Supplementary Information

Molecular level engineering of heteroatom-functionalized 2D covalent organic frameworks for highly efficient supercapacitor performance

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EXPERIMENTAL SECTION

Materials

benzo[1,2-b:3,4-b':5,6-b'']trithiophene-2,5,8-tricarbaldehyde (BTT-CHO), 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TPT-NH_2), 1,3,5-tris-(4-formylphenyl)benzene (TPT-CHO), *ortho*-dichlorobenzene (*o*-DCB), *n*-butanol (*n*-BuOH), mesitylene, dioxane, acetic acid, and KOH were purchased from Finar and Merck chemicals. Chemicals were obtained from commercial sources and used without purification. Moreover, the aqueous KOH solutions were prepared by using deionized water.

Characterization

All the reagents and solvents were purchased from a commercial source without further purification. Thermogravimetric analysis (TGA) was performed on a METTLER TOLEDO (TGA/DSC1) system using STARe software at a heating rate of 10 °C/min under N_2 atmosphere to 800 °C. For the Powder X-ray diffraction (PXRD) analysis, Cu Kα (0.154 nm) monochromatic radiation was used with a Bruker D2-Phaser X-ray diffractometer. The morphologies were investigated by a Supra55 Zeiss field emission scanning electron microscope (FESEM), and HR-TEM using 300 KV (Tecnai G2 F 30). Brunauer-Emmett-Teller

(BET) surface area and Barrett-Joyner-Halenda (BJH) distribution determinations were conducted on an Autosorb iQ (Quantachrome Instruments, version 1.11). The FT-IR experiment was performed using a PerkinElmer Spectrum Two with ATR mode. ^{1}H NMR (400 MHz) spectra were recorded on a Bruker 400 MHz FT-NMR at room temperature. ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak ($CDCl_3$). Solid-state ^{13}C NMR was recorded on a JEOL Japan (JNM EC500). XPS analysis was performed on an ESCA+ instrument (Omicron Nanotechnology, Germany). The simulated PXRD data of BTT-TPT-COF was generated using Material Studio. The simulated PXRD data for TPT-COF were obtained from the literature reported below.

Reference

1. D. Ongari, M. J. Pougin, A. V. Yakutovich, L. Talirz and B. Smit, Building a consistent and reproducible database for adsorption evaluation in Covalent-Organic Frameworks, *Materials Cloud Archive*, 2023, ***165***, 2023, https://doi.org/10.24435/materialscloud:cz-kq

Preparation and Electrochemical Measurement

Carbon cloth (CC) was used as the electrode substrate, with 2 M KOH as the electrolyte, to examine the electrochemical performances of COFs. 1 mg of each electrode material was sonicated separately in 300 µL of ethanol. These samples were drop-cast onto CC (1×1 cm^2) and dried at room temperature. The modified electrodes were used for electrochemical studies performed on an Autolab PGSTAT 204N workstation. The assessments were performed at ambient temperature using a conventional three-electrode setup. Specifically, the electrochemical cell consisted of a platinum wire counter electrode, an Ag/AgCl reference electrode, and a carbon cloth (CC) working electrode. The electrochemical properties of the synthesized COFs' electroactive material were comprehensively evaluated using key techniques: cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS).

Efficiency Evaluation

The electrochemical performance of COFs was evaluated using galvanostatic charge-discharge (GCD) measurements. The specific capacitance (C_S) was calculated using the following equation:

$$C_S = \frac{I\,\Delta t}{m\Delta V} \quad (1)$$

where I/m is the current density, Δt is the discharge time, and ΔV is the potential range of the GCD profile. The specific capacity (Q) of COFs was estimated using the following equation:

$$Q = \frac{I\,\Delta t}{m} \quad (2)$$

I/m is the current density, and Δt is the discharge time.

Device Fabrication

We used COFs (active material) as the positive electrode, activated carbon as the negative electrode, cellulose paper as the separator, carbon paper (2x4 cm) as the substrate, and 1 M KOH/PVA as the gel electrolyte for device fabrication. Initially, 3 mg cm^{-2} of active material was pasted on carbon paper, and the negative electrode (3 mg cm^{-2}) was coated onto another substrate of carbon paper. The device was assembled with a separator between the positive and negative electrodes. It was then charged using a 300 mAh adapter, and the assembled device successfully powered a commercial LED bulb.

