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# Design and Assembly of a Hierarchically Micro- and Mesoporous MOF as a Highly Efficient Heterogeneous Catalyst for Knoevenagel Condensation Reaction

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#### ABSTRACT

3D А hierarchically microand mesoporous MOF.  $[Tb_6(\mu_3-OH)_8 \cdot (2 FBA_{2}$  (H<sub>2</sub>O)<sub>6</sub> (DCBA)<sub>2</sub>] · 10DMF · 4H<sub>2</sub>O (namely Tb-DCBA), was successfully constructed by the coordination self-assemble process between H<sub>4</sub>DCBA linker and Tb<sub>6</sub> hexanuclear cluster. By virtue of preferable physicochemical stability, high surface area, multiple porosity, and abundant amino functional groups, Tb-DCBA is not merely considered as a greatly potential heterogeneous catalyst for Knoevenagel condensation reaction, but also has remarkable repeatability for reusing at least four times. It is worth noting that micro- and mesoporous MOF is still an urgent and enormous challenge, because such MOFs are difficult to synthesize and determine their precise structures, and always possess relatively poor stability to limit their practical applications. Hence, this work creates a scarce opportunity for a hierarchically microand mesoporous MOF for investigating its catalytic performance.

#### **INTRODUCTION**

Metal–organic frameworks (MOFs),<sup>1,2</sup> as a booming sort of inorganic-organic hybrid porous crystal materials, have been drawn large quantity of interest and become a research focus in chemistry and material science in recent years, which is not only attributed to their abundant and fascinating structures<sup>3-5</sup> but also their potential applications in gas sorption,<sup>6,7</sup> luminescent sensor,<sup>8,9</sup> heterogeneous catalysis,<sup>10-13</sup> and optical device<sup>14,15</sup>. MOFs are constructed by the coordination self-assemble process of metal-containing secondary building units (SBUs) and bridging organic linkers with N or O-donors.<sup>16</sup> Compared with other porous materials including mesoporous silica, activated carbon, and zeolite, porous MOF materials have various unique properties, such as high surface area, adjustable pore, and attractive performance, resulting in

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vouchsafing the accurate layout of skeleton structure and regulating porous microenvironment at molecular or even atomic level.<sup>17,18</sup> Pore sizes in MOFs are in the wide range from angstrom to nanometer, leading to their widespread applications as host materials in capturing and separating small or large guest species.<sup>19-22</sup> Up to now, most MOFs only have microporous structures with pore size diameters under 2 nm, which is in favour of absorbing small gas or molecule; nevertheless, microporous MOFs are restricted to the adhibition for large molecules due to the smaller pore size than the molecular dimension of molecules. Recently, numerous efforts have been focused on designing and preparation mesoporous MOFs, including template, large organic linker or metal cluster, and post treatment.<sup>23-27</sup> On the other hand, the poor physicochemical stability of MOFs are directly limited their potential research fields because of their reversible and weak nature of coordination bond.<sup>28,29</sup> Some efficient strategies have been developed to increase the strength of skeleton to enhance the stability.<sup>30-33</sup> Especially, high-connected multicores as SBUs have high universality and effectiveness to construct mesoporous MOFs with inherent stability, but it is obviously hard to construct such MOFs due to relative harsh synthetic conditions. Rare-earth (RE) hexanuclears have been reported by Prof. Mohamed Eddaoudi to illustrate the availability of such RE hexanuclears for constructing stable MOFs.<sup>34,35</sup> Among all application fields, heterogeneous catalysis is a significantly vital and useful research hotspot for MOFs. Compared with homogeneous catalysts,<sup>36,37</sup> heterogeneous catalysts have been widely used in many fields due to size-selectivity, recyclability, and easy purify.<sup>38-41</sup> The catalysis efficiency can be remarkably accelerated by mesoporous MOFs, because mesoporous structures can directly facilitate the diffusion of substrates and products. Knoevenagel condensation reaction, as a common organic reaction, is an effective mean to synthesis ponderable C-C coupling intermediate chemicals, which can be conventionally catalyzed by

Lewis basic homogeneous catalysts.<sup>42</sup> Amino group (–NH<sub>2</sub>) is a general Lewis basic site, which can be decorated on the porous surface to catalyze Knoevenagel condensation reaction.<sup>43-46</sup> Hence, it is eagerly desirable to create a mesoporous MOF decorating –NH<sub>2</sub> as a highly efficient heterogeneous catalyst for Knoevenagel condensation reaction with excellent stability.

