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### Introduction

Anthropogenic emissions of CO<sub>2</sub> have raised serious concerns about their impact on climate.<sup>1</sup> One method to mitigate CO<sub>2</sub> impact involves chemisorption via amine scrubbing.<sup>2</sup> However, the energy penalty in regeneration motivates efforts to search for alternatives.<sup>3</sup> Recently, a family of  $SiF_6^{2-}$  (named SIFSIX) pillared square grids, termed SIFSIX-n,<sup>4</sup> were found to offer a highly efficient mechanism for carbon capture, even in the presence of moisture.<sup>5</sup> In SIFSIX-n, 2D (4,4)-grids based on octahedrally coordinated ions (e.g., Zn and Cu) and ditopic spacers (e.g., pyrazine and 4,4'-bipyridine) are pillared with  $SiF_6^{2-}$  to form 3D structures with a primitive cubic (pcu) topology. Compared to other MOFs, an outstanding feature of SIFSIXs is their SiF<sub>6</sub><sup>2-</sup> group which promotes favorable interaction with CO2 and resistance to water.5a However, beyond these isoreticular series based on linear bipyridine or its variants, few studies have been reported for other ligand types for targeting chemically and topologically different SIFSIX-type MOFs.<sup>6</sup> Given the great significance of SIFSIX-n, it is highly desirable to pursue new material types in this system.

We hypothesized that metalloporphyrins functionalized with 4 pyridine groups at the *meso* positions may form 2D layers that can be readily pillared by  ${\rm SiF_6}^{2-}$  to give 3D SIFSIX-like frameworks. We chose metalloporphyrins also because their core and periphery coordination sites permit the use of more diverse

# Porphyrinic coordination lattices with fluoropillars $\dagger$

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The combined use of porphyrins and fluorides to fabricate pillared coordination sheets is presented. Multiple features, such as coordinatively unsaturated metal sites, an optimal pore space, and a fluoridedecorated internal surface, make the new materials ideal adsorbents with high capacity and affinity for carbon dioxide. In addition, the new materials are shown to be suitable single-source precursors to afford fluorine-doped graphene analogues for application in oxygen reduction reaction electrodes.

> metal ions, either alone or in various combinations, which can greatly enrich the structure and functionality<sup>7</sup> beyond those offered by SIFSIX-pillars. Furthermore, the fluoro-pillared metalloporphyrins reported here could also offer an unprecedented opportunity for their use as single-source precursors to prepare metal-free F-doped carbons which can be potentially used as efficient oxygen reduction reaction (ORR) catalysts in fuel cells. Recently, tremendous efforts have been directed towards fabricating low-cost electrode materials.<sup>8</sup> F-doped carbons offer a promising direction.<sup>9</sup> However, the F-doped electrodes reported so far have usually been synthesized with NH<sub>4</sub>F as the F-source.<sup>10</sup> In view of its high volatility, new F-doping methods are desirable. Even though some MOF-derived electrocatalysts have been investigated,<sup>11</sup> metal-free F-doped porphyrinic carbon materials derived from robust MOFs remain largely unexplored so far.

> Here two new SIFSIX-like MOFs (denoted as CPM-131 and CPM-132) based on tetra(4-pyridyl)metalloporphyrin (TPyP-M, M = Fe and Zn, respectively) are presented. CPM-131 consists of only SiF<sub>6</sub><sup>2-</sup> pillars while CPM-132 contains mixed F<sup>-</sup>/SiF<sub>6</sub><sup>2-</sup> pillars. Both exhibited reversible adsorption with high capacity and affinity for  $CO_2$ , but sluggish  $CH_4$  and undetectable  $N_2$  uptake at near room temperature. The enhancement in CO<sub>2</sub> uptake/ selectivity was attributed to favorable interactions of sorbent hosts with gas molecules resulting from the optimized pore partition, open metal sites, and electrostatic fluoropillars. In addition to gas adsorption and separation, these materials have also been studied as single-source precursors (without additional C, N, and F sources) to prepare metal-free F-containing carbon derivatives for ORR electrodes. CPM-132/C, derived from CPM-132, showed excellent activity and superior long-term durability as a catalyst for the ORR. The incorporation of fluorine into the porphyrinic carbons contributes to the much improved ORR activity, compared to F-free CPM-133/C derived from CPM-133.