Synthetic procedure

Synthesis of BTT-TPT-COF

A Pyrex tube (10 mL) was charged with a mixture of benzo[1,2-b:3,4-b':5,6 b"]trithiophene-2,5,8-tricarbaldehyde (20 mg, 0.06 mmol), 2,4,6-tris(4-aminophenyl) 1,3,5-triazine (23mg, 0.06 mmol), 2.8 mL of butanol/1,2-dichlorobenzene (v/v, 1:1), and 0.2 mL of 6 M aqueous acetic acid. The tube was degassed by three freeze–pump–thaw cycles. The tube was sealed off and then heated at 120 °C for 3 days. The powder collected was washed with tetrahydrofuran, methanol, and tetrahydrofuran several times, and dried at 100 °C under vacuum for 12 h to obtain the **BTT-TPT-COF** sample in 87% isolated yield.

Synthesis of TPT-COF

A Pyrex tube (10 mL) was charged with a mixture of 1,3,5-tris-(4-formylphenyl) benzene (11.7 mg, 0.03 mmol) and 1,3,5-tris-(4-aminophenyl) triazine (10.6 mg, 0.03 mmol), 1.0 mL of mesitylene/1,4-dioxane (v/v, 1:1), and 0.2 mL of 6 M aqueous acetic acid. The tube was degassed by three freeze–pump–thaw cycles. The tube was sealed off and then heated at 120 °C for 3 days. The powder collected was washed with tetrahydrofuran, methanol, and tetrahydrofuran several times, and dried at 100 °C under vacuum for 12 h to obtain **TPT-COF** sample in 80% isolated yield.

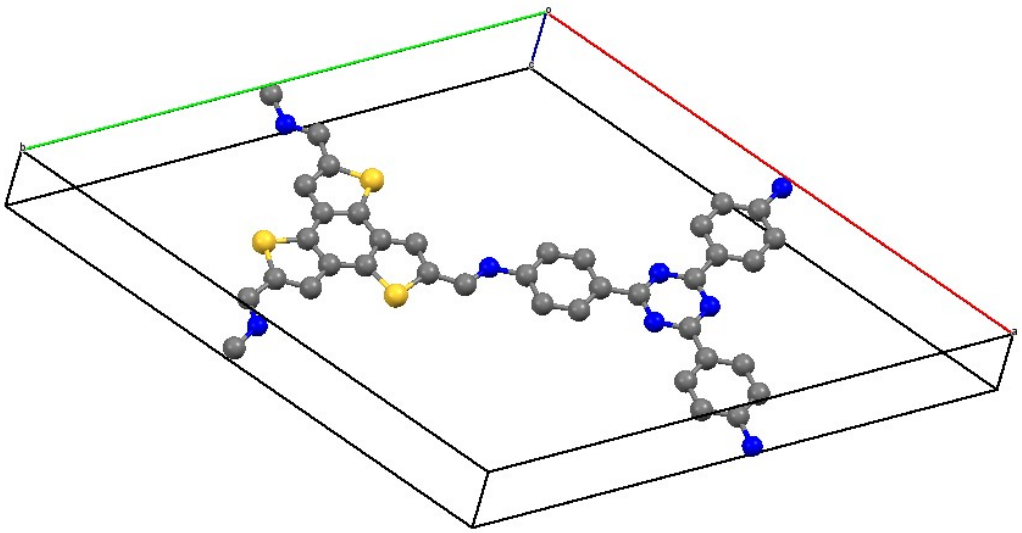

Fig. S1: Unit cell packing of modeled **BTT-TPT-COF**

Table S1: Unit cell parameters of modeled **BTT-TPT-COF**.

Crystal system: Triclinic	
Space group: P1	
a = 21.5453	α = 90°
b = 21.5453	β = 90°
c = 3.4962	γ = 120°

Table S2: Atomic coordinates of modeled BTT-TPT-COF.

C1	C	0.26186	0.64404	0.50000
C2	C	0.28390	0.59500	0.50000
S3	S	0.29248	0.78277	0.50000
C4	C	0.38145	0.84078	0.50000
C5	C	0.42295	0.80980	0.50000
C6	C	0.40975	0.91700	0.50000

