Supporting Information

Charge Redistribution in Covalent Organic Frameworks Via Linkage Conversion Enables Enhanced Selective Reduction of Oxygen to H₂O₂

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1. General information

1.1 Reagents

Unless otherwise noted, all the chemicals and reagents were purchased in analytical purity from commercial suppliers and used directly without further purification. Magnesium sulphate, 1-butanol (n-BuOH), 1,2-dichlorobenzene (o-DCB), i-propanol (*i*-PrOH), tetrahydrofuran (THF), trichloromethane (CHCl₃), N,N-dimethylformamide (DMF), petroleum ether (PE), dichloromethane (DCM), ethyl acetate, ethanol, NaHCO₃, toluene, 1,4-dioxane, Na₂SO₄, and K₂CO₃ were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Terephthalaldehyde, 1,3,6,8-tetrabromopyrene, neopentyl glycol, 4-aminophenylboronic acid pinacol ester, Pd(PPh₃)₄, p-toluenesulfonic acid (TsOH), and acetic acid (HOAc) were purchased from Bidepharm Co., Ltd. (Shanghai, China). Trifluoroacetic acid (TFA), potassium titanium oxalate, and mesitylene were obtained from Aladdin Industrial Co., Ltd. (Shanghai, China). [Cp*RhCl₂]₂ and 4,4'-biphenyldicarboxaldehyde were purchased from Adamas. Dithiooxamide was acquired from Meryer Chemical Technology Co., Ltd. (Shanghai, China).

1.2 Characterization methods

UV-vis spectra were collected on a Shimadzu UV 3600 spectrophotometer with BaSO₄ as the reference. Powder X-ray diffraction patterns were collected on a Bruker D8 Advance diffractometer with Cu K α radiation in the 2 θ range of 2-40°. Liquid-state ¹H NMR and ¹³C NMR spectra were recorded on Bruker Advance spectrometers at 298 K and chemical shift (δ) was reported in ppm with residual solvent peak as the reference. Peaks are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet,

m = multiplet or unresolved, with coupling constants in Hz. Solid-state ¹³C cross polarization magic angle spinning (¹³C-CP/MAS) NMR spectra were collected on a Bruker Avance III HD spectrometer. Fourier transform infrared (FT-IR) spectra were collected on a Nicolet 6700 spectrometer (Thermo Scientific, USA) equipped with an ATR cell. The specific Brunauer-Emmett-Teller (BET) surface area and pore size distribution were measured using a Micrometrics ASAP 2040 instrument at 77 K. High resolution transmission electron microscope (HRTEM) images were obtained on a Talos F200X G2 instrument at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha spectrometer with non-monochromatic Al K α x-rays as the excitation source and C 1s (284.6 eV) as the reference line. Thermal stability was investigated on a DZ-STA 200 (Nanjing Dazhan) thermogravimetric analyzer under N₂ atmosphere at a heating rate of 10 K min⁻¹.

1.3 Electrochemical measurements

Preparation of working electrodes: a mixture of COFs (5 mg), ethanol (0.96 mL), and 5% Nafion (0.04 mL) was sonicated for 1 h to prepare the catalyst ink. Then 30 μ L of the as-prepared catalyst ink was pipetted onto a glassy carbon electrode (0.2475 cm²) for cyclic voltammetry (CV) and rotating ring-disk electrode (RRDE) tests. In addition, 200 μ L of the as-prepared catalyst ink was dropped onto a carbon paper (1 cm²) for the H-type cell test.

CV and RRDE tests: CV and RRDE tests were performed on the CHI760E workstation (Chenhua Instruments, China), and the standard three-electrode system

included a platinum plate as the counter electrode, a commercial Ag/AgCl electrode as the reference electrode, and the catalyst-coated glassy carbon as the working electrode. 0.1 M Na₂SO₄ at pH = 3.1 (adjusted with 0.1 M H₂SO₄) was employed as the electrolyte. CV was operated in O₂ and N₂ saturated electrolytes at a scan rate of 50 mV s⁻¹. RRDE test was carried out at a scan rate of 10 mV s⁻¹ and a rotation rate of 900 rpm with a ring potential of 0.9 V (vs. Ag/AgCl). All potentials versus Ag/AgCl were calibrated to reversible hydrogen electrode (RHE) according to the following equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.199 V + 0.059 V × pH. Hydrogen peroxide selectivity and electron transfer number (*n*) were calculated according to the following equations:

$$n = \frac{|4i_d|}{|i_d| + \frac{i_r}{N}}$$
$$H_2O_2(\%) = \frac{200i_r}{N|i_d| + i_r}$$

where i_d is the disk current, i_r is the ring current, and N(0.34) is the collection efficiency.

