

# Synthesis of catalytically active porous organic polymers from metalloporphyrin building blocks†

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The synthesis of a porous organic polymer (POP) containing free-base porphyrin subunits has been accomplished by the condensation of a bis(phthalic acid)porphyrin with tetra(4-aminophenyl)methane. Metallation by post-synthesis modification affords microporous materials incorporating either Fe or Mn(porphyrins) that have been shown to be active catalysts for both olefin epoxidation and alkane hydroxylation.

## Introduction

Microporous materials have attracted considerable recent attention given their potential applications, in catalysis,<sup>1</sup> gas storage,<sup>2</sup> and chemical separations,<sup>3</sup> among many others. In addition to traditional materials such as zeolites, a number of newer classes of microporous materials have been described, including metal-organic frameworks (MOFs),<sup>4,5</sup> covalent-organic frameworks (COFs),<sup>6–9</sup> polymers of intrinsic microporosity (PIMs),<sup>10</sup> porous organic polymers (POPs),<sup>11,12</sup> and others.<sup>13–18</sup> MOFs have been the most widely studied of these newer materials—partly because of their well-defined crystalline structure and partly because of the available enormous variety of candidate organic struts. A great deal of attention has been given to catalytic applications of MOFs,<sup>1</sup> due to the potential for integrating the well-defined, single-site activity of homogenous catalysts with the shape-, size-, chemo-, and enantio-selectivity that can be designed into the micropores. However, incorporation of catalytic struts with active metal sites has proven to be a significant challenge due to the difficulty in preventing an erstwhile catalytically active center from acting as a structural node.<sup>19</sup> To avoid this complication, the synthesis of all-organic materials, where all the nodes are formed *via* organic reactions, is an attractive alternative strategy for incorporating catalytically active complexes into porous frameworks.

Metalloporphyrins are particularly desirable to use as struts in porous materials given their well-studied catalytic behavior.<sup>20–22</sup> Specifically, Fe(porphyrin) and Mn(porphyrin) are analogues of the heme cofactor in the biologically ubiquitous family of cytochrome P450 enzymes, which are responsible for catalyzing a wide variety of oxidation reactions. However, several factors limit the application of these synthetic heme analogues as oxidation catalysts. Most importantly, synthetic metalloporphyrins can rapidly become deactivated, either through the

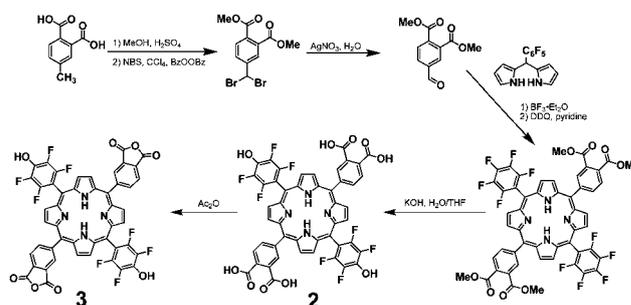
oxidative degradation of the porphyrin ring, or formation of  $\mu$ -oxo dimers.<sup>20,22</sup> Nature avoids these problems by enveloping the heme moiety within a large protein structure, which can also engender selectivity by controlling substrate access to the active site. By incorporating metalloporphyrins within microporous materials, it is hoped that these essential features of biological systems can be mimicked.

Formation of porphyrin-based polymers<sup>23</sup> and nanoparticles<sup>24,25</sup> have been reported previously, in the context of stabilizing Fe(porphyrin) catalysts in oxidation chemistry; however, examples of porous polymers based on metalloporphyrins are rare. McKeown and coworkers recently reported a condensation synthesis of polymers of intrinsic microporosity (PIMs) that incorporate Co(porphyrin) and Fe(porphyrin) and showed them to be active for the oxidations of cyclohexene and hydroquinone.<sup>26–28</sup> These findings motivated us to apply our recently reported modular strategy for synthesizing diimide-linked porous organic polymers (POPs)<sup>11,12</sup> to the challenge of constructing diimide-linked POPs containing free-base porphyrin subunits. The resulting highly rigid, all-organic porous materials should be amenable to post-synthesis modification (PSM) to yield a wide range of metalloporphyrin-based materials that are capable of catalyzing chemical reactions.

