Supplementary Information

A single-ion conducting covalent organic frameworks for aqueous rechargeable Zn-ion batteries

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Experimental details

Materials
1,4-phenylenediamine-2-sulfonic acid (Pa-SO$_3$H), 1,4-dioxane, mesitylene, acetic acid, zinc acetate and polytetrafluoroethylene (PTFE, 60 wt% dispersion in H$_2$O) were purchased from Merck. The Zn metal foil (99.98%) was purchased from Alfa Aesar. 1,3,5-triformylphloroglucinol (Tp),$^{S1}$ the sulfonic acid COF (TpPa-SO$_3$H),$^{S2,S3}$ the non-sulfonated COF (TpPa)$^{S4}$ and $\alpha$-MnO$_2$,$^{S5}$ were synthesised as previously reported. All other chemicals were obtained from commercial sources and used as received unless otherwise noted.

Synthesis of TpPa-SO$_3$Zn$_{0.5}$
TpPa-SO$_3$H (605 mg) was suspended in a 1 M aqueous zinc acetate solution (40 mL) and stirred for 72 h at room temperature, during which the solution was exchanged at an interval of 24 h. The resultant powders were collected by filtration and washed with H$_2$O to ensure the removal of excess zinc acetate. After dried under vacuum at 120 °C for overnight, the reddish powders of TpPa-SO$_3$Zn$_{0.5}$ were obtained (yield: 612 mg, 91%).

Structural and physicochemical characterisations
The elemental analysis was performed using a Leco TruSpec Micro CHN analyser. The Zn content was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Varian 700-ES. The Fourier transform infrared (FT-IR) spectrum was recorded using a Bruker ALPHA Laser class 1. The cross polarisation magic angle spinning $^{13}$C nuclear magnetic resonance (CP-MAS $^{13}$C NMR) experiment was performed using an Agilent VNMRS 600 MHz NMR spectrometer at a 20 kHz spinning rate. Chemical shifts were referenced to hexamethylbenzene at 17.3 ppm as an external standard. Morphological analyses were performed using a Hitachi S-4800 field-emission scanning electron microscope (FE-SEM) equipped with a JEOL JSM-6400 energy dispersive X-ray spectroscopy (EDS) detector and a Tecnai G2 F20 X-Twin transmission electron microscope (TEM) equipped with an Oxford INCA X-sight 7688 EDS detector. X-ray diffraction (XRD) patterns were recorded through a transmittance mode at the 6D UNIST-PAL beamline of the Pohang Accelerator Laboratory or using a Rigaku D/MAX2500. N$_2$ gas sorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 physisorption analyser. Brunauer–Emmett–Teller (BET) and non-
local density functional theory (NLDFT) methods were utilised to calculate the specific surface area and the pore size, respectively. The thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 thermogravimetric analyser under a N₂ atmosphere at a heating rate of 10 °C min⁻¹. Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) mapping images were obtained using IONTOF TOF-SIMS 5. The X-ray photoelectron spectroscopy (XPS) analysis was conducted using a Thermo Fisher Scientific ESCALAB 250Xi.

**Electrochemical characterisations**

The self-standing TpPa-SO₃Zn₀.₅ pellets were prepared by a cold-pressing method under *ca*. 40 MPa at room temperature. The flexible TpPa-SO₃Zn₀.₅ membranes were prepared by mixing PTFE (5 wt%) with the TpPa-SO₃Zn₀.₅ powders. The obtained pellets and membranes were hydrated before the electrochemical tests.

**Ionic conductivity**

Ionic conductivity was measured with Zn²⁺ blocking Ti|TpPa-SO₃Zn₀.₅|Ti cells based on an electrochemical impedance spectroscopy (EIS) analysis in a frequency range from 10⁻² to 10⁶ Hz at an applied amplitude of 10 mV using a Bio-logic VSP classic potentiostat. The ionic conductivity (σ) was determined according to the following equation:

\[
\sigma = \frac{l}{RA}
\]

where \(l\) is the pellet (or membrane) thickness, \(R\) is the resistance and \(A\) is the area in contact with the electrodes. The control experiment without Zn²⁺ was conducted using a Ti|TpPa|Ti cell.

**Zn²⁺ transference number**

The time-dependent current flowing through a Zn|TpPa-SO₃Zn₀.₅|Zn cell and the impedance of the cell before and after direct current (DC) polarisation (20 mV) were measured. The Zn²⁺ transference number (\(t_{Zn²⁺}\)) was determined according to the following equation:

\[
t_{Zn²⁺} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})}
\]

where \(I_{ss}\) is the steady-state current, \(I_0\) is the initial current, \(\Delta V\) is the applied potential, \(R_0\) and \(R_{ss}\) are the interfacial resistances before and after polarisation, respectively.
[Linear sweep voltammetry]
Linear sweep voltammetry (LSV) was conducted with a Zn|TpPa-SO₃Zn₀.₅|Ti cell operated under a sweep rate of 0.2 mV s⁻¹ in a voltage range from −0.2 to 3 V (vs. Zn/Zn²⁺) at room temperature.

