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Article

Fast and Robust Synthesis of Metalated PCN-222 and Their Catalytic Performance in Cycloaddition Reactions with CO₂

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S Supporting Information

ABSTRACT: A simple and quick setup for the synthesis of PCN-222 and of a variety of metalated PCN-222(Co, Ni, Cu, and Zn), using of a microwave reactor, is reported for CO_2 fixation. Metalation of prophyrins by microwave heating has been evaluated through UV-vis titration. PCN-222(M) were obtained in a three-step, one-pot reaction in a remarkable 72% yield in only 30 min. The materials have been characterized using a variety of techniques. A study of CO₂ fixation through cycloaddition with epoxides and azidirines using metalated PCNs as catalysts is described. Cyclic carbonates and oxazolidinones were formed using CO₂ at atmospheric pressure under mild conditions. Higher activity was observed when PCN-222(Co) was used compared to that with PCN-222(Ni, Cu, Zn).

0=0=0 $X = O, NR^2$ New route to synthetize PCN-222 and PCN-222(Co, Ni, Cu, Zn) Simple Catalytic activity study of PCN-222(M) for the cycloaddition epoxides and azidirines: Mild condition

INTRODUCTION

The development of methods for the fixation of carbon dioxide (CO_2) would allow this abundant gas to be used as a onecarbon building block for synthesis. This should be seen as a very important goal as part of a move toward the sustainable production of chemicals. CO₂ has a high thermodynamic stability, so it needs to be activated if it is to be used as a feedstock for the synthesis of added-value organic compounds.¹ Both homogeneous and heterogeneous catalytic approaches to this activation have been investigated.²⁻⁴ For example, different porous materials have been synthesized and used as heterogeneous catalysts, including metal-organic frameworks (MOFs).⁵ MOFs are porous crystalline materials that are obtained by the polymerization of organic linkers and metal ions/clusters. Adsorption capacity for CO2, catalytic efficiency for CO₂ conversion, and recyclability are the three key aspects to be considered when selecting a MOF for this goal.

The cycloaddition reaction of CO₂ with epoxides to give cyclic carbonates^{6,7} is a remarkable reaction that leads to the formation of important building blocks and proceeds with a high atom economy (Scheme 1, top left). Different organocatalysts⁸⁻¹¹ as well as metal catalysts^{2,12} have been used to catalyze this reaction under homogeneous conditions. High catalytic activity was observed when metalloporphyrins were used as catalysts. These materials show high thermal stability and straightforward formation by metal complexation, and they have been prepared with a variety of structures bearing different functional groups.^{13,14} Metalloporphyrins containing metals such as Mg, Al, Cr, Cu, and Co have been tested as Lewis acid catalysts, using, for example, ammonium salts as

cocatalysts.¹⁵ Recently, the use of bifunctional porphyrins as catalysts where the cocatalyst is already incorporated into the structure of the porphyrin has also been reported.¹⁶⁻¹⁹ In general, high temperatures and/or high pressures of CO₂ are required when metallopophyrins are used.

Turning to heterogeneous catalysts^{20–25} based on porphyrins, Zhou's group have synthesized a series of new materials, namely, PCN-224 (no metal, Ni, Co, Fe), using a linkerelimination strategy.²⁶ These MOFs consist of 3D nano-channels formed by Zr_6 clusters and metalloporphyrins. This group pioneered the use of the porphyrinic zirconium MOF, PCN-224(Co), as a catalyst for the cycloaddition reactions of propylene oxide. Recently, new porphyrinic MOFs such as CuE1,²⁷ ZnTPy-BIM4/CNTs-3,²⁸ MMPF-18,²⁹ and CuNbOF₅(TPyPNi)³⁰ have been synthesized and successfully used as catalysts in the cycloaddition reactions of epoxides. The use of azidirines instead of epoxides as substrates for cycloaddition reactions with CO₂ yields oxazolidinones, which are also important structures in pharmaceutical chemistry.^{31,32} One example of a cycloaddition reaction with an azidirine was reported using the porphyrinic Cu-containing MMPF-10 as the catalyst.³³ The products were obtained in high yields, although a high pressure of CO₂ (2 MPa) was used.

