

**Supporting Information for**

**Porphyrin-Containing Conjugated Microporous Polymer with Gradient Asymmetric Design for Efficient Oxygen Reduction**

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## 1. Structural and morphology characterization

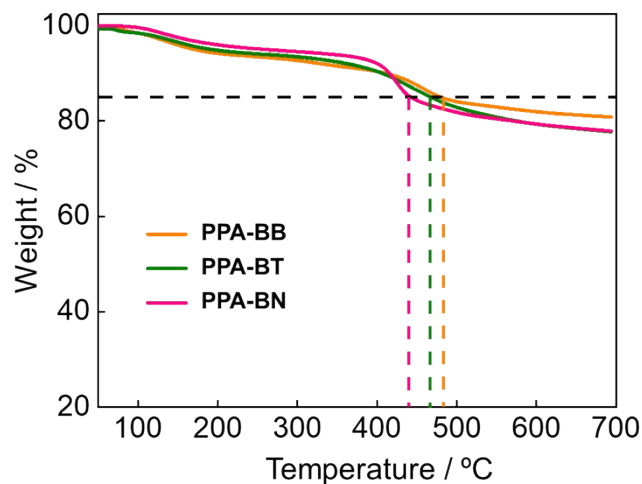


Fig. S1 Thermogravimetric analysis (TGA) of **PPA-BB**, **PPA-BT** and **PPA-BN**. They show good thermal stability with thermal decomposition temperature ( $T_d$ ) at 15% weight loss of 483 °C for **PPA-BB**, 466 °C for **PPA-BT**, and 440 °C for **PPA-BN**.

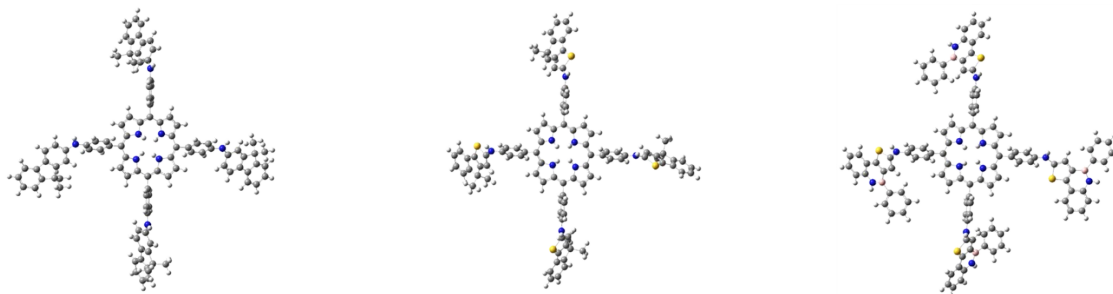


Fig. S2 Top View of model compounds of **PPA-BB**, **PPA-BT**, **PPA-BN**.

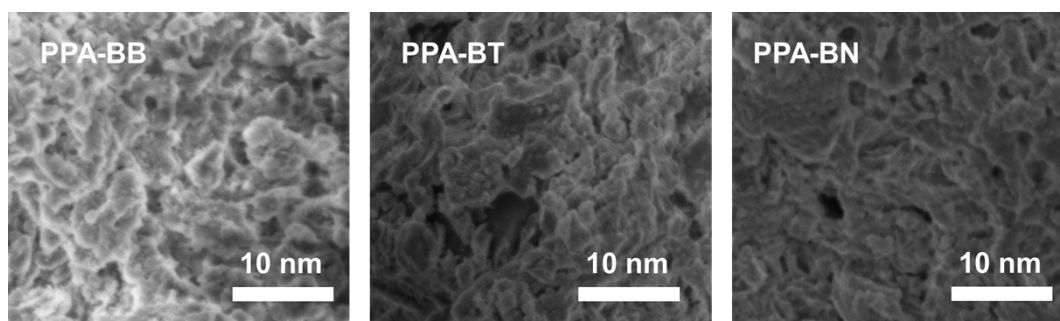


Fig. S3 SEM images of pure **PPA-BB**, **PPA-BT**, and **PPA-BN**.

