Supporting Information

Benzothiophene-Based Covalent Organic Framework for H₂O₂ Electrosynthesis: The Critical Role of Conjugated Structure

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Section 1. Experimental

Electrochemical test

ORR activity and selectivity test

The electrochemical ORR performances of as-prepared catalysts were measured in 0.1 M KOH solution using a standard three-electrode electrochemical cell on the IVIUMn-Stat electrochemical workstation at room temperature. A homogeneous catalyst ink was prepared by mixing 5 mg of catalyst powder with 470 µL of EtOH, and 30 µL of 5 *wt.*% Nafion solution, and ultrasonicated for 1 h. Then the catalyst ink (6 µL) was pipetted onto a glassy carbon disk (S = 0.1256 cm²) of rotating ring-disk electrode (RRDE) as working electrode. The Hg/HgO and graphite rod electrode were used as reference and counter electrodes, respectively.

Prior to all electrochemical tests, the electrolyte was purged by Ar gas for 30 min. Then, the pre-activation process using CV with the scan rate of 10 mV/s in O₂-saturated 0.1 M KOH solution was carried out until stable CV curves were obtained. The ORR polarization curves were collected by LSV from 1.0 to 0.0 V (vs. RHE) with the various rotation rate of 400 rpm, 900 rpm, 1600 rpm, 2500 rpm and 3600 rpm and the sweep rate of 10 mV/s. To detect the produced H_2O_2 , the Pt ring potential was maintained at 1.4 V (vs. RHE) during LSV test.

On the basis of ring current $({}^{I_r})$ and disk current $({}^{I_d})$, the electron-transfer number (*n*) and H₂O₂ selectivity $({}^{H_2O_2}\%)$ of catalysts could be calculated based on the following equations:

$$n = \frac{4 I_d}{\frac{I_r}{N} + |I_d|}$$

$$H_2 O_2 \% = \frac{200 \frac{I_r}{N}}{\frac{I_r}{N} + |I_d|}$$

where the ring collection efficiency N is 0.424. All recorded potentials were converted to the reversible hydrogen electrode (vs. RHE) based on the following equation:

E (vs. RHE) = E (vs. Hg/HgO) + 0.098 + 0.059 pH.

For the electrode reactions controlled by the mixture of mass transfer and kinetics, the disk current density j_d (the ratio of I_d to the disk area) satisfies the Koutechy-Levichequation :

$$\frac{1}{j_d} = \frac{1}{j_L} + \frac{1}{j_K}$$

$$j_L = 0.62nFD_o^2 \omega^2 v^{-\frac{1}{6}} c_o^0$$

$$\frac{1}{j_d} = \frac{1}{B\omega^2} + \frac{1}{j_K} \propto \frac{1}{\omega^2}$$

$$B = 0.62nFD_o^2 v^{-\frac{1}{6}} c_o^0$$

Where, j_d is the measured disk current density, j_L and j_K are the limiting diffusion current density and dynamic current density, repectively. ω is the rotational speed (rad/s) of RRDE, n is the electron transfer number, F is the Faraday constant (96485 C/mol). c_o^0 is the molar concentration of O₂ dissolved in 0.1 M KOH bulk solution (1.2×10⁻⁶ mol/cm³), D_o is the diffusion coefficient of O₂ in 0.1 M KOH solution (1.9×10⁻⁵ cm²/s), and v is the kinematic viscosity of electrolyte KOH (0.01 cm²/s).

When
$$\frac{1}{j_d}$$
 is used to plot the $\omega^{\frac{1}{2}}$, the value of *n* can calculated by the slope $\frac{1}{B}$.

The kinetics of electrode process satisfies the Butler-Vollmer (B-V) equation as the following (taking the cathode as an example) :

$$i_c = i_{cr} - i_{ca} = i_0 e^{\left(\frac{\alpha\eta nF}{RT}\right)} - i_0 e^{\left(\frac{-(1-\alpha)\eta nF}{RT}\right)}$$

Where i_c is the net current density flowing through the cathode, which is equal to the difference between the reduction current density i_{cr} and oxidation current density i_{ca} . i_0 is the exchange current density. α is the electron transfer coefficient. η is the overpotentia. n is the electron transfer number. F is the Faraday constant (96485 C/mol), R and T represent the molar gas constant (8.314 J/(mol·K)) and temperature, respectively. In the strongly polarized region, the overpotential of the cathode is too large resulting in i_{cr} far greater than i_{ca} . The B-V equation could be simplified as follows:

$$\eta = -\left(\frac{2.303RT}{\alpha nF}\right)\log i_0 + \left(\frac{2.303RT}{\alpha nF}\right)\log i_c$$
$$\eta = a + b\log i_c$$

This equation is considered as the Tafel formula, where b is called the tafel slop based on the linear curve of η and $\log i_c$.

