Supporting Information

Porphyric Coordination Lattices with Fluoropillars

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1. General methods

Materials: All of the reagents used were obtained from commercial supplies without further purification. 4-pyridinecarboxaldehyde (97%, C₆H₅NO, 107.11, Sigma-Aldrich), pyrrole (98%, C₄H₅N, 67.09, Sigma-Aldrich), propionic acid (99.5%, CH₃CH₂COOH, 74.08, Sigma-Aldrich), ZnSiF₆·xH₂O (99%, ~207.47, Sigma-Aldrich).

Instrumentation: Solution ¹H NMR spectroscopic data were recorded for samples in 5 mm tubes (outer diameter) with a Varian Inova 300 NMR spectrometer. Mass spectrometry (MS) was performed on a Finnigan LCQ-3 instrument, using a Pauli ion trap to collect, resolve and detect ions. Elemental Analysis (EA) was carried out with a Perkin-Elmer 2400 CHNS Elemental Analyzer (Atlantic Microlab, Inc.). Single-crystal X-ray analysis was performed on a Bruker APEX II diffractometer with nitrogen-flow temperature controller using graphite-monochromated MoKα radiation (λ = 0.71073 Å), operating in the ω and φ scan mode. The SADABS programme was used for absorption correction. The structures were solved by direct method followed by successive difference Fourier method. All atoms (except H) were refined anisotropically. Computations were performed using SHELXTL¹ and final full-matrix refinements were against $F^2$. Powder X-ray diffraction (PXRD) experiments were carried out with a Bruker D8 Advance X-ray powder diffractometer operating at 40 kV and 40 mA (Cu Kα radiation, $\lambda = 1.5418$ Å). The data collection was performed with a step size of 0.02° and counting time of 2 second per step. The simulated powder XRD pattern was obtained from the single-crystal data. Microscopic imaging was carried out at the UCR Microscopy Core at the Institute for Integrative Genome Biology (IIGB). The thermogravimetric analysis (TGA) was carried out using a TA Instruments TGA Q500 apparatus in the temperature range of 30 °C to 800 °C under N₂ flow at a heating rate of 2 °C·min⁻¹. Nitrogen, hydrogen, carbon dioxide, methane and acetylene adsorption-desorption isotherms were obtained on a Micromeritics ASAP 2020/2010 physisorption analyzer. Prior to the measurement, the as-synthesized crystal sample was dried by using the “degas” function of the surface area analyzer for 12 hr at 100 °C. Liquid N₂, acetone-dry ice, ice water, and water were used as the temperature controlling media for 77, 195, 273, and 298 K, respectively. UV-vis (liquid absorption and solid-state diffuse reflectance) spectra were recorded on a Shimadzu UV-3101PC spectrophotometer.
Fourier transformed-Infrared spectroscopy (FT-IR) was performed on a Thermo Nicolet Avatar 6700 FT-IR with cesium iodide optics allowing the instrument to observe from 525 to 4000 cm\(^{-1}\). Scanning electron microscopy (SEM) images were taken on Nova NanoSEM450 (Schottky field emission scanning electron microscope) integrated with energy-dispersive X-ray (EDX) allowing to perform qualitative and quantitative chemical analysis, and image capture. Transmission electron microscope (TEM) images were obtained on a JEM-2010 transmission electron microscope at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were made on a Kratos analytical AXIS Ultra Delay-Line Detector (DLD) Imaging XPS equipped with a vacuum ultraviolet light source, using C 1s (284.8 eV) as a reference to correct the binding energy (Francisco Zaera Surface Group, UCR). Liquid fluorescence spectra were recorded on Spex Fluorolog Tau-3 fluorescence spectrophotometer.