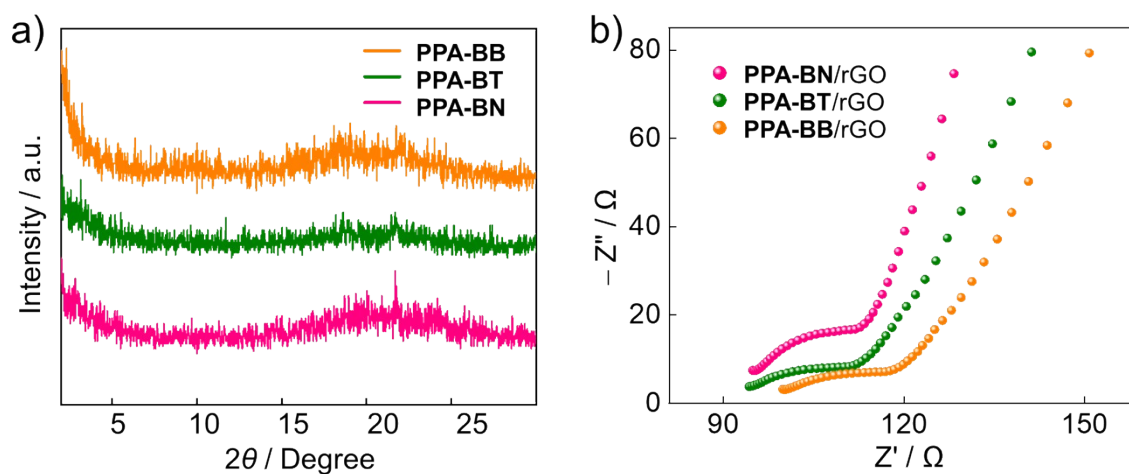


Fig. S4 a) Powder X-ray diffraction patterns of **PPA-BB**, **PPA-BT**, and **PPA-BN**. b) EIS spectra of **PPA-BB/rGO**, **PPA-BT/rGO**, **PPA-BN/rGO**.

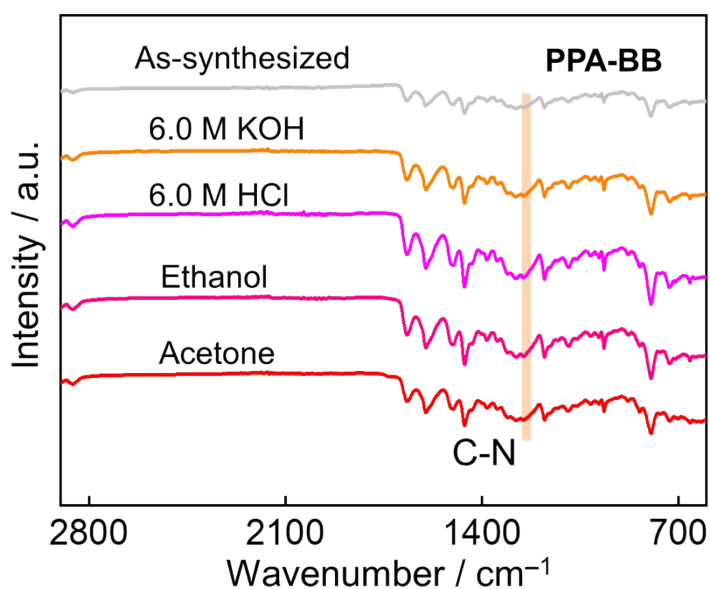


Fig. S5 FT-IR of **PPA-BB** before and after treatment under 6.0 M KOH, 6.0 M HCl, ethanol and acetone for 3 days.

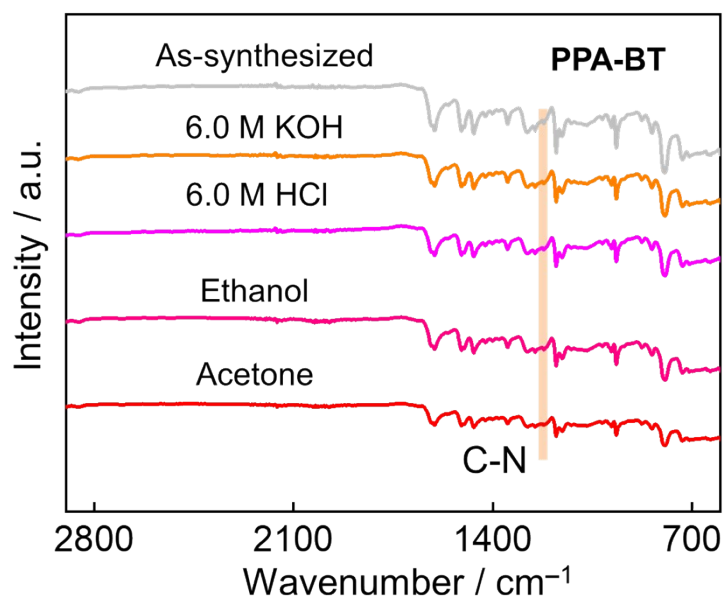


Fig. S6 FT-IR of **PPA-BT** before and after treatment under 6.0 M KOH, 6.0 M HCl, ethanol, and acetone for 3 days.