Considering these above points together, we designed and synthesized an amino-functional linker 4",6'-diamino-5',5"-bis(4-carboxyphenyl)-[1,1':3',1":3",1"'-quaterphenyl]-4,4"'-dicarboxylic acid (namely H<sub>4</sub>DCBA) by a Suzuki coupling reaction in Scheme 1, which is self-assembled with Tb<sub>6</sub> hexanuclear cluster to successfully construct a three-dimensional (3D) hierarchically micro- and mesoporous MOF,  $[Tb_6(\mu_3-OH)_8\cdot(2-FBA)_2\cdot(H_2O)_6\cdot(DCBA)_2]\cdot10DMF\cdot4H_2O$  (Tb-DCBA). The resultant sample has preferable physicochemical stability, multiple porosity, and affluent amino group simultaneously, leading in catalyzing Knoevenagel condensation reaction with preferable recyclability.



#### **Experimental Section**

**Methods and Materials.** All the chemical reagents were obtained from commercial sources and used without further purification. Powder X-ray-diffraction (PXRD) patterns were acquired on a Scintag X1 diffractometer with Cu- $K\alpha$  ( $\lambda = 1.5418$  Å) at 40 kV, 40 mA in the range of 4-50° (2 $\theta$ ). Thermogravimetric analyses (TGA) for all measurements were carried on a Perkin-Elmer TGA thermogravimetric analyser under air flow at a heating rate of 10 °C min<sup>-1</sup> in the range of 30-800 °C. Elemental analyses (C, H and N) were obtained from a Perkin-Elmer 240 analyzer. Fourier-transform infrared spectra (FT-IR) were performed on a Nicolet Impact 410 FT-IR spectrometer in the 4000-400 cm<sup>-1</sup> range using KBr pellets. All gas sorption measurements were acquired on a Surface area analyser ASAP 2020. The catalytic yields were calculated and performed on a Thermo Fisher Trace ISQ GC/MS. <sup>1</sup>H NMR spectra in ppm were collected on a Bruker AV 400 spectrometer.

**Synthesis of 3,3',5,5'-tetrabromo-[1,1'-biphenyl]-4,4'-diamine.** A sample of benzidine (1.0 g, 2.0 mmol) was dissolved in 30 mL of glacial acetic acid at room temperature. Bromine (1.2 mL) was added slowly with rapid stirring and then the mixture was continually stirred for 4 h. The brown precipitate was filtered off, washed with water several times, and dried in vacuum (yield: 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 5.31 (s, 4H), 7.53 (s, 4H).

Synthesis of 4",6'-diamino-5',5"-bis(4-carboxyphenyl)-[1,1':3',1":3",1"'-quaterphenyl]-4,4"'-dicarboxylic acid (H<sub>4</sub>DCBA). First, 3,3',5,5'-tetrabromo-[1,1'-biphenyl]-4,4'-diamine (1.98 g, 4 mmol), methyl 4-boronobenzoate (3.14 g, 19.2 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.30 g, 0.26 mmol) and K<sub>3</sub>PO<sub>4</sub> (3.82 g, 18.0 mmol) were placed in a 500 mL two-necked round bottom flask under a N<sub>2</sub> atmosphere. The flask was further charged with a 200 mL of dry 1,4-dioxane, and the contents were heated for 48 h. After the mixture was cooled to room temperature, the solvent was removed, water was added. The water phase was washed with  $CH_2Cl_2$ . The mixed organic phases were dried with MgSO<sub>4</sub>. After the solvent was removed, the crude product was purified by column chromatography with  $CH_2Cl_2$  as the eluent. Then, the above obtained dimethyl 4",6'diamino-5',5"-bis(4-(methoxycarbonyl)phenyl)-[1,1':3',1":3",1"'-quarterphenyl]-4,4"'-