Electrocatalytic activities for ORR of the as-prepared catalysts were evaluated by cyclic voltammetry (CV) and rotating disk electrode (RDE) techniques on a CHI-650 electrochemical analyzer. A three-electrode cell was employed using a glass carbon RDE (5mm in diameter, Pine) as working electrode, an Ag/AgCl, KCl (3 M) electrode as the reference electrode, and a Pt wire electrode as the counter electrode. The ORR experiments were carried out in 0.1 M KOH or 0.1 M HClO\(_4\) solution. The potential was scan between -1~+0.2 (base) or -0.2~+1 (acid) V (versus Ag/AgCl) at a scan rate of 10 mV·s\(^{-1}\) at the ambient temperature after purging O\(_2\) or Ar gas for 20 min. All the working electrodes were prepared as following: 5 mg of catalysts and 40 μL of Naflon 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 polished glassy carbon rotating disk electrode of 0.196 cm\(^2\) surface, and the electrode was dried at room temperature. Electrolyte was saturated with oxygen by bubbling O\(_2\) prior to the measurements. A flow of O\(_2\) was maintained over the electrolyte during the measurements. For the RDE recording, the working electrode was scanned cathodically at a rate of 10 mV·s\(^{-1}\) with varying rotating speed from 400 to 2500 rpm. Commercial 20 wt% Pt/C catalysts obtained from Alfa Aesar were used for comparison. The catalyst loading of active Pt-free catalysts on the working electrode is 0.2 (base) or 0.6 (acid) mg·cm\(^{-2}\) in 0.1 M KOH or HClO\(_4\) solution. For Pt/C, the loading of active material is 10
μg Pt cm$^2$ (0.1 mg Pt/C cm$^2$). All the potentials were calibrated to the potentials versus RHE (Potentials versus RHE = potential versus Ag/AgCl+0.949 (base), +0.268 (acid) V).

The Koutecky-Levich plots ($J^1$ vs $\omega^{-1/2}$) were analyzed at various electrode potentials. The slopes of the linear lines were used to calculate the number of electrons transferred ($n$) according to the following Koutechy-Levich equation.

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad \text{(K-L)}$$

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6}$$

$$J_K = nFkC_0$$

where $J$, $J_K$ and $J_L$ are the measured current density, kinetic- and diffusion-limiting current densities, respectively; $\omega$ is the angular velocity of the disk, $n$ is the electrons transferred number, $F$ is the Faraday constant (=96485 C·mol$^{-1}$), $C_0$ is the bulk concentration of O$_2$ ($C_0 = 1.2 \times 10^{-3}$ mol·L$^{-1}$ in 0.1 M KOH), $D_0$ is diffusion coefficient of O$_2$ ($D_0 = 1.9 \times 10^{-5}$ cm·s$^{-1}$ in 0.1 M KOH), $\nu$ is the kinematic viscosity of the electrolyte ($\nu = 0.01$ cm$^2$·s$^{-1}$ in 0.1 M KOH), and $k$ is the electron transfer rate constant. The number of electrons transferred ($n$) and $J_K$ can be obtained from the slope and intercept of the K–L plots. An accelerated assessment experiment by cycling CV curves from 0.2 to -1.0 V (versus Ag/AgCl) was used to measure the stability of electrode materials, with a scanning rate of 2 V·s$^{-1}$. 


2. Procedures for ligand synthesis

Ligands of 5,10,15,20-tetrapyridylporphyrin and its metallated analogues (TPyP-M, M = H₂, Fe, Zn, Cu) were synthesized based on Adler’s method with modifications. Typically, we obtained these ligands by two steps as follows:

![Scheme S1. Synthetic route for TPyP-M (M = H₂, Fe, Zn, Cu). Reagents and conditions: (i) propionic acid, reflux, 3 hr; (ii) FeCl₂·4H₂O or Zn(OAc)₂·2H₂O or Cu(OAc)₂·2H₂O, MeOH/CHCl₃, reflux, 12 hr.](image)

(1) 5,10,15,20-Tetrakis(4-pyridyl)porphyrin (TPyP-H₂): 4-pyridinecarboxaldehyde (4.28 g, 40 mmol) was stirred in propionic acid (300 mL) and heated to reflux. To refluxed solution was added pyrrole (2.77 mL, 40 mmol), then solution was refluxed for 3 hr in darkness. After cooled to room temperature, crude purple product was collected by suction-filtration. The crude product was chromatographed on silica (CH₂Cl₂/hexane = 20/1) to yield 3.5 g (49% yield). ¹H NMR (CDCl₃): δ = 9.08 (t, 8H), 8.87 (s, 8H), 8.16 (t, 8H), -2.92 (s, 2H). MS (FAB) calcd for C₄₀H₂₆N₈ [M+H]⁺ 619.2314, found 619.2372. FT-IR: ν = 3680 (w), 3310 (w), 2970 (m), 2360 (s), 1740 (m), 1590 (s), 1400 (m), 970 (m), 783 (m) cm⁻¹. EA data: C 76.13, H 4.15, N 17.65; calculated: C 77.65, H 4.24, N 18.11 %.