N7	N	0.48273	0.52277	0.50000
C8	C	0.52247	0.48707	0.50000
C9	C	0.59638	0.52241	0.50000
C10	C	0.63187	0.48441	0.50000
C11	C	0.59443	0.41052	0.50000
C12	C	0.52059	0.37556	0.50000
C13	C	0.48529	0.41369	0.50000
C14	C	0.63213	0.37023	0.50000
N15	N	0.70329	0.40424	0.50000
H16	H	0.47979	0.83829	0.50000
H17	H	0.37248	0.93532	0.50000
H18	H	0.62728	0.57893	0.50000
H19	H	0.68875	0.51280	0.50000
H20	H	0.49022	0.31873	0.50000
H21	H	0.42848	0.38628	0.50000
C22	C	0.35596	0.61782	0.50000
C23	C	0.40500	0.68890	0.50000
S24	S	0.21723	0.50971	0.50000
C25	C	0.15922	0.54067	0.50000
C26	C	0.19020	0.61315	0.50000

C27	C	0.08300	0.49275	0.50000
N28	N	0.47723	0.95996	0.50000
C29	C	0.51293	0.03540	0.50000
C30	C	0.47759	0.07397	0.50000
C31	C	0.51559	0.14746	0.50000
C32	C	0.58948	0.18391	0.50000
C33	C	0.62444	0.14503	0.50000
C34	C	0.58631	0.07160	0.50000
C35	C	0.62977	0.26190	0.50000
N36	N	0.59576	0.29905	0.50000
H37	H	0.16171	0.64150	0.50000
H38	H	0.06468	0.43716	0.50000
H39	H	0.42107	0.04835	0.50000
H40	H	0.48720	0.17595	0.50000
H41	H	0.68127	0.17149	0.50000
H42	H	0.61372	0.04220	0.50000
C43	C	0.38218	0.73814	0.50000
C44	C	0.31110	0.71610	0.50000
S45	S	0.49029	0.70752	0.50000
C46	C	0.45933	0.61855	0.50000

C47	C	0.38685	0.57705	0.50000
C48	C	0.50725	0.59025	0.50000
N49	N	0.04004	0.51727	0.50000
C50	C	0.96460	0.47753	0.50000
C51	C	0.92603	0.40362	0.50000
C52	C	0.85254	0.36813	0.50000
C53	C	0.81609	0.40557	0.50000
C54	C	0.85497	0.47941	0.50000
C55	C	0.92840	0.51471	0.50000
C56	C	0.73810	0.36787	0.50000
N57	N	0.70095	0.29671	0.50000
H58	H	0.35850	0.52021	0.50000
H59	H	0.56284	0.62752	0.50000
H60	H	0.95165	0.37272	0.50000
H61	H	0.82405	0.31125	0.50000
H62	H	0.82851	0.50978	0.50000
H63	H	0.95780	0.57152	0.50000

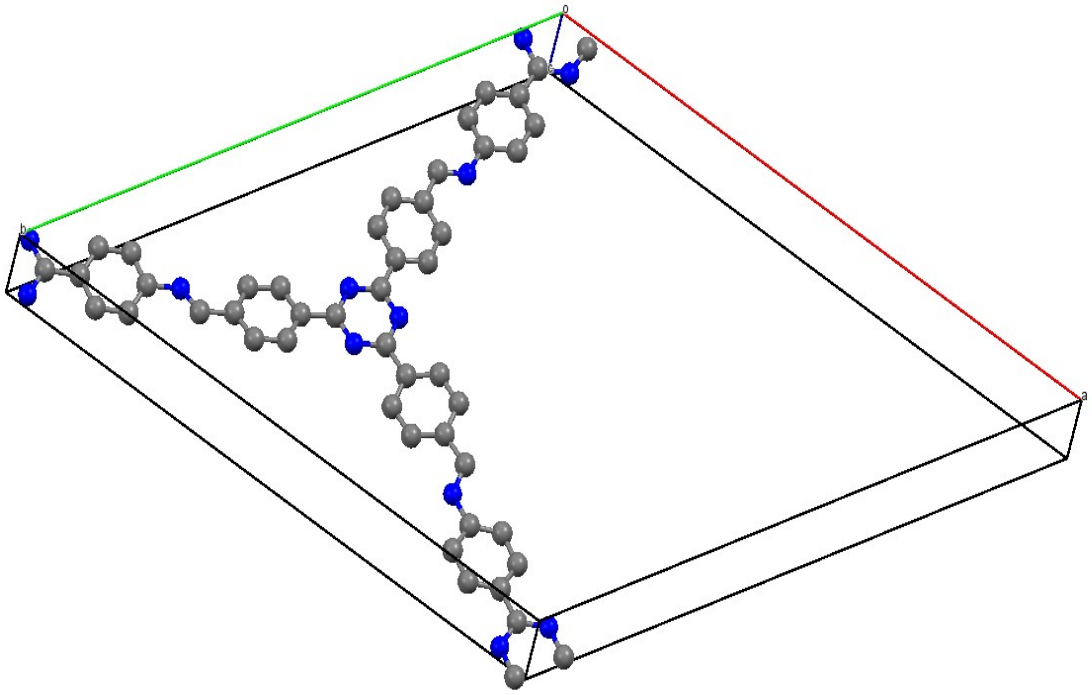

Fig. S2: Unit cell packing of modeled **TPT-COF**

Table S3: Unit cell parameters of modeled **TPT-COF** (adopted from previous literature).

