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# 2D and 3D Porphyrinic Covalent Organic Frameworks: The Influence of Dimensionality on Functionality

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Dedicated to Professor Jean-Pierre Sauvage on occasion of his 75th birthday

Abstract: The construction of 2D and 3D covalent organic frameworks (COFs) from functional moieties for desired properties has gained intensive attention. However, the influence of COFs dimensionality on their functionalities, which can further assist in COF design, has never been explored. Herein, by selecting designed precursors and topology diagrams, we reported the synthesis of 2D and 3D porphyrinic COFs (2D-PdPor-COF and 3D-PdPor-COF). By model building and Rietveld refinement of powder X-ray diffraction, 2D-PdPor-COF crystallizes as 2D sheets while 3D-PdPor-COF adopts a five-fold interpenetrated pts topology. Interestingly, compared with 2D-PdPor-COF, 3D-PdPor-COF showed interesting properties, including 1) higher CO<sub>2</sub> adsorption capacity; 2) better photocatalytic performance; 3) size-selective photocatalysis. Based on this study, we believe that with the incorporation of functional moieties, the dimensionality of COFs can definitely influence their functionalities.

#### Introduction

Covalent organic frameworks (COFs) are an emerging class of porous crystalline polymers built from molecular building blocks linked via strong covalent bonds.<sup>[11]</sup> In comparison with amorphous organic polymers, COFs can precisely assemble molecular building blocks into extended order structures through the principles of reticular chemistry. Owning to their periodic architectures, low densities, high surface areas and robust stability, COFs are considered as a highly designable and functionalized materials platform with various potential applications. Since first discovered by Yaghi and co-workers in 2005,<sup>[2]</sup> intensive attentions have been devoted to constructing functional COFs with desired properties. Thanks to the efforts of

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many groups, a large number of functional COFs have been reported over the past decade, which have found interesting applications in gas adsorption and separation,<sup>[3]</sup> heterogeneous catalysis,<sup>[4]</sup> molecular sensing,<sup>[5]</sup> energy storage,<sup>[6]</sup> proton conductivity,<sup>[7]</sup> optoelectronics,<sup>[8]</sup> etc.

In order to construct COFs with desired functionalities, a facile way is incorporating specific functional moieties during their synthesis process. From a structural viewpoint, these functional moieties can be integrated into either two-dimensional (2D) layered structures [9] or three-dimensional (3D) extended networks<sup>[10]</sup>, depending on the geometry and connectivity of the precursors. For 2D COFs, the 2D flat sheets usually stack in a face-to-face mode, and the functional moieties in the adjacent layers have strong  $\pi$ - $\pi$  interactions that could be beneficial for the charge mobility. In contrast, 3D COFs will allow the functional moieties to be three-dimensionally organized into the framework and thus feature open sites. In principle, the alignment and interaction of these functional moieties in 2D and 3D COFs are different, which may affect the properties of the resulting materials. Therefore, it will be very interesting to construct 2D and 3D COFs from the same functional moieties and then investigate the influence of dimensionality on their properties. However, to the best of our knowledge, no related work has been reported yet.





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Porphyrins and its derivatives are unique chromophores with interesting photophysical properties that have found great potentials in photocatalytic applications.[11] A unique feature of porphyrins is that their photocatalytic activity is strongly dependent on their aggregation state. With this consideration in mind, we decided to construct 2D and 3D porphyrinic COFs and then investigate their different properties to explore the dimensionality effect on COFs functionality. Herein, we report the designed synthesis and characterization of 2D and 3D palladium porphyrin-based COFs (2D-PdPor-COF and 3D-PdPor-COF) (Scheme 1), which have high crystallinity and large surface area. Interestingly, compared with 2D-PdPor-COF, 3D-PdPor-COF exhibited higher CO2 adsorption capacity. In addition, both COFs can be used as heterogeneous photocatalysts for selective oxidation of sulfides to sulfoxides, but 3D-PdPor-COF showed better photocatalytic performance as well as size-selectivity.