(2) 5,10,15,20-Tetrakis(4-pyridyl)porphyrin-Fe(II) (TPyP-Fe): A solution of TPyP-H₂ (0.62 g, 1.0 mmol) and FeCl₂·4H₂O (1.60 g, 8 mmol) in 100 mL of CHCl₃ (mixed by 30 mL of CH₃OH) and the mixture was heated to reflux for 12 hr. After cooling down to room temperature, the CHCl₃/CH₃OH was removed under reduced pressure. The obtained solid was washed three times with methanol, dried to give quantitative dark red crystals. ¹H NMR (d₆-DMSO): δ = 8.97 (t, 8H), 8.79 (s, 8H), 8.17 (t, 8H). MS (FAB) calcd for C₄₀H₂₄N₈FeCl [M+H]⁺ 708.9702, found 708.0012. FT-IR: ν = 2970 (m), 2360 (s), 1600 (s), 1490 (m), 1220 (m), 1070 (s), 858 (m), 796 (s) cm⁻¹. EA data: C 66.92, H 3.56, N 15.27; calculated: C 67.86, H 3.42, N 15.83 %.
(3) **5,10,15,20-Tetrakis(4-pyridyl)porphyrin-Zn(II)** (TPyP-Zn): A solution of TPyP-H$_2$ (0.62 g, 1.0 mmol) and Zn(OAc)$_2$·2H$_2$O (2.19 g, 10 mmol) in 100 mL of CHCl$_3$ (mixed by 30 mL of CH$_3$OH) and the mixture was heated to reflux for 12 hr. After cooling down to room temperature, the CHCl$_3$/CH$_3$OH was removed under reduced pressure. The obtained solid was washed three times with water and methanol, dried to give quantitative dark red crystals. $^1$H NMR ($d_6$-DMSO): $\delta = 8.99$ (t, 8H), 8.81 (s, 8H), 8.19 (t, 8H). MS (FAB) calcd for C$_{40}$H$_{24}$N$_8$Zn $[M+H]^+$ 681.1485, found 681.1489. FT-IR: $\nu = 2970$ (w), 2360 (m), 1590 (s), 1340 (m), 1070 (s), 991 (s), 789 (s) cm$^{-1}$. EA data: C 69.32, H 3.63, N 15.87; calculated: C 70.44, H 3.55, N 16.43 %.

(4) **5,10,15,20-Tetrakis(4-pyridyl)porphyrin-Cu(II)** (TPyP-Cu): A solution of TPyP-H$_2$ (0.62 g, 1.0 mmol) and Cu(OAc)$_2$·4H$_2$O (2.49 g, 10 mmol) in 100 mL of CHCl$_3$ (mixed by 30 mL of CH$_3$OH) and the mixture was heated to reflux for 12 hr. After cooling down to room temperature, the CHCl$_3$/CH$_3$OH was removed under reduced pressure. The obtained solid was washed three times with water and methanol, dried to give quantitative dark red crystals. $^1$H NMR ($d_6$-DMSO): $\delta = 8.96$ (t, 8H), 8.79 (s, 8H), 8.16 (t, 8H). MS (FAB) calcd for C$_{40}$H$_{24}$N$_8$Cu $[M+H]^+$ 681.2182, found 680.1519. FT-IR: $\nu = 3310$ (w), 2990 (s), 2360 (s), 1610 (s), 1400 (m), 1000 (m), 795 (s) cm$^{-1}$. EA data: C 69.05, H 3.59, N 15.97; calculated: C 70.63, H 3.56, N 16.47 %.
3. Characterization of ligands

Fig. S1 $^1$H NMR spectrum of TPyP-H$_2$ in CDCl$_3$ solution.