## Results and discussion

### Synthesis and characterization of monomers and polymers

The synthesis of POPs previously developed by our group and others takes advantage of the condensation reaction between



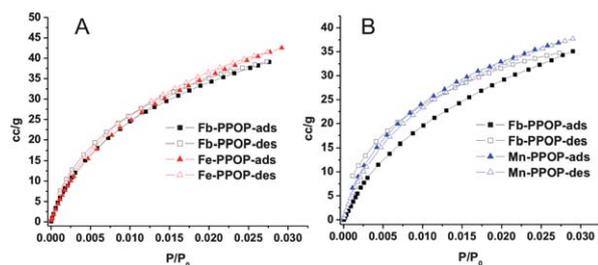
Scheme 1 Synthesis of the free-base dianhydride porphyrin monomer 3.

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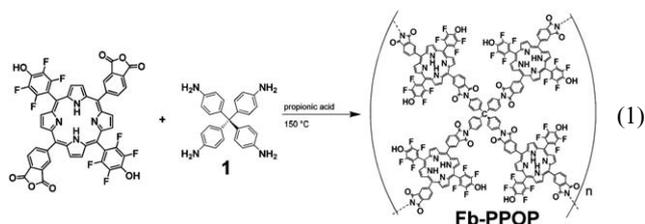
† Electronic supplementary information (ESI) available: Synthesis and characterization of porphyrin monomer and polymers, a modified synthesis of oxidant 4 and associated *safety warnings*, as well as a detailed description of catalytic conditions. See DOI: 10.1039/c0sc00339e

amines and acid anhydrides to form robust diimide bonds.<sup>11,12,15,27</sup> Porphyrins can be incorporated into these POP structures by utilizing free-base porphyrins with either pendant amine or acid anhydride groups. To introduce 3-dimensional pores into the POP network, we employed the easily accessible tetraamine monomer **1** and a bifunctional porphyrin monomer with acid anhydride groups. As outlined in Scheme 1, porphyrin **3** can be synthesized in 13% yield in six steps from 4-methylphthalic acid. The nucleophilic deprotection of the phthalate ester in step 5 led to the exchange of *p*-fluoro groups with hydroxide ions, as previously observed for perfluorophenyl porphyrins,<sup>29</sup> to form the bis(phthalic acid)-porphyrin **2**.

Condensation of the free-base porphyrin monomer (**3**) with **1** proceeded readily in refluxing propionic acid to give a dark solid that precipitated from solution in 70% yield (eqn (1)). This free-base porphyrin POP (**Fb-PPOP**) was completely insoluble in common organic solvents. Formation of the diimide linkages in **Fb-PPOP** was confirmed by FTIR spectroscopy (Fig. 2A) with a new stretch in the carbonyl region at 1724 cm<sup>-1</sup>. While some residual anhydride bonds are present in the polymeric material, as evidenced by a peak at 1853 cm<sup>-1</sup>, extending the reaction time did not eliminate them. Thermogravimetric analysis (TGA) of **Fb-PPOP** after filtration and air-drying confirmed its good porosity, with ~20% of the initial mass of the sample constituting solvent (Fig. 2C). Evidence for *permanent* porosity was obtained *via* gas adsorption measurements (CO<sub>2</sub>, 273 K) (Fig. 1). Non-local density functional theory (NLDFT) analysis of the CO<sub>2</sub> adsorption isotherms of several samples of **Fb-PPOP** yielded an average surface area of 355 ± 50 m<sup>2</sup> g<sup>-1</sup>.

