

Supporting Information

A Simple Strategy for Construction of Bi-Supported Triazine-Based Covalent Organic Frameworks as High-Performance Capacitive Materials

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Section A. Material and methods

All commercially available reagents and solvents were used as received without further purification, unless otherwise noted. 1,3,5-Tris(4-aminophenyl)-1,3,5-triazine, 2,5-dihydroxybenzenediamine, and 2,5-dibromo-3,4-ethylenedioxythiophene were purchased from San bang Chemical. Used all solvents were purchased from Aladdin. Super-P and polyvinylidene fluoride (PVDF) were purchased from Arkema.

Fourier transforms Infrared (FT-IR) spectra were recorded on a Perkin-Elmer model FT-IR-frontier infrared spectrometer. For all FT-IR tests, a small amount of sample can be directly mixed with potassium bromide and ground into a powder, compressed, and the pressed product can be directly tested. The solid-state UV-visible analyzer was used for Jasco V-770 spectrometer Solid-state. ¹³C cross-polarization/magic angle spinning nuclear magnetic resonance (CP/MAS NMR) analysis was conducted using AVANCEIII/WB-400. Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. Transmission electron microscopy (TEM) measured on Jem-2100F spectroscopy: Oxford 64T. The operating voltage is 300 kV. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 2.5^\circ$ up to 40° with 0.02° increment. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB250Xi electron spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). TGA analysis was carried out by using a Q5000IR analyzer (TA Instruments) with an automated vertical overhead thermobalance. Before measurement, the samples were heated at a rate of $10\text{ }^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. Nitrogen sorption isotherms were measured at 77 K with Bel Japan Inc. Model BELSORP-max analyzer. Before measurement, the samples were degassed in vacuum at $120\text{ }^\circ\text{C}$ for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. The nonlocal density functional theory (NLDFT) method was applied for the estimation of pore size and pore size distribution. Before measurement, the samples were also degassed in vacuum at $120\text{ }^\circ\text{C}$ for more than 10 h.

Electrochemical Characterizations: In three-electrode system, the platinum wire and Ag/AgCl electrode were used as counter electrode and reference electrode, respectively, and the 1.0 M H₂SO₄ was used as electrolyte. The working electrode was fabricated as followed. A piece of carbon cloth (CC, 1 cm × 2 cm) was thoroughly cleaned several times with DI water followed by ethanol; it was then dried in a vacuum oven. Using a mortar and pestle, as synthesized powder samples were mixed with Super-P conductive carbon as conductive additive and polyvinylidene fluoride (PVDF) as binder (weight ratio of 8:1:1) in the presence of N-methyl-2-pyrrolidone (NMP) to make a homogeneous slurry. The resultant slurry was then uniformly coated by doctor blade on the surface of freshly cleaned CC. Subsequently, it was transferred to an electric oven and dried at 60 °C overnight to be used as an electrode. A series of electrochemical measuring techniques including cyclic voltammogram (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS) and cycling stability which were performed on a CHI 660E electrochemical workstation (Shanghai CH Instruments, China). Cyclic voltammetry measurements were performed in the potential window of 0-1 V under various scan rates. The galvanostatic charge-discharge were tested at different constant current density and the charge/discharge potential-time curve was used to calculate capacitances based on $C = i \cdot \Delta t / \Delta V$, where C (F g⁻¹) is specific capacitance, i (A g⁻¹) represents charge/discharge current density, ΔV (V) represents the potential change during charge/discharge, Δt (s) is the total discharge time. EIS was conducted in the frequency range of 10⁵ -10⁻² Hz with an amplitude of 5 mV.

