## A Zn-based, pillared paddlewheel MOF containing free carboxylic acids *via* covalent post-synthesis elaboration<sup>†</sup>

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A Zn-based, mixed-ligand (pillared paddlewheel), metal-organic framework (MOF) has been covalently and quantitatively decorated with free carboxylic acids to demonstrate the utility of covalent post-synthesis modification in the construction of otherwise inaccessible carboxy-functionalized MOFs.

One of the most widely touted attractions of metal-organic framework (MOF) materials is their great potential for incorporating a wide range of chemical functionality.<sup>1</sup> From a virtually limitless library of organic ligands, appropriate chemical functionalities can be integrated into MOFs to cater to the myriad proposed applications, from catalysis and separations,<sup>2–7</sup> to drug delivery<sup>8,9</sup> and gas storage.<sup>10–12</sup> In actuality, however, many chemical functionalities are incompatible with the conditions for MOF assembly, and cannot be obtained covalently attached within MOF cavities via traditional synthetic routes. For example, MOFs with struts containing free carboxylic acids<sup>13</sup> or pyridyls<sup>2</sup> remain rare, as these moieties often serve as the key coordinating elements of the MOF frameworks. Fortunately, post-synthesis modification (PSM), recently introduced as a rational and efficient means for the generation of a series of MOFs from one "parent" MOF,  $^{2,14-26}$  appears to be the perfect approach for overcoming this hurdle. This strategy has been used to endow MOFs with chemical functionalities that are either incompatible with MOF synthesis,<sup>3,27,28</sup> or those that would have required ligands that are nonexistent in solution phase.<sup>29</sup> To establish the power of PSM in the construction of previously inaccessible MOFs, we report herein a strategy for quantitatively elaborating the struts of a MOF material with free carboxylic acids.

Incorporating free carboxylic acids into MOFs has been an outstanding challenge: because free carboxylates are often the ligating functionality of choice for framework construction, only one example of a MOF possessing these groups has been reported to date.<sup>13,30</sup> Thus, a PSM strategy that results in MOFs possessing free carboxylic acids would serve as a powerful

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demonstration of the utility of covalent modification and provide a general route to a class of functional materials that have been difficult to obtain to date. The appeal of MOF materials that have free carboxylic acids is clear: they can be further modified using a wide range of organic and inorganic reactions to afford new MOFs with different capabilities. For example, such a MOF could be functionalized with a variety of metals, generating a series of new MOF materials with metal carboxylates in their pores, where each one can be used for a particular catalytic reaction.<sup>2,28</sup> Alternatively, the varying affinities that metal carboxylates have for different chemical species could be exploited to separate specific chemical mixtures.<sup>31–33</sup>

In selecting an ideal MOF for functionalization, we looked for a material with pores large enough to accommodate the forthcoming carboxy-functionalization. This material should also possess several functionalizable handles on its struts to allow for multiple opportunities to functionalize each cavity. Thus, we chose the Zn-based, mixed-ligand (pillared paddlewheel) MOF **1** (Scheme 1),<sup>34</sup> of composition Zn<sub>2</sub>(**TCPB**)(**DPG**) (**TCPB** = 1,2,4,5-tetrakis(4-carboxyphenyl)benzene,<sup>22</sup> and **DPG** = *meso*-1,2-bis(4-pyridyl)-1,2-ethanediol). It is worth noting that nearly all pillared paddlewheel MOFs constructed with ditopic carboxylate struts are doubly (or triply) catenated, resulting in comparatively small pores.<sup>35-43</sup> In contrast, we have observed that the tetratopic strut **TCPB** often yields *non*-catenated structures featuring correspondingly larger pores.<sup>22,34,44</sup> With free hydroxyl



**Scheme 1** Top: a stick diagram showing a single network unit of **1**. Yellow polyhedra represent zinc ions. Carbon: gray; oxygen: red; nitrogen: blue. Bottom: a schematic representation of the post-synthesis reaction of **1** with succinic anhydride to give  $1_{succ}$  with free carboxylic acid groups tethered to the struts *via* ester linkages.

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Fig. 1 Left: the IR spectra of 1 and  $1_{succ}$ . The new peaks for  $1_{succ}$  at 1700–1725 cm<sup>-1</sup> and 1750 cm<sup>-1</sup> represent the carbonyls of the ester and free carboxylic acid, respectively. Middle: the <sup>1</sup>H NMR spectrum of  $1_{succ}$  in NaOD–D<sub>2</sub>O. Integration of the H<sup>d</sup> peaks *versus* the H<sup>f</sup> peak indicates quantitative conversion. Right: the MALDI-TOF spectrum of  $1_{succ}$  dissolved in pyridine. The peaks at m/z = 317 and 417 represent protonated **DPG**<sub>monosucc</sub> and **DPG**<sub>disucc</sub>, respectively. The inset is an expansion of the 200 < m/z < 230 region showing that a negligible amount of the protonated **DPG** (m/z = 217) is present.

functionalities, **DPG** would react quickly with cyclic anhydride guests, forming carboxylic acids that would remain tethered to the MOF (Scheme 1).