dicarboxylate (2.0 g, 2.8 mmol) was dissolved in 50 mL MeOH, 50 mL 2 M NaOH aqueous solution was added. The mixture was stirred at 50 °C overnight. The organic phase was removed, the aqueous phase was acidified with diluted hydrochloric acid to give yellow precipitate, which was filtered and washed with water several times. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 4.46 (s, 4H), 7.46 (s, 4H), 7.69 (d, 8H), 8.03 (d, 8H). Selected FT-IR data (KBr pellet, cm<sup>-1</sup>, see Figure S1 in the Supporting Information): 3417 (br), 2928 (br), 2364 (s), 1694 (s), 1610 (s), 1537 (s), 1451 (s), 1396 (s), 1236 (s), 1176 (s), 1107 (s), 1015 (s), 867 (s), 782 (s), 711 (s), 538 (s), 411 (s).

Synthesis of  $[Tb_6(\mu_3-OH)_8\cdot(2-FBA)_2\cdot(H_2O)_6\cdot(DCBA)_2]\cdot10DMF\cdot4H_2O$  (Tb-DCBA). A mixture of Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (16 mg, 0.035 mmol), H<sub>4</sub>DCBA (10 mg, 0.015 mmol), *N*,*N*-dimethylformamide (DMF, 2.0 mL), H<sub>2</sub>O (0.5 mL), and 2-fluorobenzoic acid (2-FBA, 140 mg) was sealed into a 23.0 mL Teflon-lined autoclave. The mixture was heated at 115 °C for 4 days and then allowed to cool to room temperature to obtain the brown block crystals with the yield of 67% (based on ligand). Element analysis (%) Calc. for C<sub>124</sub>H<sub>154</sub>O<sub>48</sub>N<sub>14</sub>F<sub>2</sub>Tb<sub>6</sub>: C, 41.4; H, 4.3; N, 5.4; Found: C, 41.6; H, 4.1; N, 5.5 Selected FT-IR data (KBr pellet, cm<sup>-1</sup>, see Figure S1 in the Supporting Information): 3431 (br), 1600 (s), 1534 (s), 1401 (s), 1269 (s), 1090 (s), 1018 (s), 866 (s), 786 (s), 716 (s), 625 (s), 547 (s), 424 (s).

**Gas Sorption Measurement.** The as-synthesized samples were soaked in dry methanol for 6 h, which was slowly activated to obtain activated Tb-DCBA by using the supercritical  $CO_2$  approach. Gas adsorption and desorption measurements for activated samples were collected on

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a surface area analyser ASAP 2020. The Brunauer-Emmett-Teller (BET) surface area and pore size distribution were both analyzed and calculated by the  $N_2$  isothermal adsorption curve at 77 K in a liquid  $N_2$  bath.

**Catalyze Knoevenagel Condensation Reaction.** Generally, aldehyde (1.0 mmol) and malononitril (1.1 mmol) were dissolved in 4 mL of  $CH_2Cl_2$  in a round-bottom flask. Activated Tb-DCBA (10 wt%) was added in the reaction system and slowly stirred at room temperature. The reaction process can be constantly monitored by TLC, illustrating that this catalytic reaction was almost completed after 6 h. Then, the reaction system was filtered and washed with fresh  $CH_2Cl_2$  for three times to recollect Tb-DCBA for the continuous catalytic reaction.