## Experimental

All reagents were purchased commercially and used without further purification, unless otherwise noted. The ligands of



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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Experimental details, characterization data (NMR, MS, FT-IR, UV-vis, PXRD, SEM, TEM, TGA, XPS, fluorescence spectra, crystal photographs, sorption isotherms, *etc.*), crystallography data (and CIFs), additional structural figures and electrochemical graphs. CCDC 1061788–1061790. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7ta06658a

TPyP-H<sub>2</sub> (5,10,15,20-tetrakis(4-pyridyl)porphyrin) and its metalcontaining variants, TPyP-M (M = Fe, Zn, or Cu), were synthesized according to Adler's method<sup>12</sup> with some modifications (detailed preparations and characterizations in the ESI<sup>†</sup>).

#### Synthetic procedure of CPM-131 ([(TPyP-Fe)Zn(SiF<sub>6</sub>)]<sub>n</sub>-fsc)

A solution of 10 mg of TPyP-Fe in 8 mL of *N*-methyl-2-pyrrolidone was layered over a solution of 10 mg of  $ZnSiF_6 \cdot xH_2O$  in 3 mL of ethylene glycol in a vial. Interdiffusion of the solutions (at room temperature or heated at 80°) for a period of 5 days yielded square-shaped crystals (42% yield based on TPyP-Fe). Selected FT-IR:  $\nu = 3680$  (m), 2990 (s), 2360 (w), 1610 (s), 1410 (s), 1070 (s), and 715 (s) cm<sup>-1</sup>.

#### Synthetic procedure of CPM-132 ([(TPyP-Zn)<sub>2</sub>F<sub>2</sub>Zn<sub>2</sub>(SiF<sub>6</sub>)]<sub>n</sub>-fsx)

A solution of 10 mg of  $\text{ZnSiF}_{6} \cdot xH_2\text{O}$  in 3 mL of propylene glycol was layered over a solution of 10 mg of TPyP-Zn in 10 mL of dimethylsulfoxide (mixed with 2 mL of chloroform) in a vial. Low temperature (60°) diffusion of the solutions for a period of 6 days yielded square-shaped crystals (62% yield based on TPyP-Zn). Selected FT-IR:  $\nu = 2990$  (s), 2360 (m), 1650 (m), 1610 (s), 1420 (m), 991 (s), and 717 (s) cm<sup>-1</sup>.

#### Synthetic procedure of CPM-133 ([TPyP-Cu]<sub>n</sub>-nbo)

First, TPyP-Cu (0.10 g) was dissolved in 4 mL of *N*,*N*-diethylacetamide solution (with 1 drop of concentrated nitric acid); then 1 mL of ethanol was added. The mixture was heated in a 120 °C oven for 3 days. After cooling down to room temperature, hexagonal prism-shaped crystals were harvested by filtration (43% yield based on TPyP-Cu). Selected FT-IR:  $\nu = 3680$  (m), 2990 (s), 2360 (m), 1590 (s), 1410 (s), 991 (s), 789 (s), and 667 (s) cm<sup>-1</sup>.

#### Crystallography

The single-crystal X-ray diffraction intensity data were collected on a Bruker APEX-II diffractometer with a nitrogen-flow temperature controller using graphite-monochromated MoK $\alpha$ radiation ( $\lambda = 0.71073$  Å), operating in the  $\omega$  and  $\varphi$  scan mode. Data reduction was carried out with the Bruker Saint program. The SADABS programme was used for absorption correction. The structures were solved by a direct method followed by the successive difference Fourier method. The full-matrix least squares technique was against  $F^2$ . Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to  $1.2 \times U_{eq}$  of the attached atom (Table 1). CCDC 1061788–1061790.†‡

#### Synthetic procedure of CPM-13X/C (X = 1, 2 and 3)

The pyrolysis reaction of CPM-13X to CPM-13X/C was carried out in a quartz tube (with two open ends) in a tube furnace under an Ar gas flow. The CPM-13X samples were heated from room temperature to a preset temperature with a heating rate of  $4 \,^{\circ}$ C min<sup>-1</sup>, and then maintained at this temperature for 4 h in an Ar atmosphere. On the basis of our initial electrocatalyst screening, 1000  $^{\circ}$ C was identified as the optimum calcination temperature for CPM-132/C and CPM-133/C, and also for comparison, CPM-13X/C-1000s (abbreviated to CPM-13X/C) were chosen for characterization by a number of experimental techniques and subsequent investigation of the performance assessment for the oxygen reduction reaction (ORR).