H-type cell test: the production of H_2O_2 was evaluated in a Nafion 117 membraneseparated dual-chamber reactor using the CS150M electrochemical station (Wuhan Corrtest Instruments). The platinum plate, commercial Ag/AgCl electrode, and the catalyst-coated carbon paper were the counter electrode, reference electrode, and working electrode, respectively. The concentration of H_2O_2 was determined by the potassium oxalate phthalate spectrophotometric method based on the absorbance at 395 nm of the yellow-brown complex formed by the reaction of titanium oxalate phthalate solution with H_2O_2 . Specifically, 1 mL of electrolyte was mixed with 0.5 mL of 3 M H_2SO_4 for acidification, and then 0.5 mL of 0.05 M potassium titanium oxalate solution was added. The mixture solution was diluted to 5 mL. After standing for 10 min, its absorbance was measured, and the concentration of H_2O_2 was converted according to the standard curve.

1.4 Theoretical calculation

All calculations were performed using the Vienna ab initio simulation package (VASP) [1]. The Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was utilized to express electron exchange correlation [2], and the projector augmented wave (PAW) method was applied to describe the pseudo-potentials [3]. Dispersion-corrected DFT-D3 schemes were employed to describe possible van der Waals (vdW) interactions [4].

The energy cut-off for the plane-wave basis was set to 400 eV. The Brillouin zone in reciprocal space was sampled using the Monkhorst-Pack scheme with $2 \times 2 \times 1$ k-point grids for geometry optimization. All structures were fully relaxed until the forces were smaller than 0.02 eV Å⁻¹, and the convergence threshold in electronic relaxation was set to 10^{-5} eV using the conjugate gradient algorithm. The vertical separation between periodically repeated images was set to be at least 20 Å to ensure no interaction between images.

Free energy diagram and activity-volcano curve were constructed to estimate the electrochemical $2e^-$ ORR performance. The $2e^-$ ORR mechanism for producing H_2O_2 comprises of two elementary steps (a and b):

*
$$+ O_{2(g)} + H^+ + e^- \rightarrow 00H *$$
 (a)
 $00H *+ H^+ + e^- \rightarrow H_2O_2(l) + *$

(b)

where the asterisk (*) denotes the active site of the catalyst.

The free energy of adsorbed specie, computed based on computational hydrogen electrode (CHE) model, is defined as (c):

$$G = E + ZPE - TS \tag{c}$$

Here *E* is the DFT-derived total ground state energy of a system. *ZPE* is the zero-point energy correction and *TS* is the entropy correction computed with standard methods and used to convert *E* into free energy (*G*) at 298.15 K. The Gibbs free energy of *OOH adsorption (ΔG_{*OOH}) at a given potential (U *vs.* reversible hydrogen electrode, RHE) are defined as (d):

$$\Delta G(*00H) = G(*00H) + \frac{3G(H_2)}{2} - G(*) - 2G(H_20) - 3eU$$
(d)

2. Synthesis of the building blocks

Scheme S1. Synthesis of TAPPy

Synthesis of 1,3,6,8-tetrakis(4-aminophenyl)pyrene (TAPPy): A round-bottom flask was charged with 1,3,6,8-tetrabromopyrene (**S1**, 2.07 g, 4.0 mmol), 4-aminophenylboronic acid pinacol ester (**S2**, 4.38 g, 20.0 mmol), Pd(PPh₃)₄ (0.12 g, 0.1 mmol), K₂CO₃ (2.07 g, 15.0 mmol), and a mixed solvent of 1,4-dioxane (100 mL) and distilled water (10 mL). After being degassed with Ar for 10 minutes, the mixture was stirred at 110 °C under an Ar atmosphere for 3 days. After cooling down, water (200 mL) was added to quench the reaction. The suspension was filtered to afford the yellow precipitate, which was further purified by Soxhlet extraction with MeOH as the solvent

for 24 hours. The final product (2.10 g, 3.7 mmol, 92%) was obtained after being dried under vacuum at 60 °C overnight. ¹H NMR (DMSO-d₆, 600 MHz) δ 8.11 (s, 4H), 7.78 (s, 2H), 7.33 (d, *J* = 8.3 Hz, 8H), 6.78 (d, *J* = 8.3 Hz, 8H), 5.27 (s, 8H).



