Supplementary Information

Ionic Covalent Organic Framework based Electrolyte for Fast-Response Ultra-Low Voltage Electrochemical Actuators

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Supplementary Methods

**Chemicals.** All starting materials and solvents, unless specified, were obtained from Sigma-Aldrich Chemicals and used without further purification.

**Analytical techniques and instruments.** Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) of solid samples was performed on a PerkinElmer Frontier spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker AV 300 Spectrometer at 300 MHz (¹H NMR). Powder X-ray diffraction (PXRD) patterns were conducted on PANalytical X’Pert Pro MPD diffractometer using Cu Kα radiation (λ = 1.5406 Å), and operating at 40 kV and 40 mA between 2 and 30° (2θ). Transmission electron microscope (TEM) was conducted on a JEM-2100 (JEOL Ltd., Japan) with an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images were collected using a JEM-7600 (JEOL Ltd., Japan). The Brunauer–Emmett–Teller (BET) surface areas were calculated from N₂ sorption isotherms at 77 K using a Micromeritics ASAP 2020 surface area and pore size analyzer. Before measurement, the samples were degassed in vacuum at room temperature for 24 h. By using the non-local density functional theory (NLDFT) model, the pore size distribution was derived from the sorption curve. Particle size analysis was performed with a particle size analyzer (SZ-100, HORIBA).

**Ionic Conductivity measurement.** Ionic conductivity measurements were performed on sample pellets using CHI 760E workstation over a frequency range from 1 MHz to 1 Hz and with an input voltage amplitude of 10 mV (30 % RH, 25 °C). The sample pellets were tightly connected between two platinum electrodes by means of spring, to ensure good contact between sample and each electrode.
Synthetic procedures

Supplementary Fig. 1. Synthesis of starting material. Synthetic route to 2,5-dihydroxyterephthalaldehyde (DHA).

Synthesis of 1,4-bis(chloromethyl)-2,5-dimethoxybenzene (1). To a mixture of 1,4-dimethoxybenzene (5.0 g, 36.1 mmol) and paraformaldehyde (1.5 g, 50 mmol) in 1,4-dioxane (20 mL), formaldehyde solution (37 wt.%, 6 mL) was introduced. The resulting mixture was heated to 90 ºC and then concentrated HCl (10 mL) was added in drops within 20 min. After being heated for another 1 h, HCl (37 wt.%, 15 mL) was added and the resulting mixture was cooled to room temperature. The resulting white precipitate was collected by filtration, washed with water, and dried under vacuum, which was further recrystallized from acetone to give product 1 as a white powder.

Synthesis of 2,5-dimethoxyterephthalaldehyde (2). A mixture of 1 (2.0 g, 8.5 mmol) and hexamethylenetetramine (2.5 g, 17.5 mmol) in chloroform (30 mL) was refluxed at 90 ºC for 24 h. After being cooled to room temperature, the pale yellow precipitate was collected by filtration, washed with CHCl₃, dried, and dissolved in water. The aqueous solution was acidified with concentrated HCl (5 mL) and heated at 90 ºC for another 24 h. The mixture was cooled to room temperature, extracted with dichloromethane, and the organic phase was dried over anhydrous MgSO₄. After solvent evaporation, the residue was recrystallized from ethanol to yield compound 2 as a yellow needle-shaped solid. Yield: (0.8 g, 40%). ¹H NMR (400 MHz, d₆-DMSO, 298K, TMS) δ (ppm) 10.4 (s, 2H), 7.44 (s, 2H), 3.94 (s, 6H).

Synthesis of 2,5-dihydroxyterephthalaldehyde (DHA). To a solution of 2 (0.5 g, 2.3 mmol) in dichloromethane (80 mL), BBr₃ (1.5 mL) diluted by CH₂Cl₂ (25 mL) was added dropwise at 0 ºC under N₂ atmosphere. After being stirred for 12 h, water (20 mL) was added to quench the reaction. The residue was extracted with dichloromethane, washed with brine, dried over MgSO₄, and evaporated under reduced pressure, giving the crude
compound which was purified by flash chromatography with hexane/ethyl acetate (5:1) as eluent to afford the title compound as a yellow solid. Yield: 0.45 g (95%). \textsuperscript{1}H NMR (400 MHz, \textit{d}_6\text{-DMSO}, 298K, TMS) \textit{\delta} (ppm) 10.30 (d, 4H, \textit{J} = 8.8 Hz), 7.23 (s, 2H).