#### **Electrocatalytic tests**

The electrocatalytic activities of the CPM-13X-derived catalysts for the ORR were evaluated by cyclic voltammetry (CV) and rotating disk electrode (RDE) techniques on a CHI-650 electrochemical analyzer. A 3-electrode cell was employed using a glassy carbon RDE (5 mm in diameter, Pine) as the working electrode, an Ag/AgCl, KCl (3 M) electrode as the reference electrode, and a Pt wire electrode as the counter electrode. All the working electrodes were prepared as follows: 5 mg of catalysts and 40 µL of Nafion solution (5 wt%) were dispersed in 600 µL of ethanol by sonication for 30 min to form a homogeneous ink. Then, 5 (base) or 15 (acid) µL of ink was loaded onto a polished glassy carbon electrode of 0.196 cm<sup>2</sup> surface, and the electrode was dried at room temperature. The ORR experiments were carried out in 0.1 M KOH or 0.1 M HClO<sub>4</sub> solution. The electrolyte was saturated and maintained with O<sub>2</sub> during the test. All the potentials were calibrated to ones versus the reversible hydrogen electrode (RHE). The Koutecky-Levich plots  $(\int^{-1} versus \ \omega^{-1/2}$ , where J is the measured current density and  $\omega$ is the angular velocity of the disk) were analyzed at various electrode potentials. The slopes of the linear lines were used to calculate the number of electrons transferred (*n*).

### **Results and discussion**

Crystals of CPM-131 were prepared by layering an N-methyl-2pyrrolidone solution of TPyP-Fe onto an ethylene glycol solution of ZnSiF<sub>6</sub>. Single-crystal X-ray diffraction revealed the formula of CPM-131 to be [(TPyP-Fe)Zn(SiF<sub>6</sub>)]<sub>n</sub>. Its framework could be simplified into a 4,6-connected fsc network (Fig. 1b and d). This is a new SIFSIX type, built of heterometalloporphyrin (4,4)-grid sheets (Fig. 1f and h). CPM-131 contains 3D interconnecting channels with a solvent accessible volume of 44.3%, as calculated using the PLATON software. Thermogravimetric analysis under a nitrogen flow (Fig. 2d) indicates the high thermal stability (up to ca. 410 °C). Its porosity was examined by nitrogen adsorption–desorption at 77 K. A N<sub>2</sub> uptake of 75 cm<sup>3</sup> g<sup>-1</sup> (STP) and a Brunauer-Emmett-Teller (BET) surface area of 226  $m^2 g^{-1}$ were observed. Evaluation using the Horvath-Kawazoe model provides a pore size distribution centered at 4.3 Å (Fig. 2e, inset), consistent with the crystallographic data when van der Waals radii are considered.

<sup>‡</sup> Crystal data for CPM-131: M = 912.00, tetragonal, P4/mmm, a = b = 13.9664(3) Å, c = 7.7060(5) Å,  $\alpha = \beta = \gamma = 90^{\circ}$ , V = 1503.1(11) Å<sup>3</sup>, Z = 1, GOF = 0.993 based on  $F^2$ , final  $R_1 = 0.0883$ ,  $wR_2 = 0.2524$  [for  $I > 2\sigma(I)$ ]; CPM-132: M = 2152.47, tetragonal, I4/m, a = b = 13.985(10) Å, c = 24.40(4) Å,  $\alpha = \beta = \gamma = 90^{\circ}$ , V = 4772.0(9) Å<sup>3</sup>, Z = 2, GOF = 0.992 based on  $F^2$ , final  $R_1 = 0.1011$ ,  $wR_2 = 0.2165$ [for  $I > 2\sigma(I)$ ]; CPM-133: M = 680.22, rhombohedral,  $R\overline{3}$ , a = b = 33.0984(19) Å, c = 9.3673(11) Å,  $\alpha = \beta = 90^{\circ}$ ,  $\gamma = 120^{\circ}$ , V = 8887.1(13) Å<sup>3</sup>, Z = 9, GOF = 1.002 based on  $F^2$ , final  $R_1 = 0.0444$ ,  $wR_2 = 0.0836$  [for  $I > 2\sigma(I)$ ].

 Table 1
 A summary of crystallographic data and porosity measurements

Code	Framework composition	a [Å]	c [Å]	S.G.	Topology	$R_1$	S.A.	$\mathrm{CO}_2^{\alpha}$	Pore size	$Q_{\rm st}$
CPM-131	[(TPyP-Fe)Zn(SiF <sub>6</sub> )] <sub>n</sub>	13.966	7.706	P4/mmm	fsc	0.0883	226/286	101 (55)	4.3 Å	35
CPM-132	[(TPyP-Zn) <sub>2</sub> F <sub>2</sub> Zn <sub>2</sub> (SiF <sub>6</sub> )] <sub>n</sub>	13.985	24.404	I4/m	fsx	0.0875	204/258	74 (40)	4.3 Å	34
CPM-133	[TPyP-Cu] <sub>n</sub>	33.098	9.367	R3̄	nbo	0.0444	390/490	75 (39)	4.8 Å	27

S.G. = space group,  $R_1 = \sum ||F_{obs}| - |F_{calc}|| / \sum |F_{obs}|$  with  $F_{obs} > 4.0 \sigma(F)$ , S.A. = (BET/Langmuir) surface area (m<sup>2</sup> g<sup>-1</sup>), <sup> $\alpha$ </sup> uptake (cm<sup>3</sup> g<sup>-1</sup>) at 1 (or 0.15) bar at 273 K,  $Q_{st}$  for CO<sub>2</sub> (kJ mol<sup>-1</sup>).



