Supplementary Information

Hydroxide Ion Conducting Polymer Organic Frameworks for Flexible Solid-State Zinc-Air Battery Applications

Deepak Rase,^{a,b†} Rajith Illathvalappil,^{a,b†} Himan Dev Singh,^{a,b} Pragalbh Shekhar,^{a,b} Liya S Leo,^{a,b} Debanjan Chakraborty, ^a Sattwick Haldar, ^{a,b} Ankita Shelke ^c, Thalasseril G. Ajithkumar ^cand Ramanathan Vaidhyanathan*^{a,b}

^aDepartment of Chemistry, Indian Institute of Science Education and Research, Dr. Homi Bhabha Road, Pashan, Pune 411008, India. ^bCentre for Energy Science, Indian Institute of Science Education and Research, Dr. Homi Bhabha Road, Pashan, Pune 411008, India. ^cCentral NMR Facility and Physical/Materials Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India. [†] D. R and R. I contributed equally to this work.

1. Materials and methods:

4-(bromomethyl) benzonitrile, Diisobutylaluminium hydride and Aluminium chloride were purchased from Spectrochem Pvt. Ltd. ; 4,4'-Bipyridine was purchased from TCI Chemicals (India) Pvt. Ltd. All other reagents were of analytical grade. All chemicals were used without any further purification.

Thermo-gravimetric analysis:

Thermo-gravimetric analysis was carried out on NETSZCH TGA-DSC system. The TGAs were performed under N_2 gas flow (20 mL/min) (purge + protective) and samples were heated from room temperature to 550 °C at a ramp rate of 5 °C/min.

¹³C Solid-State Nuclear Magnetic Resonance (NMR) Spectroscopy:

High-resolution solid-state NMR spectrum was recorded at ambient pressure on a Bruker AVANCE III spectrometer using a standard CP-TOSS pulse sequence (cross polarization with total suppression of sidebands) probe with 4 mm (outside diameter) zirconia rotors.

Infra-Red Spectroscopy:

IR spectra were obtained using a Nicolet ID5 attenuated total reflectance IR spectrometer operating at ambient temperature. The solid-state IR spectra were recorded using KBr pellets as background.

Ultra-violet Spectroscopy:

Diffused reflectance spectra of the polymer powders in the UV–visible region are recorded using a Shimadzu UV-3600 plus UV–vis–NIR spectrophotometer. Then KubelkaMunk transformation is used for the analysis of diffuse reflectance spectra. It relates the reflectance data with absorption coefficient as in equation (1): $F(R) = \alpha/S = (1-R)^2$ /2R (1) where F(R) is the Kubelka-Munk function, R is reflectance, α is absorption coefficient and S is the scattering factor.

Field Emission-Scanning Electron Microscopy (FESEM):

Electron Microscope with integral charge compensator and embedded EsB and AsB detectors. Oxford Xmax instruments 80 mm². (Carl Zeiss NTS, Gmbh), Imaging conditions: 2kV, WD= 2 mm, 200 kX, Inlens detector. For SEM images, as an initial preparation, the samples were ground thoroughly, soaked in ethanol for 30 min. and were sonicated for 2 h. These well dispersed samples were drop-casted on the silicon wafer and dried under vacuum for 12 h.

High resolution Transmission Electron Microscopy (HR-TEM):

Transmission electron microscopy (TEM) was performed using a JEM 2200FS TEM microscope operating at an accelerating voltage of 200 kV). The diffractograms were recorded at a scanning rate of 1° min⁻¹ between 20° and 80° .

Adsorption study

Adsorption studies were carried out using a Micromeritics 3-FLEX pore and surface area analyser.

Electrochemical Measurements:

The linear sweep voltammetry and the constant current charge-discharge measurements were performed using the AMETEK Battery analyzer using VERSA STUDIO (Version 2.52) software.

Impedance measurements:

The Solartron SI 1260 IMPEDANCE/GAIN-PHASE ANALYZER model was used to carry out the impedance measurement. The impedance spectra were recorded by applying a range of frequencies from 1 MHz to 0.1 Hz with an amplitude of 10 mV. Moreover, ESPEC SH-222 Bench-top Type Temperature & Humidity Chamber was used to maintain the temperature and humidity while measurement. Impedance data fitting was done using Z-view software.