Fig. S2 $^1$H NMR spectrum of TPyP-Fe in $d_6$-DMSO solution.
Fig. S3 $^1$H NMR spectrum of TPyP-Zn in $d_6$-DMSO solution.

Fig. S4 $^1$H NMR spectrum of TPyP-Cu in $d_6$-DMSO solution.
Fig. S5 Mass spectrum of TPyP-H$_2$.

Fig. S6 Mass spectrum of TPyP-Fe.
Fig. S7 Mass spectrum of TPyP-Zn.

Fig. S8 Mass spectrum of TPyP-Cu.
**Fig. S9** FT-IR spectra of TPyP-M ligands.

**Fig. S10** UV-Vis absorbance spectra of TPyP-H$_2$ (in CHCl$_3$) and TPyP-M (M = Fe/Zn/Cu, in DMSO).
Fig. S11 Fluorescence emission spectra of TPyP-(H₂, Fe, Zn, Cu) at a scan wavelength ($\lambda_{ex}$) of ca. 435 nm.
4. Synthesis of CPM-13X

(1) CPM-131 ([TPyP-Fe]Zn(SiF₆)ₙ-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 ZnSiF₆·xH₂O in 3 mL of ethylene glycol in 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). FT-IR: ν = 3680 (m), 2990 (s), 2360 (w), 1610 (s), 1410 (s), 1070 (s), 715 (s) cm⁻¹. EA data: C 49.37, H 3.14, N 11.18 %.

(2) CPM-132 ([TPyP-Zn]₂F₂Zn₂(SiF₆)ₙ-fsx): A solution of 10 mg of ZnSiF₆·xH₂O 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 vial. Low temperature (60°) diffusion of the solutions for a period of 6 days yielded square-shaped crystals (62% yield based on TPyP-Zn). FT-IR: ν = 2990 (s), 2360 (m), 1650 (m), 1610 (s), 1420 (m), 991 (s), 717 (s) cm⁻¹. EA data: C 51.45, H 3.67, N 12.35 %.

(3) CPM-133 ([TPyP-Cu]ₙ-nbo): TPyP-Cu (0.10 g) was dissolved in 4 mL of N,N-diethylacetamide solution (with 1 drop of concentrated nitric acid) firstly, then 1 mL of ethanol was added. The mixture was heated in 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). FT-IR: ν = 3680 (m), 2990 (s), 2360 (m), 1590 (s), 1410 (s), 991 (s), 789 (s), 667 (s) cm⁻¹. EA data: C 68.07, H 3.73, N 15.90 %.
5. Single crystal X-ray diffraction analysis

Materials of CPM-13X suitable for single-crystal X-ray diffraction have been obtained in our experiments. The single crystal intensity data were collected on a Bruker APEX-II diffractometer with nitrogen-flow temperature controller using graphite-monochromated MoKα radiation (λ = 0.71073 Å), operating in the ω and φ scan mode. The SADABS programme was used for absorption correction. The structures were solved by direct method followed by successive difference Fourier method. 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 × Ueq of the attached atom. CCDC 1061788-1061790 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystal Data and Structure Refinements for CPM-13X in this study.

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<th>CPM-131</th>
<th>CPM-132</th>
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<td></td>
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<td>Formula Mass</td>
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<td>13.985(10)</td>
<td>33.0984(19)</td>
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<tr>
<td>b/Å</td>
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<td>13.985(10)</td>
<td>33.0984(19)</td>
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<tr>
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<td>24.40(4)</td>
<td>9.3673(11)</td>
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<td>No. of independent reflections</td>
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<td>0.992</td>
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<td>Final R1 values (all data)</td>
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<td>0.2595</td>
<td>0.2780</td>
<td>0.0899</td>
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\[ R_1 = \frac{\sum |F_o| - |F_c|/\sum |F_o|, \quad wR = \left\{\frac{\sum w((F_o)^2 - (F_c)^2)}{\sum w((F_o)^2)}\right\}^{1/2}. \]
6. Photographs of crystals

Fig. S12 Photograph of CPM-131.
Fig. S13 Photograph of CPM-132.
Fig. S14 Photograph of CPM-133.
7. Characterization of CPM-13X

Fig. S15 Measured and simulated PXRD patterns of CPM-131.