Section B. Synthetic procedures

Synthesis of TD-COF

Weigh the monomers 1,3,5-tris(4-aminophenyl)-1,3,5-triazine (TAPT) (14.2 mg, 0.04 mmol) and 2,5-dihydroxybenzenediamine (DHTA) (10 mg, 0.06 mmol), and add them to a 5 mL Pyrex tube, respectively. Then, add 0.2 mL of anhydrous ethanol and 0.8 mL of 1,2-dichlorobenzene in sequence. Treat the above mixture in an ultrasonic instrument for 5 min to evenly disperse, and then add 0.2 mL of 6 M acetic acid aqueous solution. Use liquid nitrogen bath low-temperature pump thawing technology to degass the mixture for three cycles, then seal the tube under vacuum and heat it at 120 °C for 72 h. After the reaction is completed, the reaction tube is cooled to room temperature and the red solid product is separated by centrifugation. Then wash the solid sample with THF until the color of the washing solution becomes colorless. Finally, a red solid powder **TD-COF** was obtained by drying under dynamic vacuum for 12 h at 100 °C, with a yield of 82.3%.

Synthesis of TD-COF@CNT_x (x=0.05, 0.25, 0.45, 0.65)

The synthesis steps of the composite materials are similar to those of TD-COF. Weigh the monomers 1,3,5-tris(4-aminophenyl)-1,3,5-triazine (TAPT) (14.2 mg, 0.04 mmol), 2,5-dihydroxybenzenediamine (DHTA) (10 mg, 0.06 mmol), and carboxyl functionalized carbon nanotubes with different mass ratios (CNTs) (1.2 mg, 6.0 mg, 10.8 mg, 15.6 mg), and add them to a 5 mL Pyrex tube, respectively, followed by 0.2 mL of ethanol and 0.8 mL of 1,2-dichlorobenzene solution. Treat the above mixture in an ultrasonic instrument for 5 min to evenly disperse, and then add 0.2 mL of 6 M acetic acid aqueous solution. Use liquid nitrogen bath low-temperature pump thawing technology to degass the mixture for three cycles, then seal the tube under vacuum and heat it at 120 °C for 72 h. After the reaction is completed, the reaction tube is cooled to room temperature and the dark red solid product is separated by centrifugation. Then wash the solid sample with THF until the color of the washing solution becomes colorless. Finally, dark red solid powders **TD-COF@CNT_{0.05}**, **TD-COF@CNT_{0.25}**, **TD-COF@CNT_{0.45}**, and **TD-COF@CNT_{0.65}** were obtained by

drying under dynamic vacuum at 100 °C for 12 h.

Synthesis of TD-COF@CNT_{0.45}@PEDOT

Add 2,5-dibromo-3,4-ethylenedioxythiophene (DBrEDOT) (36 mg), and TD-COF@CNT_{0.45} (20 mg) to a 5 mL Pyrex tube, respectively, followed by 1.5 mL of acetone solution. Treat the above mixture in an ultrasonic instrument for 1 h to evenly disperse. Then, evaporate acetone under reduced pressure to obtain a red solid powder, and wash with hexane to remove excess DBrEDOT. After vacuum drying the sample for 6 h, seal it in a 5 mL Pyrex tube under nitrogen conditions, and heat it at 60 °C for 72 h, then continue to increase the reaction temperature and continue heating at 85 °C for 24 h. The purpose is to retain the product PEDOT of in situ solid-phase polymerization of monomer DBrEDOT in the nanochannels of TD-COF. After cooling, wash the mixture 5 times with acetone and dry it under dynamic vacuum at 80 °C for 12 h to obtain black red powder **TD-COF@CNT_{0.45}@PEDOT**.