Fig. 1 (a) Tetrakis(4-pyridyl)metalloporphyin, TPyP-M (M = Fe or Zn). (b, d) Simplified structure of CPM-131 built of homo-pillared sheets [(TPyP-Fe)Zn], from SiF<sub>6</sub><sup>2-</sup>, and its **fsc**-topology. (c, e) Simplified structure of CPM-132 built of hetero-pillared sheets [(TPyP-Zn)Zn], from F<sup>-</sup>/SiF<sub>6</sub><sup>2-</sup>, and its **fsx**-topology. (f, h) Top and side views of the structure of CPM-131. (g, i) Top and side views of the structure of CPM-132. C, gray; O, red; N, blue; F, aqua; Si, turquoise; metal, violet or lime; H atoms are not depicted for clarity.

Crystals of CPM-132 were prepared by low temperature  $(60^\circ)$ diffusion of a propylene glycol solution of ZnSiF<sub>6</sub> into a dimethyl sulfoxide solution of TPyP-Zn. Unlike CPM-131, CPM-132 is a rare example of porphyrin-zinc layers hetero-pillared by  $SiF_6^{2-}$  and  $F^-$  (which could arise from the degradation of  $SiF_6^{2-}$  anions during thermal treatment). The framework of CPM-132 could be simplified into a 5,6-connected fsx net (Fig. 1c and e), in which the zinc nodes have two different coordination environments. The framework can also be viewed F-intercalated zinc-tetra(pyridyl)porphyrin bilavers as (Fig. S29<sup>†</sup>), further pillared by  $SiF_6^{2-}$  in the axial direction, giving rise to a 3D framework (Fig. 2i). CPM-132 is chemically stable. Powder XRD patterns show that no change occurs during immersion in water or other solvents, such as N-methyl-2-pyrrolidone, dimethyl sulfoxide, N,N-dimethylformamide, acetone, chloroform, tetrahydrofuran, and methanol, for 24 h. The solvent-accessible volume of CPM-132 is 38.8%. N2 sorption data showed a type I isotherm with a BET surface area of 204 m<sup>2</sup> g<sup>-1</sup>, slightly lower than that of CPM-131.

For comparison with fluoropillared CPM-131/132, a F-free porphyrin MOF (CPM-133) with an **nbo**-topology and formula

[TPyP-Cu]<sub>n</sub> was also prepared. It is built of TPyP-Cu scaffolds by self-coordinating to each other (see the ESI for crystallographic details<sup>†</sup>). Isostructural metalloporphyrin-based **nbo**-nets have been reported<sup>13</sup> but not studied for CO<sub>2</sub> trapping. Notable features of CPM-133 are the honeycomb channels and pyridine-functionalized windows (Fig. S34 and S35<sup>†</sup>). The permanent porosity of CPM-133 was confirmed by N<sub>2</sub> sorption measurements at 77 K (Fig. S47<sup>†</sup>) that revealed a BET surface area of 390 m<sup>2</sup> g<sup>-1</sup>, higher than those of CPM-131/132.

#### CO<sub>2</sub> trapping

The integration of thermal/chemical stability, narrow channels, unsaturated metal sites, and a high concentration of inorganic fluorine, which can improve selectivity and affinity for CO<sub>2</sub>, inspired us to study CO<sub>2</sub> adsorption properties. Single component and low-pressure CO<sub>2</sub> and N<sub>2</sub> sorption data were collected at 273 and 298 K (Fig. 2f). The CO<sub>2</sub> uptake of CPM-131 at 1 atm and 273 K was 101 cm<sup>3</sup> g<sup>-1</sup> (equivalent to 4.5 mmol g<sup>-1</sup> or 198.4 mg g<sup>-1</sup>), whereas N<sub>2</sub> uptakes of 1.0 cm<sup>3</sup> g<sup>-1</sup> were measured. High affinity for CO<sub>2</sub> is shown by the sharp increase



Fig. 2 (a-c) Crystal photographs of CPM-13X (X = 1, 2 and 3, respectively). (d) TGA of CPM-13X. (e) N<sub>2</sub> adsorption–desorption isotherms of CPM-131 with the inset showing the pore size distribution. (f) CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> adsorption isotherms of CPM-131. (g) CO<sub>2</sub> adsorption enthalpy ( $Q_{st}$ ) of CPM-131.