For all these reactions, the catalytic activity was found to be similar to or higher than their homogeneous counterparts, but the use of such heterogeneous catalysts also has significant

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Scheme 1. Cycloaddition Reaction of CO₂, TCPP(M), and PCN-222(Co) Channels^a



^{*a*}Top, left: Cycloaddition reaction of CO_2 with epoxides and aziridines. Top, right: Schematic representation of TCPP(M). Bottom: Two projections of PCN-222(Co) channels along different axes.





advantages, such as simple catalyst separation and potential catalyst reuse. When it comes to the PCN family, their Lewis acidic character resulting from the presence of Zr metal ions as well as the metalloporphyrins within the polymeric matrix make them potential catalysts for the cycloaddition reactions of CO_2 . The PCN-222(M) family (M = metal) are ideal candidates, due to their extraordinarily large channels of 37 Å in diameter, larger than those of PCN-224, PCN-223, and MOF-525.^{34,35} Large channels and pores facilitate substratecatalyst interactions and increase the catalytic efficiency. A major drawback when it comes to the use of metalated PCN-222(M) is that tedious synthetic procedures are needed. Several steps are required to prepare the metalated porphyrins, and then the framework itself also needs to be synthesized and purified.³⁶⁻³⁸ If these materials are to be used in the development of new catalytic applications,³⁹ then the long synthetic route is a significant disadvantage. It is essential to have a fast and reliable procedure that can be used to prepare a range of materials that will allow the identification of the one with the highest catalytic activity. Our group has extensive experience in the synthesis of diverse materials and its application in catalysis.^{40–43}

In this paper, we describe a new, efficient, and general method for the synthesis of a range of metalated PCN-222 structures in one pot. The protocol allows a variety of these materials to be obtained in a simple and fast manner. Their catalytic performance in the cycload dition reactions of $\rm CO_2$ with epoxides and azidirines under atmospheric pressure is also described.

RESULTS

We developed a three-step, one-pot microwave-assisted synthesis of PCN-222 and PCN-222(Co, Ni, Cu or Zn) as shown in Scheme 2. The first step (Scheme 2, top) involves the formation of the Zr preclusters through the reaction of ZrOCl₂ with 2-fluorobenzoic acid (2FBA) (5 min, 140 °C, 70 W, 0 bar, in N,N-dimethylformamide (DMF)). Metalation of tetrakis(4-carboxyphenyl)porphyrin $[TCPP(H_2)]$ was carried out in step 2 (Scheme 2, bottom), and TCPP(M) was obtained in only 5 min at 175 °C in DMF under microwave irradiation (85 W, 1 bar). We found that a ratio of MCl_2 to $TCPP(H_2)$ of 5:1 (mol/mol) was needed for this reaction. For the preparation of nonmetalated PCN-222, step 2 was also carried out but in the absence of metal salts. The purpose of this was to solubilize the $TCPP(H_2)$. In the last step of the synthesis (step 3), the two mixtures from steps 1 and 2 were combined and treated with trifluoroacetic acid (TFA; 20 min, 150 °C, 35 W, 1 bar). Steps 2 and 3 are discussed thoroughly in the following sections. Further information on the development of this procedure is found in the Supporting Information.



Figure 1. UV–vis spectra of TCPP(H₂) (left) and TCPP(Co) (right), before (1) and after (2) adding an excess of HCl. Conditions: (1) 6.32 μ M TCPP(H₂/Co) in DMF; (2) 3.61 μ M TCPP(H₂/Co) + 8.6 mM HCl in DMF, resulting in TCPP(H₄)²⁺ and unaltered TCPP(Co).

Evaluation of the Metalation Efficiency. The metalation procedure described above (Scheme 2, step 2) was carried out under microwave conditions for 5 min at 175 °C. As our approach is based on the direct mixing of as-synthesized metalated TCPP(M) with Zr preclusters, we avoid the tedious and time-consuming purification process required to isolate the starting material. This metalation procedure is significantly simpler than those reported in the literature for the synthesis of metalated porphyrins with -COOH moieties.²⁶ The efficiency of the metalation procedure was evaluated through UV-vis titration of the reaction mixtures formed in step 2 (i.e., without any purification or isolation). The optical properties of metalated porphyrins and porphyrin derivatives are very well known.^{44,45} It is known that $TCPP(H_2)$ shows two different absorption bands in DMF as a consequence of $\pi \to \pi^*$ transitions (metal-to-linker or linker-to-metal charge transfer), one centered at 422 nm corresponding to the Soret (B) band and four Q bands at 515, 550, 590, and 646 nm (see Table S1).⁴⁶ We used the new Q-band arising at 666 nm in the fully protonated TCPP $(H_4)^{2+}$ for quantification purposes (Figure 1, left), as metalated TCPP(M) species prepared with an excess of metal salt (5:1) do not show this band in the red region of the spectra (Figure 1, right).

