# Supporting Information for

## A Three-Dimensional sp<sup>2</sup> Carbon-Conjugated Covalent Organic Framework

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#### Instrumentation and characterization

<sup>1</sup>H Nuclear Magnetic Resonance (NMR, 400 MHz) and <sup>13</sup>C NMR (100 MHz or 150 MHz) spectral data were obtained on the Bruker Avance spectrometers with tetramethylsilane (TMS) as internal reference and peak multiplicity was reported as follows: s, singlet; d, doublet; t, triplet. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF MS) were obtained with an AB 5800 system. <sup>13</sup>C cross-polarization/magic angle spinning solid-state nuclear magnetic resonance (CP/MAS ssNMR) experiments were performed on an Agilent 600 DD2 spectrometer (Agilent, USA, magnetic field strength 14.1 T) at resonance frequency of 150.72 MHz for <sup>13</sup>C using the cross-polarization (CP), magic-angle spinning (MAS), and a high-power 1H decoupling. Element Analysis system were performed on a vairo EL CUBE elementar Analysen systeme. Fourier transform infrared (FT-IR) spectra were recorded on a VERTEX 70v FTIR Spectrometer. Scanning electron microscopy (SEM) was carried out using a ZEISS MERLIN Compact scanning electron microscope. Transmission electron microscope (TEM) characterizations were conducted using a FEI TF30 with an accelerating voltage of 200 KV. Thermogravimetric analysis (TGA) were performed on a TGA/DSC3+ thermogravimetric analyzer in nitrogen atmosphere from 50 °C to 800 °C at the rate of 10 °C/min. UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded at room temperature on a UV-3600 spectrophotometer. Solution-state UV-vis spectra were measured on a TU-1901 spectrophotometer. Powder X-ray diffraction (PXRD) patterns were carried out with Bruker D8 Advance diffractometer with Cu–K $\alpha$ 1 radiation ( $\lambda = 1.5406$  Å) from  $2\theta = 3.0^{\circ}$  up to 50° at the rate of 1°/min. The sample was spread on the square recess of XRD sample holder as a thin layer. Electron paramagnetic resonance (EPR/ESR) spectra were recorded with a Bruker E500 spectrometer with X-band microwave.

**Sorption measurement** Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Instrument Corporation model ASAP2020 surface characterization analyzer. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the non-local density functional theory (NLDFT) model, the pore volume was derived from the sorption curve.

**Cyclic voltammetry (CV)** Experiments were measured on a CHI 760E in a three-electrode electrochemical cell under N<sub>2</sub> equipped with a salt bridge and a scan rate of 0.05 V s<sup>-1</sup>. The experiments were conducted in anhydrous acetonitrile (super dehydrated grade, from J&K Company) with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The auxiliary electrode was a platinum wire (diameter: 1 mm). The reference electrode was based on the Ag/Ag<sup>+</sup> couple. The working electrode was a glassy carbon electrode. Ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox potential was measured at the end of each experiment in order to calibrate the pseudo reference electrode as recommended by IUPAC. COF samples (5 mg) were dispersed in ethanol (1mL) with a few droplets (50  $\mu$ L) of 5 wt% Nafion and ultrasonicated for 3 h. The suspension was then dropped on the glassy carbon electrode and dried to form thin films for measurements.

**Conductivity measurement** The powder samples (**BUCT-COF-4**) were pressed into pellets through a 10 mm diameter mold by applying a pressure of approximately 14 MPa at room temperature and kept for 1 min at that pressure. The compressed pellets have the diameter of 10 mm and the thickness of ~0.3 mm. The conductivity and mobility (direct current) of the pellets were determined in the van der Pauw geometries in vacuum or in ambient air using a Physical Property Measurement System (PPMS) from Quantum Design. The electrode probes used gold-plated over copper materials with needle point type and the applied voltage for Hall Effect measurements was 1 V. All contacts were confirmed to be ohmic by measuring the current-voltage curves. For the sample preparation procedure photos and more information about the Hall effect measurement, please see our previous work <sup>[S1]</sup> and other related reference <sup>[S2]</sup>.