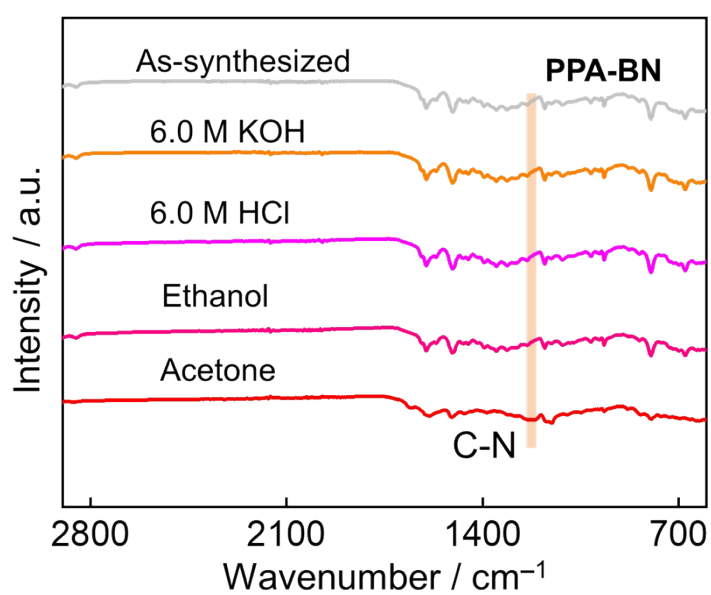


Fig. S7 FT-IR of **PPA-BN** before and after treatment under 6.0 M KOH, 6.0 M HCl, ethanol, and acetone for 3 days.

## 2. Electrochemical performance

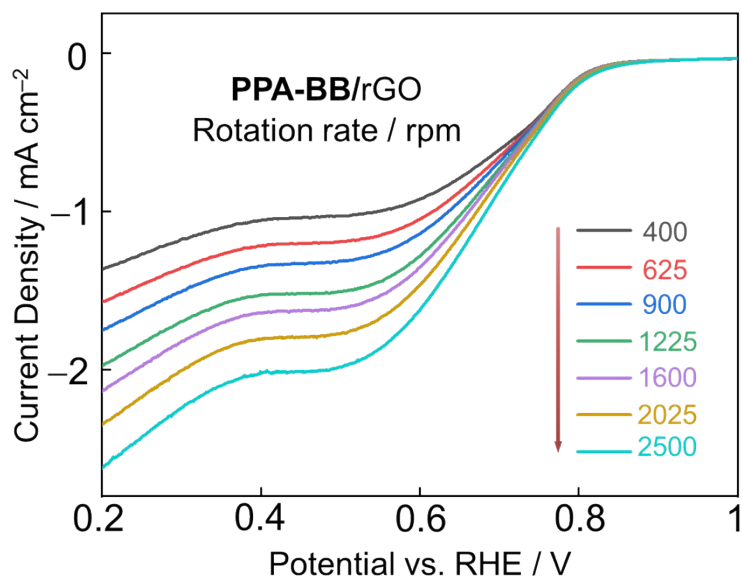


Fig. S8 LSV curves of **PPA-BB/rGO** from 400 to 2500 rpm.

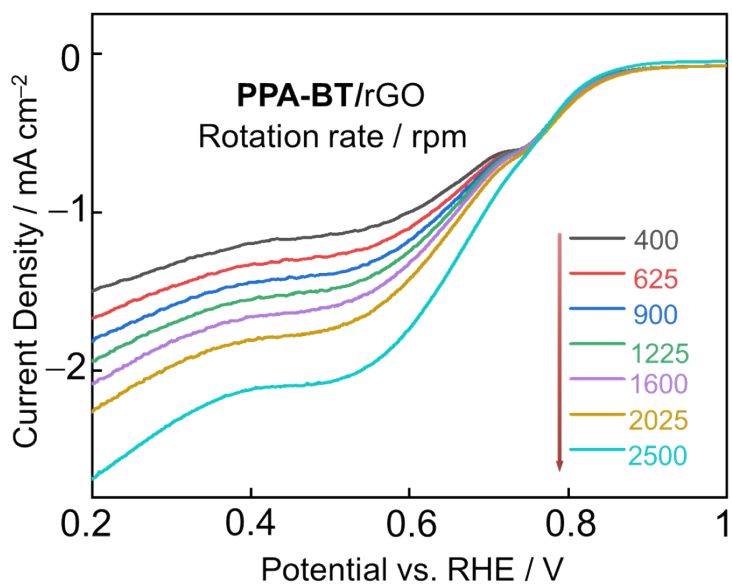


Fig. S9 LSV curves of **PPA-BT/rGO** from 400 to 2500 rpm.