By plotting the absorbance value of the band at 666 nm for nonmetalated TCPP(H₂) while adding increasing amounts of HCl (see Figure S2), it is possible to relate the degree of protonation of the porphyrin to a maximum value corresponding to the titration end point (TCPP(H₄)²⁺). When the porphyrin is fully metalated (TCPP(M)), no changes in absorbance at this wavelength should be observed, and it should not be possible to plot a titration curve (see Figure S3). Thus, the difference in absorbance between TCPP(H₄)²⁺ and TCPP(M) at 666 nm can be used to measure the efficiency of the metalation.

We tested our hypothesis by evaluating the efficiency of the metalation reaction to form TCPP(Co) using different ratios of TCPP/CoCl₂ (see Figure S3). A 1:5 excess of CoCl₂ is needed to ensure metalation of all the porphyrins in the MOF formed during step 3 (Figure 1, Table S2), as confirmed by

elemental analysis (see the Supporting Information). DMF plays a crucial role in the metalation procedure; it helps the metal to enter the ring after deprotonation of the porphyrin.⁴⁷⁴⁸ Titration curves can therefore be used to estimate the amount of Co in the system as an alternative to elemental analysis. It may be possible to extend this approach to other systems.

Optimization of the Synthesis. The influence of the reaction conditions on the outcome of the PCN-222 synthesis step was evaluated (i.e., the effects on the crystalline structure and the final yield of the reaction temperature (150 and 175 $^{\circ}$ C), reaction time (10 and 20 min), and the molar ratio modulator: Zr⁴⁺(5, 10, 25 and 50)). Benzoic acid, which is typically used as the modulator for the synthesis of PCN-222, was replaced here by 2-fluorobenzoic acid (2FBA, see the Supporting Information) (Scheme 2, step 1). The use of a modulator as well as the molar ratio modulator/Zr⁴⁺ were crucial; importantly, the amount of PCN-222 obtained decreased when increased amounts of 2FBA were used, irrespective of the other reaction parameters (see Table S3). We hypothesize that the presence of 2FBA decreases the solubility of Zr preclusters in the reaction medium;⁴⁹ this would allow less modulator to be used than in syntheses where benzoic acid was used. In general, neither reaction temperature nor reaction time had any dramatic effect on the final yield (see Table S3). We then checked the crystallinity of all the materials synthesized. The highest purity phase was obtained when a ratio of Zr⁴⁺ to 2FBA of 1:25 was used at 150 °C for 20 min (see Figure S5 and Table S3). Further optimization allowed us to decrease the amount of 2FBA to a ratio of 1:15 (Zr⁴⁺/2FBA) without losing crystallinity. Thus, we selected 150 °C, 20 min, and a 2FBA/Zr⁴⁺ ratio of 1:15 as the optimal conditions. Under these conditions, PCN-222 was obtained in 70% yield (on a scale giving ca. 100 mg). The same conditions were used for the synthesis of PCN-222(Cu, Zn, Co, Ni). PXRD confirmed that the materials formed showed the same pure crystalline phase (Figure 2), which can be attributed to the use of MW heating.⁵⁰ It is important to mention that the excess of the metal M present in the reaction mixture (TCPP/

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Figure 2. PXRD patterns of PCN-222 and PCN-222(M) compared to the theoretical pattern (in black, CCDC 893545).