Single Crystal X-ray Analysis. Crystallographic data of Tb-DCBA were taken on SuperNova CCD-based diffractometer with graphite Cu- $K\alpha$  radiation ( $\lambda = 1.54184$  Å) using  $\varphi$ - $\omega$  scan technique at 110 K. Multi-scan absorption corrections were applied with the SADABS program.<sup>47</sup> The crystal structure was determined by direct methods with *SHELXT 6* and refined with full-matrix least-squares technique using *SHELXL-2015*<sup>48,49</sup> through *OLEX2* interface program<sup>50</sup>. All non-H atoms were located successfully and refined by anisotropic thermal parameters. It was unsuccessful to locate and model the highly disordered guest DMF and H<sub>2</sub>O molecules in the porous structure. Therefore, the *SQUEEZE* routine as a part of the *PLATON* software package<sup>51,52</sup> was used to calculate the disorder areas and remove the diffraction contribution to afford a set of solvent free diffraction intensity. Solvent molecules were not included in the crystal data. The chemical formula of as-synthesized Tb-DCBA was determined based on the results of elemental analysis and TGA. Crystal data of as-synthesized Tb-DCBA are summarized in Table 1 and the selected bond lengths and bond angles are listed in Table S1.

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<b>Table 1</b> Crystallographic data and structure re	efinement for Tb-DCBA
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#### Compound **Tb-DCBA** Empirical formula C<sub>46</sub>H<sub>32</sub>O<sub>17</sub>N<sub>2</sub>Tb<sub>3</sub> Formula weight 1361.53 Crystal system Hexagonal Space group P6/mmm a (Å) 41.9264(18) *b* (Å) 41.9264(18) c (Å) 14.9781(7) $\alpha$ (°) 90.00 $\beta$ (°) 90.00 γ (°) 120.00 $V(Å^3)$ 22801 Ζ 6 $\rho$ calc g cm<sup>-3</sup> 0.598 $\mu$ (mm<sup>-1</sup>) 6.941 Nref 8510 *F*(000) 3954.0 R(int) 0.0556 Goodness-of-fit on $F^2$ 1.102 $R_1, WR_2 [I > 2\sigma(I)]$ 0.0509, 0.1745 $R_1$ , w $R_2$ (all data) 0.0633, 0.1844

#### **RESULTS AND DISCUSSION**

#### **Structural Description.**

Single-crystal X-ray diffraction analysis shows that Tb-DCBA crystallizes in hexagonal crystal system and the *P*6/mmm space group. As shown in Figure S2 in the Supporting Information, Tb-DCBA contains a quarter independent Tb1 atom, a half independent Tb2 atom, one quarter fully deprotonated DCBA<sup>4–</sup> linker, a half  $\mu_3$ -O(4)H, one second  $\mu_3$ -O(7)H, one quarter 2-FBA linker, a half terminal H<sub>2</sub>O(5) molecule, and one fourth coordinated H<sub>2</sub>O(6). A Tb<sub>6</sub> hexanuclear cluster was founded in Tb-DCBA, which is similar with some reported RE hexanuclears in MOFs (Figure 1a).<sup>32,33</sup> Each hexanuclear cluster can connect with eight –COOH groups from eight fully deprotonated DCBA<sup>4–</sup> linkers; meanwhile, the square planar DCBA<sup>4–</sup> linker can link with four hexanuclear clusters by adopting only one coordination mode as  $\mu_8$ - $\eta^1$ :  $\eta^1$ :

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(Figure 1b). More interestingly, the  $-NH_2$  group is uncoordinated and free in Tb-DCBA. All hexanuclear clusters and DCBA<sup>4–</sup> linkers are further connected with each other to generate a 3D skeleton with smaller microporous triangular channel (~1.2 nm) and larger mesoporous hexagonal channel (~3.3 nm). Figure 1c obviously shows that Tb-DCBA is a rare micro- and mesoporous MOF likely several reported MOFs. It's worth noting that the free  $-NH_2$  group is exposed on the porous surface to create a porous environment with abound Lewis basic sites (see Figure S3 in the Supporting Information). The infrequent micro- and mesoporous MOF can be considered and investigated as a heterogeneous catalyst for catalyzing Knoevenagel condensation reaction.