Crystal system: Triclinic	
Space group: P1	
a = 25.4016	α = 90°
b = 25.4016	β = 90°
c = 3.5076	γ = 120°

Table S4: Atomic coordinates of modeled **TPT-COF**.

N1	N	0.15567	0.83995	0.50893
N2	N	0.27385	0.64359	0.46693
N3	N	0.97007	0.94002	0.52920
C4	C	0.06332	0.93693	0.52705

C5	C	0.03291	0.87462	0.49761
C6	C	0.06422	0.84381	0.49265
C7	C	0.12619	0.87422	0.51492
C8	C	0.15685	0.93650	0.55035
C9	C	0.12567	0.96747	0.55463
C10	C	0.21218	0.86018	0.45980
C11	C	0.23651	0.81961	0.46320
C12	C	0.19937	0.75803	0.50679
C13	C	0.22319	0.72027	0.50747
C14	C	0.28472	0.74337	0.46627
C15	C	0.32178	0.80510	0.42394
C16	C	0.29787	0.84278	0.42168
C17	C	0.31009	0.70334	0.46695
C18	C	0.93958	0.96973	0.52929
H19	H	0.98493	0.84982	0.47642
H20	H	0.04037	0.79592	0.46843
H21	H	0.20450	0.96149	0.58097
H22	H	0.15025	0.01538	0.58248
H23	H	0.24243	0.90682	0.40816
H24	H	0.15191	0.73930	0.54043

H25	H	0.19359	0.67298	0.54246
H26	H	0.36928	0.82413	0.38993
H27	H	0.32730	0.89011	0.38686
N28	N	0.16005	0.31572	0.50893
N29	N	0.35641	0.63026	0.46693
N30	N	0.05998	0.03005	0.52920
C31	C	0.06307	0.12639	0.52705
C32	C	0.12538	0.15829	0.49761
C33	C	0.15619	0.22041	0.49265
C34	C	0.12578	0.25197	0.51492
C35	C	0.06350	0.22035	0.55035
C36	C	0.03253	0.15820	0.55463
C37	C	0.13982	0.35200	0.45980
C38	C	0.18039	0.41690	0.46320
C39	C	0.24197	0.44134	0.50679
C40	C	0.27973	0.50292	0.50747
C41	C	0.25663	0.54135	0.46627
C42	C	0.19490	0.51668	0.42394
C43	C	0.15722	0.45509	0.42168
C44	C	0.29666	0.60675	0.46695

C45	C	0.03027	0.96985	0.52929
H46	H	0.15018	0.13511	0.47642
H47	H	0.20408	0.24445	0.46843
H48	H	0.03851	0.24301	0.58097
H49	H	0.98462	0.13487	0.58248
H50	H	0.09318	0.33561	0.40816
H51	H	0.26070	0.41261	0.54043
H52	H	0.32702	0.52061	0.54246
H53	H	0.17587	0.54515	0.38993
H54	H	0.10989	0.43719	0.38686
N55	N	0.68428	0.84433	0.50893
N56	N	0.36974	0.72615	0.46693
N57	N	0.96995	0.02993	0.52920
C58	C	0.87361	0.93668	0.52705
C59	C	0.84171	0.96709	0.49761
C60	C	0.77959	0.93578	0.49265
C61	C	0.74803	0.87381	0.51492
C62	C	0.77965	0.84315	0.55035
C63	C	0.84180	0.87433	0.55463
C64	C	0.64800	0.78782	0.45980