 $MCl_2 = 1:5$) during the porphyrin metalation step did not interfere with the structural ion/ion clusters. DMF has a dual role in this reaction: It acts as a solvent, but also at the temperatures used, DMF decomposes to form dimethylamine, which is basic enough to deprotonate both the pyrroles and the carboxylic acid moieties, enabling the metalation and polymerization reactions, respectively.⁵¹

Finally, we optimized the washing procedure (Figure S7). Remarkably, only one washing step using DMF/HCl (0.5 M aqueous) was required to remove the excess of 2FBA, as confirmed by ¹H NMR spectroscopy (Figure S8). Four additional washing steps using EtOH were required to remove traces of HCl within the MOF pores. Further details about the washing procedure and the characterization of the materials prepared in this work can be found in the Supporting Information, including thermogravimetric analysis (Figure S9), nitrogen sorption isotherms (Figures S10 and S11), scanning electron microscopy (Figures S12 and S13), carbon dioxide sorption isotherms (Figure S15), elemental analysis (Table S6), and ultraviolet–visible (UV–vis, Figure S16) and infrared spectroscopies (Figure S17).

Table S4 summarizes the main procedures used to prepare all the PCN-222 and PCN-222(M) structures. This simple protocol works well, so the tedious metalation procedures reported in the literature for the preparation of PCN-222(M) MOFs, which generally involve protection of the -COOHmoieties of the TCPP, long metalation steps under harsh conditions, and then deprotection. The method presented here (Scheme 2) substantially decreases the overall time needed from typically 2 days to 30 min; it also uses low amounts of modulators and yields up to 100 mg of PCN-222 or PCN-222(M) per batch.

The reproducibility and robustness of the procedure was evaluated by synthesizing 10 batches of PCN-222(Co). These materials all gave similar diffraction patterns (see Figure S6) and were formed in yields of $(71.6 \pm 1.3)\%$ on a scale of 100 mg/batch. Thus, this procedure affords significantly increased overall yields in a short synthesis time frame.⁴⁹

It must be mentioned that this procedure cannot be extended to the synthesis of TCPP(Fe), probably as a consequence of the ability of Fe^{2+} cations to interact with the $-COO^-$ groups of the linker. Cross-linked two-dimensional polymeric Fe-TCPP structures have been reported elsewhere.⁵²

Cycloaddition of Epoxides and Azidirines with CO₂. The catalytic activity of PCN-222 and PCN-222(M = Co, Ni,

Cu, or Zn) was evaluated in the cycloaddition reactions of epoxides and azidirines with carbon dioxide. The cycloaddition reaction of 1,2-epoxydecane (1a) with CO_2 (1 atm) using tetrabutylammonium bromide (TBAB) as cocatalyst (6 mol %) at rt was investigated first (Scheme 3a). PCN-222(Co)

Scheme 3. Kinetic Profiles of Cycloaddition of 1a and 1c^a



^{*a*}(a) Kinetic profile of cycloaddition of **1a** (0.2 mmol) catalyzed by different PCN-222(M). (b) Kinetic profile of cycloaddition of **1c** (0.2 mmol) catalyzed by PCN-222(Co). Yield was determined using an internal standard.

showed higher activity than PCN-222(Cu, Ni, Zn), and 2a was obtained in 73% yield. A shorter reaction time was required for the cycloaddition reaction of 1,2-epoxypentane (1c) with CO₂ catalyzed by PCN-222(Co), and a quantitative yield was obtained after 12 h (Scheme 3b). This behavior may be attributed to the easier diffusion of smaller substrates into the channels of the porous material.^{29,30} Pore size distribution (12 and 31 Å, inset Figure S10), BET surface area (2016 m²/g, Figure S11), and affinity toward CO_2 (-17.6 kJ/mol as heat of adsorption, Figure S15) were in agreement with those values previously reported. Nonmetalated PCN-222 was also tested in the cycloaddition reactions of 1a and 1c, but lower activity was observed. This suggests that the presence of a metalated porphyrin that can act as a Lewis acid catalyst is important for the cycloaddition reaction (Table 1, entries 2 and 6). Also, lower activity was observed when a homogeneous analog (TCPP(Co)) was used as catalyst (entries 3 and 7). The difference in activity between the homogeneous and heterogeneous catalysts was greater for epoxide 1c than for 1a (32 vs 16%). This result is consistent with the idea that smaller substrates (i.e., 1c) can access the catalytic centers inside the MOF more easily. Using TBAB or CoCl₂ in the absence of the catalyst resulted in negligible yields (entries 4, 8, and 9).