**Figure 1.** Tb<sub>6</sub> hexanuclear cluster (a) and square planar DCBA<sup>4–</sup> linker (b); and (c) viewing of a 3D micro- and mesoporous structure along *c* axis (C, gray; O, red; N, blue; Tb, green).

#### TGA, PXRD, and Gas Sorption.

The TGA result of as-synthesized Tb-DCBA clearly exhibits that an apparent weight loss of  $\sim$ 25.06% before 200 °C, which is mainly attributed to losing guest and coordinated solvents in porous structure. The weight loss is well consistent with the calculated value of  $\sim$ 25.29 % (see

Figure S4 in the Supporting Information). The whole structure further starts collapse when the heating temperature reaches up to 420 °C. The purity of bulk as-synthesized samples can be confirmed by PXRD at room temperature. As displayed in Figure S5 in the Supporting Information, the diffraction peaks of solvent-formed Tb-DCBA are well consistent with those of simulated data to prove the purity of these as-synthesized crystals. The fresh Tb-DCBA was soaked in dry methanol for 6 h and then slowly activated to obtain activated samples by using the supercritical CO<sub>2</sub> approach. The PXRD profile of activated sample can well retain the diffraction peaks of original samples to prove its high crystallinity and stability after desolvating solvents (see Figure S6 in the Supporting Information). The N<sub>2</sub> adsorption isotherm of activated sample was measured at 77 K under 1 atm to in depth explore the internal porous context. The BET surface area is calculated to be ~1902 m<sup>2</sup> g<sup>-1</sup>; meanwhile, the corresponding pore size distribution can be obtained by the density functional theory (DFT) method in Figure 2. These results obviously indicate that Tb-DCBA is a rare hierarchically micro- and mesoporous MOF with high surface area.



 **Figure 2.** N<sub>2</sub> sorption isotherm at 77 K of activated samples and the corresponding pore size distribution by the DFT method.

#### **Catalytic Property.**

Benefiting of a great deal of  $-NH_2$  group in this hierarchically micro- and mesoporous Tb-DCBA, it may be implemented in a potential application in catalyzing Knoevenagel condensation reaction as an excellent heterogeneous catalyst. In a typical catalytic reaction, aldehyde (1.0 mmol) and malononitril (1.1 mmol) were both dissolved in 4 mL of CH<sub>2</sub>Cl<sub>2</sub> in a round-bottom flask, which was further added activated Tb-DCBA (10 wt%) and slowly stirred at room temperature. The reaction process can be constantly monitored by TLC, illustrating that this catalytic reaction was almost completed after 6 h. The catalytic yield is able to obtain well and truly by using the GC method and use diphenyl in the reaction system as an internal standard. As revealed in entry 1 of Table 2, benzaldehyde was firstly implemented as reaction substrate to react with malononitril in the presence of Tb-DCBA, which almost can completely react after 6 h with the high yield of >99%. The result is comparable to that of PCN-124<sup>53</sup>, Cz-MOF<sup>54</sup>, UPC-102-Zr<sup>55</sup>, and PCP-1<sup>56</sup>, which evidently shows that Tb-DCBA is a potential heterogeneous catalyst for the C-C coupling Knoevenagel condensation reaction, which encourages us to expand various aldehydes containing different functional substituent groups for this reaction. The corresponding yields of targeted products remarkably decrease from >99% for benzaldehyde to 89% for 4-fluorobenzaldehyde (entry 2), 87% for 4-methylbenzaldehyde (entry 3), 67% for 4nitrobenzaldehyde (entry 4), 19% for 4-biphenylcarboxaldehyde (entry 5), and 17% for 4phenoxybenzaldehyde (entry 6), respectively. The relative lower yields of these aldehydes with large molecule sizes are prevailingly attributed to that the large sizes will directly slow down the diffusion rate of reactants and substrates, which is similar with some reported MOFs.<sup>49-52</sup> The

control test was measured to catalyze benzaldehyde and malononitril without Tb-DCBA as catalysis. It is not found any product in the catalytic system to prove the necessary of Tb-DCBA for this reaction (entry 7). In addition, if Tb-DCBA was filtered from the reaction system of benzaldehyde and malononitril, the catalytic reaction will be terminated immediately to further illustrate that Tb-DCBA is an outstanding heterogeneous catalyst for this reaction (see Figure S7 in the Supporting Information).

