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Introduction

Covalent organic frameworks (COFs) are novel crystalline organic porous materials formed by dynamic covalent bonding.^{1–7} Compared with traditional pure inorganic molecular sieves and porous carbon materials, COFs have unique advantages such as precise design, adjustable structures and well-ordered pores.^{8–14} Porphyrin is one of the ideal building blocks for COFs because of its conjugated planar structure, strong thermal stability, high chemical stability, easy modification, high skeletal strength

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Two three-dimensional (3D) porphyrin covalent organic frameworks, PCOF-1 and PCOF-2, were synthesized via imine condensation of a planar porphyrin tetramine (TAPP or TABPP) and a rigid tetrahedral aldehyde based on the steric hindrance of 3,3',5,5'-tetrakis(4-formylphenyl)bimesityl (TFBM). The structures of PCOF-1 and PCOF-2 were studied by FT-IR and ¹³C CP-MAS solid state NMR spectroscopy. Powder X-ray diffraction patterns revealed obvious crystallinity with two intense peaks at 3.28° and 3.75° for PCOF-1, and 2.63° and 2.98° for PCOF-2. Structural simulation confirmed their 3D rutile type (pts) topological structures with two different pore sizes. X-ray single crystal diffraction revealed a distorted tetrahedral structure for the building block TFBM with two dihedral angles of 119° and 107.8°, and a planar square structure for the model compound (MC) with an outspread angle of 176.5°. PCOF-1 and PCOF-2 exhibited Brunauer-Emmett-Teller (BET) surface areas of 316 and 234 m² g⁻¹, respectively. The morphologies of PCOF-1 and PCOF-2 were investigated by scanning electron microscopy and transmission electron microscopy methods. PCOF-1 and PCOF-2 showed a high thermal stability up to 420 °C without decomposition through thermogravimetric analysis (TGA), and high chemical stability with no obvious mass loss after three days of immersion in various solutions. Due to the large surface area and the appropriate pore size, PCOF-Fe exhibited excellent biocatalytic catalytic performance, while PCOF-Co exhibited good electrocatalytic activity towards oxygen evolution reactions. These results indicate that 3D porphyrin-based COFs constructed from the tetrahedral building block with steric hindrance are promising candidates for single-site catalysis.

> and excellent catalytic performance.^{15–21} However, porphyrinbased COFs reported so far possess mainly two-dimensional layered structures, and the effective contact between the catalytic active centre and the substrate is limited by the layer-tolayer stacking.^{22–25} Three-dimensional (3D) structures could solve this issue.^{26–33} 3D porphyrin-based COFs with a controllable pore structure and adjustable catalytic performance thus have great potential application in the field of heterogeneous catalysis.

> In order to construct 3D porphyrin COFs, $T_4 + C_2$ and $T_4 + C_4$ polymerization strategies were usually adopted to generate diamond (dia) and rutile type (pts) topologies by using tetrahedral T_4 building blocks and two-connected porphyrin C_2 building blocks or four-connected porphyrin C_4 units.^{34,35} So far, most of the 3D porphyrin COFs have excellent photocatalytic properties due to the open pore structure and sufficient porphyrin active sites. However, the tetrahedral T_4 building blocks (tetra-(4-aminophenyl)methane or tetrakis(4-formylphenyl)methane) of 3D porphyrin-based COFs are non-conjugated and flexible due to sp³ carbons. The sp³ carbons in 3D COFs inhibit the transport of electrons between the conjugated units in the frameworks, and



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Scheme 1 Schematic representation of the design and synthesis of (a) tetrahedral T_4 building block (TFBM) and (b) three-dimensional porphyrin covalent organic frameworks.

the flexible structure weakens the stability of the whole 3D skeletons.^{36–41} Compared with 3D porphyrin COFs with sp³ carbons, their rigid structure can greatly improve the stability of the entire skeleton, and the porphyrin catalytic centres in the 3D framework have a good synergistic effect. However, it is challenging to improve the rigidity of 3D porphyrin-based COF skeletons. Selecting rigid tetrahedral T_4 building blocks may help construct rigid 3D porphyrin-based COFs.