Faradic efficiency could be calculated based on the following equations:

$$FE_{H_2O_2}\% = \frac{100I_r}{N \times I_d}$$

Assembly and electrochemical test of H-type cell

H-type cell consists of cathode chamber, anode chamber and proton exchange membrane. 75 mL of 0.1 M KOH electrolyte solution was installed in both the anode and cathode chambers. The 200 μ L of catalyst ink was evenly coated on carbon paper (1 cm \times 1 cm) to obtain working electrode with the load amount of 1 mg/cm². Long-term stability tests were conducted at 0.35 V (vs. RHE). The electrochemical active surface area (ECSA) measurement was conducted in Ar-saturated electrolyte using electrochemical double-layer capacitance method. In the non-Faraday region, CV curves were recorded at the sweep rate of 10 mV/s, 20 mV/s, 30 mV/s, 40 mV/s, 50 mV/s and 60 mV/s. The double-layer capacitance was calculated as follows:

$$I_{c} = \frac{dq}{dt} = \frac{d(C_{dl}\varphi)}{dt} = C_{dl}\frac{d\varphi}{dt} + \varphi\frac{dC_{dl}}{dt} \approx C_{dl}\frac{d\varphi}{dt}$$

Over a small range of scanning potential, the value of double-layer capacitance C_{dl} is a constant. I_c is the non-Faraday current, q is the mount of charge which flow through

the electrode in a period of time t. When I_c is used to plot the scan rate $\frac{d\varphi}{dt}$, the slope of the fitting curve is the C_{dl} . The value of ECSA can be estimated by the ratio of C_{dl} to the C_s following the equation:

$$ECSA = \frac{C_{dl}}{C_s}$$

Electrochemical impedance spectroscopy (EIS) was measured at open circuit voltage. Before testing, the three-electrode system was activated at the constant open circuit voltage for 30 min to establish the stable electrochemical double-layer interface. The test frequency was from 100000 to 0.01 Hz.

H_2O_2 quantification

The electrolysis was carried out in H-typed cell at 0.35 V (vs. RHE) of electrolysis voltage using chronoamperometry. The concentration of generated H_2O_2 was determined by $Ce(SO_4)_2$ titration method. Typically, the $Ce(SO_4)_2$ solution (0.5 mM) was prepared by dissolving 16.6 mg of $Ce(SO_4)_2$ in 100 mL of H_2SO_4 solution (0.5 M). Then the collected electrolyte (1 ml) was added into 10 mL of $Ce(SO_4)_2$ solution and shaken the mixed solution for 5minutes. As a control experiment, 1mL of 0.1 M KOH solution was added into 10 ml $Ce(SO_4)_2$ solution (0.5 mM) to obtain the blank mixed solution. Based on the linear relationship between the signal intensity of ultraviolet-visible (UV-vis) spectroscopy (at 319 nm) and Ce^{4+} concentration. The concentration of Ce^{4+} was measured by UV-vis. Therefore, the concentration of generated H_2O_2 can be determined by the following equation:

$$n (H_2O_2) = 1/2 \Delta n (Ce^{4+})$$

In addition, the electrolyte solution in anode region was also determined. Under identical conditions, H_2O_2 production tests were also performed in electrolyte saturated with Ar as a background for testing.

Computational Method

1. System setup

Cell structures of three COFs systems investigated by this work were optimized based on PXRD results experiment results using CP2K program (version 2024.3)^[3] with Perdew-Burke-Ernzerh (PBE)^[4] functional of generalized gradient approximation (GGA) and DZVP-MOLOPT-SR-GTH basis sets^[5]. Frequency calculations were performed under the same level-of-theory to ensure no imaginary frequency exists. Based on the optimized structure, a $2 \times 2 \times 1$ supercell was extended for each material, with intercell bonds on the boundaries terminated by corresponding monomer structures.

Solvation environments were built by LEaP program in AmberTools23^[6] package based on supercell structures. The generalized AMBER force field (GAFF)^[7] and TIP3P^[8] water model were applied for molecular dynamics. RESP^[9] charges for molecular dynamics were fitted to ensure each monomer residue to be neutral. The long-range electrostatic interactions were handled by particle-mesh Ewald (PME) ^[10]method and the cutoff value of van der Waals interactions was set to 10.0 Angstrom. Based on above parameters, molecular dynamics were performed to obtain reasonable solvation environments using GROMACS programs (version 2022.5) ^[11]accelerated by CUDA (version 12.0). The MD simulation included three stages: (1) directly minimization using steepest down algorithm; (2) 1.0 ns heating to 298.15 K; (3) 20.0 ns equilibrium simulation under 298.15 K under NPT ensemble, with v-rescale thermostat method and Berendsen method. Snapshots taken from molecular dynamics trajectories were used for further QM/MM calculations.