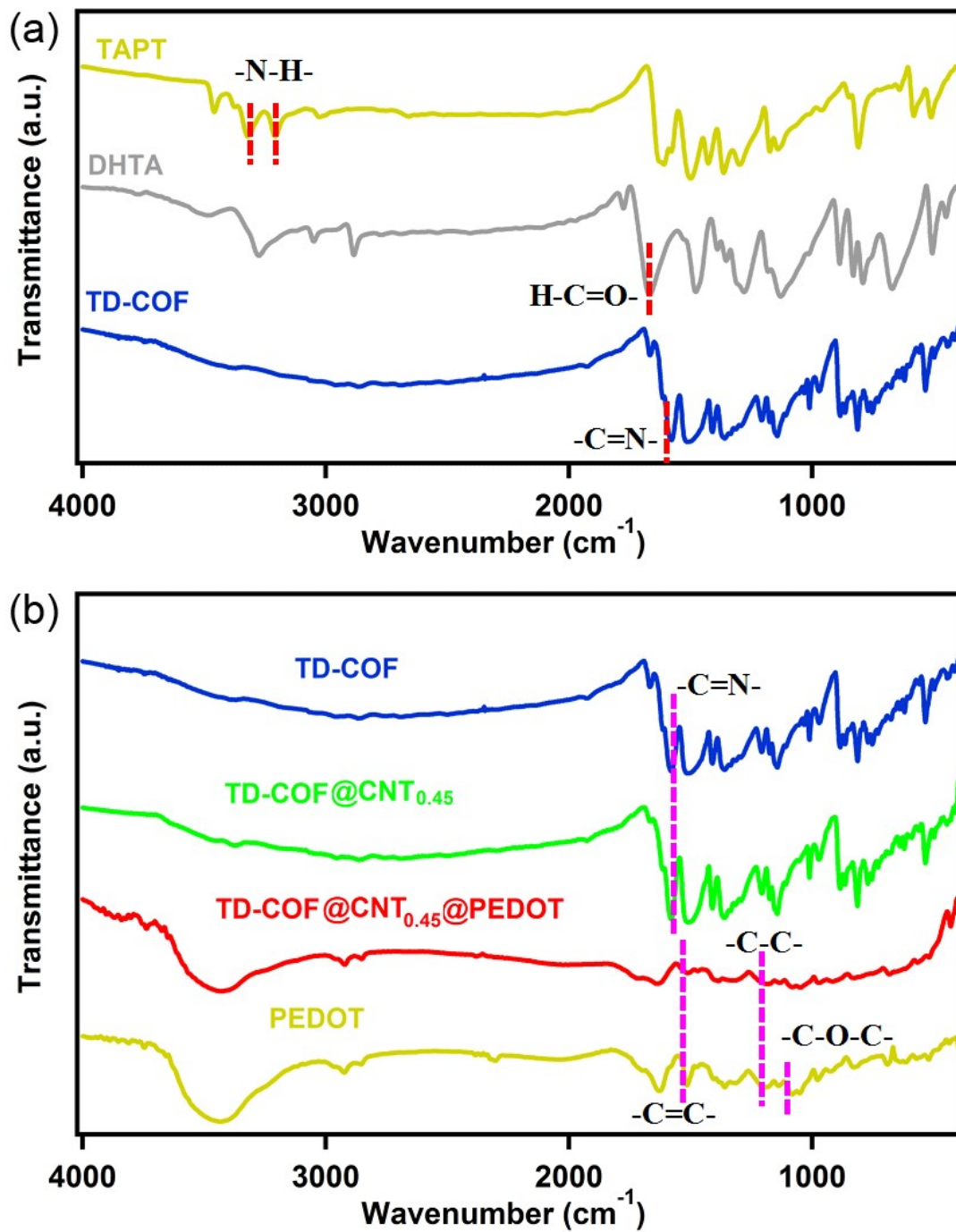


Fig. S1 FT-IR spectra of (a) TD-COF, TAPT, and DHTA; and (b) TD-COF, TD-COF@CNT_{0.45}, TD-COF@CNT_{0.45}@PEDOT, and PEDOT.