in CO<sub>2</sub> uptake in the low pressure region. In comparison, CPM-132 exhibited a lower value of 74 cm<sup>3</sup> g<sup>-1</sup> (equivalent to 3.3 mmol g<sup>-1</sup> or 145.4 mg g<sup>-1</sup>) at 1 atm and 273 K. Its N<sub>2</sub> isotherms at 273 K also showed negligible uptake (0.8 cm<sup>3</sup> g<sup>-1</sup>). For CPM-133, the volumetric CO<sub>2</sub> uptake was 75 cm<sup>3</sup> g<sup>-1</sup> at 1 atm and 273 K. Ideal adsorbed solution theory (IAST)<sup>14</sup> calculations indicated binary gas adsorption selectivity under practically relevant conditions (273 K; N<sub>2</sub> mole fractions of 0.9) to be dramatically higher for CPM-131 (1211) and CPM-132 (942) than CPM-133 (523) for CO<sub>2</sub>/N<sub>2</sub>. These findings can be attributed to the enhanced isosteric heats of adsorption ( $Q_{st}$ ). The values of  $Q_{st}$  were calculated using the adsorption data collected at 273 and 298 K (Fig. S38, S43 and S48†). At zero coverage, the enthalpy of CO<sub>2</sub> adsorption for CPM-131/132 is 35/34 kJ mol<sup>-1</sup>, greater than that of CPM-133 (27 kJ mol<sup>-1</sup>).

Similar behaviors have also been observed at room temperature. CPM-132 exhibited a CO<sub>2</sub> uptake of 59 cm<sup>3</sup> g<sup>-1</sup> (equivalent to 2.6 mmol g<sup>-1</sup> or 115.9 mg g<sup>-1</sup>) at 1 atm and 298 K, while CPM-131 exhibited a substantially higher value of 76 cm<sup>3</sup> g<sup>-1</sup> (equivalent to 3.4 mmol g<sup>-1</sup> or 149.3 mg g<sup>-1</sup>). Apart from its relevance to climate, CO<sub>2</sub> is an impurity in natural gas, biogas, and many other gas streams.<sup>3a,5a</sup> Therefore, CO<sub>2</sub>/CH<sub>4</sub> separation has also become a primary research objective. CPM-131 showed preferential adsorption of CO<sub>2</sub> over CH<sub>4</sub>, with a selectivity index of 108 (in a CO<sub>2</sub>/CH<sub>4</sub>:50/50 mixture), similar to that of CPM-132 (104), as determined from IAST simulation. The results show that open metal sites, SiF<sub>6</sub><sup>2-</sup> pillars, and small pore sizes likely contribute to the uptake and  $Q_{st}$  of CO<sub>2</sub>.

#### **ORR** activity

In addition to their potential for application in post-combustion carbon capture and energy gas purification, the fluoropillared materials reported here exhibit desirable features that support their use as single-source precursors in the synthesis of efficient

catalysts for the ORR. Carbonization was performed to convert the CPM-131/132/133 into (metallo)porphyrinic carbons, denoted as CPM-13X/C (X = 1, 2 or 3). The carbonization temperature is the key parameter that determines the trade-off between the degree of heteroatom doping, surface properties, and electrical conductivity.8c CPM-131 has active Fe-coordination species, which could be destroyed during high-temperature treatment with a concomitant reduction in catalytic activity, but for precursors without Fe-complexes, low-temperature carbonization cannot lead to a high degree of graphitization to ensure a good conductivity. As such, the optimal calcination temperature was determined to be 700 °C for CPM-131/C and 1000 °C for CPM-132/C and CPM-133/C (details in the ESI<sup>†</sup>). A comparative study showed that CPM-132/C-1000 (abbreviated to CPM-132/C) exhibited the highest catalytic efficiency and is thus described below in detail.

The powder XRD pattern (Fig. S54<sup>†</sup>) of the CPM-132-derived N-F-C composite exhibited pronounced peaks at ca. 24 and 43° corresponding to diffractions from the (002) and (100) graphitic carbon planes, respectively, suggesting the presence of long range ordering in the carbon matrix. As shown in Fig. 3b, the square layered morphology of carbonization product CPM-132/ C was seen in the scanning electron microscopy (SEM) image. To further observe the local microstructure, we also show the high-resolution transmission electron microscopy (HRTEM) image of CPM-132/C in Fig. 3d and attest to the presence of lattice fringes. Solid-state diffuse reflectance spectroscopy (Fig. 3f) indicated that the pyrolytic product did retain some porphyrinic characteristics. Elemental analysis was performed to probe the chemical composition of the CPM-132/C and the F, N, and C contents were found to be 2, 9, and 73 wt%. As shown in Fig. 3e, N<sub>2</sub> sorption isotherms at 77 K showed a steep increase at low pressure and a hysteretic trait of the desorption isotherm at high pressure, suggesting the hierarchical porosity



