 77 K. (b) PXRD patterns of NUPF-2M heated at 400 °C under Ar for 30 min. PXRD patterns of NUPF-2M in pH=2 (c) and pH=12 (d) solutions for 1 day.

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TG analysis reveals that the decomposition temperature of NUPF-2M was higher than 500 °C (Fig. S6<sup>+</sup>), demonstrating an excellent thermal stability of NUPF-2M. This high thermal stability was further authenticated by the undamaged PXRD patterns of NUPF-2M heated under Ar at 400 °C for 30 min (Fig. 2b). The high chemical and thermal stabilities may be ascribed to the high charge density (Z/r) of RE metals and highlyconnected RE clusters formed in NUPF-2M, which result in strong coordination bonds between TCPP linker and metal clusters.<sup>14-16, 23</sup> Besides the thermal stability, NUPF-2M also possess high chemical stability. Experimental results show that NUPF-2M retained their crystallinity in common organic solvents for 3 days (S11<sup>+</sup>). Remarkably, NUPF-2M could be survived in pH= 2~12 aqueous solutions for 1 day, as demonstrated by their unaltered PXRD patterns (Fig. 2c-d), exhibiting a high resistance towards acid and base solutions.

The integration of high structural stability, large solventaccessible voids and free-based porphyrinic centers in NUPF-2M make them potential versatile platforms for heterogeneous catalysis.<sup>24</sup> Among the metalloporphyrin catalyzed reactions, Fe<sup>III</sup>Cl-porphyrin showed an effective catalytic property towards N-H carbene insertion. However, such reactions were rarely explored by using MPFs as heterogeneous catalyst. In order to explore the utilization of NUPF-2M as heterogeneous catalyst in N-H carbene insertion, [FeCl] moiety, which served as catalytic active center, must be planted into the porphyrin core. We chose NUPF-2Y as an exemplified platform for post-functionalization with FeCl<sub>3</sub>. The post-metallization process was easily performed by refluxing the crystals of NUPF-2Y with FeCl<sub>3</sub> followed by filtration (denoted as NUPF-2Y-FeCl, S12<sup>+</sup>). ICP-OES measurements revealed that all the porphyrin cores were metallized (S12<sup>+</sup>), demonstrating NUPF-2Y could be facilely functionalized.

The reaction of aniline with ethyl diazoacetate (EDA) was employed as a model system to evaluate the catalytic performance of NUPF-2Y-FeCl. As shown in Table 1, compared with the trials with the blank, FeCl<sub>3</sub> and the pristine NUPF-2Y (entries 1, 2 and 3), NUPF-2Y-FeCl exhibited unequivocally catalytic activities with a high yield up to 95% (entry 4), proved the essential role of [FeCl] unit in porphyrin ligand. The catalytic activity of NUPF-2Y-FeCl was comparable to the homogeneous catalyst Fe(TPP)Cl (entry 5). However, NUPF-2Y-FeCl could be easily separated and reused for further catalytic runs. For example, the catalytic yield of NUPF-2Y-FeCl was up to 92% in the 4<sup>th</sup> run in the case of aniline (entry 6, Fig. S13<sup>+</sup> and Fig. S13<sup>+</sup>), demonstrating a huge advantage over the homogeneous catalyst. Furthermore, the catalytic activity of NUPF-2Y-FeCl could be primarily reserved in large-scale runs, as demonstrated in entry 7 which performed in 10 mmol scale with 90% yield. The high catalytic activity and good reusability of NUPF-2Y-FeCl were further verified by using more substrates bearing different groups (entries 8-15, Fig. S13<sup>+</sup> and Fig. S14<sup>+</sup>). Notably, NUPF-2Y-FeCl exhibit a slow reaction rate compared with the homogeneous reactions. For example, the reaction catalyzed by homogeneous Fe(TPP)Cl could be accomplished in 10 min (entry 5), while the same reaction was

prolonged to 30 min in NUPF-2Y-FeCl reaction (entry 4). Such slow reaction was ascribed to the inherent character of MOF-catalyzed heterogeneous reactions, in which the frameworks of MOFs served as diffusion barriers for reagents.<sup>25</sup>

 Table 1 NUPF-2Y-FeCl catalyzed N-H carbene insertion reactions.

Entry	Substrate	Catalyst	Product	Yield % <sup>a</sup>
1		blank		0
2		FeCl <sub>3</sub>		0
3		NUPF-2Y		0
4		NUPF-2Y-FeCl		96
5		Fe(TPP)Cl		93 <sup>b</sup>
6		NUPF-2Y-FeCl		92 (4 <sup>th</sup> )
7		NUPF-2Y-FeCl		90 <sup>c</sup>
8	F	NUPF-2Y-FeCl		95
9	F-NH2	NUPF-2Y-FeCl		93 (4 <sup>th</sup> )
10		NUPF-2Y-FeCl		93
11	сі–√_–№н₂	NUPF-2Y-FeCl		95
12	Br-	NUPF-2Y-FeCl		95
13	F <sub>3</sub> C-	NUPF-2Y-FeCl		96
14	NC-	NUPF-2Y-FeCl		94
15	O <sub>2</sub> N- NH <sub>2</sub>	NUPF-2Y-FeCl		93 <sup>d</sup>

Reactions were run under high-purity Ar atmosphere in dry  $CH_2Cl_2$  with 0.3 mmol of substrate, 0.36 mmol of EDA and 1 mmol% catalyst (3.7 mg for NUPF-2Y-FeCl and 2.1 mg for Fe(TPP)Cl, based on Fe-porphyrin unit) at room temperature for 30 min unless stated otherwise. <sup>a</sup> Isolated yield. <sup>b</sup> Reaction complete in 10 min. <sup>c</sup> Yield was determined by GC-MS and reaction time was 5 h. <sup>d</sup> Reaction was performed in dry acetone.

In summary, a series of porous rare-earth metalporphyrinic frameworks  $M_9O_5(TCPP)_3(solvents)_x$  (M = Y, Gd, Tb, Dy, Er, Yb) have been successfully synthesized, which represents the first examples of highly-connected RE clusterbased MPFs. These MPFs exhibit not only high permanent porosity, but also desirable chemical and thermal stabilities, which enable their utilization as versatile platforms for various applications. As an exemplification, the post-metalated NUPF-2Y-FeCl demonstrated the superior catalytic property toward the N-H carbene insertion. Considering the versatile coordination modes of multinuclear RE clusters documented by literatures and the fascinating properties of (metallo)porphyrins, it could be envisioned that more stable RE-MPFs with intriguing properties could be constructed in the near future.

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The unprecedented highly porous and stable rare earth cluster based metal-porphyrinic frameworks can be used as efficient catalysts for N-H carbene insertion.