Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Redox-active and Semi-conducting Donor-Acceptor Conjugated Microporous Polymers as Metal-free ORR Catalysts

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Physical Measurements

Infrared spectral studies were performed by making samples with KBr pellets using Bruker FT-IR spectrometer. Thermal stability of **TPA-BP-1** and **TPA-TPE-2** is analyzed using Mettler Toledo TGA 850 instrument under inert atmosphere in the temperature range of 25-850 °C at a heating rate of 3 °C /min. The elemental analyses were carried out using a Thermo Scientific Flash 2000 CHN analyzer. Fourier Transform Infrared (FTIR) spectra were recorded by making sample with KBr pellets using Bruker FT-IR spectrometer. Powder X-ray diffraction studies were recorded on a Bruker D8 discover instrument using Cu-Kα radiation. Morphological studies have been carried out using Lica-S440I Field Emission Scanning Electron Microscope (FESEM) by placing samples on a silicon wafer under high vacuum with an accelerating voltage of 10 kV. Transmission Electron Microscopy (TEM) analysis has been performed using JEOL JEM-3010 with an accelerating voltage at 300 kV. For this analysis **TPA-BP-1** and **TPA-TPE-2** were dispersed in ethanol by sonication before drop casting on a carbon-coated copper grid. Solid state ^{13}C cross-polarization magnetic angle spinning (CP/MAS) NMR spectrum measured on a varian infinity plus 300WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 1.4 ms. ^{1}H-NMR is recorded on a Bruker AV-400 spectrometer with chemical shifts reported as ppm.

Adsorption Measurements

Porosity measurements were carried out using QUNATACHROME QUADRASORD-SI analyser at 87 K for Ar and 195 K for CO_2. In the sample tube the adsorbent samples (~100-150 mg) were placed which had been prepared at 170 °C under a 1×10^{-1} Pa vacuum for about 12 h prior to measurement of the isotherms. Helium gas (99.999% purity) at a certain pressure was introduced in the gas chamber and allowed to diffuse into the sample chamber by opening the valve. The amount of gas adsorbed was calculated from the pressure difference (P_{cal}-P_e), where

P_{cal} is the calculated pressure with no gas adsorption and P_e is the observed equilibrium pressure. All the operations were computer-controlled and automatic.

Conductivity Measurements

For conductivity measurement, thin films of **TPA-BP-1** and **TPA-TPE-2** were prepared on glass substrates by spin coating method at 1200 rpm for 2 min. Two ohmic parallel electrodes were taken from the film. The dimensions of the electrodes were of 9 mm × 1 mm and the gap between two electrodes was 1mm. For conductivity measurement, a two-probe contact method was adopted to obtain a current voltage (I-V) characteristics graph, where the electrodes were connected with a Keithley 2400 source meter. The process was performed under room temperature and in open atmosphere. The conductivity was measured with the help of the slope of linear fitted I-V curve, by using equation: $\sigma = \left(\frac{\Delta I}{\Delta V}\right)\left(\frac{l}{A}\right)$

Where, σ is the conductivity, I the current, V the applied voltage, l is the distance between electrodes, A is the cross sectional area of sample.

Computational Details

We have used Gaussian 09 software[1] for all the calculations, considering M06-2X functional[2] and 6-31+G(d,p) basis set for optimization. For the energy and electronic property calculations, we have used a higher basis set of 6-311+G(d,p). M06-2X functional takes care of the long range dispersion interactions and charge transfer interactions in these systems.

Electrochemical Measurements

Electrochemical performance of TPA-BP-1 and TPA-TPE-2 was measured by using rotating disk electrode (RDE) voltammetry and rotating ring disk electrode (RRDE) voltammetry. The electrochemical measurements were performed using an Autolab PGSTAT12 potentiostat/galvanostat in a conventional three-electrode cell in combination with a Metrohm RDE-2 rotator. The catalyst inks were prepared at a concentration of 5 mg mL^{-1} of CMP and 5 mg mL^{-1} of vulcan carbon in a mixture of milliQ water, isopropanol, and Nafion (5 wt %, Sigma Aldrich) in the volume ratio of 48:48:4 as dispersion solvent. The mixture was then sonicated for