[Zn stripping/plating experiments]
The galvanostatic cyclability of a Zn|TpPa-SO₃Zn₀.₅|Zn cell and a Zn|liquid electrolyte (LE)|Zn cell (LE = 2 M ZnSO₄ in H₂O) was examined at room temperature (current density = 0.1 mA cm⁻², capacity = 0.1 mAh cm⁻²). The reversibility of Zn stripping/plating was investigated with the Zn||Ti configurations, in which Zn metal was electrochemically plated on the Ti working electrode and subsequently stripped out during a cycle (current density = 0.1 mA cm⁻², capacity = 0.1 mAh cm⁻²). The Zn||Cu configurations were used for monitoring Zn electroplating behaviour (current density = 0.3 mA cm⁻², capacity = 3 mAh cm⁻²).

[Zn||MnO₂ battery tests]
The electrode slurry composed of MnO₂, carbon black and polyvinylidene fluoride in a weight ratio of 7/2/1 was dispersed in N-methyl-2-pyrrolidone and casted onto a Ti foil current collector. The solvent was removed under vacuum at 60 °C for overnight. The prepared MnO₂ cathode was immersed with an LE (2 M ZnSO₄ + 0.2 M MnSO₄ in H₂O) and assembled with TpPa-SO₃Zn₀.₅ (or a glass fibre containing the LE) and a Zn metal anode. The resultant Zn||MnO₂ cells were tested under a current density of 0.6 A g⁻¹ at room temperature.

Simulation details

Density functional theory (DFT) calculations
The structural model of TpPa-SO₃Zn₀.₅ was constructed based on those reported for TpPa-SO₃X (X = H, Li), S²,S³ in which Zn atoms were introduced upon consideration of the charge balance between the sulfonated framework and Zn²⁺. The stable positions of Zn atoms were investigated by geometry optimisation. All DFT calculations were performed using DMol³ program. S⁷,S⁸ The generalised gradient approximation with Perdew–Burke–Ernzerhof functional (GGA-PBE) S⁹ was used for the exchange-correlation energy. The double numerical polarisation basis set with spin-polarised calculations were used, while core-electron treatment was conducted with the DFT semi-core pseudopotential. The dispersion correction pertaining to van der Waals interactions was applied with semi-empirical Tkatchenko-Scheffler (TS)
The Brillouin zone was sampled by Monkhorst-Pack\textsuperscript{11} $1 \times 1 \times 2$ $k$-point mesh for all systems. The self-consistent field (SCF) convergence for each electronic energy was set as $1.0 \times 10^{-6}$ Ha. The convergence precision of geometry optimisation for energy, force and displacement were set to $1.0 \times 10^{-5}$ Ha, 0.002 Ha Å$^{-1}$ and 0.005 Å, respectively.

**Molecular dynamics (MD) simulations**

All MD simulations were carried out in Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).\textsuperscript{12} The visualisation was conducted with 3D visualisation Open Visualisation Tool (OVITO).\textsuperscript{13} Based upon the thermodynamically stable structure of TpPa-SO$_3$Zn$_{0.5}$ obtained from DFT calculation, a $4 \times 4 \times 54$ supercell was constructed. The carbon atoms of the framework were assumed to be dynamically rigid. H$_2$O was saturated in the pores of TpPa-SO$_3$Zn$_{0.5}$ for similarity with the experimental conditions. An LE system with the same magnitude was constructed by a fixed density of 1.31 g cc$^{-1}$ for 2 M ZnSO$_4$ in H$_2$O. Both systems were equilibrated with $NVT$ ensemble at 298 K for 2 ns. After then, an external electric field of 1.0 V Å$^{-1}$ in the –z-axis direction was applied to the systems for 3 ns. The Zn$^{2+}$ number density profiles, velocity distributions and fraction of Zn–O coordination numbers were obtained by analysis of average trajectories during the last 1 ns of this stage.

The Nose–Hoover thermostat was used to control temperature.\textsuperscript{14} The Assisted Model Building with Energy Refinement (AMBER) force field\textsuperscript{15} was used for both TpPa-SO$_3$Zn$_{0.5}$ and LE systems. The optimised AMBER force field for SO$_4^{2-}$,\textsuperscript{16} the optimised non-bonded interaction for Zn$^{2+}$,\textsuperscript{17} the general AMBER force field (GAFF),\textsuperscript{18} for the other atoms were used for this analysis. The Mulliken charge\textsuperscript{19} obtained from the DFT calculation was assigned as a partial atomic charge for all systems.
Scheme S1 Synthesis of TpPa-SO$_3$Zn$_{0.5}$.