To develop rigid 3D porphyrin-based COFs, we selected rigid biphenyl to design tetrahedral T_4 building blocks through limiting the rotation of biphenyl by attaching six methyl groups at the 2, 2', 4, 4', 6 and 6' positions (Scheme 1a).⁴² And four benzaldehyde groups are decorated at the 3, 3', 5 and 5' positions of biphenyl to form rigid tetrahedral T₄ building blocks 3,3',5,5'-tetrakis(4-formylphenyl)bimesityl (TFBM). TFBM has strong steric hindrance with six methyl groups limiting the rotation to the plane, and four benzaldehyde groups can form dynamic C=N bonds with amine to constitute a rigid 3D framework. Herein, we report two 3D porphyrin-based covalent organic frameworks (PCOFs) constructed from tetrahedral TFBM building blocks and two different types of porphyrin tetramine units (5, 10, 15, 20-tetra(4-aminophenyl)porphyrin and 5, 10, 15, 20-tetra(4-aminobiphenyl)porphyrin) by aldehyde-amine condensation reactions (Scheme 1b). The metal ions were incorporated into the porphyrin centres of 3D PCOFs^{43,44} to explore the performance of biomimetic catalysis for PCOF-Fe and electrocatalytic oxygen evolution for PCOF-Co as single-site catalysts.

Experimental

All reagents and solvents were of reagent grade, purchased from commercial sources and used without further purification.

Synthesis of PCOF-1

A Pyrex tube was charged with TFBM (13.0 mg, 0.02 mmol) and TAPP (13.5 mg, 0.02 mmol) in a solution of 1.7 mL $\,$

o-dichlorobenzene, 0.3 mL mesitylene and 0.2 mL 6 M aqueous acetic acid. This mixture was sonicated for 10 min to obtain a homogeneous dispersion. After being frozen in liquid N₂, the reaction tube was degassed by freeze–pump–thaw cycles three times. Then the tube was sealed under vacuum and heated at 120 °C for 7 days. The precipitate was collected by filtration, washed with *N*,*N*-dimethyl formamide (6 × 5 mL), extracted using a Soxhlet extractor with tetrahydrofuran for 24 hours, and finally dried at 80 °C under vacuum for 12 hours to yield **PCOF-1** as a dark purple powder. Yield: 60%.

Synthesis of PCOF-2

PCOF-2 was synthesized using TABPP (19.6 mg, 0.02 mmol) following the procedures used for preparing **PCOF-1**. The **PCOF-2** was finally dried as a dark purple powder. Yield: 66%.

Synthesis of PCOF-1-Fe

PCOF-1 (40 mg) and FeCl₂·4H₂O (100 mg) were dispersed in DMF (20 mL) under a nitrogen atmosphere and refluxed for six hours. After cooling down to room temperature, powder was obtained by centrifuging. The resulting precipitate was washed with deionized water, anhydrous methanol, DMF, and anhydrous THF and finally dried at 80 °C under vacuum for 12 hours to obtain **PCOF-1-Fe**. Yield: 75%.

Synthesis of PCOF-2-Fe

PCOF-2-Fe was synthesized using **PCOF-2** (40 mg) following the procedures used for the preparation of **PCOF-1-Fe**. Yield: 69%.

Synthesis of PCOF-1-Co

PCOF-1-Co was synthesized using **PCOF-1** (40 mg) and excess $Co(CH_3COO)_2$ ·4H₂O (100 mg) following the procedures used for the preparation of **PCOF-1-Fe**. Yield: 73%.

Synthesis of PCOF-2-Co

PCOF-2-Co was synthesized using **PCOF-2** (40 mg) and excess $Co(CH_3COO)_2 \cdot 4H_2O$ (100 mg) following the procedures used for the preparation of **PCOF-1-Fe**. Yield: 79%.

Results and discussion

PCOF-1 and **PCOF-2** were synthesized by $T_4 + C_4$ aldehydeamine condensation polymerization reactions (Fig. 1). Starting with metallized porphyrins as monomers would lead to metal detachment and amorphous **PCOFs**, and the method of postmodification was thus used to coordinate the metal with the porphyrin centres of as-synthesized **PCOFs**. In order to enhance the crystallinity of the imine condensation reaction, it is necessary to adjust the solvent selection and the ratio, and use a suitable concentration of acetic acid solution as a catalyst to trigger the polymerization at a suitable temperature (Tables S1, S2 and Fig. S11, S12, ESI†). **PCOF-1** and **PCOF-2** were crystallized through condensation between TFBM (0.02 mmol) and TAPP (0.02 mmol) or TABPP (0.02 mmol) under solvothermal conditions in a mixture of *o*-dichlorobenzene (1.7 mL), mesitylene (0.3 mL)



