Supporting Information

Electron Highways into Nanochannels of Covalent Organic Frameworks for High Electrical Conductivity and Energy Storage

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Section A. Material and Method

All the solvents were purchased from Kanto Chemicals. All chemicals including DAAQ and DBrEDOT were purchased from TCI.

Synthesis of triformylephloroglucinol (TFP)

Anhydrous phloroglucinol (6.0 g, 49 mmol) and hexamethylenetetramine (15.0 g, 108 mmol) were added into the flask under the N_2 atmosphere. 90 mL of trifluoroacetic acid was slowly added to the reaction mixture and stirred for 5 h at 100 °C. Then 150 mL of 3 M HCl was added into the reaction vessel and the reaction was continued for another 2 h under the same condition. After that, the reaction mixture was allowed to cool down to room temperature and filtered through celite. The desired product was extracted from the solution with 380 mL of dichloromethane. The organic layer was washed with water and saturated aqueous sodium chloride, dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent using a rotary evaporator, TFP was yielded as off-white solid (2 g).

Preparation of AQ-COF

AQ-COF was synthesized under typical solvothermal condition. A 10 mL Pyrex tube was charged with 2,4,6-Triformylphloroglucinol (TFP) (40 mg, 0.2 mmol), 2,6-diaminoanthraquinone (DAAQ) (68 mg, 0.3 mmol), Dimethylacetamide/mesitylene (2.4 mL, 3/1 by vol.) and 6 M acetic acid (0.1 mL). The resulting mixture was sonicated for 1 minute at room temperature and degassed via 3 freeze-pump-thaw cycles. The tube was sealed under vacuum heated at 120 °C for 3 days. The reaction mixture was cooled to room temperature and the dark-red precipitate was collected by centrifugation and washed with DMF and acetone. The powder was exhaustively washed by Soxhlet extractions with THF for 24 hours and then dried under vacuum at 120 °C overnight. The AQ-COF was isolated as a red powder in 80% yield.

Preparation of PEDOT@AQ-COF

In a 30 mL glass vial, a solution was prepared by dissolving 360 mg of 2,5-dibromo-3,4-ethylenedioxythiophene (DBrEDOT) in 15 mL of acetone. 200 mg of AQ-COF was added to
the solution and stirred at 25°C for 1 hour. The acetone was then evaporated under reduced pressure (20 kPa, 25°C). The obtained red powder was then rinsed was hexane (5 mL) to remove the surface DBrEDOT, dried under vacuum and sealed into glass vial under nitrogen. After that, the glass vial was heated in an oven at 60 °C for 3 days and 85 °C for 1 day. The reaction temperature is lower than the melting point of the DBrEDOT. So, the product of the in situ solid-state polymerization, PEDOT, will be remained in the nanochannels of COF. After cooling down, the black powder was washed with 10 mL of acetone, 20 mL of aqueous sodium hydrosulfite (1 M), 20 mL of water and 10 mL of acetone. Then the powder was dried under vacuum at 120 °C overnight. The PEDOT@AQ-COF composite was obtained as black powder (300 mg). Elemental analysis of the calculated \([[(C_{60}H_{30}N_{6}O_{12})\cdot(C_{6}H_{4}O_{2}S)_{10.08}\cdot(H_{2}O)_{10.5}\cdot(Br)_{2}]\): C (51.89 %), H (3.30 %), N (3.01 %), S (11.59 %); found: C (49.50 %), H (3.30 %), N (3.01 %), S (11.58 %).

**Calculation based on Elemental analysis**

1) Results from Structure:

   a. Chemical Formula for Unit cell of AQ-COF:

   \[C_{60}H_{30}N_{6}O_{12}\] (Molecular Weight: 1026.93)

   b. Chemical Formula for Repeating unit of PEDOT:

   \[C_{6}H_{4}O_{2}S\] (Molecular Weight: 140.16)

2) Results from Elemental analysis:

   C (49.50 wt%), H (3.30 wt%), N (3.01 wt%), S (11.58 wt%)

3) Atomic mass \((m_a)\) from periodic table of elements:

   C:12.01; H:1.01; N:14.01; S:32.06; O:16.00; Br:79.90

4) Calculate the molar ratio of N: S

   \[\frac{(3.01 \text{ wt%})}{(14.01 \text{ wt%})} = 1:1.68\]
5) Calculate the molar ratio of Unit cell of AQ-COF(C60H30N6O12): Repeating unit of PEDOT(C6H4O2S)

\[
\frac{(1/6)}{1.68} = 1:10.08
\]

6) Calculate the mass ratio of AQ-COF: PEDOT

\[
1026.93:(140.16 \times 10.08) = 1:1.38 \approx 1:1.4
\]

7) Calculate the composition:

Assume the composition to be \((\text{C}_{60}\text{H}_{30}\text{N}_{6}\text{O}_{12}) \cdot (\text{C}_6\text{H}_4\text{O}_2\text{S})_{10.08} \cdot (\text{H}_2\text{O})_x \cdot (\text{Br})_y\)

When \(x = 10.5\) and \(y = 2\), the calculated elemental composition is C (51.89 %), H (3.30 %), N (3.01 %), S (11.59 %), which is very close to the experimental result.