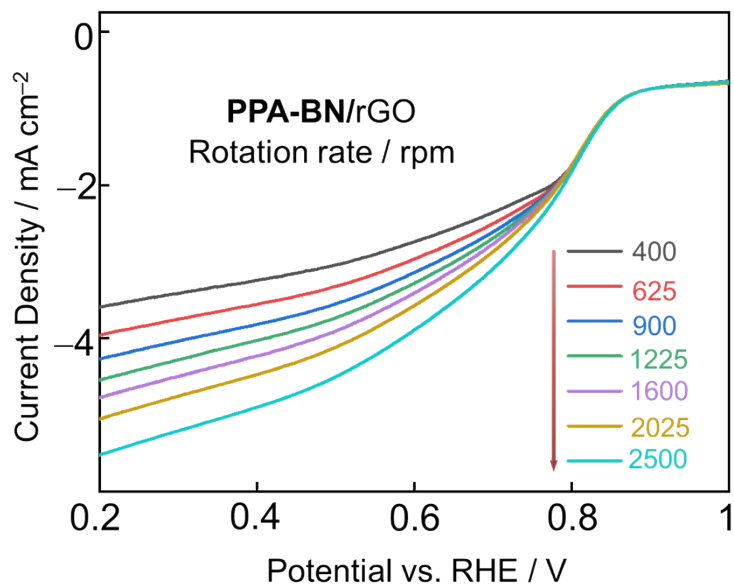


Fig. S10 LSV curves of **PPA-BN/rGO** from 400 to 2500 rpm.

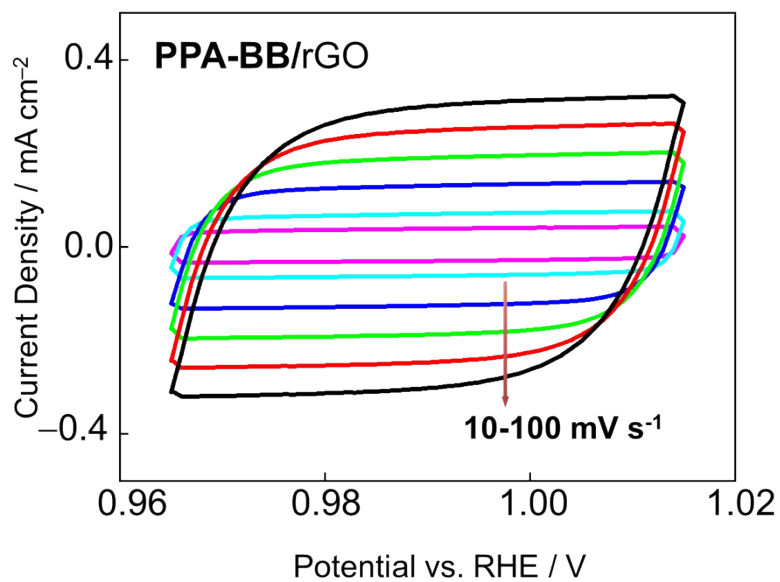


Fig. S11 CV curves of **PPA-BB/rGO** with the scan rate from 10 mV s<sup>-1</sup> to 100 mV s<sup>-1</sup>.

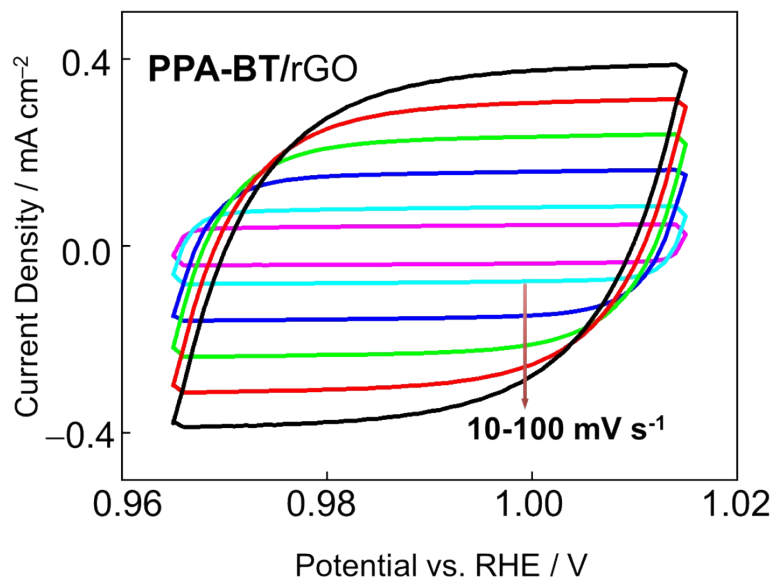


Fig. S12 CV curves of **PPA-BT/rGO** with the scan rate from 10 mV s<sup>-1</sup> to 100 mV s<sup>-1</sup>.