Synthesis of S5: A round-bottom flask equipped with a Dean-Stark apparatus was charged with terephthalaldehyde (S3, 4.51 g, 33.6 mmol), neopentyl glycol (S4, 3.50 g, 33.6 mmol), TsOH (22.4 mg, 0.13 mmol), and toluene (75 mL). Subsequently, the mixture was stirred at 140 °C under an air atmosphere for 24 hours. After cooling down, the suspension was transferred to a separatory funnel and washed with aqueous NaHCO₃ solution (50 mL). This was followed by the addition of deionized water (50 mL) to obtain two immiscible layers. The organic layer was collected in a beaker and the aqueous layer was extracted three times with ethyl acetate (25 mL) and DCM (25 mL). The combined organic layer was added with Na₂SO₄, which was further filtered and evaporated. Finally, the concentrated residue was purified by flash chromatography on silica gel with PE/EA as the eluent to afford the product S5 (5.13 g, 23.3 mmol, 69%). ¹H NMR (CDCl₃, 600 MHz) δ 10.03 (s, 1H), 7.89 (d, J = 7.6 Hz, 2H), δ 7.68 (d, *J* = 7.7 Hz, 2H), 5.45 (s, 1H), 3.79 (d, *J* = 10.3 Hz, 2H), 3.67 (d, *J* = 10.9 Hz, 2H), 1.29 (s, 3H), 0.82(s,3H). ¹³C NMR (151 MHz, CDCl₃) δ 192.1, 144.6, 136.7, 129.8, 127.0, 100.8, 30.3, 23.0, 21.9.



Scheme S3. Synthesis of S7

Synthesis of S7: A round-bottom flask was charged with S5 (0.92 g, 4.16 mmol), dithiooxamide (S6, 0.25 g, 2.08 mmol), and DMF (50 mL). After being degassed with Ar for 10 minutes, the mixture was stirred at 150 °C under an Ar atmosphere for 6 hours. After cooling down, the suspension was filtered to afford the light-yellow precipitate, which was then washed with water until the filtrate was colorless. The final product (0.45 g, 0.87 mmol, 42%) was obtained after being dried under vacuum at 60 °C overnight. ¹H NMR (CDCl₃, 600 MHz) δ 8.00 (d, *J* = 8.2 Hz, 4H), 7.61(d, *J* = 8.2 Hz, 4H), 5.44 (s, 2H), 3.79 (d, *J* = 10.9 Hz, 4H), 3.66 (d, *J* = 10.9 Hz, 4H), 1.30 (s, 6H), 0.81(s, 6H).



Scheme S4. Synthesis of S8

Synthesis of S8: A round-bottom flask was charged with **S7** (0.50 g, 0.96 mmol) and a mixed solvent of TFA (50 mL), CHCl₃ (50 mL), and distilled water (50 mL). After being degassed with Ar for 10 minutes, the mixture was stirred at 80 °C under an Ar atmosphere for 24 hours. After cooling down, the suspension was filtered to afford the yellow precipitate, which was then washed with water and dichloromethane until the filtrate was colorless. The final product (0.31 g, 0.88 mmol, 92%) was obtained after

being dried under vacuum at 60 °C overnight. ¹H NMR (CDCl₃, 600 MHz) δ 10.09 (s, 2H), 8.20 (d, J = 8.3 Hz, 4H), 8.01 (d, J = 8.2 Hz, 4H).

3. Synthesis of COFs

Synthesis of I-COF_{TAPPy-TzDA}: A Pyrex glass tube (10 mL) was charged with TAPPy (28.3 mg, 0.05 mmol), **S8** (35 mg, 0.1 mmol), mesitylene (0.7 mL), 1,4-dioxane (0.3 mL), and HOAc (6 mol, 0.1 mL). Subsequently, the tube was sonicated for 10 minutes, degassed by three freeze-pump-thaw cycles (liquid nitrogen), and sealed under vacuum. After being heated in an oven at 120 °C for 3 days, the cooled suspension was centrifuged to separate the solid, which was repeatedly washed by THF until the solvent was colorless. The I-COF_{TAPPy-TzDA} was finally obtained as the red powder (65.3 mg, 74.3%) after being dried under vacuum at 80 °C.