So the calculated formula is \((\text{C}_{60}\text{H}_{30}\text{N}_{6}\text{O}_{12}) \cdot (\text{C}_6\text{H}_4\text{O}_2\text{S})_{10.08} \cdot (\text{H}_2\text{O})_{10.5} \cdot (\text{Br})_2\)

**Preparation of PEDOT**

300 mg of 2,5-Dibromo-3,4-ethylenedioxythiophene (DBrEDOT) was sealed into a 10 mL glass vial under nitrogen. After that, the glass vial was heated in an oven at 60 °C for 3 days and 85 °C for 1 day. After cooling down, the black powder was washed with 10 mL of acetone, 20 mL of aqueous sodium hydrosulfite (1 M), 20 mL of water and 10 mL of acetone. Then the powder was dried under vacuum at 120 °C overnight. The PEDOT was obtained as black powder (100 mg).

**Preparation of the electrodes**

The active material slurry was prepared by dispersing PEDOT@AQ-COF (91 wt%) and polyvinylidene fluoride (PVDF) binder (9 wt%) in N-Methyl-2-Pyrrolidone (NMP). The slurry was coated on the top of a glassy carbon (GC) electrode. The geometric surface area of the GC electrode is 0.07 cm\(^2\) and active materials loading measured to be 0.29 mg/cm\(^2\).

**Characterization methods**
High-resolution transmission electron microscopy (HR-TEM) images and Energy dispersive X-ray fluorescence (EDX) spectra were obtained on a JEOL JEM-2100plus Field Emission Electron Microscope equipped with EDS system. Scanning electron microscope (SEM) images were obtained on a Hitachi S-4300 field emission SEM. Powder X-ray diffraction (PXRD) measurement was performed on a Rigaku MultiFlex X-ray diffractometer, the scanning speed was 2 ° min⁻¹, and the diffraction angle range was from 1.5 to 60 ° with 0.02 ° increment. Thermal gravimetical analysis (TGA) was carried out on an Exstar TG/DTA 6200 thermal analyzer under N₂, by heating to 900 °C at a rate of 5 °C min⁻¹. Elemental analysis of activated framework was performed on a PerkinElmer 2400 series II CHNS/O elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer using ATR. Nitrogen (N₂) gas adsorption and desorption measurement was carried out on a BELSORP-min surface area and pore size analyzer. The saturation pressure is 101kPa. The adsorption and desorption were performed at 77 K, and the adsorption/desorption data were analyzed by BELmasterTM software in which Brunauer-Emmett-Teller (BET) method and NL-DFT analysis were integrated. Electrochemistry experiments were conducted on a BioLogic SP-150 single potentiostat electrochemical analyzer using a standard three-electrode system in 1M H₂SO₄ aqueous solution. Active material coated GC electrode, Pt wire and an aqueous Ag/AgCl electrode were considered as working, counter and reference electrodes, respectively.
Section B. Supporting Figures

Figure S1. Redox active AQ unit and β-ketoenamine linkage.
Figure S2. FT-IR spectra AQ-COF, PEDOT and PEDOT@AQ-COF.

For AQ-COF, the characteristic absorbances of β-ketoenamine linkage at 1235, 1555 and 1615 cm\(^{-1}\), are attributed to the C-N, C=C and C=O bonds, respectively. The absorption band at around 1675 cm\(^{-1}\) is assigned to the C=O stretching in anthraquinone (AQ) group. For PEDOT, the characteristic peaks at 1500 and 1270 cm\(^{-1}\) are attributed to the asymmetric C=C stretching and inter-ring C-C stretching, respectively. The absorbances at 1165, 1120, 1070, and 1000 cm\(^{-1}\) are due to bending vibrations of C-O-C bond in ethylenedioxy group. The peaks at 950, 865, and 720 cm\(^{-1}\) are the characteristic absorbances of C-S-C stretching vibrations in thiophene ring. The spectrum of PEDOT@AQ-COF shows characteristic absorbances of both AQ-COF and PEDOT. The characteristic bands of β-ketoenamine linkage and anthraquinone group are identical to that of AQ-COF, which indicated the preservation of the AQ-COF during the polymerization. The peaks appear around 1510 and 1315 cm\(^{-1}\) corresponding to the asymmetric C=C stretching and inter-ring C-C stretching, respectively, which indicates the formation of PEDOT. The broad absorption observed for PEDOT (1600 to 4000 cm\(^{-1}\)) and PEDOT@AQ-COF (1700 to 4000 cm\(^{-1}\)) could be assigned to the electronic excitation due to the low band gap of both PEDOT and PEDOT@AQ-COF.