1 hour to obtain a well-dispersed suspension. Glassy carbon electrodes (4 mm diameter) were used as rotating disk electrodes (RDEs). Before experiment, the glassy carbon electrodes were polished on a polishing cloth, using different alumina pastes (3.0 to 0.05 μm) to obtain a mirror-like surface, followed by ultrasonic cleaning in water. About 5 μL of the catalyst ink was drop-cast on a glassy carbon electrode and left overnight to dry under ambient conditions. The catalyst loading for each electrode was about 350 $\mu g cm^{-2}$. A 0.1 M KOH aqueous solution was used as electrolyte. The counter and reference electrodes were a platinum foil and an Ag/AgCl/3M KCl electrode, respectively. The reference electrode was calibrated with respect to the reversible hydrogen electrode (RHE). Electrochemical impedance spectroscopy was recorded at the corresponding open circuit potential using an AC perturbation of 10 mV in the frequency range from 50 kHz to 1 Hz. The solution resistance was determined from the resulting Nyquist plot, and later used for ohmic drop correction according to the relation,

$$E_c = E_m - iR_s,$$

Where, E_c is the corrected potential and E_m is the measured potential. All current densities were calculated using the geometric surface area of the electrode. All potentials were rescaled to the pH-independent reversible hydrogen electrode (RHE). The long-term stability was evaluated chronopotentiometrically at a current density of -1 mA cm^{-2} on a graphite rotating disk electrode (5 mm diameter) modified with the catalyst in 0.1 M KOH solution. During the measurements, the electrode was maintained at a rotation of 900 rpm to avoid accumulation of gas bubbles on the electrode surface. The electrolyte was purged for ~30 min with Ar prior to measurements to determine the background current, and later O_2 flow was maintained over the electrolyte throughout the timeframe of the experiment. All measurements were carried out at room temperature. Linear sweep voltammetry (LSV) was performed at rotation speeds of 400, 900, 1600, 2500 and 3600 rpm at a sweep rate of 10 mV s^{-1}. The number of electrons involved in the reduction process was calculated using the Koutecký–Levich (K–L) equation:

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_K}$$

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

$$j_K = nF\kappa C_o$$

where, j is the measured current density, j_K and j_L are the kinetic and diffusion-limited current densities, ω is the angular frequency of the RDE in radians per second, n is the number of electrons involved in the reaction, F is the Faraday constant (96485 C mol^{-1}), D_0 is the diffusion coefficient of O_2 in the electrolyte (1.93×10^{-5} cm^2 s^{-1}), v is the kinematic viscosity of the electrolyte (1.01×10^{-2} cm^2 s^{-1}), C_0 is the concentration of O_2 in the electrolyte (1.26×10^{-6} mol cm^{-3}) and k is the electron transfer rate constant. Rotating ring disk electrode (RRDE) voltammetry was used to calculate the number of electrons and the amount of H_2O_2 formed during ORR based on the ratio of the disk and the ring current as shown in the equations given below. For the RRDE experiments, the ring electrode was held at a potential of 1.5 V (vs. RHE) to oxidize hydrogen peroxide.

$$n_e = \frac{4I_D}{I_D + \frac{I_R}{N}}$$

$$H_2O_2(\%) = \frac{\frac{I_R}{N}}{I_D + \frac{I_R}{N}} \times 200$$

Where, N = 0.2678 is the collection efficiency, I_D is the Faradaic disk current, and I_R is the Faradaic ring.

Experimental Section

1. **Material and Methods**

All reagents and chemicals were purchased from Sigma-Aldrich chemical Co. Ltd. and used without further purification. Solvents used were purified by standard procedures.

2. Synthesis

2.1 Synthesis of TPA-BP-1

4, 4’-diethynylbiphenyl was synthesized according to reported procedures.[3] The Sonogoshira–Hagihara coupling reaction of Tris (4-bromophenyl)amine ($TPABr_3$) and 4, 4’-diethynylbiphenyl in N, N’-dimethylformamide (DMF) resulted in the desired conjugated microporous polymer. $TPABr_3$ (0.126 mmol, 60 mg) and 4,4’-diethynylbiphenyl (0.37 mmol,75 mg) were weighed and taken in a 25 mL schlenck flask. They were then dissolved in 5 mL dry DMF and 2mL triethylamine, and the mixture was degassed by three vacuum cycles and purged with nitrogen. To this, $Pd(PPh_3)_4$ (0.037 mmol, 43 mg) and CuI (0.078 mmol, 12mg) were added under continuous nitrogen flow. The reaction mixture was refluxed for 24 h at 140 °C under nitrogen atmosphere and cooled to room temperature. The yellow precipitates were collected through filtration and washed with methanol and THF. Further purification was done using Soxhlet extraction to remove traces of catalysts with methanol for 96 h. Yield 75%, 84 mg.