![Chemical structure](image)

Supplementary Fig. 2. Synthesis of starting material. Synthetic route to 1,3,5-tris-(4-aminophenyl)benzene (TAB).

\textbf{1,3,5-tris(4-nitrophenyl)benzene (3).} 4-Nitroacetophenone (50 g), toluene (200 mL), and CF\textsubscript{3}SO\textsubscript{3}H (2.0 mL) were added to a flask equipped with a water separator and a cooling condenser. The mixture was refluxed for 48 h, during this time the formed water was eliminated as a toluene azeotrope. After being cooled to room temperature, the mixture was filtered and washed with DMF under refluxing to yield a grey-green solid product after drying. This product is insoluble in any common solvent.

\textbf{1,3,5-tris-(4-aminophenyl)benzene (TAB).} A suspension of 1,3,5-tris(4-nitrophenyl)benzene (12.5 g, 28.4 mmol) and Pd/C (5 wt\%, 2.0 g) in ethanol (200 mL) was heated to reflux. Hydrazine hydrate (30 mL) was added in portions, and the resulting mixture was refluxed overnight. After that, the mixture was hot filtered through celite, and the filtrate was left undisturbed to fully crystallize the product. The solid was collected by filtration and washed with cold ethanol. Yield: 8.3 g (84%). \textsuperscript{1}H NMR (400 MHz, \textit{d}_6\text{-DMSO}, 298K, TMS): \textit{\delta}(ppm) 7.50 (t, 9H), 6.69 (d, 6H), 5.22 (s, 6H).

\textbf{Structure modelling.} The structure of COF-DT was determined by modeling, powder indexing, and Pawley refinement based on powder X-ray diffraction (PXRD) pattern. The resulting structure was geometrically optimized using the Forcite module, with a Universal forcefield. The as-obtained model was in good agreement with experimental data. Pawley
refinement was performed on the eclipsed (AA) COFs model in space group $P6/m$ against experimental data. The refinement was based on the Debye-Scherrer geometry and the Thompson-Cox-Hastings peak profile function. The refinement results are depicted in Figure 3a, and the final atomic coordination is enumerated in supplementary table 1.

**Supplementary Equation 1**

**Ionic conductivity.** The ionic conductivity ($\sigma$) can be calculated with the following equation 1:

$$\sigma = \frac{l}{RA} \cdots \cdots \cdots \cdots \cdots (1)$$

where $R$ is the ionic resistance, and $l$ and $A$ are the thickness and area of the pellet.

**Supplementary Equation 2**

**Bending strain difference (%)**. The bending strain difference ($\varepsilon$, %) generated in the actuator was estimated by the following equation 2:

$$\varepsilon = \frac{2d\delta}{l^2+\delta^2} \cdots \cdots \cdots \cdots (2)$$

where $d$, $\delta$, and $l$ are the thickness, the tip displacement, and the free length of the actuator.
Supplementary Table

**Supplementary Table 1.** Fractional atomic coordinates of the structural model of COF-DT with eclipsed (AA) stacking mode, resulting from Pawley refinement against experimental PXRD data.