Fluorescence Microscopy:

Macro Zoom Fluorescence Microscope System (OLYMPUS- MVX10) with the microscopic lens (OLYMPUS-MV PLAPO 1X JAPAN) and camera (OLYMPUS-DP 80), the captured images were processed by Cellsens software.

1. Experimental Section

2.1 Synthesis of 4-(bromomethyl)benzaldehyde

The synthesis of the compound is based on a previous report.^[S1] A 500 mL flask was charged with 5 g of 4-(bromomethyl) benzonitrile (25.5 mmol) and vacuumed at ambient temperature for 2 h. About 140 mL Toluene was used to dissolve 4- (bromomethyl)benzonitrile, the obtained solution was then cooled to 0 °C and stirred under N₂ atmosphere for 8 h. 36.0 mL DIBAl-H (1 M in hexane) was added dropwise to the solution cautiously, immediately, the solution turned yellow and becomes clear. After stirring for 2 h, the solution was added with 66 mL CHCl₃ and then added with 200 mL 10 % HCl solution. After stirring for one more hour, the organic phase was extracted from the mixture and washed with water twice. The solution was dried with Na₂SO₄ and further dried under a vacuum oven to obtain the pale-yellow clear oil. After cooling down to ambient temperature, the white solid was immediately observed after the addition of ice-cold hexane. The whole mixture was placed in the refrigerator (4 °C) overnight and then filtrated to obtained the white crystals with a yield of 84%. NMR results are in good agreement with the literature. ¹H (400 MHz, CDCl₃) δ = 10.01 (s, 1H), 7.87 (d, J = 7.5 Hz, 2H), 7.56 (d, J = 7.5 Hz, 2H), 4.52 (s, 2H) ppm. ¹³C NMR (400 MHz, CDCl₃) δ = 191.25, 143.98, 135.86, 129.98, 129.41, 31.68 ppm.





¹³C NMR of 4-(bromomethyl)benzaldehyde

2.2 Synthesis of 1,1'-bis(4-formylbenzyl)-4,4'-bipyridiniumdibromide (VBrBA)

A solution of 0.39 g 4,4'-Bipyridine (2.50 mmol) and 1 g 4-(bromomethyl)-benzaldehyde (4.97 mmol) in 15 mL of acetonitrile was heated at 75 °C for 6 h. After cooling down to room temperature, the precipitate

was filtered off, washed with acetonitrile and ether, and dried in an oven, and obtained the yield of nearly 1.30 g (94%) of a yellow powder.



1,1'-bis(4-formylbenzyl)-[4,4'-bipyridine]-1,1'-diium dibromide



¹H NMR of 1,1'-bis(4-formylbenzyl)-4,4'-bipyridiniumdibromide



¹³C NMR of 1,1'-bis(4-formylbenzyl)-4,4'-bipyridiniumdibromide

2.3 Synthesis of 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(benzene-1,3-diol) (TRIRES)

The synthesis of the compound is based on a previous report.^[S2] 2 g (10.8 mmol) of cyanuric chloride and 3.58 g (32.5 mmol) of resorcinol were dispersed in 100 mL of 1,2-dichloroethane. Contents were dissolved by heating at 75 °C, following this, the mixture was cooled to 0 °C. To this, about 4.35 g (32.5 mmol) anhydrous AlCl₃ was slowly added in 30 minutes. This mixture was refluxed for 36 h. The reaction mixture was cooled to room temperature and the solvent was removed using a rota-evaporator. The solid was then stirred in 100 mL of 10% HCl for 3 h and kept it for an additional 3 h. A yellow solid was precipitated, which was filtered under vacuum and washed with about 250 mL of diethyl ether to remove any unreacted starting materials. The product was dried in a vacuum oven. About 3.2 g (yield: 88%) of the product was obtained.



4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(benzene-1,3-diol)



HRMS of RMS data of 4,4',4"-(1,3,5-triazine-2,4,6-triyl)tris(benzene-1,3-diol) shows only a single intense peak of [M+H]+:406.10. The exact molecular mass of bispyridine-s-tetrazine diamine $(C_{21}H_{15}N_3O_6)$ is 405.37.