#### **Results and Discussion**

In order to study the dimensionality effect, the major concern is how to rationally select the proper topology diagram and then design the functional precursors to construct the desired 2D and 3D COFs. However, unlike the well-established 2D COFs, the construction of 3D COFs have been proved to be a big challenge,<sup>[12]</sup> and only a few topology diagrams for 3D COFs has been reported until now.<sup>[1b]</sup> After careful consideration, we decided to choose the reported [ $C_4 + C_2$ ] diagram to synthesize 2D COFs,<sup>[1b]</sup> whereas for 3D COFs we used our reported topology strategy starting from tetrahedral ( $T_d$ ) and quadrilateral ( $C_2$  or  $C_4$ ) building blocks.<sup>[13]</sup> Since we aimed to construct porphyrinic COFs, we accordingly designed and synthesized the functional precursor, [5,10,15,20-Tetrakis(4-benzaldehyde)porphyrin]palladium (*p*-PdPor-CHO),<sup>[14]</sup> which can form 2D or 3D COFs by condensation with *p*-phenylenediamine (PPDA) or tetra(*p*-aminophenyl)methane (TAPM)<sup>[15]</sup>, respectively.

As can be seen in Scheme 1, 2D-PdPor-COF and 3D-PdPor-COF were synthesized under solvothermal conditions by reacting p-PdPor-CHO with PPDA and TAPM in a mixture of odichlorobenzene, n-butanol and aqueous acetic acid at 120 °C for several days. After washed by the Soxhlet extraction method, both COFs were isolated as powders insoluble in common organic solvents and water. From the solid-state <sup>13</sup>C NMR spectra (Figure S1 and S2), 2D-PdPor-COF and 3D-PdPor-COF showed a characteristic signal at ~158 ppm, which should be assigned to the imine carbon atom and indicates the formation of imine-linked materials. In addition, the Fourier transform infrared (FT-IR) spectra of both COFs exhibited a stretching vibration band at ~1626 cm<sup>-1</sup> (Figure S3), confirming again the existence of imine bonds. Furthermore, the thermogravimetric analysis (TGA, Figure S4) revealed that both COFs have high thermal stability up to 500 °C under nitrogen atmosphere. According to the scanning electron microscopy (SEM) images (Figure S5), 3D-PdPor-COF possesses an irregular polyhedral morphology while 2D-PdPor-COF is plate-like.



Figure 1. PXRD patterns of 2D-PdPor-COF (a) and 3D-PdPor-COF (d) with the experimental profiles in black, Rietveld refinement in red, their difference in green, and the Bragg position in blue. Structural representations of 2D-PdPor-COF (b) and 3D-PdPor-COF (e), in which the former has an eclipsed AA stacking 2D structure and the latter adopts a five-fold interpenetrated **pts** topology. The schematic diagrams of stacking manners of palladium porphyrin units in 2D-PdPor-COF (c) and 3D-PdPor-COF (f).

The high crystallinity of 2D-PdPor-COF and 3D-PdPor-COF was revealed by powder X-ray diffraction (PXRD) analysis (Figure 1a and 1d). Their structures were then reliably solved and confirmed based on PXRD data by a combination of real space method (model building) and Rietveld refinement.<sup>[16]</sup> For 2D-PdPor-COF, from its PXRD pattern, a triclinic unit cell (a = 4.29 Å, b = 23.51 Å, c = 25.47 Å,  $\alpha$  = 88.6°,  $\beta$  = 97.7°,  $\gamma$  = 87.9°, space group P-1) could be indexed. With the determined unit cell a topologically reasonable eclipsed AA stacking 2D structure model (Figure 1b) was built straightforwardly by employing the chemical information from real space such as basic building blocks and connection manners (-C=N-). The simulated PXRD pattern of the structure model fits well with the experimental PXRD pattern of 2D-PdPor-COF in peak positions and intensities (Figure S8), indicating the reliability of the structure model. The structure model was then further validated by the Rietveld refinement using the program Topas V6.[17] The final agreement residuals for the refinement were  $R_l = 0.005$ ,  $R_{wp} =$ 0.076, and Rexp =0.028 (Figure 1a, Table S1). For 3D-PdPor-COF, its PXRD pattern could be indexed by a C-centered monoclinic unit cell (a = 28.37 Å, b = 7.50 Å, c = 39.9 Å,  $\beta$  = 99.75°, space group C2/c), which is highly consistent with the one revealed by single-crystal electron diffraction data<sup>[18]</sup> (Figure S9, Table S2). A structure model with a five-fold interpenetrated pts topology (Figure 1e, Figure S11) was then established indisputably using model building. The Rietveld refinement of 3D-PdPor-COF converged with agreement values  $R_{i}$ = 0.007,  $R_{wp}$ = 0.064, with  $R_{exp}$ = 0.030 (Figure 1d, Table S3). It should be mentioned here, in the refined structures of 2D-PdPor-COF and 3D-PdPor-COF, all bond lengths and angles are consistent with those expected for COF materials. Furthermore, according to their crystal structures, the palladium porphyrin units in 2D-PdPor-COF and 3D-PdPor-COF stack in totally different manners (Figure 1c and 1f).