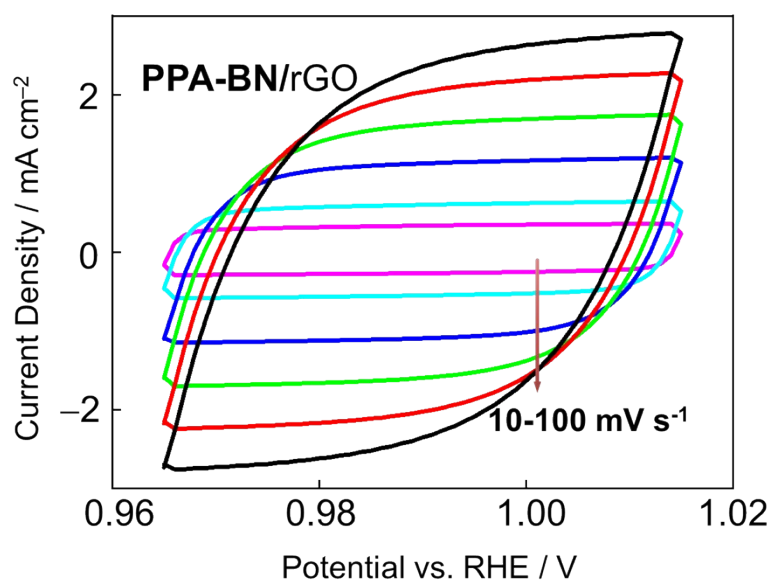


Fig. S13 CV curves of **PPA-BN/rGO** with the scan rate from 10 mV s<sup>-1</sup> to 100 mV s<sup>-1</sup>.

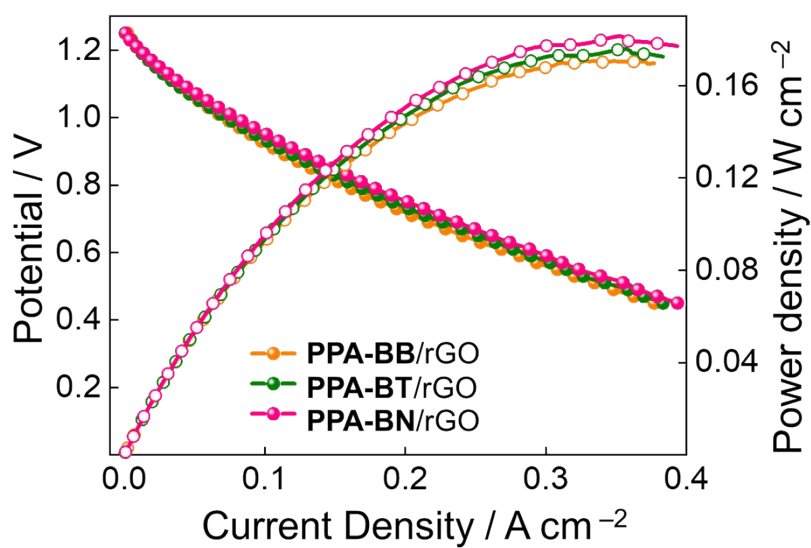


Fig. S14 Discharge polarization curve and corresponding power density plot of **PPA-BB/rGO**, **PPA-BT/rGO**, and **PPA-BN/rGO**.

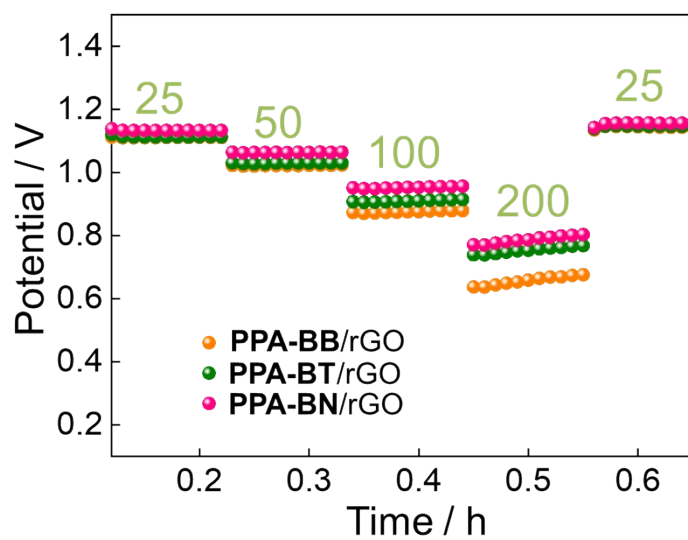


Fig. S15 Discharge curves of **PPA-BB/rGO**, **PPA-BT/rGO**, and **PPA-BN/rGO** based ZABs at different current densities (25, 50, 100, 200  $\text{mA cm}^{-2}$ ).