2.4 Synthesis of cationic polymer IISERP-POF11 (1)

The polymer has been synthesized according to the optimized protocol by our group.^[S3] The solvothermal reaction between 0.2 mmol phenolic compound and 0.15 mmol viologen aldehyde in a mixture of 3 mL THF and 3 mL 1,4- dioxane at 200 °C for 72 h yielded a brown-colored precipitate which was sequentially washed with DMF, THF, MeOH and finally acetone. The product was dried in the vacuum oven for 6 h and the obtained material was named hereafter as **1**. CHN analysis: **1**: C=80.71%, H=10.83%, N=8.46%.



Schematic showing the structure of **1**. Inset showing the photographic image of the compound.

2.5 Anion exchange with IISERP-POF11 to form IISERP-POF11_OH (1_OH)

The as-made polymer 1 (100 mg) was dispersed in 10 mL of 3 M KOH and sonicated for 10 minutes. After sonication, the mixture was stirred for 24 h at room temperature for hydroxide ion (OH⁻) incorporation. Hydroxide ion exchanged polymer was filtered and washed with an ample amount of water to remove the excess KOH. The product was dried in a vacuum oven for 12 h at 80 °C and obtained a yield of 88 %. A significant colour change was observed after the exchange with the hydroxide ions to obtain 1_OH. 1 was exchanged with 6 M KOH followed by the above procedure to obtain 1_6OH.



1_OH with inset showing the photographic image of the compound

Analytical Characterizations



Fig. S1: Comparative Solid-state Cross-Polarization Magic Angle Spinning Carbon-13 Nuclear Magnetic Resonance (¹³C CP-MAS NMR) spectra of **1**, **1_OH** and **1_6OH**.



Fig. S2: Field Emission-Scanning Electron Microscopy (FESEM) images of 1 at different magnifications.



Fig. S3: FESEM images of 1_OH at different magnifications.



Fig. S4: FESEM-EDX elemental mapping of 1.



Fig. S5: FESEM-EDX elemental mapping of 1_OH.



Fig. S6: High Resolution Transmission Electron Microscopy (HR-TEM) images of **1** at different magnifications.



Fig. S7: HRTEM images of 1_OH at different magnifications.



Fig. S8: (a) Comparative thermogravimetric analysis plot for **1**, **1_OH** and **1_6OH**. (b) and (c): Contact angle of the droplet of water sitting on the surface of the **1**. $CA = 148^{\circ} \pm 3^{\circ}$.



Fig. S9: Adsorption isotherms and plot of the pore width vs. incremental pore volume of 1 and 1_OH.

2. Hydroxide ion conductivity Analysis

4.1 Temperature-dependent hydroxide ion conductivity analysis of 1_OH:

The hydroxide ion conductivity (σ) of the **1_OH** was investigated by the electrochemical impedance spectroscopy method from a frequency range of 1–10⁶ Hz using the Solartron Impedance Analyzer. For this, **1_OH** was made into a pelletized form. The conductivity measurements were carried out three times on different pellet thicknesses (0.6 to 0.8 mm) and diameters of 10 mm to validate the consistency in the obtained results. Before each measurement, the sample was equilibrated at the particular temperature and humidity for 2 h throughout the experiment. The hydroxide ion conductivity of the pellet was measured from 30 to 80 °C in relative humidity (RH) of 95% and calculated using the following equation;

$$\sigma \left(\mathbf{S} \ \mathbf{c} \mathbf{m}^{-1} \right) = \frac{\mathbf{l}}{\mathbf{R} \mathbf{A}}$$

where *l* is the thickness of the pellet (cm), R is the resistance of the sample (Ω) obtained from the x-axis intercept, and A is the cross-sectional area of the pellet (cm²). The humidity dependent OH⁻ ion conductivity of **1_OH** was also measured at 80 °C with variable relative humidity under similar conditions.