Succinic anhydride proved to be an ideal substrate for our purposes, reacting readily with 1 in DMF at 80 °C to yield 1<sub>succ</sub>. Success of the esterification was determined by rinsing  $\mathbf{1}_{succ}$  with THF using a Soxhlet extractor and analyzing the rinsed sample by <sup>1</sup>H NMR spectroscopy, MALDI-TOF mass spectrometry, and IR spectroscopy. The IR spectrum of a powder sample of  $\mathbf{1}_{succ}$  exhibited strong  $\nu_{CO}$  stretches corresponding to the carbonyls of an ester and a free carboxylic acid, which were absent in that of 1 (Fig. 1, left panel). In the proton NMR spectrum of 1<sub>succ</sub> that had been dissolved in NaOD-D<sub>2</sub>O, integration of the protons  $\alpha$  to the pyridyl nitrogen in **DPG** versus the methylene hydrogens of the succinic acid revealed that close to 100% of the hydroxyl groups had been functionalized (Fig. 1, middle panel). In addition, the MALDI-TOF mass spectrum of a solution of pyridinedissolved 1<sub>suce</sub> clearly showed a large peak corresponding to the doubly functionalized **DPG**, **DPG**<sub>disuce</sub>,  $([M + H]^+ = 417,$ Fig. 1, right panel). Also present was a smaller peak for the mono-functionalized **DPG**, **DPG**<sub>monosucc</sub>  $([M + H]^+ = 317)$ . However, there was little evidence of the parent ligand  $([M + H]^+ = 217)$ . The differing solubilities of the two esterification products in pyridine are most likely responsible for the disproportionate prominence of the MALDI-TOF peak corresponding to the mono-carboxylated DPG<sub>monosucc</sub>.

The PXRD spectrum of  $1_{succ}$  matched that of 1 precisely and indicated a high level of crystallinity (Fig. 2, top left) that was unchanged after reaction with succinic anhydride. The extra stability afforded the tetrakisbenzoate struts by cooperative binding would favor maintaining the framework structure and tilting the equilibrium significantly towards the protonated succinic acid derivative in  $1_{succ}$ . That is, protonation of one of the benzoates of the **TCPB** ligand would not result in its disassociation from the Zn cluster, as the other three carboxylates are still bound firmly within the framework. Furthermore, since **TCPB** is a rigid ligand, the only way that one protonated benzoate could disassociate from the Zn-cluster node would be for its benzene ring to rotate into the plane of the central benzene ring of **TCPB**, resulting in unfavorable hydrogen interactions. While attempts at obtaining a N<sub>2</sub> isotherm for  $1_{succ}$  proved unsuccessful, (Fig. 2, top right), CO<sub>2</sub> uptake at 273 K confirmed that the evacuated material contains accessible micropores (Fig. 2, bottom right), giving an NLDFT surface area of 200 m<sup>2</sup> g<sup>-1</sup> and an average pore diameter of 5.5 Å (The CO<sub>2</sub> isotherm of 1 at 273 K (Fig. 2, bottom right) gave a surface area of 740 m<sup>2</sup> g<sup>-1</sup> and an average pore diameter of 8.3 Å). Thermogravimetric analyses (TGA) point to diminished pore volume in the framework after functionalization: as-synthesized 1<sub>succ</sub> loses 20% of its weight as DMF, as opposed to as-synthesized 1, which loses 55% (Fig. 2, bottom left). Additionally, solvent loss from 1<sub>succ</sub> occurs over a larger temperature range than from 1, suggesting smaller pores and stronger interactions between DMF and the framework.



Fig. 2 Top left: powder X-ray diffraction data showing that the esterification reaction does not undermine the structural integrity of the original framework in 1. Bottom left: TGA curves confirming that  $1_{succ}$  has less solvent-accessible volume than 1. Right: the gas adsorption isotherms for 1 and  $1_{succ}$ . Due to presumably smaller pores,  $1_{succ}$  is unable to uptake N<sub>2</sub> (top right). However, it can take up CO<sub>2</sub> (bottom right), though to a lesser extent than 1, as is to be expected.



Fig. 3 Top: a schematic representation of the  $Cu^{2+}$  chelation. Bottom left:  $1_{succ}$  in 50 ppm  $Cu^{2+}$  (aq). Bottom right: sample after 4 h.

To demonstrate the utility of the free carboxylic acids in  $1_{succ}$ , we immersed a sample of it in a 75 ppm aqueous solution of CuCl<sub>2</sub>. After 1 h, the supernatant solution was subjected to ICP-AES analysis, which showed a reduced Cu<sup>2+</sup> concentration of 20 ppm. A control experiment using 1 confirmed that the sequestration by  $1_{succ}$  was largely due to the presence of the carboxylic acids: 1 only reduced the Cu<sup>2+</sup> concentration to 46 ppm even though it has greater surface area, and, with a smaller formula weight, has more unit cells present per mass. Most impressively,  $1_{succ}$  can effectively remove Cu<sup>2+</sup> ions at lower concentrations. Upon exposure to a 50 ppm CuCl<sub>2</sub> solution, a sample of  $1_{succ}$  turned blue-green after a few hours though the initial solution had appeared colorless to the naked eye (Fig. 3).

In conclusion, we have demonstrated the power of post-synthesis modification to engender free carboxylic functionalities, inaccessible *via* traditional MOF synthesis, into MOF **1**. The new MOF material retains the basic physical properties of **1** but with additional carboxylic acid groups that can be further modified. While we only illustrated the free carboxylates' ability to chelate metals, the potential for tailoring MOFs post-synthesis using organic chemistry should open a plethora of opportunities for generating new functional materials.

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