**Doping BUCT-COF-4 with iodine** An open small glass vial (10.0 mL) containing the **BUCT-COF-4** powder samples (20.0 mg) was placed in a large vial (50.0 mL) containing iodine (~1.0 g). The large vial was capped tightly and kept in an oven at 65 °C. After 36 h, the system was cooled to room temperature and the samples was dried in vacuum to remove the excess amorphous I<sub>2</sub>. Then certain amount of doped samples were separated for electrical or magnetic measurement experiments. **Magnetic properties** Data were collected using a Quantum Design 9 Tesla PPMS-VSM magnetometer. Powder samples of iodine-doped **BUCT-COF-4** (the samples were maintained at iodine-saturated vapor pressure until the magnetic measurement experiments) with a weight of  $\approx 10$  mg were sealed in a plastic capsule. Magnetic moment was measured in the temperature range of 2.4 to 300 K. The empty plastic capsule exhibited diamagnetic and its magnetic moment was measured for correction.

## Synthesis section



Scheme S1. Synthesis of the C=C-linked fully conjugated 3D COF the BUCT-COF-4.

Synthesis of the C=C-linked fully conjugated 3D COF (BUCT-COF-4). The building block COThP-CHO was synthesized according to our previous work.<sup>[S1]</sup> The COThP-CHO (14.9 mg, 0.02 mmol) and 1,4-phenylenediacetonitrile (PDAN) (4.4 mg, 0.04 mmol) were dissolved in 1,2-Dichlorobenzene (1.0 mL) in a Pyrex tube. After sonicated for two minutes, 0.2 mL of EtONa in anhydrous methanol (super dehydrated grade) (0.5 mM) was added and the mixture was further sonicated for 10 min. The mixture was then degassed through freeze-pump-thaw cycles for three times,

warmed to room temperature, sealed in nitrogen atmosphere and kept at 40 °C in an oven without disturbance for 6 h, then 90 °C for 48 h, 110 °C for 24 h. The mixture was cooled to room temperature and the precipitate was collected by filtration, washed with deionized water, Methanol and dichloromethane for several times. Soxhlet extracted in tetrahydrofuran for 48 h and dried under vacuum at 120 °C for 12 h to afford reddish powder (13 mg) in 73% isolated yield. Elemental analysis (%): calcd. for C<sub>64</sub>H<sub>32</sub>N<sub>4</sub>S<sub>4</sub>: C 78.02, H 3.27, N 5.69; found: C 72.51, H 2.95, N 3.70. Solid-state <sup>13</sup>C CP/MAS NMR (150 MHz):  $\delta$  = 142.32, 138.54, 135.67, 131.51, 126.67, 124.51, 117.13, 106.78.



Scheme S2. The synthesis illustration of the Model Compound.

**Synthesis of the Model Compound**. The synthetic process is similar to that of **BUCT-COF-4**. **COThP-CHO** (14.9 mg, 0.02 mmol) and phenylacetonitrile (**PAN**) (10  $\mu$ L, 0.087 mmol) were dissolved in 1,2-Dichlorobenzene (1.0 mL) in a Pyrex tube. After sonicated for two minutes, 0.2 mL of EtONa in anhydrous methanol (super dehydrated grade) (0.5 mM) was added and the mixture was further sonicated for 10 min. The mixture was then degassed through freeze-pump-thaw cycles for three times, warmed to room temperature, sealed in nitrogen atmosphere and kept at 40 °C for 6 h, then 90 °C for 48 h, 110 °C for 24 h. After cooled to room temperature, the precipitate was collected by centrifugation, washed with Methanol, deionized water, and Methanol for several times, dried under vacuum at 70 °C for 12 h to afford reddish powder (19 mg) in 83% isolated yield. <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>, TMS):  $\delta$  = 7.95 (d, *J* = 8.4 Hz, 8H), 7.72 (s, 4H), 7.69 (d, *J* = 8.0 Hz, 8H), 7.52 (s, 4H),

7.48~7.44 (m, 8H), 7.42~7.36 (m, 12H). <sup>13</sup>C NMR (150 MHz, 298 K, CDCl<sub>3</sub>, TMS): δ = 144.91, 141.14, 135.38, 134.46, 133.32, 130.09, 129.30, 129.12, 128.88, 127.89, 126.71, 126.01, 125.82, 118.07, 111.51. MS (MALDI-TOF): 1140.0 [M]<sup>+</sup>; HR-MS (MALDI-TOF): m/z calcd. for C<sub>76</sub>H<sub>44</sub>N<sub>4</sub>S<sub>4</sub> [M]<sup>+</sup>: 1140.2449, found: 1140.2459.

## **Figures and Tables**



#### **Fig. S1.**

Fourier Transform Infrared spectra of (A) **BUCT-COF-4**, (B) **COThP-CHO** and (C) 1,4phenylenediacetonitrile (**PDAN**). The band corresponding to C=O vibration (~1695 cm<sup>-1</sup>) in **BUCT-COF-4** was still observed, which was attributed to the terminal aldehyde groups at the edges of the COFs.