4.2 Activation energy calculation for 1_OH

The activation energy was obtained using the Arrhenius equation where m is the slope of the plot between $\ln \sigma$ Vs 1000/T and the R is the gas constant with the value of 8.314 J/mol.

$$\ln\sigma = (-E_a/RT) + \ln A$$

Table S1: Hydroxide ion conductivity of **1_OH** at variable temperatures and a constant relative humidity of 95%.

Sr. No.	Humidity (%)	Temperature (°C)	Conductivity (S/cm)
1	95	30	2.7 x 10 -4
2	95	40	1.4 x 10 ⁻³
3	95	50	2.3 x 10 ⁻³
4	95	60	3.4x 10 ⁻³
5	95	70	5.3 x 10 ⁻³
6	95	80	1.4 x 10 ⁻²



Fig. S10: (a) Humidity dependent Nyquist plots of **1_OH** at 80 °C. (b) **1_OH** impedance anlysis measured at 80 °C and 95 % RH for 15 h.



Fig. S11: Cyclic voltammogram of 1 measured using a three-elctrode system in 1M KOH electrolyte with Hg/HgO as reference and Pt wire as counter electrode.



Fig. S12: Linear sweep voltammogram (LSV) of 1_OH measured using a two-probe set-up.



Fig. S13: A plot of the Z' versus $\omega^{-1/2}$ for **1_OH** at 95% RH at different temperatures.

3. Development of IISERP-POF11_OH@Filter Paper (1_OH@FP)

The obtained **1_OH** was dispersed in 10 mL DI water and 100 μ L Nafion binder (10% in H₂O) was added to increase the adherence. This mixture was stirred for 2 h and poured into a petri dish of diameter 50 mm. A 5 x 5 cm Whatman filter paper grade 1 (approx. thickness 0.2 mm) was dried and weighed before soaking it into the dispersed solution. After each 15 minute soaking, the **1_OH@FP** was dried for 30 minutes in the vacuum oven. The soaking procedure was repeated three times for each and this turned the white filter paper into a brownish yellow form.



Fig. S14: Comparison of the solid-state UV absorption spectra of neat **FP** vs. **1_OH@FP** showing significant lowering of the absorbance intensity (@280 nm) of the FP upon coating with the polymer.



Fig. S15: FESEM images of filter paper (FP) (a & b) and 1_OH@FP (c & d) at different magnifications.



Fig. S16: Cross-sectional SEM images of (a-c) Neat FP and, (d-f) 1_OH@FP at different magnifications.



Fig. S17: Comparative Nyquist plot of 1_OH and 1_OH@FP at 80 °C and 95% RH. Table shows the values for each fitting parameter.



Fig. S18: Comparative plots of the Z' versus $\omega^{-1/2}$ for **1_OH** and **1_OH@FP** at 80 °C and 95% RH.

4. Battery studies

4.1 Fabrication of Zinc-Air Battery (ZAB):

The In-situ Analytical Split Test Cell for Lithium/Zinc-Air Battery setup was used to fabricate the Zinc-air battery where, zinc dust was used as the anode which was wetted with about 500 μ L of 3 M KOH solution. The cathode was coated with Pt/C (slurry in 1:1 EtOH: H₂O) on GDL (Gas Diffusion Layer). The amount of Pt/C was maintained as 1 mg/cm² for the cathode. Finally, the cathode and anode were sandwiched with the prepared **1_OH@FP** as the separator-cumelectrolyte. The battery setup was assembled with screws and a continuous flow of O₂ gas was provided throughout the measurements. The polarization curves were obtained by performing the linear sweep voltammetry (LSV) from OCV to 0.4 V at a scan rate of 10 mV s⁻¹ using the AMETEK battery analyzer.



Zinc-air Battery Assembly

Fig. S19: Photographic images of the ZAB assembly.



Fig. S20: Comparison of the Nyquist plots for the **1_OH@FP** measured in the zinc-air battery set-up. Table shows the values for each fitting parameter.



Fig. S21: Comparison of the Nyquist plots for the neat paper measured in the zinc-air battery set-up. Table shows the values for each fitting parameter.