Fig. S16 Measured and simulated PXRD patterns of CPM-132.
Fig. S17 Measured and simulated PXRD patterns of CPM-133.

Fig. S18 SEM images of (a) CPM-131, (b) CPM-132, and (c) CPM-133.
**Fig. S19** EDX of the crystal CPM-131 (coated with Pd/Pt).

**Fig. S20** EDX of the crystal CPM-132 (coated with Pd/Pt).
Fig. S21 EDX of the crystal CPM-133 (coated with Pd/Pt).

Fig. S22 Normalized solid-state diffuse reflectance spectra of the CPM-13X.
Fig. S23 FT-IR spectra of CPM-13X.

Fig. S24 TGA curves of CPM-13X.
8. Additional structural pictures

**Fig. S25** Layer of [(TPyP-Fe)Zn]$_n$ in CPM-131.

**Fig. S26** Projection of structure of CPM-131 along c axis.
Fig. S27 Side view of 3D structure of CPM-131.

Fig. S28 Space-filling model of CPM-131 along c axis.
**Fig. S29** Bi-layer (pillared by F\(^-\) ions) in CPM-132.

**Fig. S30** Bi-layer (pillared by SiF\(_6^{2-}\) ions) in CPM-132.
**Fig. S31** Side view of the structure of CPM-132.

**Fig. S32** Projection of structure of CPM-132 along c axis.
**Fig. S33** Space-filling model of CPM-132 along c axis.

**Fig. S34** Projection of the framework of CPM-133 along c axis.
Fig. S35 Hexagonal channel of CPM-133 along $c$ axis.

Fig. S36 Space-filling model of CPM-133 along $c$ axis.
9. Gas sorptions

Fig. S37 N₂ adsorption-desorption isotherms with inset of pore size distribution (using Horvath-Kawazoe model) of CPM-131 at 77 K.

Fig. S38 CO₂ sorption with inset of $Q_{st}$ of CPM-131.
**Fig. S39** CO$_2$ and N$_2$ adsorption of CPM-131 at 273 K.

**Fig. S40** C$_2$H$_2$ sorption with inset of $Q_{st}$ of CPM-131.
**Fig. S41** CH$_4$ sorption of CPM-131.

**Fig. S42** N$_2$ adsorption-desorption isotherms with inset of pore size distribution (using Horvath-Kawazoe model) of CPM-132 at 77 K.
**Fig. S43** CO$_2$ sorption with inset of $Q_{st}$ of CPM-132.

**Fig. S44** CO$_2$ and N$_2$ adsorption of CPM-132 at 273 K.
Fig. S45 C$_2$H$_2$ sorption with inset of $Q_{st}$ of CPM-132.

Fig. S46 CH$_4$ sorption of CPM-132.
Fig. S47 $\text{N}_2$ adsorption-desorption isotherms with inset of pore size distribution (using Horvath-Kawazoe model) of CPM-133 at 77 K.

Fig. S48 $\text{CO}_2$ sorption with inset of $Q_{st}$ of CPM-133.
Fig. S49 CO₂ and N₂ adsorption of CPM-133 at 273 K.

Fig. S50 C₂H₂ sorption with inset of $Q_{st}$ of CPM-133.
Fig. S51 CH₄ sorption of CPM-133.

Fig. S52 H₂ sorption of CPM-13X at 77 K.
Table S2 A summary of porosity measurements.