Synthesis of NQ-COF_{TAPPy-TzDA}-PSM: A 10 mL Schlenk pressure tube was charged with the corresponding I-COF_{TAPPy-TzDA} (30 mg, 0.1 mmol theoretical content of imine linkage), vinylene carbonate (25.8 mg, 0.3 mmol), [Cp*RhCl₂]₂ (3 mg, 0.0045 mmol), and *i*-PrOH (2.5 mL). Subsequently, the tube was sonicated for 5 minutes, degassed by three freeze-pump-thaw cycles (liquid nitrogen), and sealed under vacuum. The reaction mixture was stirred at 110 °C for 12 h. After cooling to room temperature, the solid was separated by filtration under reduced pressure, and washed with water and CH₃OH successively. Finally, NQ-COF_{TAPPy-TzDA}-PSM (26.5 mg, 86.5%) was afforded as the brown powder after being dried under vacuum at 80 °C.

Synthesis of NQ-COF_{TAPPy-TzDA}-OPR: A Pyrex glass tube (10 mL) was charged with TAPPy (28.3 mg, 0.05 mmol), S8 (35 mg, 0.1 mmol), MgSO₄ (72 mg), vinylene

carbonate (25.8 mg, 0.3 mmol), $[Cp*RhCl_2]_2$ (3 mg, 0.0045 mmol), *o*-DCB (0.1 mL), and HOAc (6 mol, 0.1 mL). Subsequently, the tube was sonicated for 10 minutes, degassed by three freeze-pump-thaw cycles (liquid nitrogen), and sealed under vacuum. After being heated in an oven at 120 °C for 3 days, the cooled suspension was centrifuged to separate the solid, which was repeatedly washed by THF and water until the solvent was colorless. The NQ-COF_{TAPPy-TzDA}-OPR was finally obtained as the brown powder (58.7 mg, 66.8%) after being dried under vacuum at 80 °C.



Scheme S5. Synthesis of I-COF_{TAPPv-BPDA} and NQ-COF_{TAPPv-BPDA}-OPR

Synthesis of I-COF_{TAPPy-BPDA}: A Pyrex glass tube (10 mL) was charged with TAPPy (28.3 mg, 0.05 mmol), 4,4'-biphenyldicarboxaldehyde (21 mg, 0.1 mmol), *o*-DCB (0.5 mL), *n*-BuOH (0.5 mL), and HOAc (6 mol, 0.1 mL). Subsequently, the tube was sonicated for 10 minutes, degassed by three freeze-pump-thaw cycles (liquid nitrogen), and sealed under vacuum. After being heated in an oven at 120 °C for 3 days, the cooled suspension was centrifuged to separate the solid, which was repeatedly washed by THF until the solvent was colorless. The **I-COF_{TAPPy-BPDA}** was finally obtained as the yellow

powder (31.2 mg, 79.5%) after being dried under vacuum at 80 °C.

Synthesis of NQ-COF_{TAPPy-BPDA}-OPR: A Pyrex glass tube (10 mL) was charged with TAPPy (28.3 mg, 0.05 mmol), 4,4'-biphenyldicarboxaldehyde (21 mg, 0.1 mmol), MgSO₄ (48 mg), vinylene carbonate (25.8 mg, 0.3 mmol), [Cp*RhCl₂]₂ (3 mg, 0.0045 mmol), *o*-DCB (0.1 mL), and HOAc (6 mol, 0.1 mL). Subsequently, the tube was sonicated for 10 minutes, degassed by three freeze-pump-thaw cycles (liquid nitrogen), and sealed under vacuum. After being heated in an oven at 120 °C for 3 days, the cooled suspension was centrifuged to separate the solid, which was repeatedly washed by THF and water until the solvent was colorless. The NQ-COF_{TAPPy-BPDA}-OPR was finally obtained as the brown powder (26.5 mg, 66.6%) after being dried under vacuum at 80 °C.

4. Characterization of COFs



Fig. S1 HRTEM image of (a) NQ-COF_{TAPPy-TzDA}-PSM and (b) line intensity profile of NQ-COF_{TAPPy-TzDA}-PSM along the direction marked by the red arrow in (a).



Fig. S2 FT-IR spectra of TzDA and TAPPy.



Fig. S3 PXRD patterns of (a) NQ-COF_{TAPPy-TzDA}-OPR and (b) I-COF_{TAPPy-TzDA} before and after different chemical treatments.



Fig. S4 FT-IR spectra of NQ-COF_{TAPPy-TzDA}-OPR before and after different chemical treatments.