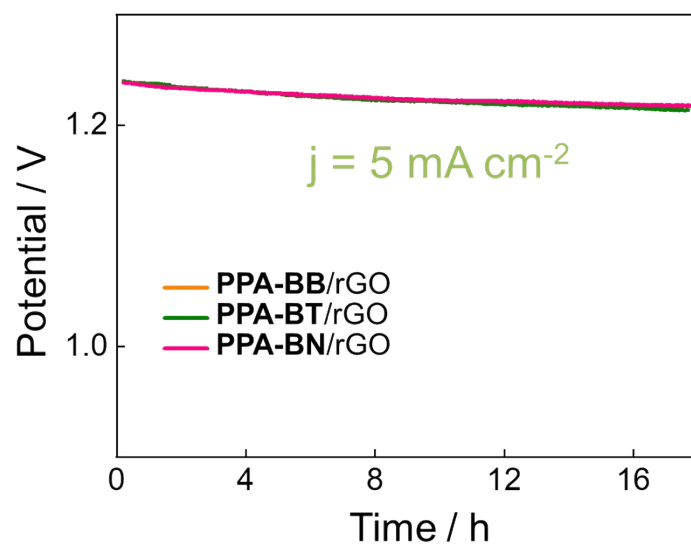


Fig. S16 Galvanostatic discharge curve of **PPA-BB/rGO**, **PPA-BT/rGO**, and **PPA-BN/rGO** based ZABs (6.0 M KOH electrolyte).

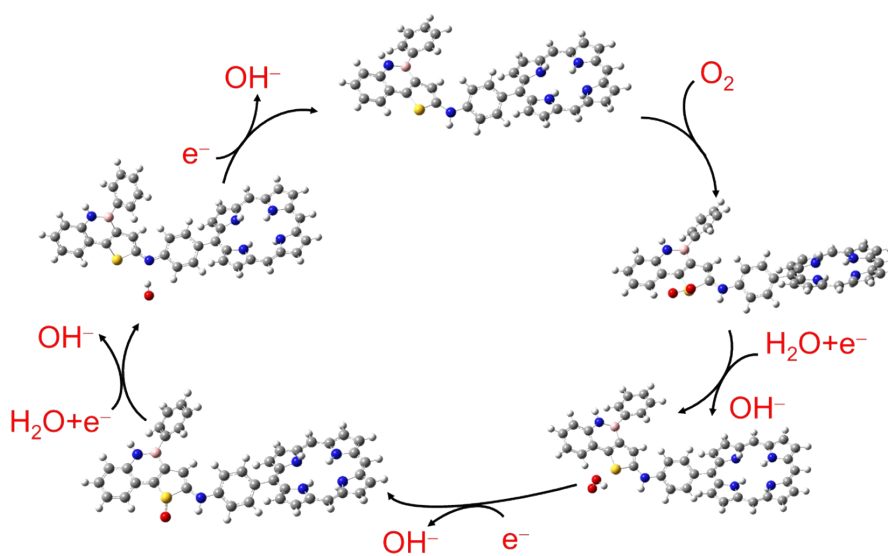


Fig. S17 Theoretical ORR catalytic process of active site-5 in **PPA-BN**.

Table S1. The free energy values of different sites in **PPA-BN**.

Site	1	2	3	4	5	6
Overpotential	1.85	3.12	1.01	0.74	0.71	0.93
$\Delta G1$	0.21	1.36	0.81	0.56	0.71	0.93
$\Delta G2$	-2.44	-3.59	-1.58	-1.39	-0.79	-1.02
$\Delta G3$	1.85	3.12	1.01	-0.74	-0.63	0.45
$\Delta G4$	-0.38	-0.89	-0.24	0.09	0.71	-0.36

Table S2. The free energy values of different sites in **PPA-BT**.

Site	2	3	4	5	6
Overpotential	1.32	1.21		0.78	0.77
$\Delta G1$	0.88	0.93		0.49	0.72
$\Delta G2$	-1.89	-1.71		-0.58	-1.31
$\Delta G3$	1.32	1.21		-0.70	0.77
$\Delta G4$	-0.32	-0.43		0.78	-0.18

Table S3. The free energy values of different sites in **PPA-BB**.