<table>
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<th>Code</th>
<th>Framework Composition</th>
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<th>CO\textsubscript{2}\textsuperscript{b}</th>
<th>N\textsubscript{2}\textsuperscript{a}</th>
<th>CH\textsubscript{4}\textsuperscript{a}</th>
<th>Selectivity\textsuperscript{c}</th>
<th>Pore Size</th>
<th>Q\textsubscript{st}</th>
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<td>CPM-131</td>
<td>[(TPyP-Fe)Zn(SiF\textsubscript{6})]\textsubscript{n}</td>
<td>fsc</td>
<td>226/286</td>
<td>101/55</td>
<td>76/31</td>
<td>1.0/0.39</td>
<td>13/2.9</td>
<td>1211[108]</td>
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<td>35</td>
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<td>CPM-132</td>
<td>[(TPyP-Zn)\textsubscript{2}F\textsubscript{2}Zn\textsubscript{2}(SiF\textsubscript{6})]\textsubscript{n}</td>
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<td>204/258</td>
<td>74/40</td>
<td>59/23</td>
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<td>8/2.8</td>
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<td>nbo</td>
<td>390/490</td>
<td>75/39</td>
<td>59/22</td>
<td>1.7/0.45</td>
<td>13/2.2</td>
<td>523[99]</td>
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S.A. = (BET/Langmuir) surface area (m\textsuperscript{2}g\textsuperscript{-1}), \textsuperscript{a}uptake @ 1/0.15 bar (cm\textsuperscript{3}g\textsuperscript{-1}) at 273 K, \textsuperscript{b}uptake @ 1/0.15 bar (cm\textsuperscript{3}g\textsuperscript{-1}) at 298 K, \textsuperscript{c}selectivity for CO\textsubscript{2}:N\textsubscript{2} (10:90) [selectivity for CO\textsubscript{2}:CH\textsubscript{4} (50:50)] at 0.01 bar (273 K) by IAST, Q\textsubscript{st} for CO\textsubscript{2} (kJmol\textsuperscript{-1}).
10. Pyrolysis of CPM-13X (to CPM-13X/C)
The pyrolysis reaction of CPM-13X to CPM-13X/C was carried out in quartz tubes (with two open ends) in tube furnace under Ar atmosphere. The CPM-13X samples were heated from the room temperature to 700, or 800, or 900 or 1000 °C with a heating rate of 4 °C·min⁻¹, then kept the temperature for 4 hr in Ar gas, respectively. The carbonization products were denoted to CPM-13X/C-700, CPM-13X/C-800, CPM-13X/C-900 and CPM-13X/C-1000. FT-IR: ν = 3680 (m), 2990 (s), 2360 (s), 1390 (m), 1250 (m), 1070 (s), 879 (m) cm⁻¹ for CPM-131/C; ν = 3680 (m), 2990 (s), 2360 (s), 1390 (m), 1070 (s) cm⁻¹ for CPM-132/C; ν = 3680 (m), 2990 (s), 2340 (m), 1390 (m), 1230 (m), 1070 (s), 879 (w) cm⁻¹ for CPM-133/C.
11. Characterization of CPM-13X/C

Fig. S53 PXRD patterns of CPM-131/C pyrolized at different temperature.
Fig. S54 PXRD patterns of CPM-132/C pyrolized at different temperature.

Fig. S55 PXRD patterns of CPM-133/C pyrolized at different temperature.
Fig. S56 SEM images of (a) CPM-131/C, (b) CPM-132/C, and (c) CPM-133/C.

Fig. S57 EDX of CPM-131/C (coated with Pd/Pt).

Fig. S58 EDX of CPM-132/C (coated with Pd/Pt).
**Fig. S59** EDX of CPM-133/C (coated with Pd/Pt).

**Fig. S60** TEM image of CPM-131/C.
Fig. S61 TEM images of CPM-132/C.
**Fig. S62** TEM images of CPM-133/C.

**Fig. S63** SAED pattern of CPM-131/C.
**Fig. S64** FT-IR spectra of CPM-13X/C-700.

**Fig. S65** Normalized solid-state diffuse reflectance spectra of CPM-13X/C-700.
Fig. S66 XPS survey spectrum of CPM-131/C-700.

Fig. S67 XPS F 1s spectrum of CPM-131/C-700.
Fig. S68 XPS N 1s spectrum of CPM-131/C-700.

Fig. S69 XPS Fe 2p spectrum of CPM-131/C-700.
Fig. S70 XPS C 1s spectrum of CPM-131/C-700.

Fig. S71 XPS survey spectra of CPM-132/C-700.
Fig. S72 XPS F 1s spectrum of CPM-132/C-700.