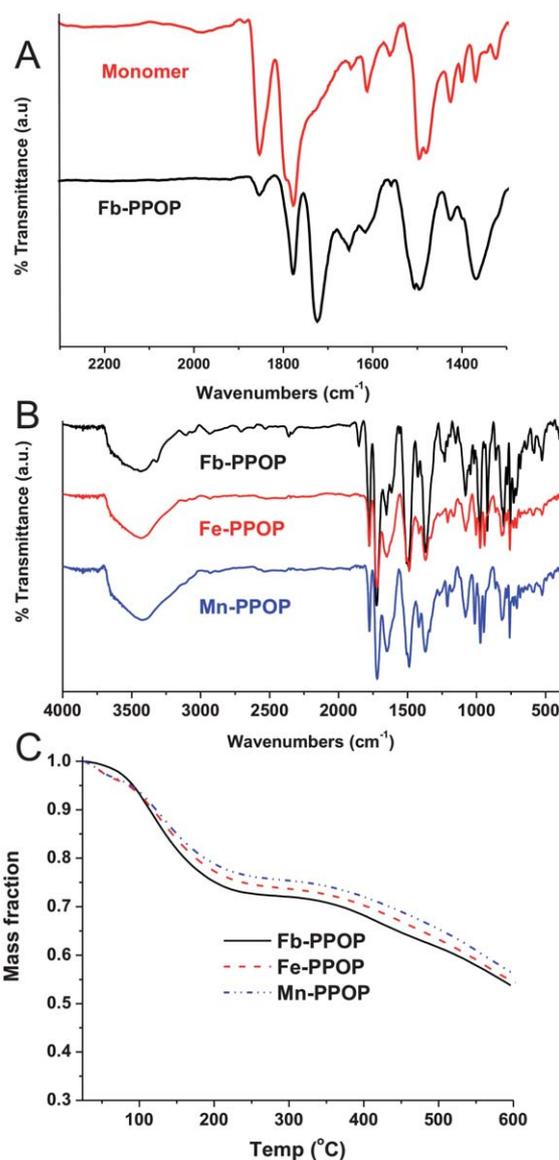


**Fig. 1** CO<sub>2</sub> gas adsorption isotherms of **Fb-PPOPs** and **M-PPOPs**, carried out at 0 °C. Each plot include the isotherms for the **Fb-PPOP** starting materials and the subsequently metallated PPOP. NLDFT surface areas: A) **Fb-PPOP**: 415 m<sup>2</sup> g<sup>-1</sup>; **Fe-PPOP**: 453 m<sup>2</sup> g<sup>-1</sup>. B) **Fb-PPOP**: 376 m<sup>2</sup> g<sup>-1</sup>; **Mn-PPOP**: 399 m<sup>2</sup> g<sup>-1</sup>.



### Metalation of PPOPs

Reaction of **Fb-PPOP** with either anhydrous FeCl<sub>2</sub> or MnCl<sub>2</sub>·4H<sub>2</sub>O in DMF at 100 °C under nitrogen produced **Fe-** or

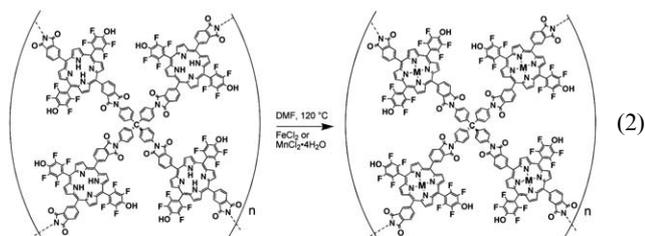


**Fig. 2** A) FTIR spectra of monomer **3** and **Fb-PPOP**. B) FTIR spectra of **Fb-PPOP**, **Fe-PPOP**, and **Mn-PPOP**. C) TGA profiles of **Fb-PPOP**, **Fe-PPOP**, and **Mn-PPOP**.

**Mn-PPOP** (eqn (2)). FTIR analysis of the **M-PPOPs** shows a significant decrease in the intensity of the N–H stretch at 3318 cm<sup>-1</sup> upon metallation of the PPOP (Fig. 2B). Analysis with inductively coupled plasma atomic emission spectroscopy (ICP-AES) confirmed metallation of the polymer with up to 3.6 wt% of Fe or 2.8 wt% of Mn. While these are below the theoretical metallation capacities of the **Fb-PPOP** (4.75 and 4.65 wt% for Fe and Mn, respectively), longer reaction times did not increase the metal content.

There are two likely explanations for the aforementioned observed low metal contents in our metallated PPOP materials. Either a significant number of porphyrins remain unmetallated after treatment with the metal salt, or the actual structure of our **Fb-PPOP** is far from ideal, such that there are fewer available porphyrin sites per mass of the polymer than we expect from an idealized stoichiometry of 2:1 mol mol<sup>-1</sup> **3**:1. UV-vis analysis

would have been a valuable tool for addressing the first hypothesis; unfortunately, the size of our polymer particles (~100–500 nm) prevented the collection of useful data from diffuse-reflectance measurements. The second hypothesis is more difficult to address given the amorphous, solid-state nature of the PPOPs. We are currently carrying out X-ray scattering experiments in an attempt to interrogate the real structure of these materials; these results will be reported in due course.