The permanent porosities of 2D-PdPor-COF and 3D-PdPor-COF were evaluated by nitrogen adsorption isotherms at 77 K. As shown in Figure 2a and 2b, both COFs exhibited a typical I isotherm, indicating micro-porosity. Accordingly, the Brunauer-Emmett-Teller (BET) surface areas were calculated to be 1120 m<sup>2</sup> g<sup>-1</sup> for 2D-PdPor-COF and 1406 m<sup>2</sup> g<sup>-1</sup> for 3D-PdPor-COF. From density functional theory calculations, both COFs showed a narrow pore distribution with the peak at 1.9 nm for 2D-PdPor-COF and 0.58 nm for 3D-PdPor-COF, which is in agreement with the calculated pore size from crystal structures (1.87 nm for 2D-PdPor-COF and 0.63 nm for 3D-PdPor-COF, Figure S12). Furthermore, we investigated their CO<sub>2</sub> adsorption with pressures up to 1 bar and at temperature of 273 K and 298 K (Figure 2c and 2d). Interestingly, 3D-PdPor-COF exhibited a capacity of 105.0 cm<sup>3</sup> g<sup>-1</sup> at 273 K and 47.7 cm<sup>3</sup> g<sup>-1</sup> at 298 K, which is 3.1-fold and 2.4-fold greater than those of 2D-PdPor-COF. Therefore, compared with 2D-PdPor-COF, 3D-PdPor-COF has advantages in CO<sub>2</sub> adsorption.

For exploring the dimensional effect of 2D-PdPor-COF and 3D-PdPor-COF, we decided to investigate their photocatalytic as photocatalysts based on the following activities considerations: 1) palladium porphyrins are good photosensitizer; 2) from the crystal structures, the alignments of palladium porphyrins in these two COFs are significantly different, which can affect their photochemical properties; and 3) the smaller pore size of 3D-PdPor-COF may show certain selectivity. Their photocatalytic performances were then studied by the visible-light-induced aerobic oxidation of sulfides to sulfoxides, which plays a pivotal role in synthesizing a series of important organic compounds.<sup>[19]</sup> As shown in Table 1, by using

 Table 1. Photocatalytic seletive Oxidation of thioanisole to methyl phenyl sulfoxide by both COFs [a]
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a)	b)
c)	$\mathbf{d}_{1,0}^{u}$
G G G G G G G G G G G G G G	ADS at 273K ADS at 273K ADS at 273K ADS at 273K ADS at 273K ADS at 273K ADS at 278K ADS at 298K DES at 298K 0 0 0 0 0 0 0 0 0 0 0 0 0

Figure 2. N<sub>2</sub> adsorption and desorption isotherms of 2D-PdPor-COF (a) and 3D-PdPor-COF (b) at 77K. The inset is their pore size distributions.  $CO_2$  adsorption and desorption isotherms of 2D-PdPor-COF (c) and 3D-PdPor-COF (d) at 273K and 298K.

Blue LED, Air, RT								
Entry	Light	Photocatalyst	Air	Additive	Yield (%) <sup>#</sup>			
1	on	3D-PdPor-COF	+	-	98			
2	off	3D-PdPor-COF	+	-	0			
3	on	none	+	-	0			
4	on	3D-PdPor-COF	-	-	0			
5	on	2D-PdPor-COF	+	-	48			
6	on	3D-PdPor-COF	+	Superoxide scavenger <sup>c</sup>	13			
7	on	2D-PdPor-COF	+	Superoxide scavenger <sup>c</sup>	7			
8	on	p-PdPor-CHO	+	-	23			

 $^{[a]}$  Conditions: thioanisole (0.2 mmol), photocatalyst (0.01 mmol), CF<sub>3</sub>CH<sub>2</sub>OH (1 mL), chlorobenzene (10 µL), irradiation with 3W blue LEDs, 0.4 h.  $^{[b]}$  Yield determined by GC-FID with chlorobenzene as internal standard.  $^{[c]}$  *p*-Benzoquinone as superoxide scavenger (1 mg).