Fig. 3 (a, b) SEM images of CPM-132 and its carbonization product CPM-132/C. (c, d) TEM images of CPM-132/C. (e)  $N_2$  adsorption-desorption isotherms of CPM-132/C with the inset showing the pore size distribution. (f) UV-vis spectra of CPM-132 and CPM-132/C. XPS (g) N 1s and (h) F 1s spectra of CPM-132/C.

of the nanocomposite CPM-132/C. CPM-132/C exhibited a BET surface area of 278 m<sup>2</sup> g<sup>-1</sup>, slightly greater than that of its crystalline precursor. The pore size distribution was centered at 1.0 and 3.8 nm, as determined from the adsorption isotherm using the Horvath–Kawazoe model and desorption isotherm using the Barrett–Joyner–Halenda model, respectively.

Because the surface chemistry is of particular interest for catalytic applications, the electronic states of F, N, and C were examined by X-ray photoelectron spectroscopy (XPS). As revealed in Fig. 3g, the high-resolution N 1s XPS spectrum is deconvoluted into 3 peaks at 398.5, 399.6 and 400.8 eV, corresponding to pyridinic, metal-coordinated, and graphitic nitrogen species, respectively, indicating 3 different bonding configurations.<sup>84,9e</sup> As shown in the high-resolution F 1s XPS of CPM-132/C (Fig. 3h), a dominant peak at 689.3 eV, assigned to semi-ionic F–C bonding,<sup>10a</sup> was also observed. Overall, the well dispersed N and F-codoped active sites, combined with the easily accessible porous structure, are highly beneficial for the electrocatalytic performance described below.

The ORR catalytic activity and kinetics of CPM-13X/C, along with 20% Pt/C reference catalysts (Alfa Aesar), were evaluated using cyclic voltammetry (CV) and rotating-disk electrode (RDE) techniques in 0.1 M KOH and 0.1 M HClO<sub>4</sub>. All potentials were referenced to the reversible hydrogen electrode (RHE). Prior to each experiment, the electrolytes were saturated with Ar or O<sub>2</sub>, respectively. In an Ar-saturated solution of 0.1 M KOH, the CV curves of the composites CPM-13X/C within the entire potential range showed nearly nonsense shapes, while well-defined cathodic peaks occurred in the O<sub>2</sub>-saturated solution (Fig. 4a), illustrating their effective ORR activities in alkaline medium. Among the 3 samples, N–F–C based CPM-132/C showed an ORR peak at the most positive potential of 0.83 V, which is close to that of Pt/C (0.85 V).

Their electrocatalytic activity sequence was further supported by linear sweep voltammetry on a RDE. As shown in Fig. 4b, non-fluorinated CPM-133/C exhibited an onset

potential of 0.89 V and a half-wave potential of 0.74 V, determined using the polarization curves at 1600 rpm. A more substantial improvement in ORR activity, reflected by much more positive onset/half-wave ORR potentials (0.94/0.79 V), is achieved in CPM-132/C, showing a synergetic effect from N–F codoping. The electrocatalytic capacity of N–F binary-doped CPM-132/C even matched that of CPM-131-derived Fe–N–F ternary-doped carbon. The superior performance of the CPM-132/C electrode is attributed to its precursor's unique features of high density of fluorine, ionic bonding of F<sup>-</sup> to Zn<sup>2+</sup> (boosting the framework stability), macrocyclic porphyrins with a layered network, and microporosity.

To assess the mechanism of the electrocatalytic activity of CPM-132/C, the Koutecky–Levich (K–L) plots were calculated from RDE polarization curves (Fig. 5b). The electron transfer number (*n*) was calculated from the slopes of the K–L plots to be  $4.0 \pm 0.1$ , suggesting a 4-electron transfer process. However, the ORR process catalysed by CPM-133/C likely involves mixed 2-and 4-electron pathways, as the number of electrons transferred per O<sub>2</sub> is 3.6 at 0.5 V. The CPM-132/C catalyst exhibited long-term durability, superior to that of Pt/C (Fig. 5c and d). Through continuous potential cycling, the deterioration of the cathodic peak current of CVs underwent a non-significant change with



Fig. 4 (a) CVs and (b) LSV curves at a rotation rate of 1600 rpm on CPM-13X/C and 20% Pt/C in  $O_2\mbox{-saturated}$  0.1 M KOH.