(Ref.: \textit{J. Am. Chem. Soc.} 2004, \textbf{126}, 426; and \textit{Science} 2001, \textbf{293}, 79.)
Figure S3. Chemical stability experiment of AQ-COF. (A) FT-IR, (B) PXRD and (C) N\textsubscript{2} sorption isotherms of AQ-COF before and after 1 M H\textsubscript{2}SO\textsubscript{4} treatment. In the chemical stability experiment, 50 mg of AQ-COF was immersed in 1 M H\textsubscript{2}SO\textsubscript{4} (5 mL) at room temperature for 5 days. Then, the AQ-COF was collected by centrifugation and washed with water and acetone. About 99% of AQ-COF was recovered after being dried under vacuum at 120 °C overnight.
Figure S4. TGA curves of AQ-COF, PEDOT and PEDOT@AQ-COF. The weight loss before 100 °C is the evacuation of adsorbed water.
Figure S5. SEM image of AQ-COF.
Figure S6. SEM image of PEDOT@AQ-COF.
Figure S7. HR-TEM image of AQ-COF.
Figure S8. HR-TEM image of PEDOT@AQ-COF.
Figure S9. EDX elemental mapping results for AQ-COF.
Figure S10. EDX elemental mapping results for PEDOT@AQ-COF.

The elements carbon and oxygen come from both AQ-COF and PEDOT. The element nitrogen was attributed to AQ-COF, element sulfur was assigned to PEDOT, and element bromine can be attributed to the bromine at the end of PEDOT chains and doped bromine ions.
Figure S11. Schematic diagram of (A) the two-probe measurement and (B) the four-probe measurement. The conductivity ($\sigma$) value was calculated by as $\sigma = 1 / \rho = L / (R \times W \times H)$, where $\rho =$ resistivity, $R =$ resistance, $H =$ height, $L =$ length, $W =$ width, $I =$ current, $V =$ voltage.

To prepare the pressed sample pellets, firstly, the sample (about 50 mg) was grinded into a homogeneous powder with a mortar and pestle. The powder was then added to a standard 10 mm die and then pressed at 100 kN for 60 min to form a membrane. The pellet was cut into a rectangle. To the rectangle-shaped pellet, gold wires with a diameter of 25 μm were attached by gold paste. The pellet was then connected and mounted to a sample probe and placed in a cryostat. Conductivity measurements were performed under nitrogen atmosphere. Conductivity were investigated in the four-probe current-applying voltage measurement (V-I) method and the voltage-applying current measurement (I-V) method by an ADVANTEST R6245 source meter in direct current mode controlled by a PC through the GP-IB interface with custom-made software. The temperature dependence of the conductivity was measured upon cooling in the temperature range from 298 to 77 K.
Figure S12. Conductivity measurements by two-probe method. (A) Room-temperature I–V plots of PEDOT@AQ-COF. (B) Time-dependent resistance at room-temperature. (C) Temperature-dependent conductivity profiles of PEDOT@AQ-COF.
Figure S13. CV curves of AQ-COF/PEDOT recorded at different scan rates.
Figure S14. CV curves of PEDOT@AQ-COF recorded at different scan rates.
Figure S15. Nyquist plot of AQ-COF/PEDOT (black) and PEDOT@AQ-COF (red) electrode with the inset showing high-frequency region. ESR was obtained from the x-interception of the Nyquist plot.
Figure S16. GCD profiles AQ-COF/PEDOT at different current densities.
Section C. Supporting Tables

Table S1. Summary of electrical conductivity (room-temperature) of different COF-based materials reported to date.