C65	C	0.58310	0.76349	0.46320
C66	C	0.55866	0.80063	0.50679
C67	C	0.49708	0.77681	0.50747
C68	C	0.45865	0.71528	0.46627
C69	C	0.48332	0.67822	0.42394
C70	C	0.54491	0.70213	0.42168
C71	C	0.39325	0.68991	0.46695
C72	C	0.03015	0.06042	0.52929
H73	H	0.86489	0.01507	0.47642
H74	H	0.75555	0.95963	0.46843
H75	H	0.75699	0.79550	0.58097
H76	H	0.86513	0.84975	0.58248
H77	H	0.66439	0.75757	0.40816
H78	H	0.58739	0.84809	0.54043
H79	H	0.47939	0.80641	0.54246
H80	H	0.45485	0.63072	0.38993
H81	H	0.56281	0.67270	0.38686

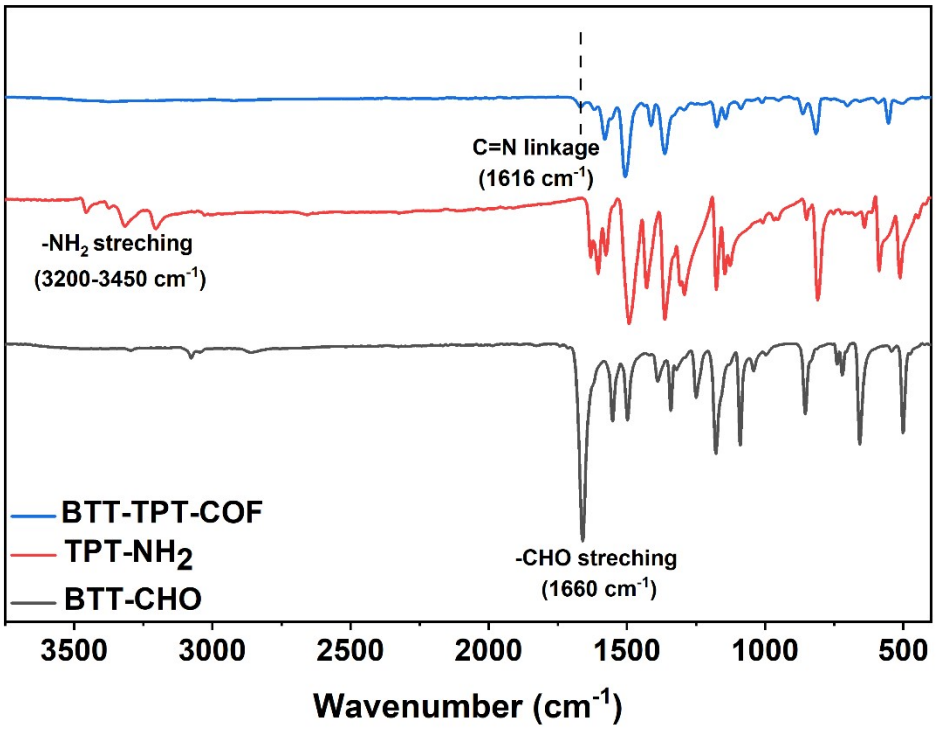

Fig. S3: comparative FTIR spectrum of **BTT-TPT-COF** with organic monomers