2.2 Synthesis of TPA-TPE-2

1, 1, 2, 2-tetrakis-(4-ethynylphenyl)ethene was synthesized according to reported procedures.[4] The Sonogoshira- Hagihara coupling reaction of 1, 1, 2, 2-tetrakis (4-ethynylphenyl)ethene and $TPABr_3$ in N, N’-dimethylformamide (DMF) and triethylamine (Et_3N) resulted in the desired conjugated microporous polymer. TPE triple bond precursor (0.105 mmol, 45 mg) and $TPABr_3$ (0.139 mmol, 67 mg) were weighed and taken in a 25 ml schlenk flask. They were then dissolved in 3 mL of dry DMF and 1.5 mL of anhydrous triethylamine, and the mixture was degassed by three vacuum cycles and purged with nitrogen. To this, $Pd(PPh_3)_4$ (0.018 mmol, 21 mg) and CuI (0.052 mmol, 8mg) were added under continuous nitrogen flow. The reaction mixture was refluxed for 28 h at 140 °C under nitrogen atmosphere and cooled to room temperature. The yellow precipitates were collected through filtration and washed with methanol and THF. Further purification was done using Soxhlet extraction to remove traces of catalysts with methanol and THF for 48 h each. Yield is 85%, 142 mg.

IR Spectra

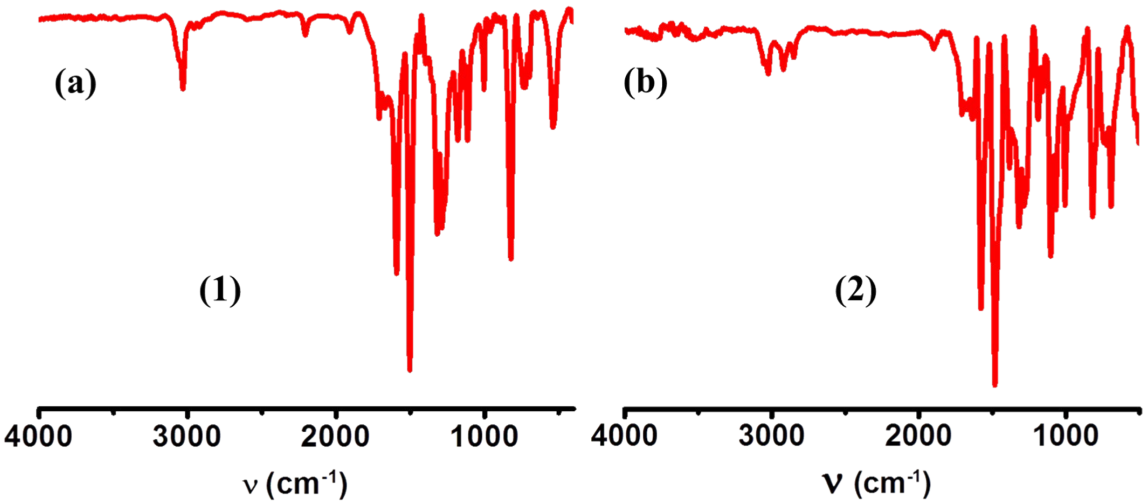

Figure S1. IR spectrum of (a) **TPA-BP-1** and (b) **TPA-TPE-2.**

PXRD

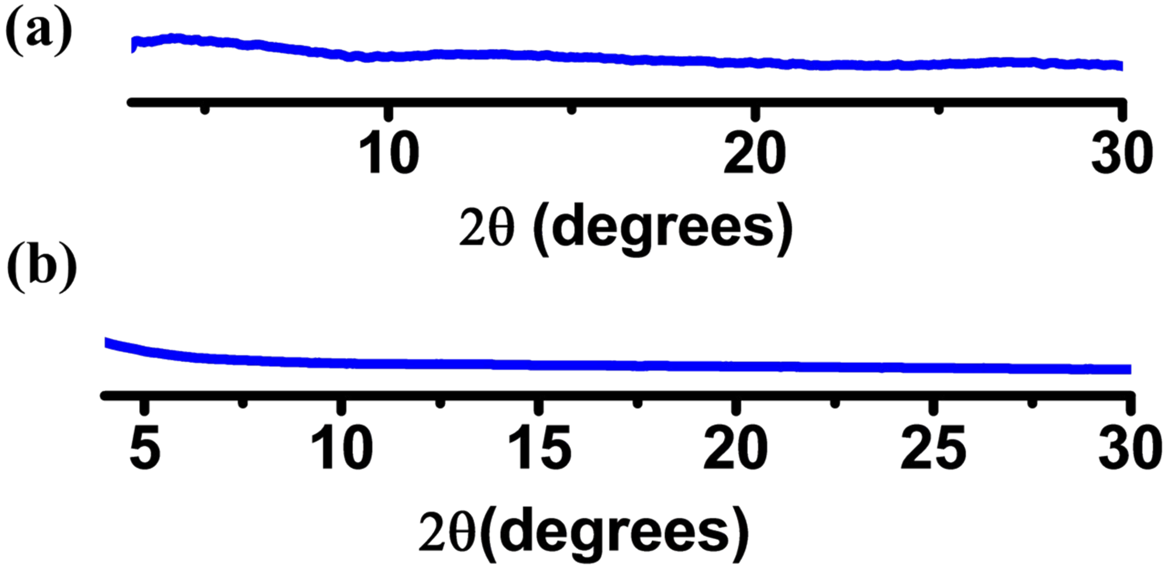