| COF-DT  | Hexagonal, \( P6/m, a = 38.19 \, \text{Å}, b = 38.19 \, \text{Å}, c = 3.48 \, \text{Å}, \alpha = \beta = 90^\circ, \gamma = 120^\circ \) |
|---------|-------------------------------------------------------------------------------------------------------------------------------------|
| Atom    | \( x \)  | \( y \)  | \( z \)  |
| C1      | 0.51811  | 1.04296  | 1.00000  |
| C2      | 0.54259  | 1.02446  | 1.00000  |
| C3      | 0.52411  | 0.98243  | 1.00000  |
| C4      | 0.46729  | 0.91279  | 1.00000  |
| N5      | 0.42929  | 0.88546  | 1.00000  |
| C6      | 0.41193  | 0.84226  | 1.00000  |
| C7      | 0.43497  | 0.82300  | 1.00000  |
| C8      | 0.41612  | 0.78078  | 1.00000  |
| C9      | 0.37337  | 0.75597  | 1.00000  |
| C10     | 0.35090  | 0.77640  | 1.00000  |
| C11     | 0.37002  | 0.81860  | 1.00000  |
| C12     | 0.35271  | 0.70987  | 1.00000  |
| C13     | 0.37527  | 0.68980  | 1.00000  |
| O14     | 0.41521  | 0.95520  | 1.00000  |

**Supplementary Table 2.** Fractional atomic coordinates of the structural model of COF-DT-SO\(_3\)H with eclipsed (AA) stacking mode, resulting from Pawley refinement against experimental PXRD data.