3D-PdPor-COF as photocatalyst (entry 1), the photo-induced oxidation of thioanisole to methyl phenyl sulfoxide can reach to a yield of 98% in 0.4 h. This performance is comparable to many reported heterogeneous photocatalysts (Table S7). In addition, without any special treatment, 3D-PdPor-COF was still highly active after 3 runs (Figure S17) with the framework retained (Figure S18). We also evaluated the factors that may influence the photocatalytic reaction. According to entries 2-4, it can be concluded that the photocatalyst, light irradiation and oxygen source are all indispensable.

However, when 2D-PdPor-COF was used as the photocatalyst (entry 5) under same condition, the reaction yield is only 48%, much lower than that of 3D-PdPor-COF. In order to figure out the mechanism for this difference, we first performed spin-trapping experiment by using electron spin resonance (ESR) spectroscopy. After photoirradiation of the air saturated CF<sub>3</sub>CH<sub>2</sub>OH solution containing 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2D-PdPor-COF or 3D-PdPor-COF, the signal for the adduct of superoxide radical anion with DMPO was detected (Figure S20) for both COFs, indicating the formation of the superoxide radical anion. In addition, when the superoxide scavenger *p*-benzoguinone was added into the reaction system (entries 6 and 7), the conversion of thioanisole in the presence of 3D-PdPor-COF and 2D-PdPor-COF reduced to 13% and 7%, respectively. Therefore, the key oxidative intermediate in this photocatalytic reaction is the superoxide radical anion, which is generally accepted that it is formed through the electron transfer of the excited triplet state of porphyrins to molecular oxygen.<sup>[20]</sup> We then studied the triplet state lifetimes of these two COFs by using transient absorption spectroscopy. As shown in Figure 3, 3D-PdPor-COF exhibited longer lifetime (26.34 µs) than that of 2D-PdPor-COF (0.41 µs). This difference can be explained from their crystal structures (Figure 1), as the stacking mode of palladium porphyrin units in 2D-PdPor-COF can efficiently quench the triplet excited states. Consequently, compared with 2D-PdPor-COF, 3D-PdPor-COF has better photosensitizing activity to produce superoxide radical anion, which results in better photocatalytic performance.



Figure 3. Transient absorption decay curves of the triplet states of 2D-PdPor-COF (a) and 3D-PdPor-COF (b) at 546 nm.

We further studied the applicability of both COFs as photocatalysts, staring from substrates with different substituents and sizes. As shown in Table 2 entries 1-4, in the presence of 3D-PdPor-COF, these tested substrates can be efficiently converted to the desired products with high yields. As 3D-PdPor-COF exhibited better usual. photocatalvtic performance than 2D-PdPor-COF under same conditions, due to its better photosensitizing activity mentioned above. However, when substrates with larger sizes were used (entries 5-6), the reaction yield of 3D-PdPor-COF decreased sharply while 2D-PdPor-COF still showed reasonable yield. For example, by changing the substrates from methyl p-tolyl sulfide (entry 2) to 4tert-butylphenyl methyl sulfide (entry 5), the yield of 3D-PdPor-COF decreased from 99% to 48%, but for 2D-PdPor-COF, it is almost the same. Accordingly, compared with 2D-PdPor-COF, 3D-PdPor-COF can exhibit certain size-selective photocatalysis. This is reasonable, as the pore size of 3D-PdPor-COF is much smaller than that of 2D-PdPor-COF.

Table 2. Substrate scope of the photocatalytic selective oxidation of sulfides to sulfoxides by both COFs  $^{\left[ a\right] }$ 

Entry	Substrate	Product	3D-PdPor-COF Yield (%) <sup>[b]</sup>	2D-PdPor-COF Yield (%) <sup>[b]</sup>
1	€) <sup>s</sup> ∖	0:0	98	48
2	,€) <sup>s</sup> `	↓ S S	99	60
3	~S~		99	60
4	F S	F C S	94	39
5	$\gamma^{\text{r}}$		48	59
6	CC <sup>s</sup>	CCC <sup>S</sup>	38	58

 $^{[a]}$  Conditions: sulfides (0.2 mmol), photocatalyst (0.01 mmol), CF<sub>3</sub>CH<sub>2</sub>OH (1 mL), chlorobenzene (10  $\mu$ L), irradiation with 3W blue LEDs, 0.4 h.  $^{[b]}$  Yield determined by GC-FID with chlorobenzene as internal standard.