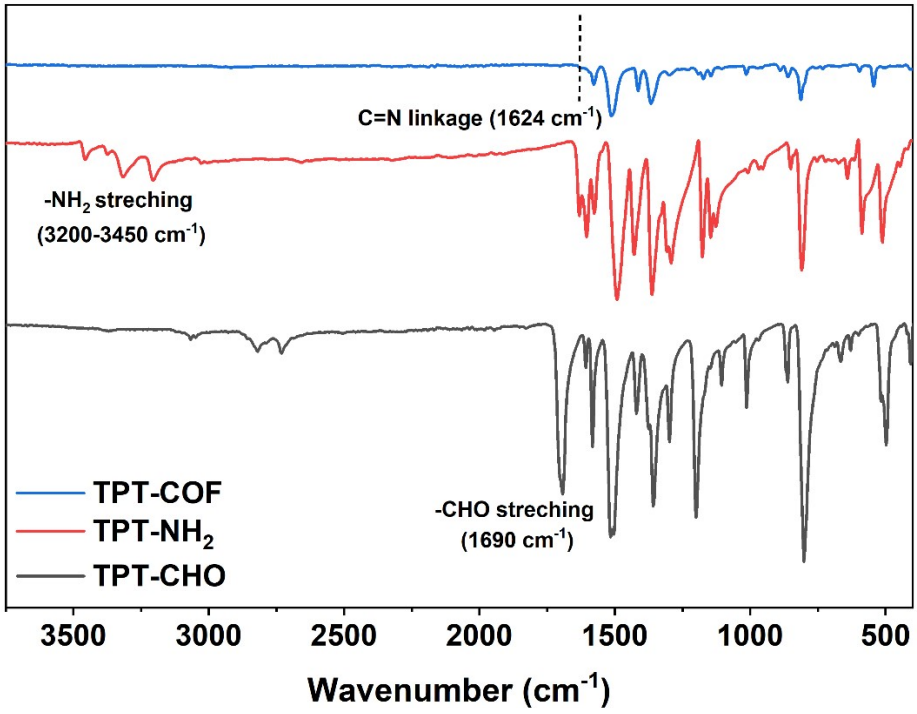

Fig. S4: comparative FTIR spectrum of **TPT-COF** with organic monomers

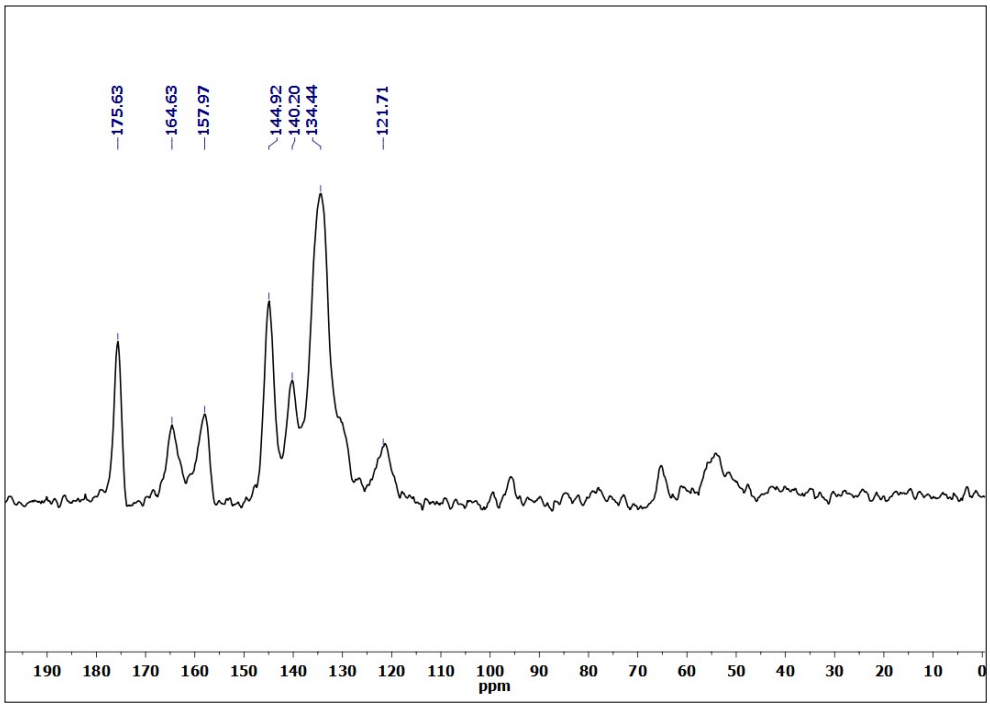

Fig. S5: Solid-state ^{13}C NMR of **TPT-COF**

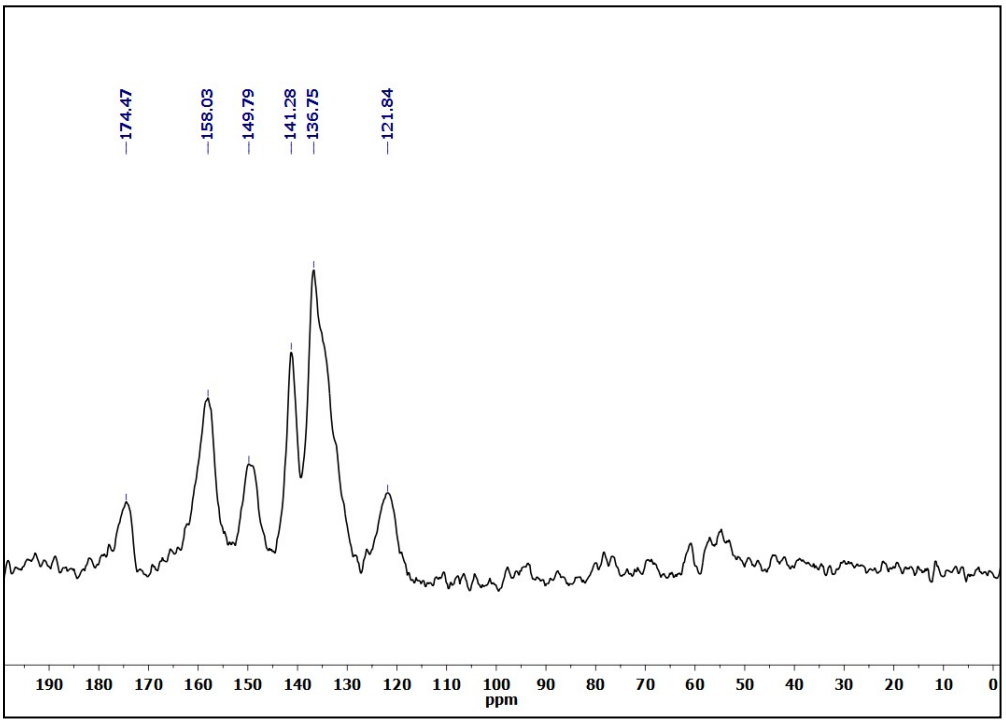

Fig. S6: Solid-state ^{13}C NMR of **BTT-TPT-COF**