Site	2	3	4	5	6
Overpotential	1.29	1.01	1.16	1.12	1.32
$\Delta G1$	1.29	1.01	1.16	1.12	1.32
$\Delta G2$	-1.47	-1.02	-1.20	-1.12	-1.11
$\Delta G3$	0.90	0.64	0.66	-0.67	0.61
$\Delta G4$	-0.73	-0.63	-0.60	0.67	-0.83

### 3. NMR spectra

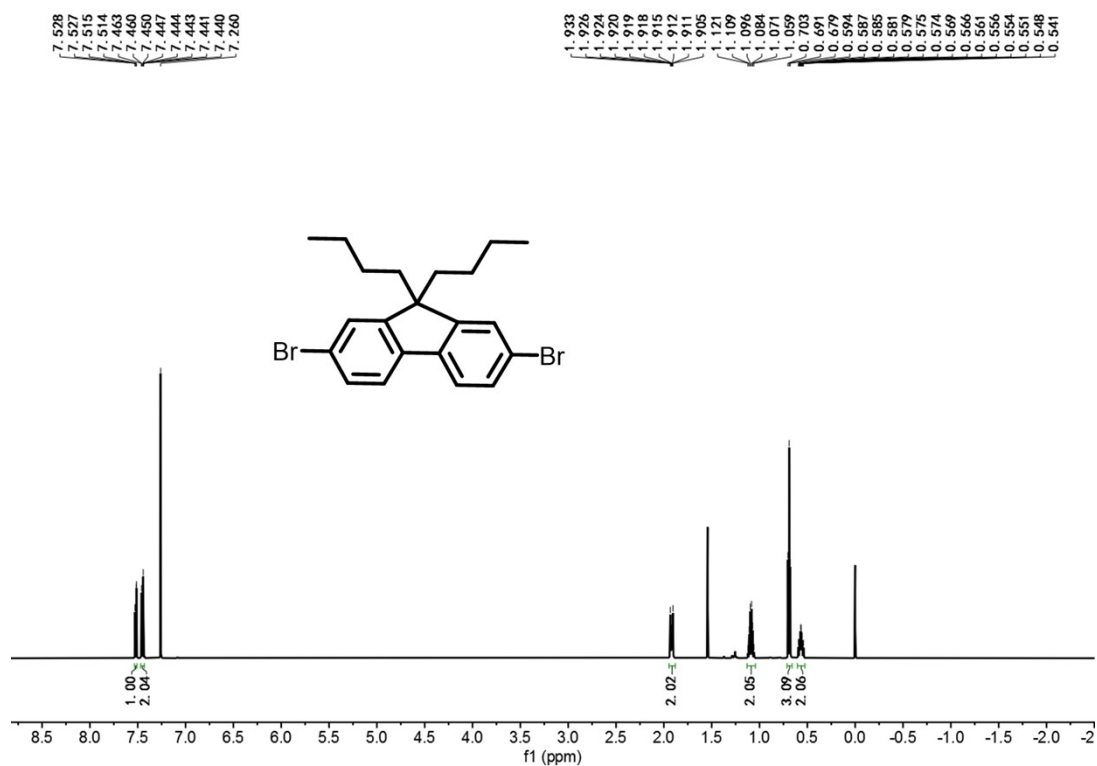


Fig. S18. <sup>1</sup>H NMR spectrum of BB.