| COF-DT-SO\(_3\)H | Triclinic, \( P1, a = 4.45 \, \text{Å}, b = 37.25 \, \text{Å}, c = 37.35 \, \text{Å}, \alpha = 119.75^\circ, \beta = \gamma = 90^\circ \) |
|-------------------|-------------------------------------------------------------------------------------------------|
| Atom              | \( x \)  | \( y \)  | \( z \)  |
| C1                | 0.58960  | -0.37441 | 0.45950  |
| C2                | 0.55046  | -0.33138 | 0.48214  |
| C3                | 0.51730  | -0.30830 | 0.46206  |
| C4                | 0.52834  | -0.32869 | 0.41885  |
| C5                | 0.55950  | -0.37188 | 0.39552  |
| C6                | 0.59004  | -0.39451 | 0.41624  |
| C7                | 0.55547  | -0.39301 | 0.34969  |
| C8                | 0.46627  | -0.26303 | 0.48599  |
| C9                | 0.62231  | -0.39817 | 0.48138  |
| C10               | 0.73628  | -0.42786 | 0.32581  |
| C11               | 0.73382  | -0.44694 | 0.28272  |
| C12               | 0.55622  | -0.43130 | 0.26276  |
| C13               | 0.36921  | -0.39717 | 0.28641  |
|   |      |      |      |
|---|------|------|------|
| C14 | 0.36902 | -0.37829 | 0.32938 |
| C15 | 0.25850 | -0.24434 | 0.47206 |
| C16 | 0.21754 | -0.20160 | 0.49368 |
| C17 | 0.38376 | -0.17653 | 0.52909 |
| C18 | 0.58869 | -0.19508 | 0.54370 |
| C19 | 0.62719 | -0.23806 | 0.52245 |
| C20 | 0.45708 | -0.43461 | 0.46896 |
| C21 | 0.47131 | -0.45512 | 0.49176 |
| C22 | 0.65311 | -0.43959 | 0.52715 |
| C23 | 0.47937 | -0.43566 | 0.19614 |
| C24 | 0.48747 | -0.45961 | 0.15052 |
| N25 | 0.56687 | -0.45144 | 0.21858 |
| N26 | 0.35030 | -0.13259 | 0.54719 |
| C27 | 0.47937 | -0.43566 | 0.19614 |
| C28 | 0.33829 | -0.44282 | 0.12902 |
| C29 | 0.46303 | -0.10420 | 0.58177 |
| C30 | 0.41896 | -0.05981 | 0.59572 |
| C31 | 0.61052 | -0.52033 | 0.08508 |
| C32 | 0.63358 | -0.49833 | 0.12840 |
| C33 | 0.46287 | -0.03125 | 0.63779 |
| C34 | 0.44191 | 0.01160 | 0.65278 |
| C35 | 0.35725 | 0.02566 | 0.62541 |
| C36 | 0.31476 | -0.00276 | 0.58345 |
| C37 | 0.35488 | -0.04531 | 0.56794 |
| C38 | 0.44373 | -0.52622 | 0.01854 |
| C39 | 0.33739 | 0.07024 | 0.63914 |
| O40 | 0.80537 | -0.51287 | 0.15041 |
| O41 | 0.17901 | -0.44778 | 0.06359 |
| O42 | 0.34105 | -0.07293 | 0.52512 |
| O43 | 0.51626 | 0.04125 | 0.69369 |
| N44 | 0.28183 | 0.09712 | 0.67741 |
| C45 | 0.29099 | 0.14109 | 0.69500 |
| C46 | 0.13273 | 0.16562 | 0.73148 |
| C47 | 0.15414 | 0.20873 | 0.75143 |
| C48 | 0.34067 | 0.22794 | 0.73552 |
| C49 | 0.50087 | 0.20315 | 0.69893 |
| C50 | 0.47664 | 0.16012 | 0.67886 |
| C51 | 0.37259 | 0.27359 | 0.75728 |
| C52 | 0.39151 | 0.29444 | 0.73476 |
|   |       |       |       |
|---|-------|-------|-------|
| C57 | 0.42806 | 0.33743 | 0.75480 |
| C58 | 0.43563 | 0.35993 | 0.79801 |
| C59 | 0.41830 | 0.33972 | 0.82127 |
| C60 | 0.38982 | 0.29642 | 0.80051 |
| C61 | 0.46306 | 0.35857 | 0.73035 |
| C62 | 0.43289 | 0.36376 | 0.86708 |
| C63 | 0.30789 | 0.39544 | 0.74131 |
| C64 | 0.33729 | 0.41473 | 0.71751 |
| C65 | 0.52415 | 0.39747 | 0.68255 |
| C66 | 0.67379 | 0.36074 | 0.67160 |
| C67 | 0.64949 | 0.34152 | 0.69540 |
| C68 | 0.26147 | 0.35190 | 0.89119 |
| C69 | 0.27414 | 0.37482 | 0.93428 |
| C70 | 0.45100 | 0.41036 | 0.95390 |
| C71 | 0.62447 | 0.42223 | 0.93019 |
| C72 | 0.61746 | 0.39897 | 0.88716 |
| N73 | 0.45643 | 0.43365 | 0.99798 |
| N74 | 0.54988 | 0.41462 | 0.65584 |
| C75 | 0.48581 | 0.45211 | 0.66477 |
| C76 | 0.51048 | 0.46500 | 0.63325 |
| C77 | 0.50287 | 0.50741 | 0.64641 |
| C78 | 0.52217 | 0.52163 | 0.61805 |
| C79 | 0.55470 | 0.49276 | 0.57556 |
| C80 | 0.55809 | 0.45027 | 0.56231 |
| C81 | 0.53464 | 0.43607 | 0.59065 |
| C82 | 0.57326 | 0.50580 | 0.54409 |
| O83 | 0.56185 | 0.39371 | 0.57716 |
| O84 | 0.53406 | 0.56422 | 0.63199 |
| C85 | 0.52004 | -0.06174 | 0.50029 |
| C86 | 0.54839 | -0.09889 | 0.45697 |
| C87 | 0.68699 | -0.13602 | 0.45794 |
| S88 | 0.80372 | -0.17579 | 0.40639 |
| C89 | 0.66102 | 0.02914 | 0.72000 |
| C90 | 0.78119 | 0.06849 | 0.75672 |
| C91 | 0.85983 | 0.06210 | 0.79304 |
| S92 | 1.02532 | 0.10890 | 0.83513 |
| C93 | 0.19418 | -0.40402 | 0.08017 |
| C94 | 0.08412 | -0.39461 | 0.04696 |
| C95 | 0.15229 | -0.35000 | 0.05722 |
| S96 | -0.03977 | -0.31093 | 0.10387 |
| C97 | 0.91895 | -0.55405 | 0.12982 |
| C98 | 1.07452 | -0.56118 | 0.16209 |
| C99 | 1.14377 | -0.60706 | 0.14544 |
|   |   |   |   |
|---|---|---|---|
| S100 | 1.32048 | -0.61525 | 0.18494 |
| C101 | 0.36351 | 0.36598 | 0.54529 |
| C102 | 0.55809 | 0.33281 | 0.51151 |
| C103 | 0.37912 | 0.29797 | 0.47647 |
| S104 | 0.24323 | 0.25947 | 0.48953 |
| C105 | 0.32358 | 0.59051 | 0.66274 |
| C106 | 0.17972 | 0.61828 | 0.64820 |
| C107 | 0.07282 | 0.65931 | 0.68448 |
| S108 | -0.08108 | 0.69339 | 0.66694 |
| O109 | 1.54048 | -0.65216 | 0.16566 |
| O110 | -0.28296 | -0.32897 | 0.11986 |
| O111 | -0.23207 | -0.28314 | 0.09307 |
| O112 | 0.15316 | -0.27619 | 0.14741 |
| O113 | 1.53438 | -0.57966 | 0.21292 |
| O114 | 1.10853 | -0.62339 | 0.21878 |
| O115 | 1.01341 | -0.15851 | 0.38561 |
| O116 | 1.01157 | -0.20777 | 0.40863 |
| O117 | 0.54926 | -0.20574 | 0.36869 |
| O118 | 1.25012 | 0.09836 | 0.86006 |
| O119 | 1.23173 | 0.13158 | 0.81957 |
| O120 | 0.80420 | 0.14741 | 0.87192 |
| O121 | -0.30146 | 0.72492 | 0.69913 |
| O122 | -0.28833 | 0.67088 | 0.62907 |
| O123 | 0.14961 | 0.72292 | 0.65491 |
| O124 | -0.00752 | 0.23388 | 0.45897 |
| O125 | 0.07433 | 0.27743 | 0.53100 |
| O126 | 0.47472 | 0.22222 | 0.48887 |
**Supplementary Table 3.** Fractional atomic coordinates of the structural model of COF-DT-SO$_3$Na with eclipsed (AA) stacking mode, resulting from Pawley refinement against experimental PXRD data.