Figure S2. PXRD of (a) **TPA-BP-1** and (b) **TPA-TPE-2.**

FESEM

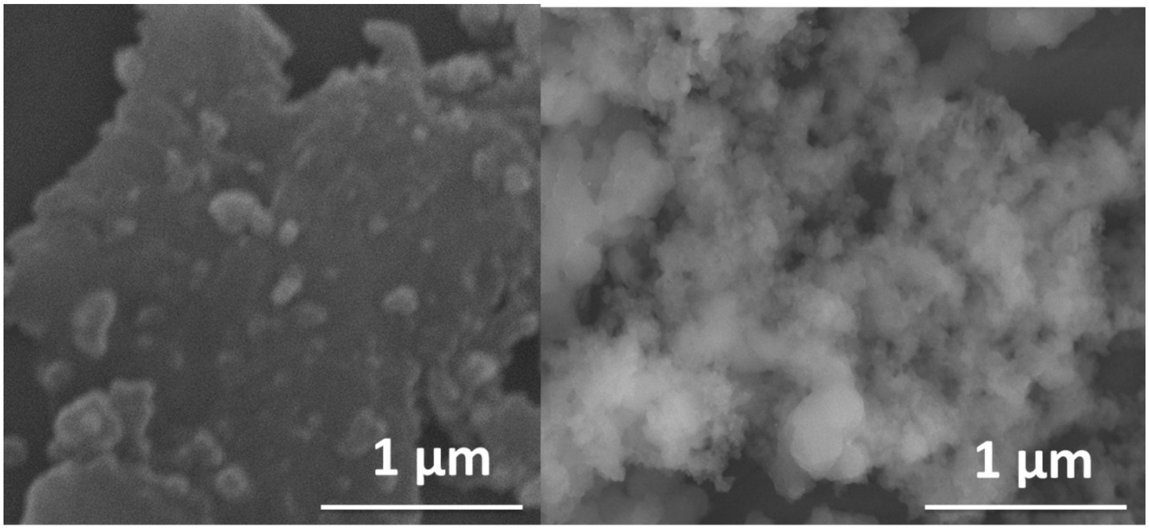

Figure S3. FESEM images of (a) **TPA-BP-1** and (b) **TPA-TPE-2.**

TGA

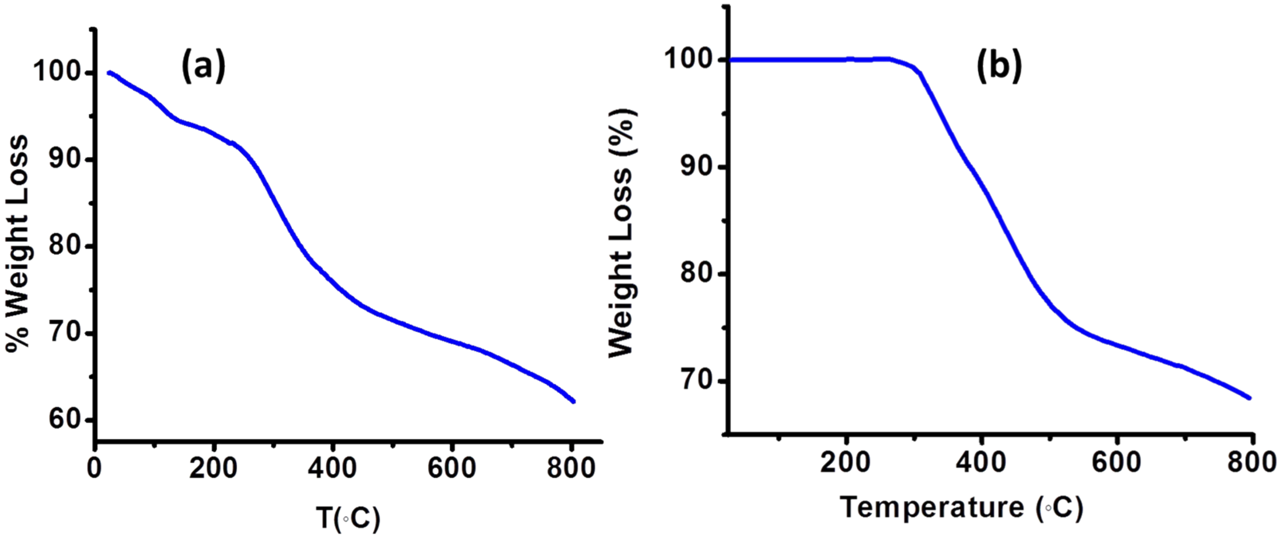

Figure S4. TG curves of (a) **TPA-BP-1** and (b) **TPA-TPE-2**.

Pore Size Distribution plots

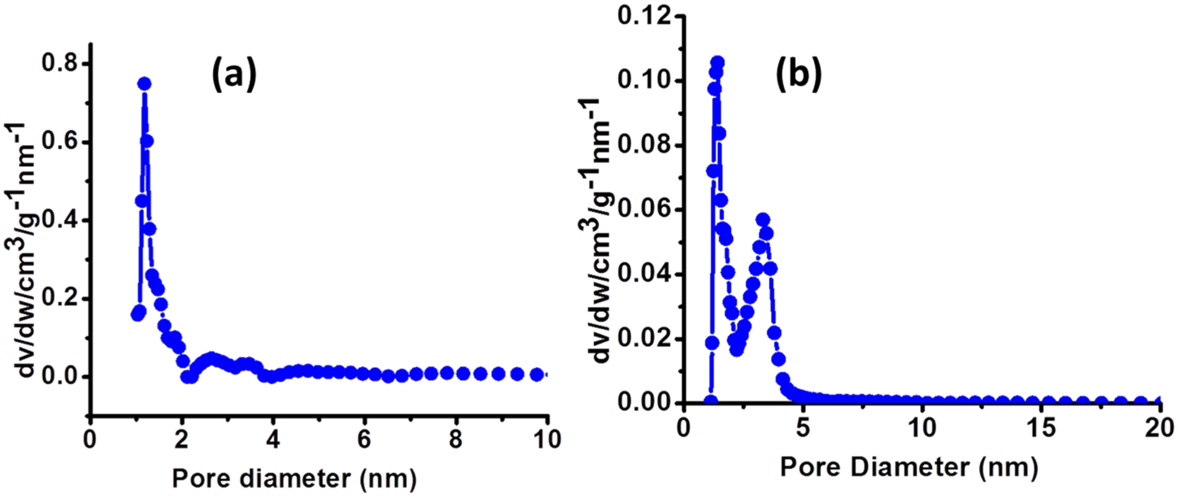

Figure S5. Pore size distribution curves of (a) **TPA-BP-1** and (b) **TPA-TPE-2**.

Geometry optimization of CMP building units

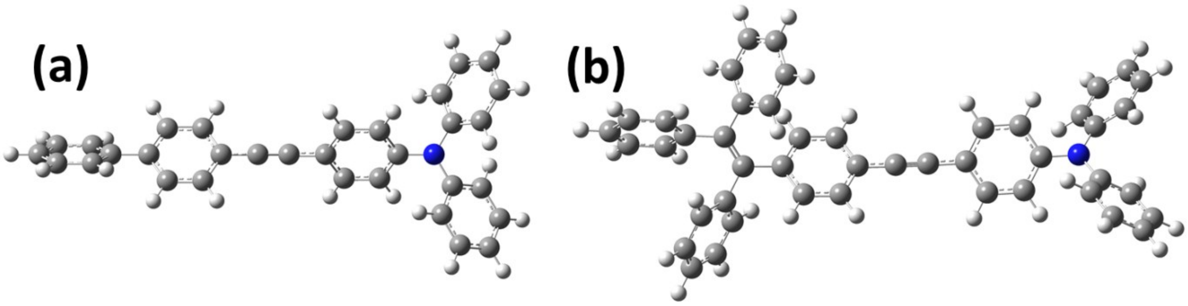

Figure S6. Optimized structures of the monomers of (a) **TPA-BP-1** and (b) **TPA-TPE-2**.