and 6 M acetic acid (0.2 mL) at 120 °C for 7 days. For the synthesis of **PCOFs**, *o*-dichlorobenzene and mesitylene that increase the solubility of porphyrin, 6 M acetic acid and a suitable temperature (120 °C) promote the Schiff base reaction of aldehyde and amine. **PCOF-1** and **PCOF-2** were separated by filtration and washed with various solvents to afford a dark purple solid. The **PCOF** products are insoluble in water and common organic solvents such as ethanol, tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF). The metal ions (Fe or Co) were introduced into the porphyrin centres of **PCOFs** by the method of post-modification. **PCOFs** and excess FeCl₂·4H₂O or Co(CH₃COO)₂·4H₂O were refluxed in a DMF solution at 150 °C for six hours under a nitrogen atmosphere, then filtered and washed to obtain **PCOF-Fe** and **PCOF-Co**.

Structural and morphological characterization

In order to determine the structure of the obtained COFs, powder X-ray diffraction (PXRD) experiments and theoretical simulations were carried out. The experimental results are similar to the theoretical simulation. As shown in Fig. 2a, the PXRD pattern of **PCOF-1** shows diffraction peaks at 3.30°, 3.73°, 4.80°, 6.84°, 8.18° and 9.06°, corresponding to the (010), (110), (210), (120), (212) and (312) facets, respectively. The peaks at 2.63°, 2.99°, 3.89°, 4.72°, 5.46° and 7.53° for **PCOF-2** correspond to the (010), (110), (210), (211), (120) and (312) facets, respectively (Fig. 2b). After metalation (**PCOF-1-Fe, PCOF-2-Fe, PCOF-1-Co** and **PCOF-2-CO**), the crystallinity was well-maintained as shown in the

PXRD pattern (Fig. S14, ESI⁺). The simulations were carried out by using Materials Studio version-7. Only a few nets (e.g., pth, pti, pts, etc.) are reasonable for PCOF-1 and PCOF-2 according to Reticular Chemistry Structure Resource.45 After comparing these possible spatial structures, it is proposed that both PCOF-1 and PCOF-2 adopt the Pmc_{21} space group (a = 50.60 Å, b = 26.70 Å, c = 26.69 Å for PCOF-1; a = 61.65 Å, b = 33.51 Å, c = 32.99 Å for PCOF-2) (Tables S7 and S8, ESI⁺). According to the optimized simulation, the extension angles between the positions 3 and 3', 3 and 5, 5 and 5', 3' and 5' in the tetrahedral unit were about 109° , 114° , 105° and 112° in **PCOF-1** and **PCOF-2**. The tetrahedral T_4 building blocks (TFBM) with four joint points and the square C_4 units (TAPP for PCOF-1 and TABPP for PCOF-2) with four joint points form a pts topology with two-fold interpenetration. PCOF-1 mainly possesses a hexagonal pore with a size of 42.3 Å and quadrilateral pores with a size of 18.4 Å, while they are 53.3 Å and 25.23 Å for PCOF-2. The porphyrin units orientate the channel, helping to maximize the available active sites. To the best of our knowledge, PCOF-1 and PCOF-2 are the first reported full-rigid three-dimensional porphyrin COFs.

The structures of TFBM and MC have been characterized by single-crystal X-ray diffraction structural analysis (Tables S3–S6, ESI†). Fig. 2c shows the structures of TFBM and MC. TFBM has a distorted tetrahedral structure with two dihedral angles of 107.8° and 119° due to the steric effect from its own six methyl groups, which are similar to the angles of the theoretical structure. The crystal structure of MC unambiguously proves



Fig. 2 (a) PXRD pattern and simulated structure of **PCOF-1**. (b) PXRD pattern and simulated structure of **PCOF-2**. (c) Single-crystal X-ray structure of TFBM (left. grey, C; red, O) and the model compound MC (right. grey, C; blue, N). (d) Infrared spectra of TFBM (red), **PCOF-1** (green), **PCOF-2** (blue). (e) ¹³C CP/MAS NMR spectra of **PCOF-1** (red) and **PCOF-2** (black). N₂ adsorption/desorption isotherms (77 K) and pore size distribution profiles (insert) of (f) **PCOF-1** and (g) **PCOF-2**.

the reaction of aldehyde–amine condensation, and it has a planar structure with an approximate straight angle of 176.5°. The distorted tetrahedral structure of TFBM and the planar structure of MC further confirm the feasibility of the theoretical structures of **PCOF-1** and **PCOF-2**. During polymerization, the four amino groups on the square TAPP and the four aldehyde units on the tetrahedral TFBM control the growing direction of the segments and result in 3D frameworks.