| COF-DT-SO$_3$Na |
|------------------|
| Triclinic, $P1$, $a = 4.93$ Å, $b = 35.36$ Å, $c = 36.55$ Å, $\alpha = 62.61^\circ$, $\beta = \gamma = 90^\circ$ |
| Atom | $x$     | $y$     | $z$     |
|------|---------|---------|---------|
| C1   | 0.66341 | 0.84122 | -0.44379|
| C2   | 0.64125 | 0.82640 | -0.47361|
| C3   | 0.61679 | 0.78262 | -0.46193|
| C4   | 0.62253 | 0.75336 | -0.41961|
| C5   | 0.64167 | 0.76694 | -0.38898|
| C6   | 0.66479 | 0.81113 | -0.40163|
| C7   | 0.63331 | 0.73677 | -0.34689|
| C8   | 0.58260 | 0.76766 | -0.49128|
| C9   | 0.66579 | 0.88552 | -0.45693|
| C10  | 0.82384 | 0.73843 | -0.31882|
| C11  | 0.81161 | 0.70897 | -0.27682|
| C12  | 0.60637 | 0.67783 | -0.26130|
| C13  | 0.42201 | 0.67488 | -0.28953|
| C14  | 0.43451 | 0.70413 | -0.33171|
| C15  | 0.36850 | 0.73921 | -0.48665|
| C16  | 0.34530 | 0.72098 | -0.51341|
| C17  | 0.53336 | 0.73099 | -0.54536|
| C18  | 0.73546 | 0.76180 | -0.55230|
| C19  | 0.76199 | 0.77956 | -0.52500|
| C20  | 0.47406 | 0.90420 | -0.44126|
| C21  | 0.44027 | 0.94872 | -0.45991|
| C22  | 0.59900 | 0.97510 | -0.49446|
| C23  | 0.81176 | 0.95697 | -0.50673|
| C24  | 0.84481 | 0.91253 | -0.48834|
| N25  | 0.59662 | 0.65408 | -0.21986|
| N26  | 0.51171 | 0.70708 | -0.56508|
| C27  | 0.43537 | 0.62132 | -0.19496|
| C28  | 0.43883 | 0.60323 | -0.15139|
| N29  | 0.54866 | 1.01648 | -0.51989|
| C30  | 0.65365 | 0.70612 | -0.59604|
| C31  | 0.60885 | 0.67247 | -0.60561|
| C32  | 0.29875 | 0.56427 | -0.12858|
| C33  | 0.28838 | 0.54438 | -0.08516|
| C34  | 0.40948 | 0.56449 | -0.06348|
| C35  | 0.54647 | 0.60359 | -0.08598|
| C36  | 0.57000 | 0.62227 | -0.12926|
|   |        |        |        |
|---|--------|--------|--------|
| C37 | 0.59216 | 0.68179 | -0.64758 |
| C38 | 0.55110 | 0.64916 | -0.65899 |
| C39 | 0.52413 | 0.60639 | -0.62786 |
| C40 | 0.54143 | 0.59738 | -0.58603 |
| C41 | 0.58701 | 0.62963 | -0.57419 |
| C42 | 0.40389 | 0.54433 | -0.02008 |
| C43 | 0.49767 | 0.57173 | -0.63668 |
| O44 | 0.72170 | 0.65824 | -0.14985 |
| O45 | 0.16913 | 0.50540 | -0.06307 |
| O46 | 0.61969 | 0.61925 | -0.53328 |
| O47 | 0.54157 | 0.65778 | -0.69944 |
| N48 | 0.38779 | 0.57559 | -0.67204 |
| C49 | 0.39114 | 0.54834 | -0.68841 |
| C50 | 0.20912 | 0.55659 | -0.72082 |
| C51 | 0.21902 | 0.53262 | -0.74260 |
| C52 | 0.41379 | 0.49989 | -0.73239 |
| C53 | 0.58896 | 0.49046 | -0.69859 |
| C54 | 0.57731 | 0.51432 | -0.67673 |
| C55 | 0.43584 | 0.47763 | -0.75587 |
| C56 | 0.44995 | 0.43278 | -0.73648 |
| C57 | 0.47205 | 0.41000 | -0.75952 |
| C58 | 0.47563 | 0.43317 | -0.80299 |
| C59 | 0.46125 | 0.47829 | -0.82369 |
| C60 | 0.44501 | 0.49981 | -0.79934 |
| C61 | 0.47898 | 0.36503 | -0.73865 |
| C62 | 0.46130 | 0.50132 | -0.86728 |
| C63 | 0.29699 | 0.34085 | -0.74948 |
| C64 | 0.28153 | 0.29632 | -0.72570 |
| C65 | 0.44758 | 0.27518 | -0.69059 |