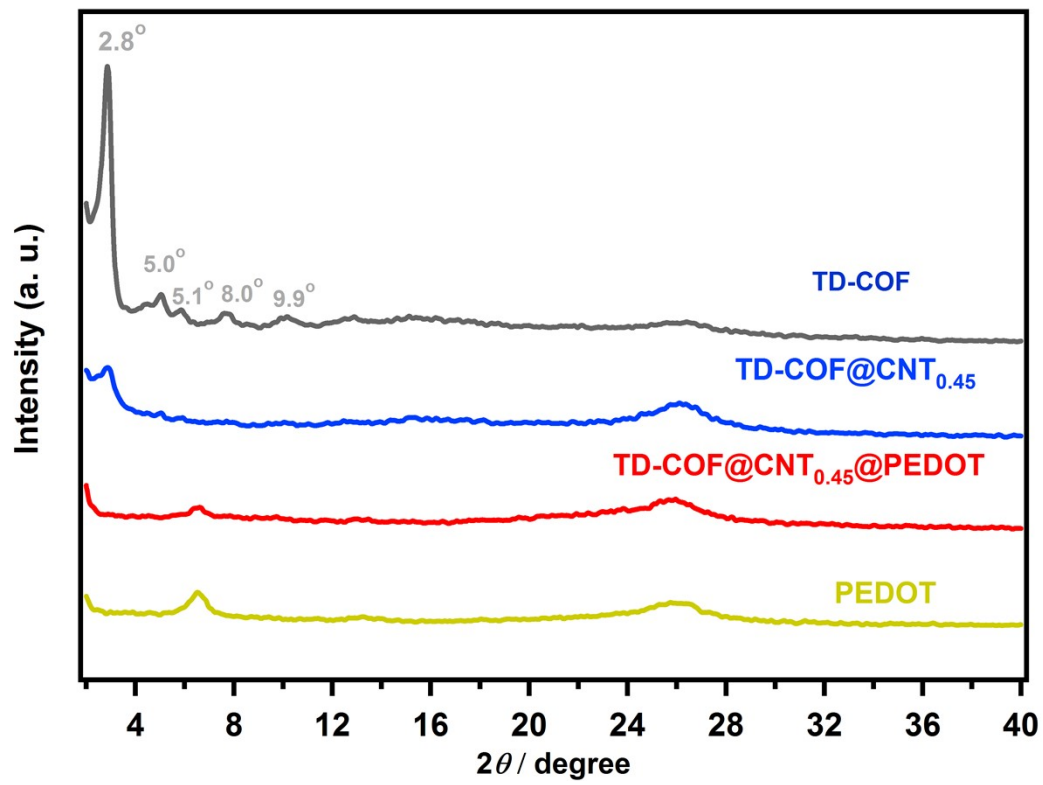


Fig. S2. PXRD patterns of TD-COF, TD-COF@CNT_{0.45}, TD-COF@CNT_{0.45}@PEDOT, and PEDOT.