**Fig. S2.** 

Solid-state <sup>13</sup>C cross-polarization/magic angle spinning (<sup>13</sup>C CP-MAS) NMR spectrum of the **BUCT-COF-4**. The peak assignment was referred to the <sup>13</sup>C NMR spectrum of **Model Compound**.



## Fig. S3.

Scanning electron microscopy (SEM) images of BUCT-COF-4.



## Fig. S4.

Transmission electron microscopy (TEM) images of BUCT-COF-4.





Thermogravimetric analysis (TGA). Weight loss of the BUCT-COF-4 under nitrogen.



**Fig. S6.** 

PXRD patterns of **BUCT-COF-4** after immersed in different organic solvents and 3 M NaOH and 3 M HCl aqueous solutions for 24 h. After treatment, the powders were filtrated and dried in vacuum at 120 °C for 12 h and measured PXRD again.



**Fig. S7** The simulated PXRD patterns of **BUCT-COF-4** with different interpenetrations of a diamond net. It can be seen that only the 9-fold interpenetrated structure with *Imma* spacing group fits well with the experimental data.

**Note:** Wang et al. recently reported a universal formula of  $N = 2\sqrt{4L^2 - a^2}/c$  to calculate the interpenetration number N in *dia-cN* 3D COF structures, where the L is the length of the organic linker between two tetrahedral nodes, while a and c are the unit cell parameters. The lattice structure could be determined as I lattice space group when N is odd number, while it is P lattice when N is even number (Wang, et al. J. Am. Chem. Soc. **2018**, 140, 6763–6766). <sup>[S3]</sup> As for our BUCT-COF-4, the L = 26.7 Å, a = 30.6 Å, c = 10.04 Å. Based on this formula, the interpenetration number N is calculated to be 9.2, and the space group is I lattice structure, matched well with simulated results (*dia-c9*, Imma space group). Based on the simulated PXRD fitting and the formula calculation results, our BUCT-COF-4 is determined to be the *dia-c9* net.



#### Fig. S8.

Comparison of PXRD patterns for **BUCT-COF-4**: experimental (black) as well as calculated (red) from the 9-fold interpenetrated *dia* net (spacing group: *Imma*).

**Note:** The BUCT-COF-4 in this work is 9-fold interpenetration, while our previously reported BUCT-COF-1 which was synthesized from Schiff-base condensation of COThP-CHO and with 1,4-diaminobenzene (*Angew. Chem. Int. Ed.* **2021**, *60*, 9321–9325) is assigned to be 13-fold.<sup>[S1]</sup> The reason why these two 3D COFs have different interpenetrations although they have similar node-node distances, may be ascribed to the following reasons. First, the synthetic conditions. BUCT-COF-1 is acid catalyzed Schiff-base condensations in DMA/mesitylene, while the BUCT-COF-4 is base catalyzed Knoevenagel condensation in o-DCB. Previously, Wang et al. found that the well-known 3D COF, COF-300, was 5-fold, but could transform into 7-fold interpenetration isomerism when adding an aging process (Wang et al, *J. Am. Chem. Soc.* **2018**, *140*, 6763–6766.),<sup>[S3]</sup> which illustrates the great influence of synthesis procedure. Second, the introduced CN substituted groups. The CN groups on the backbones have disordered orientations and could introduce the steric hindrance among framework layers, which would influence the packing.



**Fig. S9.** Simulated crystal structures of **BUCT-COF-4** (a,b). Chemical structure and stereo chirality of the saddle-shaped building block COThP-CHO (c,d).

**Note:** The built modeling structure of **BUCT-COF-4** has the low-symmetry orthorhombic system with *Imma* space group (No.74). In the crystal structure, eight S atoms are displayed in each central cyclooctatetrathiophene core. However, the building block COThP-CHO only contains four S atoms. This difference would be ascribed to the following reasons: 1) the cyclooctatetrathiophene is not centrosymmetric; 2) the chirality of saddle-shaped COThP-CHO.<sup>[S4]</sup> Therefore, there exists racemic mixtures and different orientations of cyclooctatetrathiophene derivatives, resulting in the difficult resolution of S atom positions in each thiophene ring of cyclooctatetrathiophene cores. Consequently, the crystal structures of **BUCT-COF-4** exhibits low symmetry and statistically show eight S atoms in each node. On the other hand, the CN substituted groups on each C=C linkage in the polymer backbones deriving from the Knoevenagel condensations also have different disordered orientations, which also lowers the symmetry of crystal system.



Fig. S10.