4.2 Fabrication of flexible solid-state ZAB:

For the flexible solid-state Zinc-air battery, Zn foil with 0.25 mm thickness was employed as the anode, Pt/C coated carbon cloth was used as the air-breathing cathode and hydroxide ion conducting **1_OH@FP** as the solid-state separator-cum-electrolyte. During the fabrication of the battery, **1_OH@FP** was wetted with 3 M KOH solution. The anode and cathode were separated with **1_OH@FP** and the sandwich is sealed. The backside of the cathode was kept it open for the passage of air and the battery was operated without providing any additional O_2 supply.



Fig. S22: (a) Photographic images of the electrodes and the separator employed for the flexible battery, (b) Photographic images of the single flexible battery, (c) Two flexible batteries connected in series and, (d) Combination of three devices in series.

5. Post ZAB measurement sample characterizations



Fig. S23: Comparison of the PXRD patterns of the **FP**, **1_OH@FP** and the pyrolyzed product of the **1_OH@FP** (burnt at 600°C under N₂). The inorganic species in this pyrolyzed sample includes ZnO(\bigstar), K₂CO₃ (**•**)and Pt₃O₄ (**•**)(from cathode).

Note: It was impossible to identify the elements deposited on the paper-based electrolyte-cum-separator during the measurement from a direct PXRD. This is because the amount of inorganics deposited on the surface is minimal compared to the paper itself. Hence we resorted to pyrolysis of the electrolyte-cum-separator to shed light on the post-battery SEI layer composition.



Fig.S24: Comparison of the IR spectra showing the integration of the polymer (1) with the **FP** and the functionalities remain intact even after the ZAB measurements.



Fig. S25: The FESEM and EDAX images of the post-battery measurement electrolyte (**1_OH@FP**) showed the presence of a few additional components compared to the pristine **1_OH@FP**.



Fig. S26: Comparison of the confocal microscopy images of the neat (a) FP, (b) **1_OH@FP** and (c) post ZAB 1_OH@FP.

6. Computational details:

The crystallographic modeling of the structure of the 1_OH and its DFT optimization was carried out using the DMOL³ package embedded in the Materials Studio (Accelrys) V.8.0.^[S4,S5] The initial structure of the polymer containing two triazine-triresorcinol units linked to two viologen units terminated with a tolyl ring was constructed using atomic manipulation. Four hydroxide ions were introduced to counterbalance the protonated viologen nitrogens. In the initial configuration, the hydroxides were positioned adjacent to the protonated nitrogen centers and were allowed to find their final atomic positions freely during the optimization. The optimized structure of this polymer's representative unit and its frontier orbitals was calculated using the DMOL minimization routine. To calculate the frontier orbitals, we used the DMOL³ module S6 with a high tolerance of 1×10^{-6} for the SCF convergence and a global cut-off of 3.7 Å. UFF-based Lennard-Jones dispersion corrections were included in Energy, Force and Displacement calculations. All calculations are at 0 K and were spin-unrestricted, adopting the formal spin as the initial spin. The final configuration converged with acceptable geometries and bond parameters.

We created an amorphous cell consisting of four oligomeric chains and the charge-balancing hydroxide ions. The cell parameters, as well as the geometries, were optimized using the DMOL³. In the optimized configuration, the cross-linked chains packed efficiently and possessed ample spaces capable of accommodating the extra-framework hydroxide anions and with very few solvent-accessible voids. This is consistent with the experimental observations, which point to the material being non-porous to nitrogen gas but comprises some solvent molecules in the as-synthesized form.

Core elements were treated with all-electron pseudopotentials and the DNP basis set with a basis cut-off of 3.7 Å. For our dispersion corrections, we used Generalized Gradient Approximation (GGA) for calculating the exchange and the correlation energies and employed the Perdew-Wang 91 (PW91) functional.^[S6] Density mixing was done using the Pulay scheme. The final configuration considered in the analysis converged well. We used this final optimized structure for the molecular dynamics simulations.