Fig. S73 XPS N 1s spectrum of CPM-132/C-700.
Fig. S74 XPS C 1s spectrum of CPM-132/C-700.

Fig. S75 XPS survey spectra of CPM-133/C-700.
Fig. S76 XPS N 1s spectrum of CPM-133/C-700.

Fig. S77 XPS C 1s spectrum of CPM-133/C-700.
**Fig. S78** $N_2$ sorption of CPM-131/C.

**Fig. S79** $N_2$ sorption of CPM-132/C.
Fig. S80 N$_2$ sorption of CPM-133/C.
12. Electrocatalytic activities for ORR

![Graph showing LSV curves for ORR](image1)

**Fig. S81** LSV curves at rotation rate of 1600 rpm on CPM-131/C calcined at different temperature in O₂-saturated 0.1 M KOH solution.

![Graph showing CVs for ORR](image2)

**Fig. S82** CVs on CPM-131/C calcined at different temperature in O₂-saturated 0.1 M KOH solution.
Fig. S83 LSV curves at rotation rate of 1600 rpm on CPM-132/C calcined at different temperature in O$_2$-saturated 0.1 M KOH solution.

Fig. S84 CVs on CPM-132/C calcined at different temperature in O$_2$-saturated 0.1 M KOH solution.
**Fig. S85** LSV curves at rotation rate of 1600 rpm on CPM-133/C calcined at different temperature in O$_2$-saturated 0.1 M KOH solution.

**Fig. S86** CVs on CPM-133/C calcined at different temperature in O$_2$-saturated 0.1 M KOH solution.
**Fig. S87** LSV curves at rotation rate of 1600 rpm on CPM-13X/C and 20% Pt/C in O$_2$-saturated 0.1 M KOH solution.

**Fig. S88** CVs on CPM-13X/C and 20% Pt/C in O$_2$-saturated 0.1 M KOH solution.
Fig. S89 LSV curves at different rotation rates with inset of K-L plots of $J^1$ versus $\omega^{-1}$ on CPM-131/C-1000 in O$_2$-saturated 0.1 M KOH solution.

Fig. S90 LSV curves at different rotation rates with inset of K-L plots of $J^1$ versus $\omega^{-1}$ on CPM-132/C-1000 in O$_2$-saturated 0.1 M KOH solution.
Fig. S91 LSV curves at different rotation rates with inset of K-L plots of $J^1$ versus $\omega^{-1}$ on CPM-133/C-1000 in O$_2$-saturated 0.1 M KOH solution.

Fig. S92 Cycling CVs and methanol-poisoning effects over CPM-132/C-1000 in O$_2$-saturated 0.1 M KOH solution.
**Fig. S93** Current-time (i-t) chronoamperometric response over CPM-132/C-1000 and 20% Pt/C in O₂-saturated 0.1 M KOH solution.

**Fig. S94** LSV curves at rotation rate of 1600 rpm on CPM-13X/C and 20% Pt/C in O₂-saturated 0.1 M HClO₄ solution.
Fig. S95 CVs on CPM-13X/C and 20% Pt/C in O₂-saturated 0.1 M HClO₄ solution.

Fig. S96 LSV curves at different rotation rates with inset of K-L plots of $J^1$ versus $\omega^{-1}$ on CPM-131/C in O₂-saturated 0.1 M HClO₄ solution.
Fig. S97 LSV curves at different rotation rates with inset of K-L plots of $J^1$ versus $\omega^{-1}$ on CPM-132/C in O$_2$-saturated 0.1 M HClO$_4$ solution.

Fig. S98 LSV curves at different rotation rates with inset of K-L plots of $J^1$ versus $\omega^{-1}$ on CPM-133/C in O$_2$-saturated 0.1 M HClO$_4$ solution.
Fig. S99 Cycling CVs and methanol-poisoning effects over CPM-132/C-1000 in O$_2$-saturated 0.1 M HClO$_4$ solution.

Fig. S100 Current-time ($i$-$t$) chronoamperometric response over CPM-132/C-1000 and 20% Pt/C in O$_2$-saturated 0.1 M HClO$_4$ solution at a scan rate of 10 mV s$^{-1}$. 
13. Supplementary reference