Fig. S5 TGA curves of I-COF_{TAPPy-TzDA} and NQ-COF_{TAPPy-TzDA}-OPR.



Fig. S6 (a) LSV curve of Pt/C in oxygen saturated 0.1 M Na_2SO_4 (pH = 3.1) solution.

(b) The dependence of electron transfer number on the potential.



Fig. S7 (a) Concentration of H_2O_2 produced over I-COF_{TAPPy-TzDA}, NQ-COF_{TAPPy-TzDA}-PSM, NQ-COF_{TAPPy-TzDA}-OPR, and I-COF_{TAPPy-TzDA}-Rh. (b) Faradaic efficiency of I-COF_{TAPPy-TzDA}, NQ-COF_{TAPPy-TzDA}-PSM, NQ-COF_{TAPPy-TzDA}-OPR, and I-COF_{TAPPy-TzDA}-Rh.



Fig. S8 CV curves of I-COF_{TAPPy-TzDA} (a), NQ-COF_{TAPPy-TzDA}-PSM (b), and NQ-COF_{TAPPy-TzDA}-OPR (c) at different scan rates. Plots of current density *versus* scan rates of I-COF_{TAPPy-TzDA} (d), NQ-COF_{TAPPy-TzDA}-PSM (e), and NQ-COF_{TAPPy-TzDA}-OPR (f).



Fig. S9 Nyquist plots of I-COF_{TAPPy-TzDA}, NQ-COF_{TAPPy-TzDA}-PSM, and NQ-COF_{TAPPy-TzDA}-OPR.



Fig. S10 (a) UV-vis DRS spectra of NQ-COF_{TAPPy-TzDA}-PSM and NQ-COF_{TAPPy-TzDA} OPR. (b) The Kubelka-Munk-transformed reflectrance spectra of NQ-COF_{TAPPy-TzDA}-PSM and NQ-COF_{TAPPy-TzDA}-OPR. Mott-Schottky plots of NQ-COF_{TAPPy-TzDA}-PSM (c) and NQ-COF_{TAPPy-TzDA}-OPR (d).



Fig. S11 (a) LSV curves of I-COF_{TAPPy-TzDA} and I-COF_{TAPPy-TzDA}-Rh in oxygen saturated 0.1 M Na₂SO₄ (pH = 3.1) solution. (b) The dependence of electron transfer number on the potential. (c) The dependence of H_2O_2 selectivity on the potential



Fig. S12 (a) LSV curve of NQ-COF_{TAPPy-TzDA}-OPR in oxygen saturated 0.1 M KOH solution. (b) The dependence of H_2O_2 selectivity on the potential.



Fig. S13 (a) Stability test of NQ-COF_{TAPPy-BPDA}-OPR at the potential of -0.9 V (vs. Ag/AgCl) for 48 h. PXRD patterns (b) and FT-IR spectra (c) of NQ-COF_{TAPPy-BPDA}-OPR before and after stability test. (d) Optical image of rhodamine B solution before and after degradation.



Fig. S14 FT-IR spectra of I-COF_{TAPPy-BPDA} and NQ-COF_{TAPPy-BPDA}-OPR.



Fig. S15 XRD patterns of (a) I-COF_{TAPPy-BPDA} and (b) NQ-COF_{TAPPy-BPDA}-OPR.



Fig. S16 Concentration of H_2O_2 produced over I-COF_{TAPPy-BPDA} and NQ-COF_{TAPPy-BPDA}-OPR.



Fig. S17 (a) The optimized structure of $I-COF_{TAPPy-TzDA}$. The optimized structures of *OOH adsorbed at S (b), N (c), and N1 (d) sites of $I-COF_{TAPPy-TzDA}$.



Fig. S18 (a) The optimized structure of NQ-COF_{TAPPy-TzDA}. The optimized structures of *OOH adsorbed at S (b), N (c), and N1 (d) sites of NQ -COF_{TAPPy-TzDA}.

5. Copies of NMR spectra



Fig. S20 ¹H NMR spectra of S5.



Fig. S21 ¹³C NMR spectra of S5.



Fig. S22 ¹H NMR spectra of S7.



Fig. S23 ¹H NMR spectra of TzDA.

6. References

- [1] J. Hafner, J. Comput. Chem., 2008, 29, 2044–2078.
- [2] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865–3868.
- [3] P. E. Blöchl, Phys. Rev. B, 1994, 50, 17953–17979.
- [4] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys., 2010, 132, 154104.