The Fourier transform infrared (FT-IR) spectra of PCOF-1 and PCOF-2 showed significantly weakened signals from the C=O vibration (1701 cm⁻¹) and the appearance of the C=N bond (1622 cm^{-1}) (Fig. 2d). As shown in the solid-state ¹³C cross-polarization magic-angle-spinning (CP/MAS) NMR spectra of PCOF-1 and PCOF-2 (Fig. 2e), a resonance signal at 155 ppm from the carbon in the C=N group was observed. These results also indicate the formation of PCOF-1 and PCOF-2. The UV/vis absorption spectrum of PCOF-1 or PCOF-2 nearly corresponds to TAPP or TABPP, except for stronger Q-bands at λ = 590 and 650 nm (Fig. S13, ESI[†]). In addition, the ratio of the relative intensities of the Q-bands versus the Soret band increased from 0.49 and 0.35 for TAPP and TABPP to 0.71 and 0.6 for PCOF-1 and PCOF-2, respectively. This enhanced absorption can be attributed to the fact that the 3D pore structure avoids the accumulation of porphyrins and promotes the interaction of porphyrins.46,47 Moreover, compared with PCOFs, the stretching vibrational frequency of the N-H bond (3320 cm^{-1}) of the porphyrin ring disappeared, indicating that the porphyrin rings are coordinated with Fe or Co ions in **PCOF-Fe** or **PCOF-Co** (Fig. S15, ESI[†]).³⁴ The powder electrical conductivity of **PCOFs** was measured to be 10^{-6} S cm⁻¹ and improved to 10^{-5} S cm⁻¹ after metal incorporation.

The porous structures of PCOF-1 and PCOF-2 were investigated by the physisorption of nitrogen at 77 K. The N₂ adsorption/ desorption isotherms of PCOF-1 and PCOF-2 demonstrate a combination of type I and type IV sorption isotherms according to the IUPAC classification, indicative of the presence of both micropores and mesopores. The sharp nitrogen adsorption at low relative pressures $(P/P_0 < 0.001)$ indicates the presence of abundant micropores. The slight adsorption hysteresis may be due to the spatial network interspersed structure or the restricted access of adsorbate molecules through a narrow pore opening.⁴⁸ The Brunauer-Emmett-Teller (BET) surface areas (Fig. 2f and g) are 316 and 234 m² g⁻¹ for **PCOF-1** and **PCOF-2**, respectively. The pore size distribution calculated by the non-local density functional theory (NLDFT) of PCOF-1 shows the coexistence of two different pores, 2.3 and 4.3 nm, which was consistent with the simulated structures (42.3 and 18.4 Å). The pore size of PCOF-2 is concentrated at 1.9 nm, similar to the theoretical simulation (25.23 Å). After metalation (PCOF-1-Fe, PCOF-2-Fe, PCOF-1-Co and PCOF-2-Co), the porous structures and BET surface areas were well-maintained according to the nitrogen adsorption isotherms (Fig. S16, ESI[†]).

Fig. 3 shows the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of **PCOF-1** and



Fig. 3 (a) SEM and (b) TEM images of **PCOF-1**. (c) SEM and (d) TEM images of **PCOF-2**.

PCOF-2. Both **PCOF-1** and **PCOF-2** are agglomerates of tiny spheres (Fig. 3a and c). The TEM images show that there are nanopore channels throughout the whole networks of **PCOF-1** and **PCOF-2** (Fig. 3b and d). Thermogravimetric analysis (TGA) showed that **PCOF-1** and **PCOF-2** have good thermal stability with small mass losses below 420 °C, and only about 30% mass loss in a nitrogen atmosphere up to 800 °C (Fig. S19, ESI†). Their chemical stability was investigated by immersing 15 mg of **PCOF-1** and **PCOF-2** in THF, DMF, HCl solution (6 M) or NaOH solution (6 M). After three days, the polymer was filtered, washed and dried, and showed a slight mass loss and a similar FT-IR spectrum (Fig. S20, ESI†) to the original polymers. These results indicate that **PCOF-1** and **PCOF-2** have high chemical stability.