[Diagram showing the synthesis process involving Tp and Pa-SO$_3$H in 1,4-dioxane/mesitylene (1/4 v/v) with acetic acid (6 M) at 120°C for 72 h, followed by addition of Zn(OAc)$_2$ in water at room temperature for 72 h.]
Table S1 CHN analysis and ICP-OES (for Zn) results for TpPa-SO₃Zn₀.5

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcd. (wt%) for</td>
<td>44.49</td>
<td>2.18</td>
<td>8.65</td>
<td>10.09</td>
</tr>
<tr>
<td>$C_{72}H_{42}N_{12}O_{30}S_6Zn_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Found (wt%)</td>
<td>44.32</td>
<td>2.62</td>
<td>8.79</td>
<td>9.82</td>
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</table>
### Table S2 Unit cell parameters of TpPa-SO$_3$Zn$_{0.5}$

<table>
<thead>
<tr>
<th></th>
<th>TpPa-SO$<em>3$Zn$</em>{0.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C$<em>{72}$H$</em>{42}$N$<em>{12}$O$</em>{30}$S$_6$Zn$_3$</td>
</tr>
<tr>
<td><strong>Symmetry</strong></td>
<td>Triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>$P1$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>22.8345</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>22.9434</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>6.8744</td>
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<tr>
<td>$\alpha$ (º)</td>
<td>89.8514</td>
</tr>
<tr>
<td>$\beta$ (º)</td>
<td>89.7964</td>
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<tr>
<td>$\gamma$ (º)</td>
<td>120.5433</td>
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Table S3 $t_{Zn^{2+}}$ values of TpPa-SO$_3$Zn$_{0.5}$ and previously reported Zn$^{2+}$ conducting polyanions

<table>
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<th>Anionic host</th>
<th>Guest</th>
<th>$t_{Zn^{2+}}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc sulfonated COF (TpPa-SO$<em>3$Zn$</em>{0.5}$)</td>
<td>H$_2$O</td>
<td>0.91</td>
<td>This study</td>
</tr>
<tr>
<td>Zn$^{2+}$-paired anionic MOF (ZnMOF-808)</td>
<td>H$_2$O</td>
<td>0.93</td>
<td>S20</td>
</tr>
<tr>
<td>Zinc sulfonated poly(ether ether ketone) (Zn-SPEEK)</td>
<td>H$_2$O</td>
<td>0.89</td>
<td>S21</td>
</tr>
<tr>
<td>Sulfonated perfluoro polyolefin (3M-Nafion)</td>
<td>3 M ZnSO$_4$ in H$_2$O</td>
<td>0.52</td>
<td>S22</td>
</tr>
<tr>
<td>Zinc sulfonated perfluoro polyolefin (ZPSAM)</td>
<td>H$_2$O</td>
<td>0.2</td>
<td>S23</td>
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</table>
Table S4 Details on model systems constructed for MD simulations

<table>
<thead>
<tr>
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<th>TpPa-SO$<em>3$Zn$</em>{0.5}$</th>
<th>LE (2 M ZnSO$_4$ in H$_2$O)</th>
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<tr>
<td><strong>Number of species</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>2592</td>
<td>3216</td>
</tr>
<tr>
<td>TpPa-SO$_3$$^-$</td>
<td>1 (139968 atoms)</td>
<td>–</td>
</tr>
<tr>
<td>SO$_4$$^{2-}$</td>
<td>–</td>
<td>3216</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>46656</td>
<td>89208</td>
</tr>
<tr>
<td><strong>Total number of atoms</strong></td>
<td>282528</td>
<td>286920</td>
</tr>
<tr>
<td><strong>Cell parameters</strong></td>
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<td></td>
</tr>
<tr>
<td>$a$ (Å)</td>
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</tr>
<tr>
<td>$b$ (Å)</td>
<td>91.77</td>
<td></td>
</tr>
<tr>
<td>$c$ (Å)</td>
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<td>$\alpha$ (°)</td>
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<td>$\beta$ (°)</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>120</td>
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</tr>
</tbody>
</table>
**Table S5** Characteristics of electrochemical cells containing TpPa-SO$_3$Zn$_{0.5}$ compared with those containing previously reported single Zn$^{2+}$ conductors