| C66 | 0.64107 | 0.29872 | -0.68122 |
| C67 | 0.65786 | 0.34319 | -0.70510 |
| C68 | 0.28720 | 0.53681 | -0.88859 |
| C69 | 0.28325 | 0.55886 | -0.93197 |
| C70 | 0.44735 | 0.54529 | -0.95524 |
| C71 | 0.62681 | 0.51084 | -0.93439 |
| C72 | 0.63500 | 0.48937 | -0.89113 |
| N73 | 0.42808 | 0.56501 | -0.99681 |
| N74 | 0.42696 | 0.23361 | -0.66334 |
| C75 | 0.27284 | 0.20182 | -0.66284 |
| C76 | 0.27445 | 0.16237 | -0.62728 |
| C77 | 0.32286 | 0.12512 | -0.63138 |
| C78 | 0.34405 | 0.08511 | -0.59640 |
| C79 | 0.31856 | 0.08255 | -0.55649 |
|   |   |   |   |
|---|---|---|---|
| C80 | 0.25262 | 0.11962 | -0.55265 |
| C81 | 0.23031 | 0.15969 | -0.58773 |
| C82 | 0.35149 | 0.04343 | -0.52080 |
| O83 | 0.16615 | 0.19644 | -0.58582 |
| O84 | 0.38721 | 0.04884 | -0.60035 |
| C85 | 0.65937 | 0.57794 | -0.49881 |
| C86 | 0.69485 | 0.58052 | -0.45802 |
| C87 | 0.89265 | 0.61565 | -0.46046 |
| S88 | 0.95488 | 0.60888 | -0.40837 |
| C89 | 0.64454 | 0.47581 | -0.07645 |
| C90 | 0.82189 | 0.66937 | -0.75588 |
| C91 | 0.87118 | 0.69641 | -0.80284 |
| S92 | 1.07837 | 0.66884 | -0.82378 |
| C93 | 0.06798 | 0.47581 | -0.07645 |
| C94 | 0.00808 | 0.43359 | -0.03719 |
| C95 | 0.05827 | 0.39303 | -0.04250 |
| S96 | -0.17714 | 0.38567 | -0.07644 |
| C97 | 0.84981 | 0.68709 | -0.13777 |
| C98 | 1.02029 | 0.71661 | -0.17562 |
| C99 | 1.09005 | 0.76069 | -0.17886 |
| S100 | 1.29767 | 0.79158 | -0.22355 |
| C101 | 0.07751 | 0.20703 | -0.55423 |
| C102 | 0.28994 | 0.23790 | -0.55169 |
| C103 | 0.20261 | 0.26410 | -0.52924 |
| S104 | -0.01362 | 0.30940 | -0.55860 |
| C105 | 0.35387 | 0.03827 | -0.63351 |
| C106 | 0.18122 | -0.00270 | -0.61485 |
| C107 | 0.13612 | -0.02261 | -0.64437 |
| S108 | -0.08899 | -0.06795 | -0.62274 |
| O109 | 1.48226 | 0.82531 | -0.21819 |
| O110 | -0.36086 | 0.42548 | -0.10363 |
| O111 | -0.37336 | 0.34705 | -0.05071 |
| O112 | -0.06744 | 0.37096 | -0.11122 |
| O113 | 1.50085 | 0.76247 | -0.23270 |
| O114 | 1.16601 | 0.82014 | -0.27056 |
| O115 | 1.21205 | 0.58012 | -0.38772 |
| O116 | 1.19768 | 0.63985 | -0.43223 |
| O117 | 0.98698 | 0.65083 | -0.39868 |
| O118 | 1.22042 | 0.69976 | -0.86584 |
| O119 | 1.32274 | 0.64524 | -0.79423 |
| O120 | 0.95413 | 0.63022 | -0.83334 |
| O121 | -0.25269 | -0.07305 | -0.65746 |
| O122 | -0.31144 | -0.06457 | -0.59327 |
|     |     |     |     |
|-----|-----|-----|-----|
| O123 | 0.03355 | -0.11696 | -0.59433 |
| O124 | -0.18127 | 0.32118 | -0.52829 |
| O125 | -0.23238 | 0.30254 | -0.58655 |
| O126 | 0.11339 | 0.35741 | -0.59008 |
| Na205 | 1.43411 | 0.62362 | -0.85325 |
| Na206 | -0.37318 | 0.38149 | -0.59809 |
| Na207 | 1.65512 | -0.16302 | -0.29138 |
| Na208 | -0.56387 | -0.62994 | -0.12670 |
| Na209 | 1.46865 | -0.36419 | -0.37191 |
| Na210 | -0.44887 | -0.14237 | -0.58893 |
**Supplementary Table 4.** Comparison of bending performance of ionic soft actuators.