Table 1. Control Experiments^a

1a 1c	R R ; R = -(CH ₂) ₆ CH ; R = -CH ₂ CH ₃	Catalyst TBAB (6 mol%), CO ₂ (1 I ₃	atm), rt R	0 0 4 2a-2c
entry	epoxide	catalyst	time (h)	yield (%) ^b
1	1a	PCN-222(Co)	27	73
2	1a	PCN	27	58
3	1a	TCPP(Co)	27	57
4	1a		27	<5
5	1c	PCN-222(Co)	12	99
6	1c	PCN	12	67
7	1c	TCPP(Co)	12	67
8	1c		12	<5
9	1c	CoCl ₂	12	41

^{*a*}Reaction conditions: epoxide 1 (0.2 mmol), CO_2 (1 atm), catalyst (1 mol % based on Co), TBAB (6 mol %), no solvent, room temperature. ^{*b*}Yield determined by ¹H NMR spectroscopy using an internal standard.

The scope of the reaction was then studied (Scheme 4). Epoxide substrates bearing alkyl chains of different lengths were tested, and the corresponding products were obtained in excellent yields (2a-d). Smaller epoxides required lower

Scheme 4. Reaction Scope^a

temperatures and shorter times than epoxides with longer carbon chains, even though their electronic properties were similar (i.e., 1b-d vs 1a). Additionally, halogenated substituted epoxides (1e,f), styrene (1g), and 2-(phenoxymethyl)-oxirane (1h) gave cyclic carbonates in excellent yields. The efficiency of PCN-222(Co) in the fixation of CO₂ was further tested by reaction with aziridines to give oxazolidinones. Under mild conditions, a variety of azidirines were tested, and the corresponding oxazolidinones 4a-e were obtained in good yields.

The recyclability of the catalyst is an important subject in heterogeneous catalysis. The catalytic activity toward 1c remains constant after 4 runs (ca. 95% yield after 24 h, Figure 3). Furthermore, to prove the catalytic perfomance of the material, the yield of 2c is checked at shorter times (12 h) showing ca. 40% yield in consecutive runs (Figure S18), confirming a similar reaction rate for different runs. Both the crystallinity and morphology were maintained (Figures S19 and S20). Using scanning electron microscopy, we demonstrated that after 4 catalytic runs, the hexagonal rods were unaltered. The sizes of the crystals decreased slightly from 1.3 to 0.9 μ m, and the edges became rounded, but the aspect ratio remained similar (3.5).⁵³

PCN-222(Co) showed a high catalytic activity in the cycloaddition reactions, and a wide range of products were obtained under milder conditions compared to other



^{*a*}Conditions: substrate 1 or 3 (0.2 mmol), CO₂ (1 atm), catalyst (1 mol % based on Co), TBAB (6 mol %), and no solvent. Yield determined by ¹H NMR spectroscopy using an internal standard, isolated yields in parentheses. ^{*b*}Ratio of regioisomers.



Figure 3. Study of recyclability. Conditions: epoxide 1c (2 mmol), CO_2 (1 atm), catalyst (1 mol % based on Co), TBAB (6 mol %), no solvent, room temperature for 24 h. Yield determined by ¹H NMR spectroscopy using an internal standard.

porphyrin-based catalysts (see Table S9). Furthermore, the recyclability study demonstrates the efficiency and robustness of the material.

CONCLUSIONS

We have described a new microwave-assisted synthesis of metalated PCN-222. By optimizing different synthetic parameters such as reaction time, reaction temperature, and the amount of modulator, we were able to obtain PCN-222 as a pure crystalline phase in excellent yields and in very short reaction times. The simple and straightforward procedure for the synthesis of metalated PCN-222(M = Co, Ni, Cu, and Zn) avoids tedious protection/deprotection steps of the carboxylic acid functional groups of TCPP. A new in situ UV-vis titration procedure was established for the quantification of the metalation efficiency. A general washing/activation procedure was also developed, vielding 100 mg of PCN-222(M) per batch. The catalytic activity of PCN-222(Co) was demonstrated in the cycloaddition of epoxides and azidirines with CO₂ under remarkably mild reaction conditions under CO₂ at atmospheric pressure. Furthermore, the material can be recycled for up to 4 runs, maintaining its catalytic activity and crystallinity.

ASSOCIATED CONTENT

S Supporting Information

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Experimental details, characterization data, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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