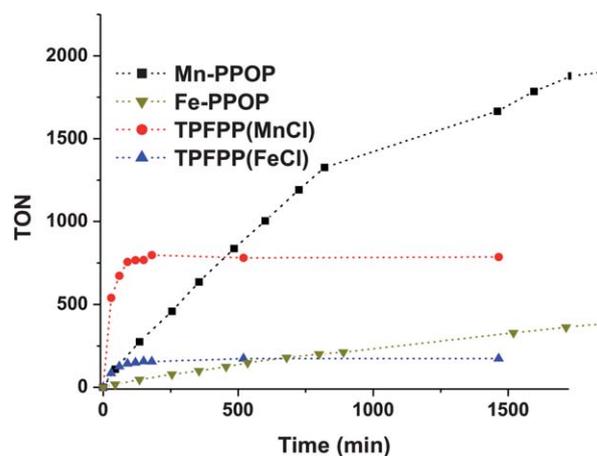


Metallation had little effect on the material's porosity—the CO<sub>2</sub> adsorption isotherms for **Fe-** and **Mn-PPOPs** are quite similar to that of **Fb-PPOP** (Fig. 1). TGA indicates that the metallated PPOPs absorb the same amount of solvent as the unmetallated material (Fig. 2C), further supporting this conclusion. The similar porosity of the metallated materials compared to **Fb-PPOP** additionally suggests that the metal uptake is mostly due to selective metallation of the porphyrin ligands and not adsorption of metal ions within the micropores of the material. In addition, powder X-ray diffraction data of the PPOP materials shows no peaks (see ESI†), suggesting that crystalline metal nanoparticles were not formed during the metallation.

### Catalytic activity of Fe- and Mn-PPOP

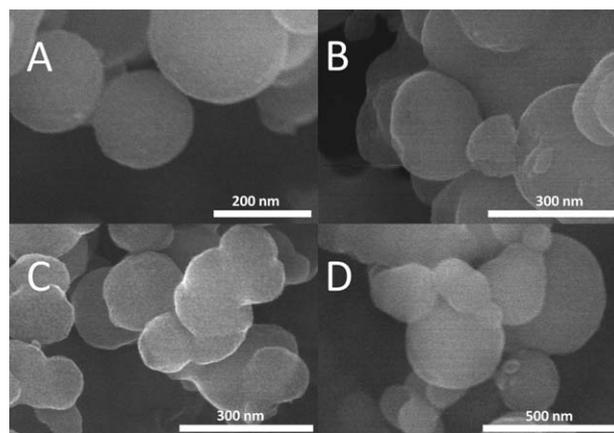
In the presence of a variety of terminal oxidants, Fe and Mn(porphyrin) complexes are well-known to function as catalysts for a range of oxidation reactions. To test the catalytic activity of the metallated PPOPs (M-PPOPs), we examined the epoxidation of styrene (eqn (3)) by a soluble analogue of iodosylbenzene<sup>30</sup> (**4**, this oxidant is known to be unreactive with olefins in the absence of a catalyst, see ESI† for important *safety warnings* regarding the synthesis of this oxidant). As a control, these epoxidations were compared against reactions catalyzed by the corresponding metallated *meso*-tetrapentafluorophenylporphyrin homogenous complexes ((TPFPP)M, M = FeCl, MnCl). At 0.025 mol% catalyst loading, the homogenous catalysts rapidly produce epoxides, but with facile deactivation and degradation of the catalyst (after 780 turnovers in the case of (TPFPP)Mn, and 170 in the case of (TPFPP)Fe (Fig. 3)). In contrast, both the **Fe-** and **Mn-PPOP** show greater stability than the analogous homogenous catalysts: **Mn-PPOP** is active for more than 2000 turnovers without displaying any signs of decomposition. As would be expected for heterogeneous catalysts, M-PPOPs generally display a much slower initial rate than the homogeneous analogs.