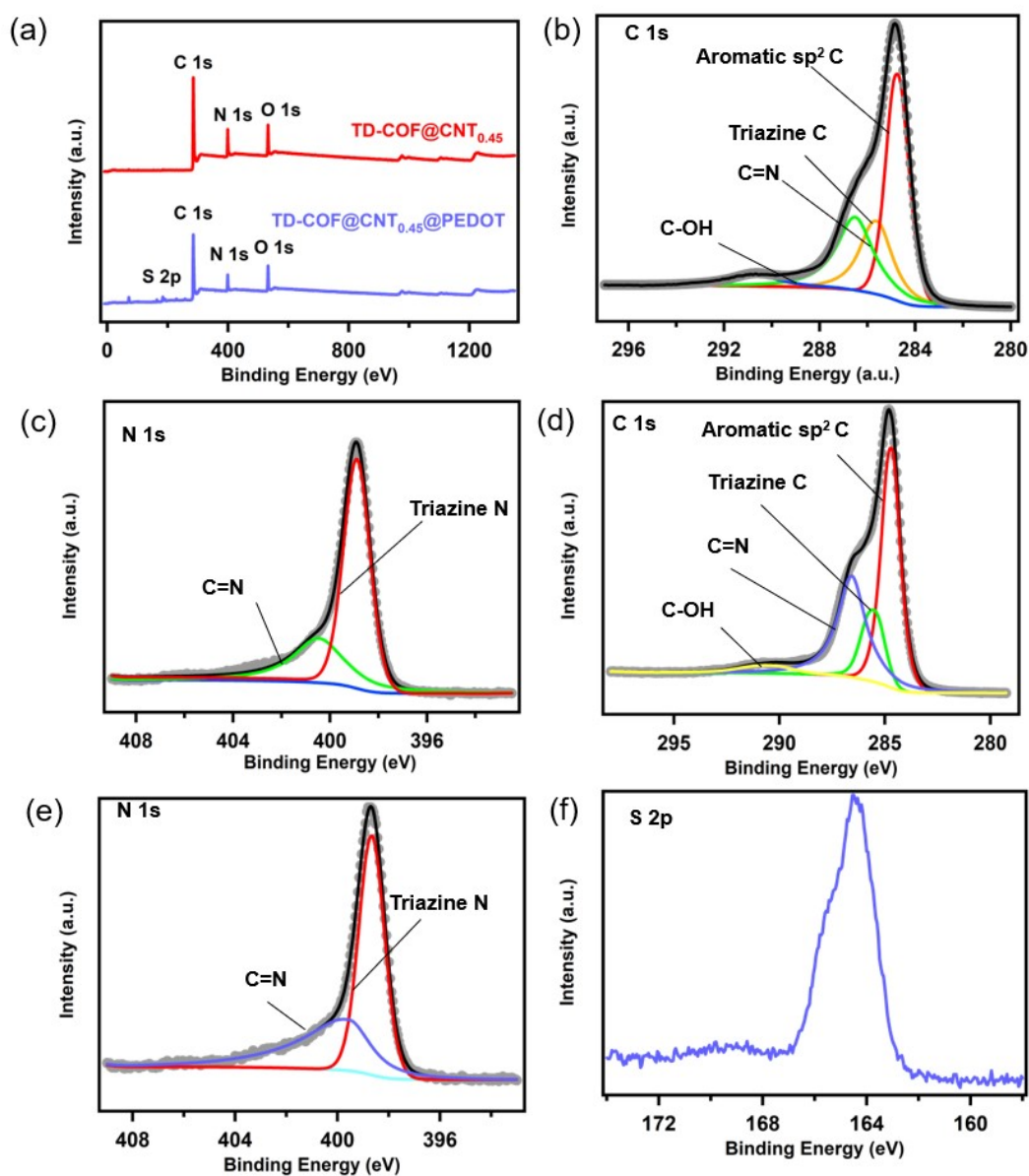


Fig. S3. (a) XPS survey spectra of the TD-COF@CNT_{0.45} and TD-COF@CNT_{0.45}@PEDOT. (b) C 1s and (c) N 1s of TD-COF@CNT_{0.45}. (d) C 1s, (e) N 1s and (f) S 2p of TD-COF@CNT_{0.45}@PEDOT.