In order to confirm the elemental composition of the polymer and the oxidation states of the Fe and Co elements, X-ray photoelectron spectroscopy (XPS) (Fig. S17, ESI[†]) and energy dispersive X-ray spectroscopy (EDX) (Fig. S18, ESI[†]) analyses were performed. The XPS survey spectra clearly showed the presence of carbon, nitrogen and oxygen in both COFs, while Fe(III) and Co(II) were detected in **PCOF-Fe** and **PCOF-Co**, respectively. As shown in Fig. 4a and b, the binding energy of Fe $2p_{1/2}$ in **PCOF-1-Fe** and **PCOF-2-Fe** is ~724.5 eV, while the binding energy of Fe $2p_{3/2}$ in **PCOF-1-Fe** and **PCOF-2-Fe** is ~711.0 eV, suggesting the presence of Fe(III)–N_x species.⁴⁹ The peaks at 781.0 eV (Co $2p_{3/2}$) and 796.0 eV (Co $2p_{1/2}$) in **PCOF-1-Co** and **PCOF-2-Co** (Fig. 4c and d) are assigned to the Co(II)–N_x species.⁵⁰

Biocatalytic properties

Porphyrin is a good single-site catalytic unit due to its conjugated planar structure. The biomimetic catalysis and electrocatalysis of porphyrin are studied in this paper. Fe–porphyrin is an important class of biomimetic catalysts, which can simulate cytochrome *P*450 monooxygenase and activate molecular oxygen under mild conditions, so that hydrocarbons can be catalytically oxidized with high efficiency and selectivity in air.⁵¹ **PCOF-1** and **PCOF-2** meet all the prerequisites of a biomimetic system: large pore size, high chemical stability, and potentially numerous active



Fig. 4 High resolution XPS spectra for Fe 2p of the (a) **PCOF-1-Fe** and (b) **PCOF-2-Fe** hybrid. The high resolution XPS spectra for Co 2p of the (c) **PCOF-1-Co** and (d) **PCOF-2-Co** hybrid.

centres. We loaded the porphyrin centres of **PCOF-1** and **PCOF-2** with ferric iron and evaluated their biomimetic catalytic performance by catalytic oxidation of two substrates, that is 2,2'-azinodi(3-ethylbenzothiazoline)-6-sulfonate (ABTS) and 3,3',5,5'-tetramethylbenzidine (TMB) (Scheme 2). These are commonly used to characterize the catalytic properties of heme-like enzyme mimics. The contents of the active centres in **PCOF-1-Fe** and **PCOF-2-Fe** were found to be 0.663×10^{-3} mol g⁻¹ (the ratio of metallization was 91%) and 0.554×10^{-3} mol g⁻¹ (the ratio of metallization was 93%) by ICP-MS, respectively.

The two catalytic oxidation reactions followed the conventional enzymatic dynamic regulation of the Michaelis-Menten equation and were monitored by absorption spectroscopy. These reactions are catalyzed by PCOF-1-Fe with constant hydrogen peroxide and catalyst concentrations, but variable substrate concentrations. We performed the same experiment on PCOF-2-Fe for comparison. The Lineweaver-Burk plots can be obtained based on reaction rates at varied substrate concentrations, and important kinetic parameters such as k_{cat} and $K_{\rm m}$ can be obtained. The $k_{\rm cat}$ value is the maximum number of substrate molecules transformed per catalyst molecule per unit time under optimal conditions, and directly measures the catalytic activity. Km is the Michaelis constant usually related to the affinity of the catalyst molecule for the substrate and a measure of the substrate concentration required for efficient catalysis. The catalytic efficiency (k_{cat}/K_m) was obtained using a Michaelis-Menten curve fit.



Scheme 2 Biomimetic catalysis of the ABTS oxidation and TMB oxidation.



Fig. 5 (a) The fitting curves of the initial ABTS oxidation profiles at marked concentrations by **PPOP-1-Fe**. (b) The Lineweaver–Burk plots of ABTS oxidation catalyzed by **PPOP-1-Fe**. (c) The fitting curves of the initial TMB oxidation profiles at marked concentrations by **PPOP-1-Fe**. (d) The Lineweaver–Burk plots of TMB oxidation catalyzed by **PPOP-1-Fe**. (e) The fitting curves of the initial ABTS oxidation profiles at marked concentrations by **PPOP-1-Fe**. (e) The fitting curves of the initial ABTS oxidation profiles at marked concentrations by **PPOP-2-Fe**. (f) The Lineweaver–Burk plots of ABTS oxidation catalyzed by **PPOP-2-Fe**. (g) The fitting curves of the initial TMB oxidation profiles at marked concentrations by **PPOP-2-Fe**. (h) The Lineweaver–Burk plots of TMB oxidation catalyzed by **PPOP-2-Fe**.