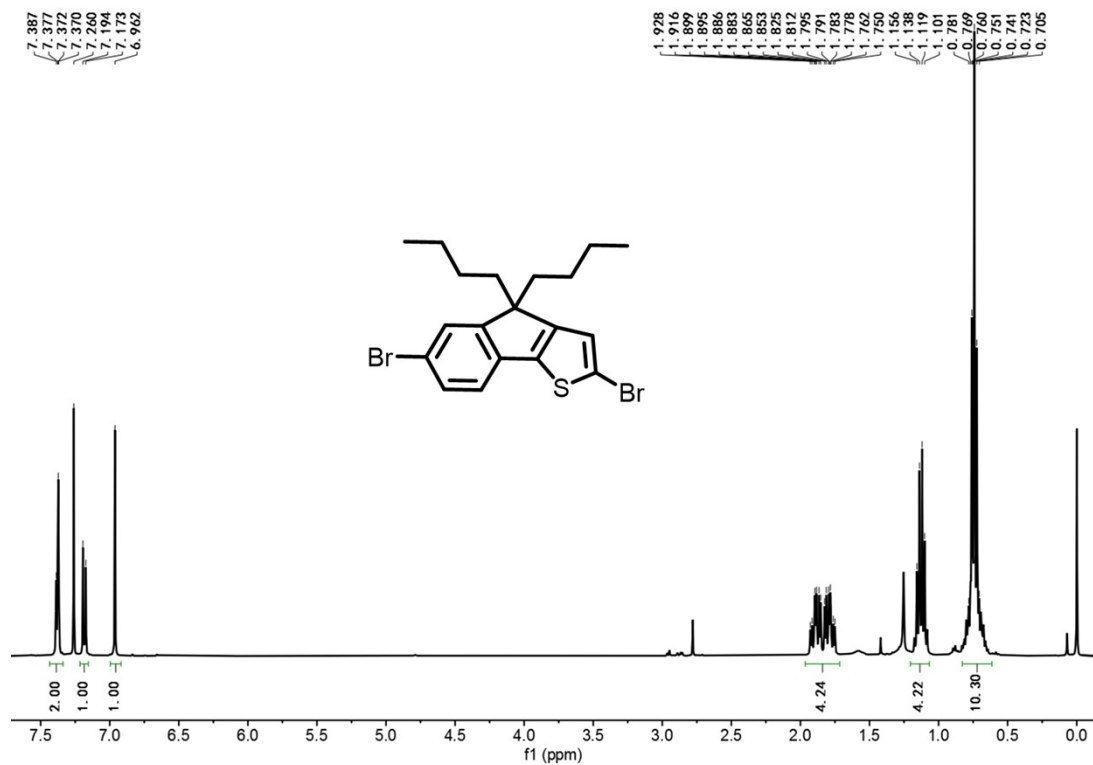


Fig. S19. <sup>1</sup>H NMR spectrum of BT.

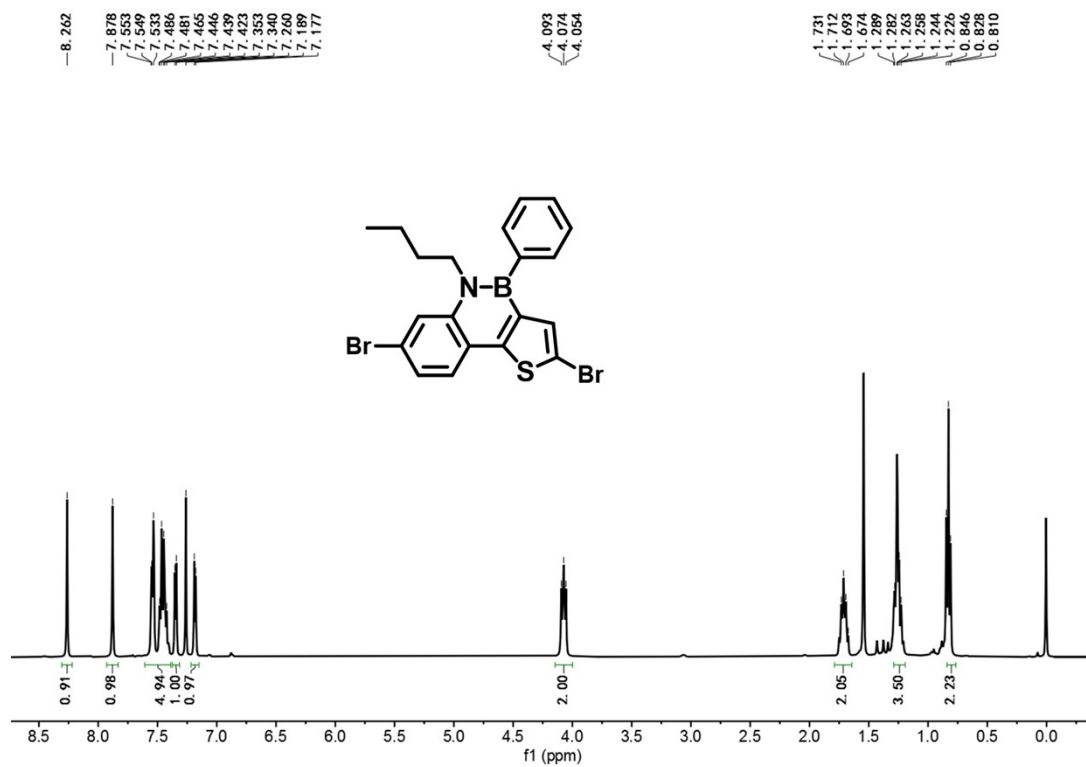


Fig. S20. <sup>1</sup>H NMR spectrum of BN.