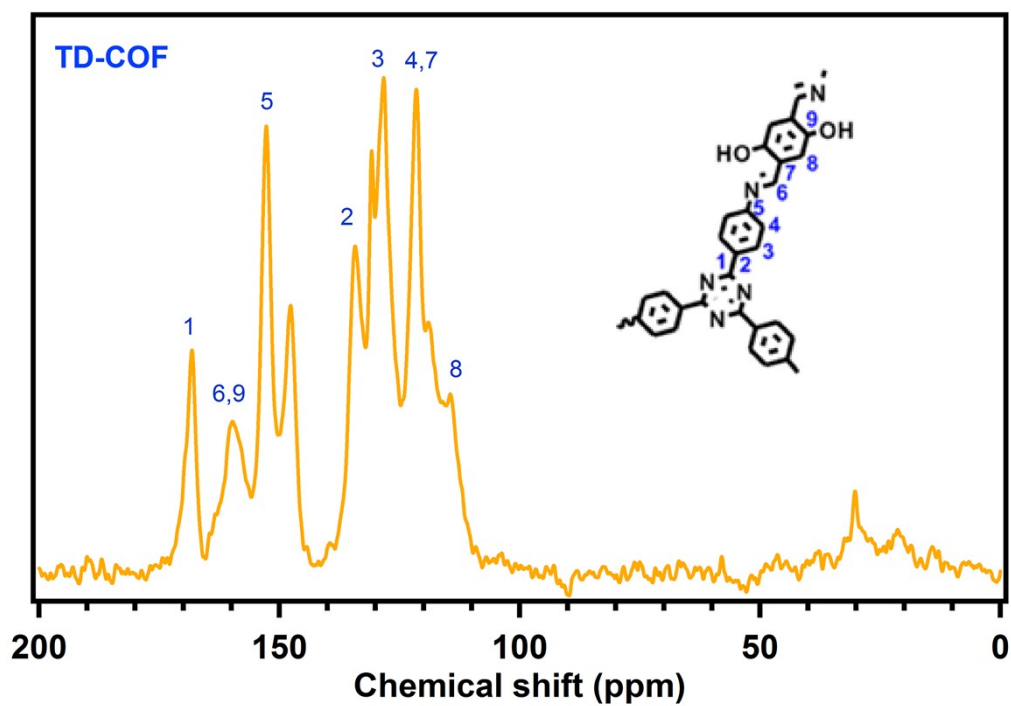


Fig. S4. ^{13}C NMR spectrum of TD-COF.

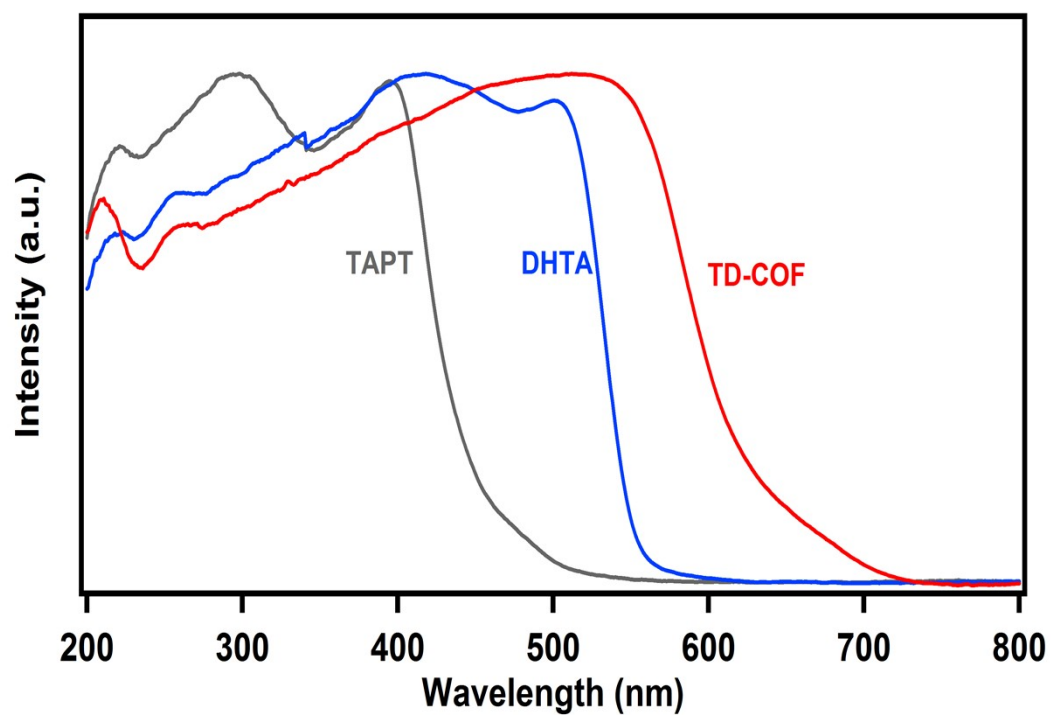


Fig. S5. UV-vis spectra of TD-COF, TAPT and DHTA.