For the oxidation reaction of ABTS with ABTS^{•+} which was confirmed by scanning the UV-vis absorbance using a spectrophotometer, we studied a series of reactions that proceeded with different concentrations of ABTS (2 to 10 mM) in the presence of H₂O₂ (40 mM) and PCOF-1-Fe or PCOF-2-Fe catalyst $(40 \ \mu g)$ (Fig. 5a, b, e and f). The solvent was 3 mL HEPES buffer solution. The color of the solution rapidly changed in a short time when PCOF-1-Fe was added. This indicates that the ABTS reaction can occur rapidly with PCOF-1-Fe catalysts. For the ABTS oxidation reaction, as shown in Table 1, the k_{cat} of **PCOF-1-Fe** and **PCOF-2-Fe** shows a value of 23.4 \min^{-1} and 3.96 min⁻¹, respectively (Table 1). Since k_{cat} represents the initial rate, PCOF-Fe has a higher initial rate than the recently reported excellent enzyme mimics CHF-1.52 The catalytic efficiency of **PCOF-1-Fe** ($k_{\rm cat}/K_{\rm m} \approx 1.5 \times 10^4$) was comparable to that of CHF-1 ($k_{\rm cat}/K_{\rm m} \approx 2.0 \times 10^4$). Compared with that of horseradish peroxidase (HRP),⁵³ the lower catalytic efficiency of PCOF-Fe may be due to its hydrophobicity. Considering the

 Table 1
 Kinetic parameters for the oxidation of substrates by different catalysts

Substrate	Catalyst	$K_{\rm m}$ [mM]	$k_{\rm cat} [{\rm min}^{-1}]$	$k_{\text{cat}}/K_{\text{m}} \left[\text{M}^{-1} \text{min}^{-1} \right]$
ABTS	PCOF-1-Fe PCOF-2-Fe CHF-1 ⁵² HRP ⁵³	1.56 0.75 0.022 0.64	$23.4 \\ 3.96 \\ 0.45 \\ 2.7 \times 10^{3}$	$\begin{array}{c} 1.5 \times 10^4 \\ 0.5 \times 10^4 \\ 2.0 \times 10^4 \\ 4.26 \times 10^6 \end{array}$
ТМВ	PCOF-1-Fe PCOF-2-Fe Hemin ⁵⁴ PCN-222(Fe) ⁵⁵	1.14 1.2 0.78 1.63	3.8 2.44 0.1 14.0	$\begin{array}{c} 3.3 \times 10^{3} \\ 2.0 \times 10^{3} \\ 1.26 \times 10^{3} \\ 8.59 \times 10^{3} \end{array}$

diffusion rate of the substrate from the solution to the **PCOF-Fe** channel, the actual k_{cat} value of the catalytic centres in **PCOF-Fe** is even higher. After consecutive reactions, the resultant powders could be easily recovered by centrifugation and were thoroughly washed with CH₃CH₂OH. It could be reused for three cycles without losing catalytic activity (Fig. S21, ESI[†]). The infrared spectrum (Fig. S22, ESI[†]) and PXRD (Fig. S23, ESI[†]) pattern of **PCOF-Fe** showed no significant changes after three cycles of catalytic reaction, indicating that the catalysis remained stable. Moreover, the contents of Fe in **PCOF-1-Fe** and **PCOF-2-Fe** were found to exhibit only a little reduction by ICP-MS after three cycles of catalytic reaction.