Table 2. The Knoevenagel condensation reaction.<sup>a</sup>

R		+ NC CN -		CN CN
Entry	R–	Catalyst	Product	Yield(%) <sup>t</sup>
1	H–	Tb-DCBA	CN CN	>99
2	4-F-	Tb-DCBA	F CN CN	89
3	4-Me-	Tb-DCBA	Me CN	87
4	4-NO <sub>2</sub> -	Tb-DCBA	O <sub>2</sub> N CN	67
5	4-Ph-	Tb-DCBA	CN CN	19
6	4-PhO-	Tb-DCBA		17



<sup>a</sup> Reaction conditions: aldehyde (1.0 mmol), Tb-DCBA (10 wt%), malononitril (1.1 mmol),  $CH_2Cl_2$  (4 mL) at room temperature. <sup>b</sup> Calculated by GC with diphenyl as internal standard.

The repeatability is a significantly critical factor for heterogeneous catalysts in the practical application. After each Knoevenagel condensation reaction of benzaldehyde and malononitril, Tb-DCBA can be directly collected by centrifugation at 8000 r min<sup>-1</sup> for 2 min and regenerated by washing with fresh  $CH_2Cl_2$  for several times. The recycled Tb-DCBA can well keep the catalytic performance even after reusing four times, which has high catalytic yield of >99% (entry 8 and Figure 3a). On the other hand, all PXRD profiles of Tb-DCBA after recycling several times are matched well with that of pristine crystals exhibiting that Tb-DCBA can keep well structure during the catalytic process (Figure 3b). Meanwhile, the FT-IR spectra of recycled samples are consistent well with the original spectrum to further prove the stability of reused Tb-DCBA (see Figure S8 in the Supporting Information).



Figure 3. (a) Reusability and (b) PXRD profiles of reused Tb-DCBA.

Referring to the early similar research work,<sup>57-63</sup> the assumptive mechanism of catalytic reaction mainly consists several parts in Figure 4. The full catalytic process can be firstly activated the O atom of aldehyde by interacting with  $-NH_2$  as the Lewis basic acid catalytic site on the linker. An amide intermediate state is generated by removing a H<sub>2</sub>O molecular. Subsequently, malononitril can be quickly interacted with the amide intermediate to form the targeted product. Finally, the catalytic center of Lewis basic site ( $-NH_2$ ) can be regenerated for the next catalytic reaction. Nonetheless, the catalytic mechanistic for this Knoevenagel condensation reaction still far surpasses than our scope to accurately understand the authentic catalytic mechanism, which require more investigations in the future work and more advanced characterization techniques.



Figure 4. Assumptive catalytic mechanism of Knoevenagel condensation reaction by Tb-DCBA.

CONCLUSION

In conclusion, a 3D hierarchically micro- and mesoporous MOF based on  $Tb_6$  clusters has been successfully designed and synthesized, which has lots of Lewis basic site ( $-NH_2$ ) on the porous surface. The resultant sample can highly efficient catalyze Knoevenagel condensation reaction and also has preferred recyclability. We really hope that this work can create an interesting and useful method to prepare such mesoporous MOFs in terms of special catalytic application areas.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The FT-IR, PXRD, TGA, crystal structure and crystal data (CIF) were provided in the supporting information. The crystallographic data was deposited in the Cambridge Crystallographic Data Centre (CCDC) as CCDC No. 1970448. This material is available free charge *via* the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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## Design and Assembly of a Hierarchically Micro- and Mesoporous MOF as a Highly Efficient Heterogeneous Catalyst for Knoevenagel Condensation Reaction

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This work presents a hierarchically micro- and mesoporous MOF with preferable stability as a potential excellent heterogeneous catalysis for Knoevenagel condensation reaction with excellent recyclability.