| Electrode layer | Electrolyte layer | Input potential and frequency | Length (mm) | Thickness (µm) | Peak-to-peak displacement (mm) | Bending strain difference (%) | Force (mN) | References |
|-----------------|--------------------|-------------------------------|-------------|----------------|------------------------------|------------------------------|------------|------------|
| BS-COF-C900/PEDOT:PSS | Nafion/EMIMBF₄ | ±0.5 V, 1 Hz | 20 | >85 | ~3.8 | ~0.28 | - | *Adv. Funct. Mater.* **29**, 1900161 (2019)¹ |
| BS-COF-C700/PEDOT:PSS | Nafion/EMIMBF₄ | ±0.5 V, 1 Hz | 20 | >85 | ~3.0 | ~0.23 | - | |
| TP6/PEDOT:PSS | Nafion/EMIMBF₄ | ±0.5 V, 1 Hz | 25 | ~115 | ~3.8 | ~0.13 | ~1.20 | *Nat. Commun.* **11**, 5358 (2020)² |
| PVdF/Graphdiyne | PVdF/EMIMBF₄ | ±0.5 V, 0.1 Hz | 25 | ~80 | ~18.0 | ~0.78 | 3.37 | *Nat. Commun.* **9**, 752 (2018)³ |
| PVdF/CNT | PVdF/EMIMBF₄ | ±0.5 V, 0.1 Hz | 25 | ~80 | ~2.0 | ~0.04 | 1.38 | |
| PVdF/Graphene | PVdF/EMIMBF₄ | ±0.5 V, 0.1 Hz | 25 | ~80 | ~6.0 | ~0.12 | 1.92 | |
| Ni-CAT NWAs/CNF | PVdF/EMImTFSI | ±3 V, 1 Hz | 25 | ~80 | ~6.0 | ~0.22 | 1.45 | *J. Am. Chem. Soc.* **143**, 4017-4023 (2021)⁴ |
| RGO/MWCNT | PVdF/BMIMBF₄ | ±2 V, 1 Hz | 30 | ~130 | ~0.7 | ~0.03 | 0.41 | *Adv. Mater.* **24**, 4317-4321 (2012)⁵ |
| MWCNT | PVdF/BMIMBF₄ | ±2 V, 1 Hz | 30 | ~130 | ~0.3 | ~0.01 | 0.22 | |
| RGO | PVdF/BMIMBF₄ | ±2 V, 1 Hz | 30 | ~130 | ~0.3 | ~0.01 | 0.5 | |
| PEDOT:PSS | COF-DT-SO₃Na | ±0.5 V, 1 Hz | 20 | ~60 | ~9.6 | ~0.38 | 1.5 | *This work* |
Supplementary Figures