For oxidation of 3,3',5,5'-tetramethylbenzidine (TMB), acidic aqueous solution (pH = 3) was selected due to the favorable reaction conditions. The concentrations of the substrate varied from 0.18 to 2.10 mM along with a fixed amount of PCOF-1-Fe or PCOF-2-Fe catalysts (10 µg) and a hydrogen peroxide concentration of 40 mM (Fig. 5c, d, g and h). For the TMB oxidation reaction, the derived k_{cat} values of the PCOF-1-Fe and PCOF-2-Fe catalyst were 3.8 and 2.44 min⁻¹, respectively (Table 1), which are dozens of times higher than the k_{cat} of free hemin (0.1 min⁻¹).⁵⁴ Moreover, the K_m values of PCOF-1-Fe (1.14 mM) and PCOF-2-Fe (1.2 mM) are lower than those of porphyrin-based metal-organic frameworks PCN-222(Fe) (1.63 mM),55 which are indicative of a better affinity of the substrate to PCOF-Fe. At the same time, the metallized porphyrin monomers Fe-TAPP were tested for the oxidation of ABTS and TMB, and exhibited lower catalytic efficiency than PCOF-Fe (Fig. S24, ESI[†]). The excellent catalytic performance of PCOF-Fe is attributed to the stable 3D structure with high-density porphyrin active centres which effectively promote the reaction.

Electrocatalytic properties

Co-porphyrin has attracted much attention in the field of electrocatalysis. **PCOF-1** and **PCOF-2** with partial conjugation facilitate the transport of electrons. We loaded the porphyrin centres of **PCOF-1** and **PCOF-2** with Co(π) and evaluated their electrocatalytic activities towards oxygen evolution reactions (OERs) in 1 M KOH using a three-electrode system.⁵⁶

Fig. 6a shows the linear sweep voltammograms (LSVs) of **PCOF-Co**. To achieve a current density of 10 mA cm⁻², an overpotential of 473 mV was required for **PCOF-1-Co**, which is lower than that of **PCOF-2-Co** (487 mV). Notably, this value is comparable to that of cobalt porphyrin-based conjugated



Fig. 6 OER activity: (a) LSV curves using **PCOF-1-Co** and **PCOF-2-Co** as catalysts under 1.0 M KOH at 20 mV s⁻¹ with *iR* compensation. (b) Tafel plot of **PCOF-1-Co** and **PCOF-2-Co** in 1.0 M KOH. (c) Nyquist plots of **PCOF-1-Co** and **PCOF-2-Co** with a potential of 1.65 V (vs. RHE). (d) Chronopotentiometry data for **PCOF-1-Co** and **PCOF-2-Co** as the catalyst at a current density of 10 mA cm⁻² for 50 hours.

mesoporous polymers CoP-4ph-CMP-800.⁵¹ The higher catalytic activity of PCOF-1-Co can be attributed to its higher active site content. Overpotential values of 386 mV (PCOF-1-Co) and 396 mV (PCOF-2-Co) were needed to generate an anodic current density of 1 mA cm⁻² (Fig. S25, ESI^{\dagger}), which could be found to be in good agreement with other documented Co-based OER catalysts such as cobalt-modified laminar COF Co-TpBpy.57 Under the same experimental conditions, the metallized porphyrins showed a higher overpotential (Fig. S26, ESI⁺), indicating the advantages of the three-dimensional structure of PCOFs exposing more active sites. To further understand the OER dynamics of PCOF-Co, the Tafel plot (Fig. 6b) was acquired. The values of the Tafel slope were estimated to be 89 mV dec⁻¹ (PCOF-1-Co) and 95 mV dec⁻¹ (PCOF-2-Co), which were comparable to and even lower than those of many other reported catalysts such as CoP-2ph-CMP-800,⁵⁰ Ni₃S₂/Ni foam⁵⁸ and CsCo₉/carbon composites.⁵⁹ Electrochemical impedance spectroscopy (EIS) analysis was also performed. Fig. 6c depicts the Nyquist plot of PCOF-Co. The charge transfer resistance (R_{ct}) of the catalysts is determined by the diameter of the high frequency semicircle. PCOF-1-Co and PCOF-2-Co have similar $R_{\rm ct}$ values. In addition, catalyst stability is a key factor for their practical applications. The long-term chronopotential curve showed no significant changes in potential over 50 hours at a catalytic current density of 10 mA cm⁻² (Fig. 6d), suggesting good catalytic stability.

Conclusions

In summary, we have constructed two 3D porphyrin-based covalent organic frameworks based on tetrahedral building blocks with steric hindrance. **PCOF-1** and **PCOF-2** can be used as platforms for single-site catalysis owing to their high-density porphyrin centres, open pores, suitable pore size, stable structure and rigid backbone, and exhibit excellent biomimetic catalytic and electrocatalytic activity by adjusting the coordination metal. The design and synthesis of other 3D porphyrin-based COFs with interesting features and promising applications are underway in our lab.

Conflicts of interest

There are no conflicts to declare.

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