Cyclic Voltammetry

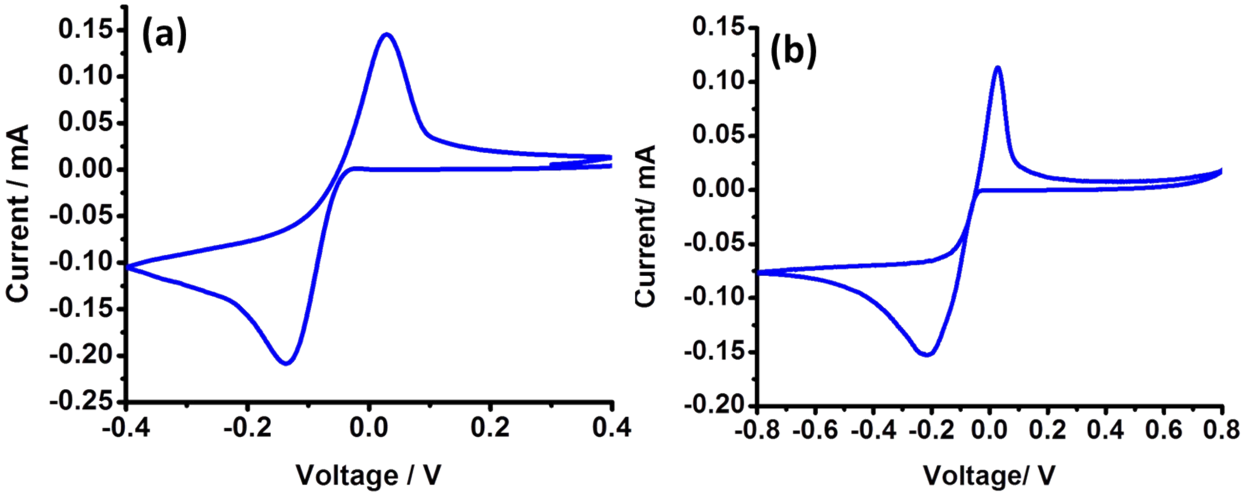

Figure S7. Cyclic voltammogram of (a) **TPA-BP-1** and (b) **TPA-TPE-2** on a glassy carbon electrode in anhydrous acetonitrile solution containing TBAP as a supporting electrolyte at a scan rate of 50 mV/sec.

As the cyclic voltammogram was obtained under non-aqueous conditions, Ag/Ag$^+$ reference electrode was used and hence conversion into RHE voltages was required to carry out the band gap calculations. The following standard equation was used for the conversion:

$$E_{RHE}=E_{Ag/Ag+} + E + 0.059*pH\ldots\ldots(1) \text{ where}$$

E_{RHE}= the corresponding potential for RHE

$E_{Ag/Ag+}$= the standard electrode potential for the Ag/Ag$^+$ couple

and E= the observed potential using the Ag/Ag$^+$ couple

For TPA-BP-1

Using the above equation, the onset oxidation and reduction potentials were found to be 1.240 and 0.952 V, respectively.

$$E_{oxRHE}=0.799 + 0.028 + 0.413 = 1.240 \text{ V}$$

$$E_{redRHE}=0.799 - 0.26+ 0.413 = 0.952 \text{ V}$$

Hereon, the following formula was utilized to determine the experimental electrochemical HOMO and LUMO levels in terms of eV unit:

$$E\,(\mathrm{HOMO}) = -e\,[E_{ox}^{onset} + 4.4] \ldots..(2)$$

$$E\,(\mathrm{LUMO}) = -e\,[E_{red}^{onset} + 4.4] \ldots\ (3)$$

And the HOMO and LUMO levels were found to be -5.23 and -3.03 eV respectively having a band gap of 2.19 eV.

$$E\,(\mathrm{HOMO}) = -e\,[1.342 - 0.41 + 4.4] = -5.23\ \mathrm{eV}$$

$$E\,(\mathrm{LUMO}) = -e\,[-0.842 - 0.41 + 4.4] = -3.03\ \mathrm{eV}$$

For TPA-TPE-2

Using the above equation, the onset oxidation and reduction potentials were found to be 1.242 and 0.762 V respectively.