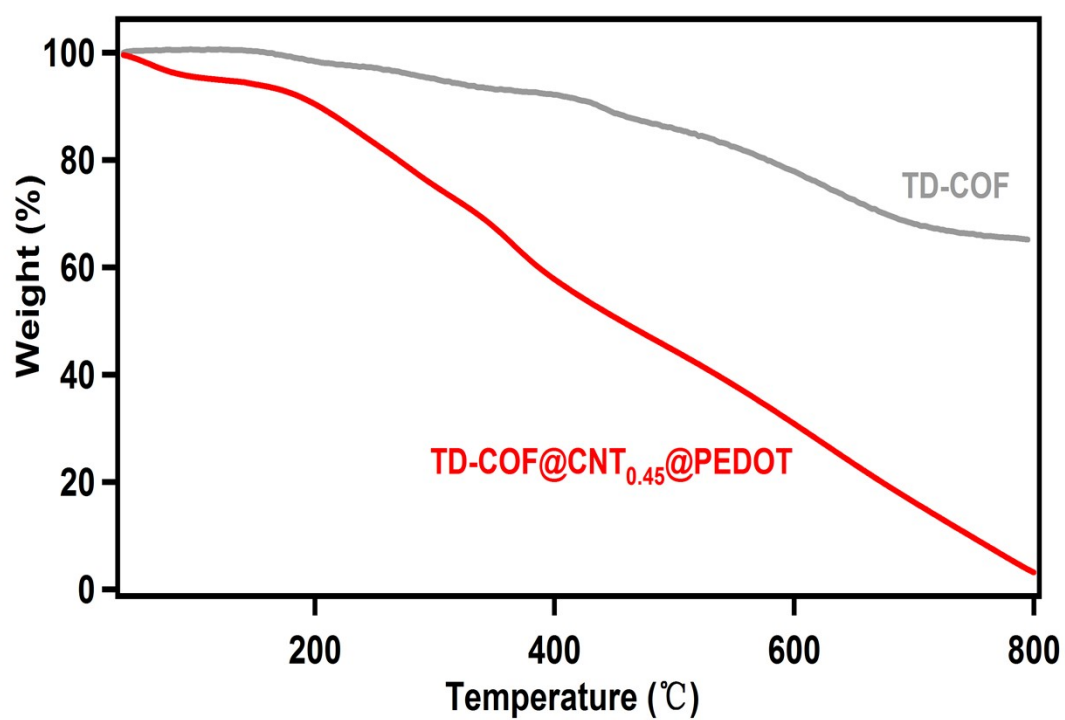


Fig. S6. TGA curves of TD-COF and TD-COF@CNT_{0.45}@PEDOT.