Fig. 5 (a) RDE polarization curves at different rotation rates, (b) K–L plots, and (c) cycling CVs on CPM-132/C, and (d) current–time chronoamperometric response on CPM-132/C with reference 20% Pt/C, in  $O_2$ -saturated 0.1 M KOH. (e) LSV curves at a rotation rate of 1600 rpm on CPM-13X/C and 20% Pt/C, and (f) current–time chronoamperometric response on CPM-132/C with reference 20% Pt/C, in  $O_2$ -saturated 0.1 M HClO<sub>4</sub>.

only 7% drop after 50 000 cycles. The tolerance of CPM-132/C to methanol was also proved in 0.1 M KOH solution.

Finally, we also investigated the ORR performance of the CPM-13X-derived catalysts in 0.1 M HClO<sub>4</sub> media. Again, the CPM-132/C-electrode showed a better electrocatalytic activity with an onset potential (0.86 V) higher than that of non-fluorinated CPM-133/C (0.74 V). Compared with Fe-N-F triple-doped CPM-131/C, the N-F double-doped CPM-132/C exhibited lower onset/half-wave potentials but much higher current density (Fig. 5e). Based on the K-L equation, the number of electrons transferred (*n*) per  $O_2$  molecule for the CPM-132/C in the acidic medium was calculated to be 3.9 at 0.5 V (Fig. S97<sup>†</sup>), suggesting a 4-electron pathway even under acidic conditions. In addition to the activity, the materials also show long-term durability and resistance to methanol fuel. The prominent performance of the CPM-132-derived electrode, on the same level as best metal-free catalysts,<sup>9,10b,15</sup> may come from advantages of its CPM-132 precursor, such as robust porosity, high thermal stability, uniform distribution and high content of N/F hetero-dopants with a synergistic effect, porphyrinic coordination sheets, and hard-templating effects by ionic Zn-F. In addition, it was also suggested that variations in the charge and spin densities of the carbon lattice could be significant factors for the excellent performance observed with multiple doped nanocarbons.16

# Conclusions

In summary, we have fabricated two SIFSIX-like porphyrinic MOFs, endowed with coordinatively unsaturated metal centers, periodic arrays of fluorine-enriched anions, resistance to heat/ water, and an optimized pore size. By comparison with the reported hexafluorosilicate-pillared versions, CPM-131/132 synthesized in this work are topologically and chemically different MOFs, offering another paradigm for investigation in carbon capture and separation. With a favourable electrostatic

internal surface, such unique hybrids exhibited high uptake capacity and selectivity for  $CO_2$  over  $N_2/CH_4$  at low pressure. Significantly, such robust F-enriched porphyrinic architectures could be self-supporting precursors for F-doped porphyrinic carbon composites. Their carbonization products exhibited good ORR activity and durability in both alkaline and acidic electrolytes. Moreover, the design concept presented here could be amenable to the expansion of the compositional scope of the heteroatom-doped catalysts, through crystal engineering of the precursors of (metallo)porphyrinic MOFs.

# Conflicts of interest

There are no conflicts to declare.

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## Notes and references

- 1 R. Quadrelli and S. Peterson, Energy Policy, 2007, 35, 5938.
- 2 G. T. Rochelle, Science, 2009, 325, 1652.
- 3 (a) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald,
  E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724; (b) W. Wang and D. Yuan, *Sci. Rep.*, 2014, **4**, 5711; (c) Z. R. Jiang, H. W. Wang, Y. L. Hu, J. L. Lu and H. L. Jiang, *Chemsuschem*, 2015, **8**, 878; (d) S. T. Zheng,
  J. T. Bu, Y. F. Li, T. Wu, F. Zuo, P. Y. Feng and X. H. Bu, *J. Am. Chem. Soc.*, 2010, **132**, 17062; (e) B. L. Hu, C. Y. Wang,
  J. X. Wang, J. K. Gao, K. Wang, J. S. Wu, G. D. Zhang,
  W. Q. Cheng, B. Venkateswarlu, M. F. Wang, P. S. Lee and
  Q. C. Zhang, *Chem. Sci.*, 2014, **5**, 3404; (f) K. Sumida,

D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724.