$$E_{oxRHE} = 0.799 + 0.03 + 0.413 = 1.242\ \mathrm{V}$$

$$E_{redRHE} = 0.799 - 0.45 + 0.413 = 0.762\ \mathrm{V}$$

Hereon, the following formula was utilized to determine the experimental electrochemical HOMO and LUMO levels in terms of eV unit:

$$E\,(\mathrm{HOMO}) = -e\,[E_{ox}^{onset} + 4.4] \ldots..(2)$$

$$E\,(\mathrm{LUMO}) = -e\,[E_{red}^{onset} + 4.4] \ldots\ (3)$$

And the HOMO and LUMO levels were found to be -5.23 and -3.53 eV respectively having a band gap of 1.69 eV.

$$E\,(\mathrm{HOMO}) = -e\,[1.342 - 0.41 + 4.4] = -5.232\ \mathrm{eV}$$

$$E\,(\mathrm{LUMO}) = -e\,[-0.842 - 0.41 + 4.4] = -3.538\ \mathrm{eV}$$

Koutechy-Levich Plots

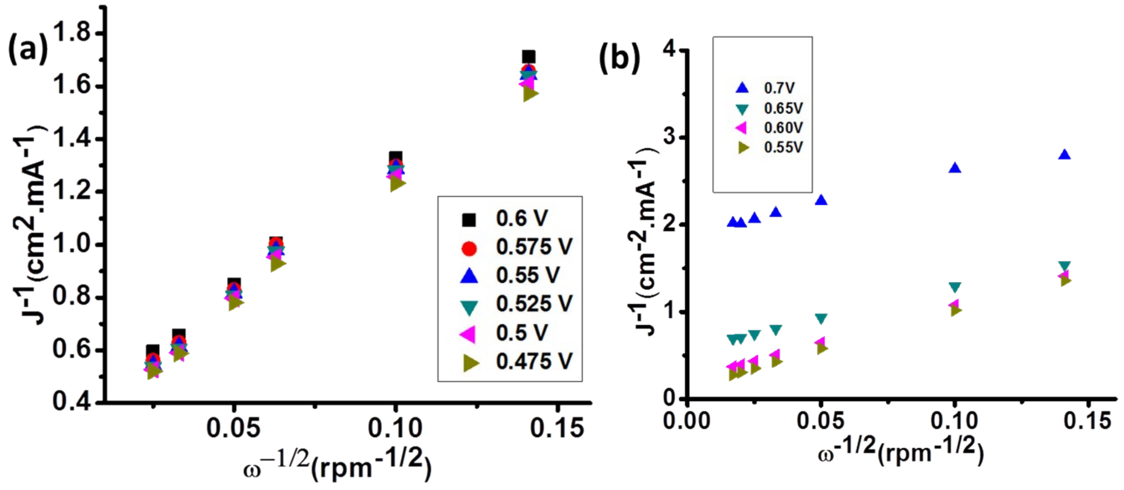

Figure S8. K-L plot of (a) **TPA-BP-1** and (b) **TPA-TPE-2** showing good parallelism and linearity.