While both M-PPOPs can be recycled, their activities are greatly reduced. **Fe-PPOP** retains only 70% of its initial activity in the second cycle of epoxidation and 23% in the third cycle (Fig. 5). **Mn-PPOP** also displays a substantial difference between the first and second cycles, with only 60% activity retained in the

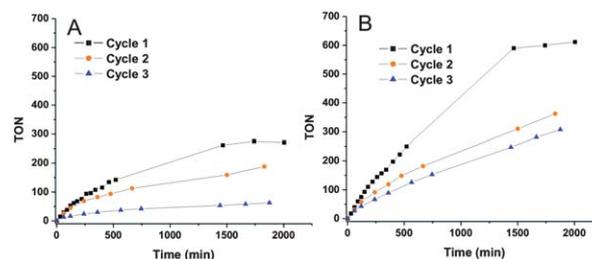


**Fig. 3** The epoxidation of styrene catalyzed by homogenous M-TPFPP and heterogeneous M-PPOP catalysts (0.025 mol% catalyst, by metal).

second cycle. However, after the second cycle, **Mn-PPOP** shows much less additional degradation than **Fe-PPOP**, with very similar activity evident for the third and second cycles. The loss of catalytic activity can be attributed to the oxidation of individual pyrrolic rings, not destruction of the polymer framework. While both materials are visibly bleached after a single cycle of catalysis, turning from a dark color into a light tan, SEM analysis of the polymer after bleaching shows identical spherical morphology and particle size (100–500 nm) as the pristine M-PPOPs (Fig. 4). Surprisingly, bleaching is not accompanied by

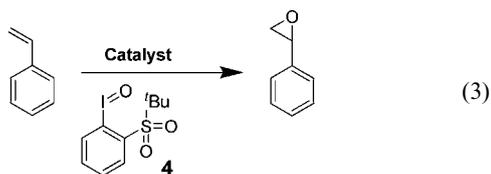


**Fig. 4** SEM images of pristine **Fe-PPOP** (A) and **Mn-PPOP** (B) for comparison to after-catalysis **Fe-PPOP** (C) and **Mn-PPOP** (D).



**Fig. 5** The catalytic recycling profiles of M-PPOP catalysts: A) **Fe-PPOP**. B) **Mn-PPOP**.

demetallation of the material, as ICP-OES analysis shows similar Fe and Mn contents (See ESI†).



The new M-PPOPs also proved catalytic for alkane oxidation, albeit with much lower activity than for exoxidation (see Fig. S6 in ESI†), as expected for iodosylbenzene oxidant.<sup>22</sup> The oxidation of cyclohexane with 1 mol% of Fe- and Mn-PPOP produced 12% and 48% yields of product (based on oxidant), respectively. In both cases, the product was a mixture of cyclohexanol and cyclohexanone (97 : 3 in the case of Fe; 95 : 5 for Mn).

We note that porphyrin nanoparticles have recently been reported with impressive enhancement of catalytic oxidation activity from the respective building blocks.<sup>24,25</sup> However, the manner in which porphyrin molecules are ordered in these nanoparticle materials is also unknown, rendering them difficult to study and improve. While our PPOPs display lower catalytic activity than the aforementioned porphyrin nanoparticles, the modularity of our synthesis strategy lends itself readily for systematic modifications that can aid in future structure-property investigations using solid-state techniques such as density measurements, pore-size distribution analysis, and X-ray scattering. The resulting data can then be used to improve the materials design and catalytic behavior of both types of porphyrin-based materials.

## Conclusions

In summary, we have demonstrated a modular method for incorporating metalloporphyrin catalysts as structural components of microporous POPs and demonstrated the feasibility of using these materials as oxidation catalysts that display significantly greater activity than their homogenous counterparts. The ability to prepare porphyrin-based porous organic polymers in free-base form, and then metallate them subsequently, overcomes a problem often encountered with related coordination polymers. Indeed, for the latter, microporous materials featuring coordinatively unsaturated metal sites can be directly synthesized only with appreciable difficulty. **Fb-PPOP** and similar materials should be modifiable to incorporate nearly any transition metal, as well as many main groups elements, using well-established porphyrin chemistry. Such studies, along with investigations into the catalytic properties of these materials using environmentally friendly reagents and oxidants, will be reported in the near future.

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