- 4 (a) S. D. Burd, S. Ma, J. A. Perman, B. J. Sikora, R. Q. Snurr, P. K. Thallapally, J. Tian, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2012, **134**, 3663; (b) S. Subramanian and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 1995, **34**, 2561.
- 5 (a) P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, 495, 80;
  (b) O. Shekhah, Y. Belmabkhout, Z. Chen, V. Guillerm, A. Cairns, K. Adil and M. Eddaoudi, *Nat. Commun.*, 2014, 5, 4228.
- 6 (a) P. S. Nugent, V. L. Rhodus, T. Pham, K. Forrest, L. Wojtas, B. Space and M. J. Zaworotko, J. Am. Chem. Soc., 2013, 135, 10950; (b) A. Cadiau, K. Adil, P. M. Bhatt, Y. Belmabkhout and M. Eddaoudi, Science, 2016, 353, 137; (c) X. L. Cui, K. J. Chen, H. B. Xing, Q. W. Yang, R. Krishna, Z. B. Bao, H. Wu, W. Zhou, X. L. Dong, Y. Han, B. Li, Q. L. Ren, M. J. Zaworotko and B. L. Chen, Science, 2016, 353, 141; (d) X. Cui, Q. Yang, L. Yang, R. Krishna, Z. Zhang, Z. Bao, H. Wu, Q. Ren, W. Zhou, B. Chen and H. Xing, Adv. Mater., 2017, 29, 1606929.
- 7 (a) H. J. Son, S. Jin, S. Patwardhan, S. J. Wezenberg, N. C. Jeong, M. So, C. E. Wilmer, A. A. Sarjeant, G. C. Schatz, R. Q. Snurr, O. K. Farha, G. P. Wiederrecht and J. T. Hupp, *J. Am. Chem. Soc.*, 2013, 135, 862; (b) D. Feng, Z. Y. Gu, J. R. Li, H. L. Jiang, Z. Wei and H. C. Zhou, *Angew. Chem., Int. Ed.*, 2012, 51, 10307.
- 8 (a) G. Wu and P. Zelenay, *Acc. Chem. Res.*, 2013, 46, 1878; (b)
  F. Jaouen, E. Proietti, M. Lefèvre, R. Chenitz, J.-P. Dodelet,

G. Wu, H. T. Chung, C. M. Johnston and P. Zelenay, *Energy Environ. Sci.*, 2011, **4**, 114; (c) X. J. Zhou, J. L. Qiao, L. Yang and J. J. Zhang, *Adv. Energy Mater.*, 2014, **4**, 1301523; (d) J. Liang, X. Du, C. Gibson, X. W. Du and S. Z. Qiao, *Adv. Mater.*, 2013, **25**, 6226.

- 9 (a) Y. Ito, W. Cong, T. Fujita, Z. Tang and M. Chen, Angew. Chem., Int. Ed., 2015, 54, 2131; (b) J. Liang, Y. Jiao, M. Jaroniec and S. Z. Qiao, Angew. Chem., Int. Ed., 2012, 51, 11496; (c) W. Wei, H. Liang, K. Parvez, X. Zhuang, X. Feng and K. Mullen, Angew. Chem., Int. Ed., 2014, 53, 1570.
- 10 (a) X. Sun, Y. Zhang, P. Song, J. Pan, L. Zhuang, W. Xu and W. Xing, ACS Catal., 2013, 3, 1726; (b) L. Hao, S. S. Zhang, R. J. Liu, J. Ning, G. J. Zhang and L. J. Zhi, Adv. Mater., 2015, 27, 3190.
- 11 H. X. Zhong, J. Wang, Y. W. Zhang, W. L. Xu, W. Xing, D. Xu, Y. F. Zhang and X. B. Zhang, *Angew. Chem., Int. Ed.*, 2014, 53, 14235.
- 12 A. D. Adler, Shergali.W and F. R. Longo, J. Am. Chem. Soc., 1964, 86, 3145.
- 13 (a) K. J. Lin, Angew. Chem., Int. Ed., 1999, 38, 3415; (b)
  H. Krupitsky, Z. Stein, I. Goldberg and C. E. Strouse, J. Inclusion Phenom. Mol. Recognit. Chem., 1994, 18, 177.
- 14 A. L. Myers and J. M. Prausnitz, AlChE J., 1965, 11, 121.
- 15 (a) C. H. Choi, S. H. Park and S. I. Woo, ACS Nano, 2012, 6, 7084; (b) Z. W. Liu, F. Peng, H. J. Wang, H. Yu, W. X. Zheng and J. Yang, Angew. Chem., Int. Ed., 2011, 50, 3257; (c) H. L. Fei, R. Q. Ye, G. L. Ye, Y. J. Gong, Z. W. Peng, X. J. Fan, E. L. G. Samuel, P. M. Ajayan and J. M. Tour, ACS Nano, 2014, 8, 10837.
- 16 J. Y. Cheon, J. H. Kim, J. H. Kim, K. C. Goddeti, J. Y. Park and S. H. Joo, *J. Am. Chem. Soc.*, 2014, **136**, 8875.