| Single Zn$^{2+}$ conductor | Cycling time of the Zn||Zn cell, h (current density, mA cm$^{-2}$; capacity, mAh cm$^{-2}$) | Battery application (operating voltage, V) | Cycle number (current density, A g$^{-1}$) | Ref. |
|----------------------------|-------------------------------------------------------------------------------------------------|---------------------------------------------|---------------------------------------------|------|
| Zinc sulfonated COF (TpPa-SO$_3$Zn$_{0.5}$) | 500 (0.1; 0.1) | Zn||MnO$_2$ (*ca.* 1.4) | 800 (0.6) | This study |
| Zn$^{2+}$-paired anionic MOF (ZnMOF-808) | 360 (0.1; 0.05) | Zn||VS$_2$ (*ca.* 0.7) | 250 (0.2) | S20 |
| Zinc sulfonated poly(ether ether ketone) (Zn-SPEEK) | 50 (1; 0.5) | – | – | S21 |
| Sulfonated polyacrylonitrile (PAN-S) | 350 (0.5; 0.25) | – | – | S24 |
Fig. S1 (a) CP-MAS $^{13}$C NMR and (b) FT-IR spectra of TpPa-SO$_3$Zn$_{0.5}$. 
**Fig. S2** TEM image of TpPa-SO$_3$Zn$_{0.5}$. 
Fig. S3 Theoretical unit cell structure of TpPa-SO$_3$Zn$_{0.5}$ displayed along (a) c- and (b) a-axes. (c) Optimal geometry of Zn$^{2+}$.
**Fig. S4** Electrostatic potential (ESP) for TpPa-SO$_3$Zn$_{0.5}$ mapped on the electron density surface.
Fig. S5 Pore size distribution of TpPa-SO$_3$Zn$_{0.5}$. 
**Fig. S6** Cross-sectional SEM images of (a) a TpPa-SO$_3$Zn$_{0.5}$ pellet and (b) a TpPa-SO$_3$Zn$_{0.5}$–PTFE composite membrane (arrows: PTFE fibres).
**Fig. S7** EIS profiles of the hydrated TpPa-SO$_3$Zn$_{0.5}$ measured at varied temperatures.
Fig. S8 (a) Chemical structure, (b) XRD patterns and (c) N₂ gas isotherms of TpPa.
**Fig. S9** EIS profile of the hydrated TpPa measured at room temperature.
Fig. S10 (a) Velocity distribution of Zn$^{2+}$ in TpPa-SO$_3$Zn$_{0.5}$ and LE (2 M ZnSO$_4$ in H$_2$O) in the z-axis. (b) Fraction of Zn–O coordination numbers in TpPa-SO$_3$Zn$_{0.5}$ and LE. O$_w$ belongs to H$_2$O, O$_f$ belongs to TpPa-SO$_3^-$ and O$_s$ belongs to SO$_4^{2-}$. 
Fig. S11 TGA curve of TpPa-SO$_3$Zn$_{0.5}$.

Fig. S12 LSV profile of TpPa-SO$_3$Zn$_{0.5}$. 
**Fig. S13** XRD patterns of TpPa-SO$_3$Zn$_{0.5}$ (as a PTFE composite membrane) before and after the Zn plating/stripping test. *PTFE.
Fig. S14  (a) XPS spectra (Zn 2p\textsubscript{3/2} and S 2p) of Zn metal electrodes after Zn plating/stripping tests in contact with TpPa-SO\textsubscript{3}Zn\textsubscript{0.5} (top) or LE (2 M ZnSO\textsubscript{4} in H\textsubscript{2}O; bottom). (b) XRD patterns of Zn metal electrodes before (black) and after Zn plating/stripping tests in contact with TpPa-SO\textsubscript{3}Zn\textsubscript{0.5} (purple) or LE (green). *Zn\textsubscript{4}SO\textsubscript{4}(OH)\textsubscript{6}·5H\textsubscript{2}O (PDF 39-0688).
**Fig. S15** (a) SEM and TEM (the inset) images, (b) XRD pattern (PDF 44-0141) and (c) cyclic voltammograms of α-MnO₂.
Fig. S16 (a) Cycling performance of a Zn|LE|MnO$_2$ cell (LE = 2 M ZnSO$_4$ + 0.2 M MnSO$_4$ in H$_2$O). (b) SEM image of the Zn metal anode after the 400$^{th}$ cycle. (c) TEM (left) and EDS mapping (for Mn; right) images of the MnO$_2$ cathode after the 400$^{th}$ cycle.
**Fig. S17** XPS spectra (Mn 2p<sub>3/2</sub>) of MnO<sub>2</sub> cathodes cycled in contact with TpPa-SO<sub>3</sub>Zn<sub>0.5</sub> (top) or LE (2 M ZnSO<sub>4</sub> + 0.2 M MnSO<sub>4</sub> in H<sub>2</sub>O; bottom).
References


S27