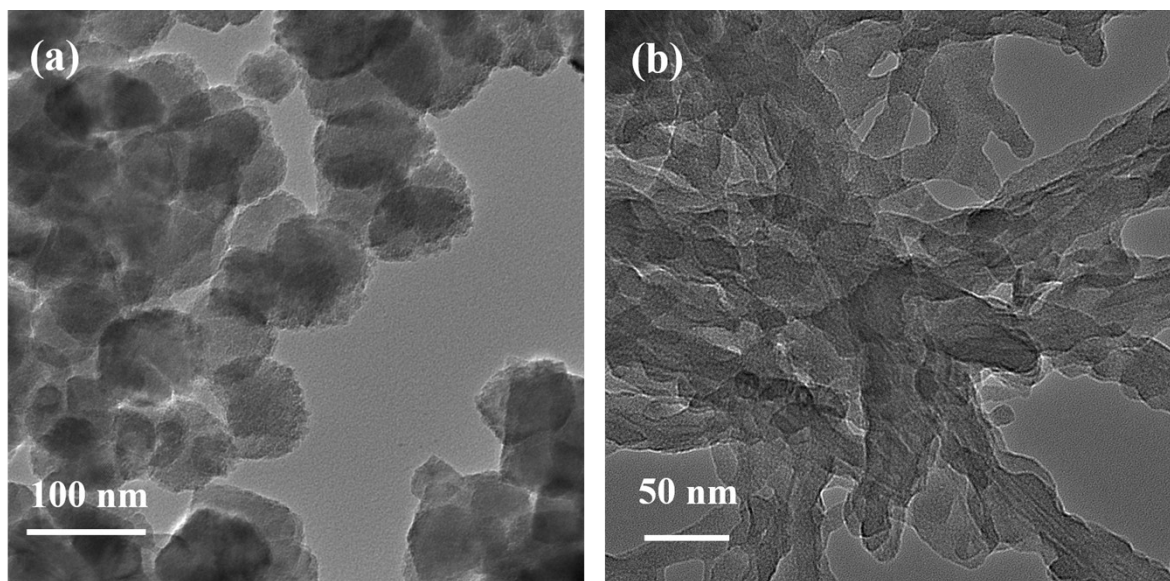


Fig. S7. TEM images of (a) TD-COF and (b) TD-COF@CNT_{0.45}@PEDOT.

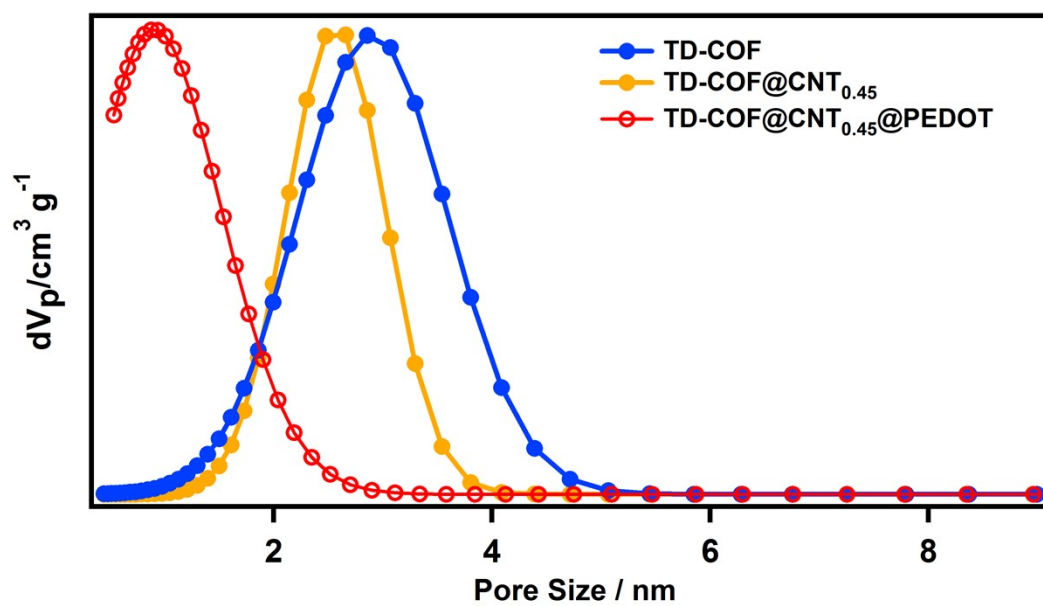


Fig. S8. Pore size distributions of TD-COF, TD-COF@CNT_{0.45}, and TD-COF@CNT_{0.45}@PEDOT.