Supplementary Fig. 3. ATR FT-IR spectra. Full width stacked ATR FT-IR spectra of COF-DT (green line), COF-DT-SO$_3$H (blue line), and COF-DT-SO$_3$Na (orange line).
Supplementary Fig. 4. SEM and elemental mappings. SEM mapping of a COF-DT, b COF-DT-$SO_3$H, and c COF-DT-$SO_3$Na, respectively. Elemental mapping of d COF-DT, e COF-DT-$SO_3$H, and f COF-DT-$SO_3$Na.
Supplementary Fig. 5. Pore size distribution (PSD). a COF-DT, b COF-DT-SO$_3$H, and c COF-DT-SO$_3$Na by using Non-Local Density Functional Theory (NLDFT) modeling, cumulative volume (blue circle line), dV/dw (orange circle line).
Supplementary Fig. 6. Electrochemical impedance spectroscopy (EIS) of the COF-DT (blue circle).

Supplementary Fig. 7. Electrochemical impedance spectroscopy (EIS) of the COF-DT-SO$_3$H (blue circle).
Supplementary Fig. 8. The peak-to-peak displacement (blue circle line) of the actuator reach the equilibrium-bending motion under 0.5 V DC voltage.

Supplementary Fig. 9. Comparison of peak-to-peak displacement of the actuators under different applied frequencies (0.1-20 Hz). Nafion based actuator (red cycle line), COF-DT-SO$_3$Na based actuator (blue circle line).
Supplementary Fig. 10. Size distribution of COF-DT-SO$_3$Na (blue bar).
Supplementary References

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