RRDE plots

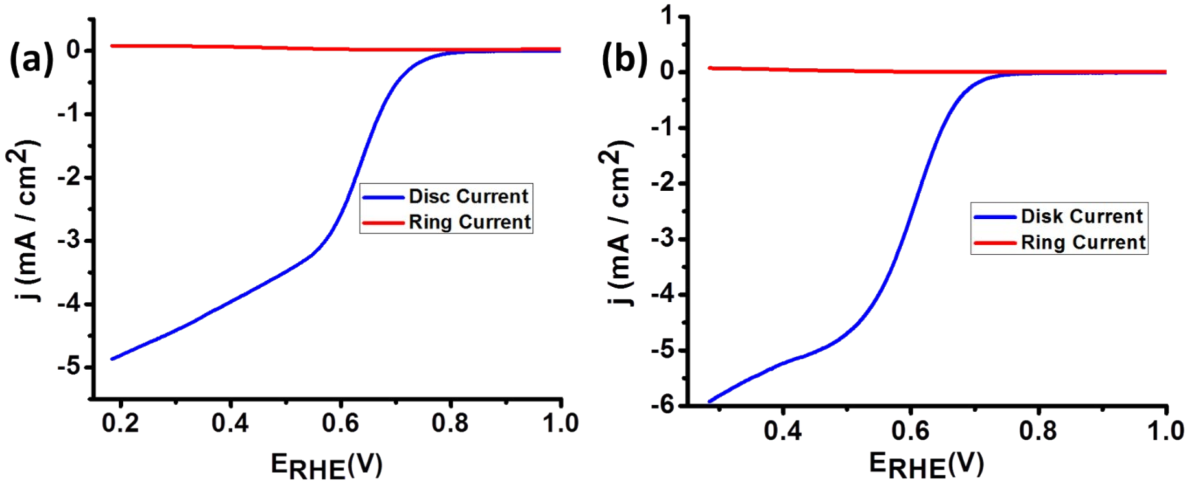

Figure S9. RRDE plots (a) **TPA-BP-1** and (b) **TPA-TPE-2** showing the change in disk and ring currents on oxygen reduction.

O_2 binding calculations

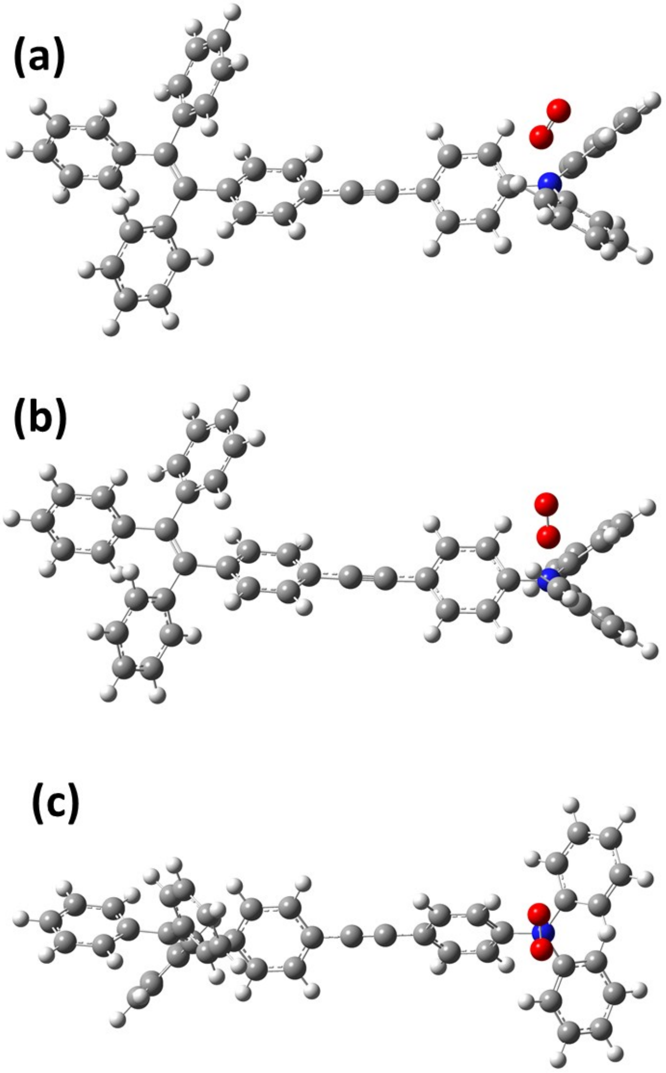

Figure S10. (a) O_2 binding modes on the modeled structures used for the calculation in (a) bent (b) head-on and (c) side-on fashion.

Table showing the importance of metal-free and assynthesized electrochemical performance of TPA-BP-1 and TPA-TPE-2

Table S1. Comparison of the several porous organic and hybrid materials showing ORR activity.

Name	**Material**	**Post-synthetic modification**	**Metal-free**	**High stability and low overpotential**	**Reference**
$Ni_3(HITP)_2$	MOF	No	No	Yes	5
(700, 800.900)-N,P-CNT	CNT coated COF	Yes	Yes	Yes	6a
Co-COF	Metallated COF	No	No	Yes	6e
PTEB	Pyrolized CMP	Yes	Yes	Yes	6h
M-CMPs	Pyrolyzed MoS_2 templated CMPs	Yes	Yes	Yes	6a
CMP-DBN	CMPs pyrolyzed to generate B and N co doped porous carbons	Yes	Yes	Yes	6b
CoP-CMP	Pyrolyzed	Yes	No	Yes	6c
TPA-BP-1 and TPA-TPE-2	Prisitne CMPs	No	Yes	Yes	This work

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