Molecular Dynamics Simulations (MD):

The optimized amorphous cell containing four polymer chains was investigated using the Forcite Dynamics module embedded in the Accelrys Package. For the MD, the initial velocities were made Random. A 5 ns NPT MD simulation (1.0 fs time step, 300K) was used to generate were used to reach an equilibrium state. The COMPASS force field was employed, and the Coulumbic interactions were treated with Group-based summation methods with a considerable cut-off distance of 40 Å, considering the large unit-cell. We did not alter the charge group size. Nose-Hoover Thermostat was employed to control the temperature, while Berendsen barostat helped control the pressure. Energy tolerance of 5 x 105 kcal/mol was applied. Finally, a 5 ns NVE simulations (1.0 fs time step) were used to generate the low-energy trajectory from which we analyzed the radial distribution function (RDF). We used the COMPASS force field (V 2.8) for these simulations with the NVE ensemble and treated the Coulumbic interactions with Group-based summation methods. The electrostatic and van der Waals summation were calculated to a

cut-off distance of 18.5 Å. Similar MD simulation parameters were employed for all the other temperatures used to calculate the activation energy from the slope of the MSD.



Fig. S27: (a) Mean Square Displacement (MSD) vs. time plot calculated at variable temperature using MD simulations and the derived hydroxide ion self-diffusion coefficient. (b) Plot of $\log(D_{OH})$ vs 1000/T from experimental and computational for **1_OH**. The data points were fitted to a straight line.

Table S2: Comparison of the hydroxide ion conductivity of the 1_OH with relevant literature reports.

S. No.	Membrane	Electrolyte (Conc. of KOH)	Catalyst	Application	Maximum Power Density (in mW/cm ²)	OH ⁻ Conductivity (in S/cm)	Reference
1.	25 μm polypropylene membrane, Celgard 5550	6 M	Pt/C	Zinc-air battery	30	-	J. Electrochem. Soc. 160, no. 9 (2013): F910
2.	Celgard® 3501	6 M	Pt/C	Zinc-air battery	90	1.70 x 10 ⁻²	Molecules 26, no. 13 (2021): 4062
3.	Perfluorinated piperazinium	2 M	Pt/C	Fuel Cell	77	4.70 x 10 ⁻²	J. Mater. Chem. 21, no. 17 (2011): 6158-6160
4.	polymeric ionomer TPQPOH with a tris(2,4,6- trimethoxyphenyl) phosphonium	-	Pt/C	Fuel Cell	138	2.70 x 10 ⁻²	Angewandte Chemie 121, no. 35 (2009): 6621- 6624
5.	poly(vinyl alcohol) (PVA)/poly(acrylic acid) (PAA)	32 wt%	-	Zinc-air battery	50	1.42 x 10 ⁻¹	J. Membr. Sci. 280, no. 1-2 (2006): 802-808
6.	semi-IPN MOF	2 M	-	(Fuel cell)	42.5	12 x 10 ⁻²	Energy & Fuels 2019, 33, 5749–5760
7.	KI–PVAA–GO GPE	4 M KOH + 2 M KI	CO ₃ O ₄	Zinc-air battery	78.6	1.55 x 10 ⁻¹	Adv. Mater. 32, no. 22 (2020): 1908127.
8.	polyacrylamide (PAM) based alkaline gel electrolyte (AGE)	20 wt%	MnO2/N RGO- Urea	Zinc-air battery	105.0	2.15 x 10 ⁻¹	J. Power Sources 450 (2020): 227653 (2020)
9.	IISERP-POF11_OH	3 M	Pt/C	Zinc-air battery	115	1.47 x 10 ⁻²	This Work

7. References

[S1] R. E. Gawley, H. Mao, M. M. Haque, J. B. Thorne, J. S. Pharr, J. Org. Chem. 2007, 72, 2187.

- [S2] S. Nandi, J. Rother, D. Chakraborty, R. Maity, U. Werner-Zwanziger, R. Vaidhyanathan, J. Mater. Chem. A 2017, 5, 8431.
- [S3] D. Chakraborty, S. Nandi, R. Kushwaha, D. Kaleeswaran, R. Vaidhyanathan, Mater. Res. Bull. 2021, 111614.
- [S4] B. Delley, J. Chem. Phys. 92, 508 (1990).
- [S5] B. Delley, J. Chem. Phys. 113, 7756 (2000).
- [S6] P91 exchange: Perdew, Physica B 172, 1 (1991).