BET plot of BUCT-COF-4 calculated from  $N_2$  adsorption isotherm at 77 K.





THF vapor adsorption and desorption isotherms of BUCT-COF-4 at 283 K at different cycles.

**Note:** The measured pore volume of **BUCT-COF-4** at 283 K from THF vapor sorption isotherms is  $0.50 \text{ cm}^3 \text{ g}^{-1}$ , bigger than the value ( $0.17 \text{ cm}^3 \text{ g}^{-1}$ ) from N<sub>2</sub> sorption isotherm at 77 K. This could be attributed to the fact that at lower temperature, there exist some contracted forms of **BUCT-COF-4**, resulting in smaller pore volume.





The normalized UV-vis spectrum of the **Model Compound** in dilute Chloroform solution  $(1.8 \times 10^{-5} \text{ mol } \text{L}^{-1})$ .



#### Fig. S13.

The comparison of UV-vis RDS spectra of -C=C- linked **BUCT-COF-4** (red curve) and the -C=N-linked **BUCT-COF-1** (black curve) synthesized through the COThP-CHO with 1,4-diaminobenzene reported in our previous work <sup>[S1]</sup>.





Cyclic voltammetry of (A) BUCT-COF-4 and (B) ferrocene for calibration. (0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN under N<sub>2</sub> atmosphere, Ag/AgCl as the reference electrode, scan rate 0.05 V s<sup>-1</sup>). The half-wave potential of BUCT-COF-4 was -0.81 V, and the ferrocene was 0.47 V under this condition. The lowest unoccupied molecular orbital (LUMO) level of BUCT-COF-4 was calculated through the equation <sup>[85]</sup>:  $E_{LUMO} = -(E^{1/2}_{red} - E_{Ferrocene} + 4.8)$  eV.



#### Fig. S15.

Mott-Schottky plots of **BUCT-COF-4** (in 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution) with inset of energy diagram of the LUMO and HOMO levels (vs. Ag/AgCl).

Considering the conduction band minimum (CBM)(LUMO) position in the n-type semiconductors was approximately equal to the flat band positions, <sup>[S6]</sup> the LUMO (CBM) and HOMO (VBM) positions of the **BUCT-COF-4** were roughly determined to be -0.71 V and 1.14 V (vs. Ag/AgCl), comparable to these from CV measurements (Fig. S14).



## Fig. S16.

(A) Images of one compressed **BUCT-COF-4** sample (~20 mg) with a diameter of 10 mm and a thickness (inserted image) of 0.22 mm. (B) The XRD pattern of **BUCT-COF-4** powder (red curve) and compressed pellet (black curve) samples.





(A) Current (I)-Voltage (V) characteristics of the intrinsic **BUCT-COF-4** pellet sample at 298 K. (**B**) The *I-V* curves of **BUCT-COF-4** after I<sub>2</sub> doping; Inset: the photo of thickness of one compressed I<sub>2</sub>doped **BUCT-COF-4** pellet sample (thickness: 0.32 mm, diameter: 10 mm). The intrinsic **BUCT-COF-4** sample was conducted in vacuum condition in order to avoid the influence of humidity and other interfering gases, and the I<sub>2</sub>-doped sample was measured in ambient air. The linear *I-V* profiles suggested the ohmic contact between the COF pellets and the electrode probes (needle point probes with gold-plated over copper)





The Hall effect measurement of  $I_2$ -doped **BUCT-COF-4** pellet sample in ambient air at 298 K (thickness: 0.32 mm, diameter: 10 mm). Data were summarized in table S2.





The PXRD patterns of intrinsic **BUCT-COF-4** powder sample (black), and the  $I_2$ -doped BUCT-COF-4 sample after dried in vacuum at 120 °C for 12 h (red) to remove the amorphous  $I_2$ .



Fig. S20.

<sup>1</sup>H NMR spectrum of the Model Compound (400 MHz, 298 K, CDCl<sub>3</sub>, TMS).



Fig. S21.

<sup>13</sup>C NMR spectrum of compound the **Model Compound** (150 MHz, 298 K, CDCl<sub>3</sub>, TMS).



Fig. S22.

<sup>1</sup>H/<sup>13</sup>C HSQC NMR spectrum of **Model compound** (298 K, CDCl<sub>3</sub>, TMS).



### Fig. S23.

<sup>1</sup>H/<sup>13</sup>C HMBC NMR spectrum of **Model compound** (298 K, CDCl<sub>3</sub>, TMS).





MALDI-TOF Mass spectrum of Model Compound.