#### Conclusion

In conclusion, in order to demonstrate the influence of dimensionality on COF functionality, we reported the designed synthesis of 2D-PdPor-COF and 3D-PdPor-COF as well as their properties characterization. Our results showed that, compared with 2D-PdPor-COF, 3D-PdPor-COF can not only display higher  $CO_2$  adsorption capacity, but also exhibit better photocatalytic performance and size-selectivity. From this study, it can be concluded that the incorporation of functional moieties into 2D or 3D COFs can definitely allow the resulting materials with different properties, indicating the dimensionality of COFs can influence the functionality through different arrangements of

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functional groups. Although the construction of 3D COFs has been considered as a big challenge,<sup>[12]</sup> this study will definitely encourage us to synthesize functional 3D COFs for interesting applications in future.

#### **Experimental Section**

**Synthesis of 2D-PdPor-COF.** A Pyrex tube was charged with *p*-phenylenediamine (12.8 mg, 0.12 mmol), *p*-PdPor-CHO (50 mg, 0.06 mmol), 2 mL *o*-dichlorobenzene, 2 mL *n*-butanol, and 0.4 mL of 3 M aqueous acetic acid. After being degassed by freeze-pump-thaw technique for three times and then sealed under vacuum, the tube was placed in an oven at 120 °C for 3 d. The resulting precipitate was filtered off, exhaustively washed by Soxhlet extractions with tetrahydrofuran and dichloromethane for 2 d, dried at 80 °C under vacuum for overnight. The 2D-PdPor-COF was isolated as a crimson powder (55.4 mg, 88% yield). Elemental analysis for the calculated formula ( $C_{60}H_{36}N_8Pd$ )<sub>n</sub>: C, 73.88%; H, 3.72%; N, 11.49%. Found: C, 72.08%; H, 3.60%; N, 10.86%.

**Synthesis of 3D-PdPor-COF**. A Pyrex tube was charged with TAPM (22.8 mg, 0.06 mmol), *p*-PdPor-CHO (50 mg, 0.06 mmol), 3.6 mL o-dichlorobenzene, 0.4 mL *n*-butanol, and 0.4 mL of 6 M aqueous acetic acid. After being degassed by freeze-pump-thaw technique for three times and then sealed under vacuum, the tube was placed in an oven at 120 °C for 7 d. The resulting precipitate was filtered off, exhaustively washed by Soxhlet extractions with tetrahydrofuran and dichloromethane for 2 d, dried at 80 °C under vacuum for overnight. The 3D-PdPor-COF was isolated as a tibetan orange powder (60.3 mg, 83% yield). Elemental analysis for the calculated formula (C<sub>73</sub>H<sub>44</sub>N<sub>8</sub>Pd)<sub>n</sub>: C, 76.94%; H, 3.89%; N, 9.83%. Found: C, 73.66%; H, 4.39%; N, 8.95%.

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**Keywords:** dimensionality effect  $\bullet$  functional moieties  $\bullet$  COFs  $\bullet$  size-selective catalysis  $\bullet$  CO<sub>2</sub> adsorption

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#### Entry for the Table of Contents (Please choose one layout)

Layout 2:

## **RESEARCH ARTICLE**



Yi Meng, Yi Luo, Ji-Long Shi, Huimin Ding, Xianjun Lang, Wei Chen, Anmin Zheng, Junliang Sun\* and Cheng Wang\*

#### Page No. – Page No.

2D and 3D Porphyrinic Covalent Organic Frameworks: The Influence of Dimensionality on Functionality

**2D vs 3D COFs:** In order to demonstrate the influence of dimensionality on COF functionality, we reported the designed synthesis of 2D-PdPor-COF and 3D-PdPor-COF. Our results showed that, compared with 2D-PdPor-COF, 3D-PdPor-COF can not only display higher CO<sub>2</sub> adsorption capacity, but also exhibit better photocatalytic performance and size-selectivity.