| Materials          | Conductivity (S cm⁻¹) | Ref.              |
|--------------------|-----------------------|-------------------|
| PEDOT@AQ-COF       | 1.1                   | This Work         |
| I₂@TTF-Ph-COF      | 10⁻⁵                 | Chem. Eur. J. 2014, 20, 14608 |
| I₂@TTF-Py-COF      | 10⁻⁶                 | Chem. Eur. J. 2014, 20, 14608 |
| TTF-COF            | 1.2×10⁻⁶             | Chem. Sci. 2014, 5, 4693 |
| I₂@TTF-COF         | 1×10⁻⁵               | Chem. Sci. 2014, 5, 4693 |
| TCNQ@TTF-COF       | 2.8×10⁻³             | Chem. Sci. 2014, 5, 4693 |
| I₂@TTF-COF         | 1.8×10⁻⁶             | Chem. Eur. J. 2014, 20, 14614 |
| sp²c-COF           | 6.1×10⁻¹⁶            | Science 2017, 357, 673 |
| I₂@sp²c-COF        | 7.1×10⁻⁴             | Science 2017, 357, 673 |
| PyVg-COF           | 4×10⁻³               | Chem. Sci. 2019. DOI: 10.1039/C8SC04255A |
Table S2. Summary of supercapacitor performance of different COF-based materials reported to date.

| Active material                  | Capacitance | Experiment parameter | Electrodes                            | Ref.                                      |
|----------------------------------|-------------|----------------------|---------------------------------------|-------------------------------------------|
| PEDOT@AQ-COF                    | 1663 F g⁻¹  | 1 A g⁻¹               | Active material (91 wt. %)             | This Work                                 |
|                                  | 998 F g⁻¹   | 500 A g⁻¹             | PVDF (9 wt. %)                        |                                           |
| AQ-COF/PEDOT                    | 274 F g⁻¹   | 1 A g⁻¹               |                                       |                                           |
| DAAQ-TFP COF                    | 42 F g⁻¹    | 0.1 A g⁻¹             | Active material (35 wt. %)             | J. Am. Chem. Soc. 2013, 135, 16821       |
|                                  | 14 F g⁻¹    | 2 A g⁻¹               | carbon black (60 wt. %)                |                                           |
|                                  | 14 F g⁻¹    | 0.1 A g⁻¹             | carbon black (25 wt. %)                |                                           |
| DAB-TFP COF                     | 5 F g⁻¹     | 2 A g⁻¹               | PTFE (10 wt. %)                       |                                           |
| TaPa–Py COF                     | 102 F g⁻¹   | 0.5 A g⁻¹             | Active material (65 wt. %)             | J. Mater. Chem. A 2016, 4, 16312         |
|                                  | 62 F g⁻¹    | 10 A g⁻¹              |                                        |                                           |
| DAB-TFP COF                     | 43 F g⁻¹    | 0.5 A g⁻¹             |                                        |                                           |
|                                  | 15 F g⁻¹    | 10 A g⁻¹              |                                        |                                           |
| NiNWs@TpPa-COF                  | 426 F g⁻¹   | 2 A g⁻¹               | Active material (35 wt. %)             | Nanotechnology 2017, 28, 33LT01           |
|                                  | 314 F g⁻¹   | 50 A g⁻¹              | carbon black (60 wt. %)                |                                           |
|                                  |             |                      | PVDF (5 wt. %)                        |                                           |
| TFP-NDA-COF                     | 348 F g⁻¹   | 0.5 A g⁻¹             | ---                                   | Micropor. Mesopor. Mat. 2018, 266, 109    |
| TpOMe-DAQ COF                   | 169 F g⁻¹   | 1600 mF cm⁻²          | Active material (100 %)                | J. Am. Chem. Soc. 2018, 140 (35), 10941. |
|                                  | 3.3 mA cm⁻² |                      |                                        |                                           |
| [TEMPO]50% NiP-COF              | 124 F g⁻¹   | 0.1 A g⁻¹             | Active material (20 wt. %)             | Angew. Chem., Int. Ed. 2015, 54, 6814    |
| [TEMPO]100% NiP-COF             | 167 F g⁻¹   | 0.1 A g⁻¹             | carbon black (70 wt. %)                |                                           |
|                                  |              |                      | PTFE (10 wt. %)                       |                                           |
| DAAQ-TFP COF thin film          | 3.0 mF cm⁻² | 0.4 mA cm⁻²           | Active material (100 %)                | ACS Nano 2015, 9, 3178                    |
| DAAQ-TFP/PEDOT                  | ~110 F g⁻¹  |                      |                                        |                                           |
|                                  | 350 F cm⁻³  |                      |                                        |                                           |
|                                  | 34 mF cm⁻²  |                      |                                        |                                           |
|                                  | 20 mV s⁻¹   |                      |                                        | ACS Cent. Sci. 2016, 2, 667              |