## Table S1.

Summary of the intrinsic charge mobilities of COF materials at ambient temperature reported in literature. Some data were referred to the literature S2 (Table S3 in S2).

COF type	COF Name	Method	Hole	Electron	Ref.	
(Dimension)			Mobility	Mobility		
			$\mu_{h}$	$\mu_{e}$		
			$(cm^2 V^{-1} s^{-1})$	$(cm^2 V^{-1} s^{-1})$		
3D	BUCT-COF-4	Hall effect	-	1.97±0.06	This work	
	BUCT-COF-1	Hall effect	-	2.75±0.22	S1	
	CuPc-pz COF	Hall effect	0.9±0.2	-	S2	
	ZnPc-pz COF	Hall effect	4.8±0.7	-		
	COF-366	FP-TRMC	8.1	-	S7	
2D	COF-66	FP-TRMC	3.0	-		
	CS-COF	FP-TRMC	4.2	-	S8	
	H <sub>2</sub> P-COF	FP-TRMC	3.5	-	S9	
	NiPc COF	FP-TRMC	1.3	-	S10	
	HBC-COF	FP-TRMC	0.7	-	S11	
	2D-NiPc-	FP-TRMC	-	0.6	S12	
	BTDA COF					
	ZnP-COF	FP-TRMC	0.032	0.016	S9	
	CuP-COF	FP-TRMC	-	0.19		
	TTF-Ph-COF	FP-TRMC	0.2	-	S13	
	TTF-Py-COF	FP-TRMC	0.08	-		
	2D D-A COF	FP-TRMC	0.01	0.04	S14	

## Table S2.

The Hall effect measurements by van der Pauw methods (298 K, applied magnetic field: -4 T~4 T).

Sample	Thickness	Carrier	Carrier density	Hall	Resistivity	Electron
No.	(mm)	type	(cm <sup>-3</sup> )	coefficient	(Ω cm)	Mobility
				(cm <sup>3</sup> /C)		(cm²/Vs)
1 <sup>a</sup>	0.22	n	1.81±0.05 ×10 <sup>11</sup>	-3.44 ×10 <sup>7</sup>	1.74 ×10 <sup>7</sup>	1.97±0.06
2 <sup>b</sup>	0.32	n	6.63±0.03 ×10 <sup>12</sup>	-9.41 ×10 <sup>5</sup>	3.58 ×10 <sup>5</sup>	2.62±0.03

<sup>a</sup> the intrinsic BUCT-COF-4 pellet sample, measured under vacuum.

<sup>b</sup> the I<sub>2</sub>-doped **BUCT-COF-4** pellet sample, measured in ambient air.

## Table S3

Unit cell parameters and fractional atomic coordinates for the BUCT-COF-4.

Crystal system		Orthorhombic		
Space group		Imma (NO.74)	74)	
Calculated unit cell	a = 30.6064 Å, b = 28.5330 Å, c = 10.0378 Å, $\alpha = \beta = \gamma = 90^{\circ}$			
Atoms	Х	У	Z	
C1	0.35880	0.20790	1.06493	
C2	0.45148	0.22454	0.68101	
C3	0.33314	0.20795	1.18331	
H4	0.32339	0.17474	1.22624	
C5	0.53936	0.39193	0.18182	
C6	0.52287	0.30159	0.57613	
C7	0.53933	0.41778	0.06146	
H8	0.57021	0.42766	0.01701	
C9	0.26242	0.20799	1.68528	
C10	0.53935	0.48680	-0.44013	
S11	0.58232	0.19831	0.79798	
S12	0.54808	0.33329	0.45218	
H13	0.36797	0.17439	1.02306	
H14	0.57060	0.38263	0.22464	
H15	0.27182	0.17475	1.64195	
H16	0.57027	0.47693	-0.39587	
C17	0.28969	0.25000	1.36910	
C18	0.40081	0.25000	0.87423	
C19	0.31982	0.25000	1.24542	
C20	0.30348	0.25000	1.49716	
C21	0.34930	0.25000	1.51086	
C22	0.27427	0.25000	1.62078	
N23	0.38668	0.25000	0.50841	
H24	0.24487	0.25000	0.14359	

C25	0.50000	0.46160	-0.12690
C26	0.50000	0.37852	0.24562
C27	0.50000	0.43135	-0.00039
C28	0.50000	0.44425	-0.25094
C29	0.50000	0.39515	-0.24815
C30	0.50000	0.47319	-0.37797
C31	0.50000	0.64969	0.62467
H32	0.50000	0.49834	0.87954
N33	0.50000	0.64359	0.21901
C34	0.37231	0.75000	-0.00171

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