2.QM/MM simulation

Ouantum-Mechanical/Molecular-Mechanical (OM/MM) simulations were performed by Tcl-ChemShell program (version 3.7.1)^[12], with QM part treated by ORCA program (version 5.0.4)^[13] and MM part treated by DL poly program^[14]. The interlayer interactions were treated by electrostatic embedding theory and dangling bonds on the layer boundaries were saturated using hydrogen atoms as linker atoms according to the algorithm by Morokuma et al^[15]. Geometry optimizations were performed under PBE0-D3(BJ)/def2-SVP:GAFF level of theory with DL find optimizer^[16]. The resolution-of-identity (RI) approximation and corresponding def2series auxiliary basis were applied for QM part calculations^[17]. Numerical frequency calculations were performed under the same level-of-theory for all atoms in QM region to ensure no imaginary frequency exists. Thermochemistry correction under 298.15 K was calculated by Shermo program. To obtain more accurate electronic energy, single point calculations were performed based on optimized structures under DLPNO-CCSD(T)/def2-TZVPP:GAFF level of theory with RI approximation and def2-series auxiliary basis^[18]. Multiwfn program (development version 3.8)^[19] was used for wavefunction analysis and Visual Molecular Dynamics (VMD, version 1.9.4) was used for better visualization^[20].

In situ ATR-SEIRAS measurement

In situ Attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) were performed using a Nicolet iS50 spectrometer equipped with a VeeMax III (PIKE technologies) accessory. The electrochemical test was conducted using a custom-made three-electrode electrochemical single cell, with a graphite rod and a Hg/HgO electrode as the counter and reference electrodes, respectively. The working electrode was a Si wafer coated with a thin layer of Au to load the catalysts. The potential was varied stepwise from 0 to 0.8 V (vs. RHE) in O_2 or Ar-saturated 0.1 M KOH solution. In situ FT-IR spectra were collected during the electrochemical test, with 128 scans being collected for each spectrum and a spectral resolution of 4 cm⁻¹.

ESR monitoring experiments

Electron spin resonance (ESR, Magnettech ESR5000) technique at ambient temperature was used to explore free radicals and defective states. The electrochemical test was conducted using a custom-made three-electrode electrochemical in the H-type cell, with a graphite rod and a Hg/HgO electrode as the counter and reference electrodes, respectively. The working electrode was carbon paper where the catalyst ink was evenly coated.Excess DMPO was added in cathode chamber to detect the free radical signal produced at different times of electrolysis (Mod Amp: 100 G, Mod Freq: 9.45 GHz, Mod power 10mW, Magnetic field range: 327-347 mT, Temperature: 25°C).The spectra of radicals were fitting by EPR software.

Section 2. Complementary Figures and Tables



Fig. S2 Solid-state ¹³C cross-polarization/magic angle spinning (¹³C CP-MAS) NMR spectrum of

BTT monomer.

Table S1. Structural information of AA-stacking mode of the three simulated.



Fig. S3 The FTIR spectra of BTT-PDA, BTT-BPDA and BTT-TPDA and corresponding







Fig. S5 PXRD patterns of (a) BTT-PDA, (b) BTT-BPDA and (c) BTT-TPDA before and after



treating with different solvents.

Fig. S6 FTIR spectra of (a) BTT-PDA, (b) BTT-BPDA and (c) BTT-TPDA before and after

treating with different solvents.



Fig. S7 CV plots of (a) BTT-PDA, (b) BTT-BPDA and (c) BTT-TPDA

in O₂ and Ar saturated 0.1 M KOH.



Fig. S8 LSV curves of (a) BTT-PDA, (b) BTT-BPDA and (c) BTT-TPDA at different rotation



Fig. S9 Impedance measurements

Table S2. The parameters of simulation circuit for electrode/solution interface.

EIS	BTT-PDA	BTT-BPDA	BTT-TPDA
Rs/ohm	11.18	11.18	12.46
Q/n*	0.86	0.86	0.85
Rct/Kohm	11.2	11.3	28.3

*The value of n represents the roughness of the electrode interface, usually ranging from 0 to 1. When n is equal to 1, it is shown that the electrode interface constitutes an ideal smooth capacitor.



Fig. S10. CV plots of (a) BTT-PDA, (b) BTT-BPDA and (c) BTT-TPDA at different scan rate.



Fig. S11. (a) The construction of H-type cell for electrochemical H₂O₂ production. (CE: Counter electrode; WE: Working electrode; RE: Reference electrode). (b) The UV visible spectrum and (c) the absorbance standard curve of Ce(SO₄)₂ solutions with different concentrations (0.1-0.7 mM).
(d) H₂O₂ yield in cathode chamber under Ar atmosphere. (e) H₂O₂ yield in anode chamber under air atmosphere; the insert shows oxygen bubbles generated on the graphite rod (RE).



Fig. S12 SEM and TEM images of (a) BTT-PDA, (b)BTT-PDA and (c) BTT-TPDA after long-

term electrocatalysis test.



Fig. S13 PXRD pattern of (a)BTT-PDA, BTT-BPDA (b, e) and BTT-TPDA (c, f) before and after



long-term electrocatalysis test.



Fig. S14 In situ IR spectra (the pink line represents the result of the calculation).

Fig. S15 Ex situ FTIR spctra of (a) BTT-PDA, (b) BTT-BPDA and (c) BTT-TPDA before and after long-term electrocatalysis test.

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