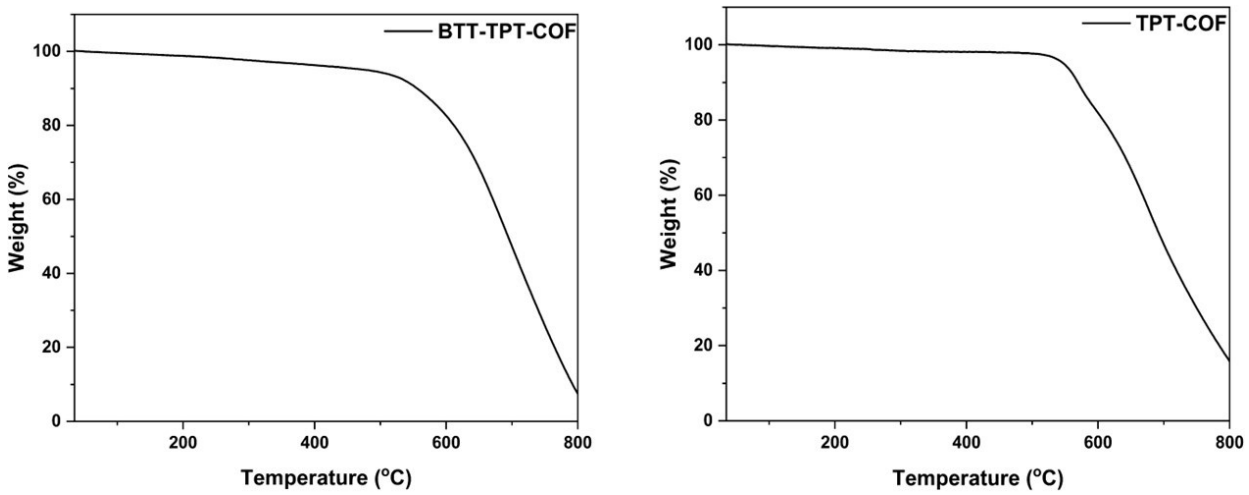

Figure S7: Thermogravimetric analysis (TGA) of **BTT-TPT-COF** and **TPT-COF**

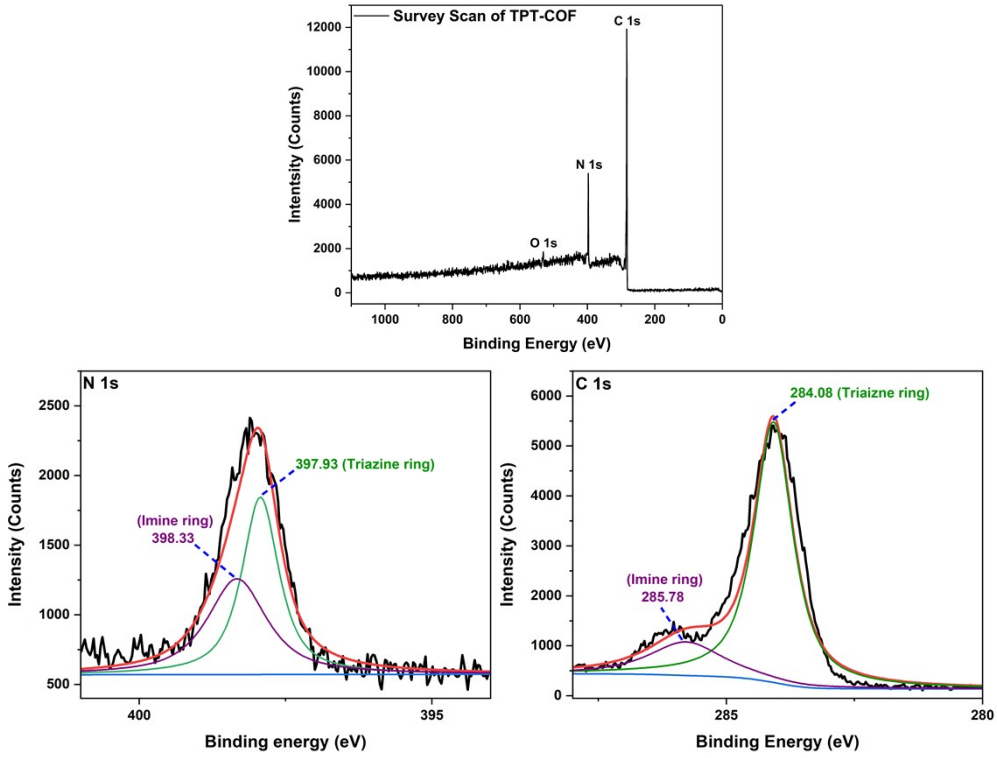

Fig. S8: XPS analysis of **TPT-COF**

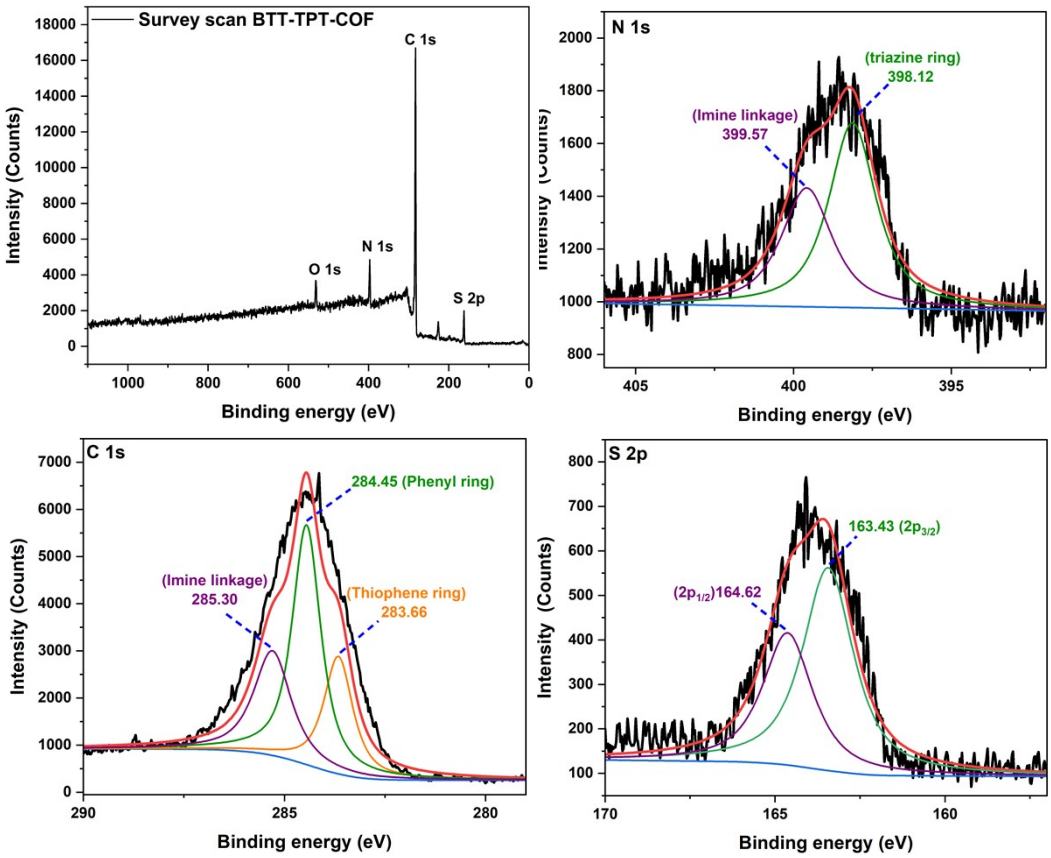

Fig. S9: XPS analysis of **BTT-TPT-COF**

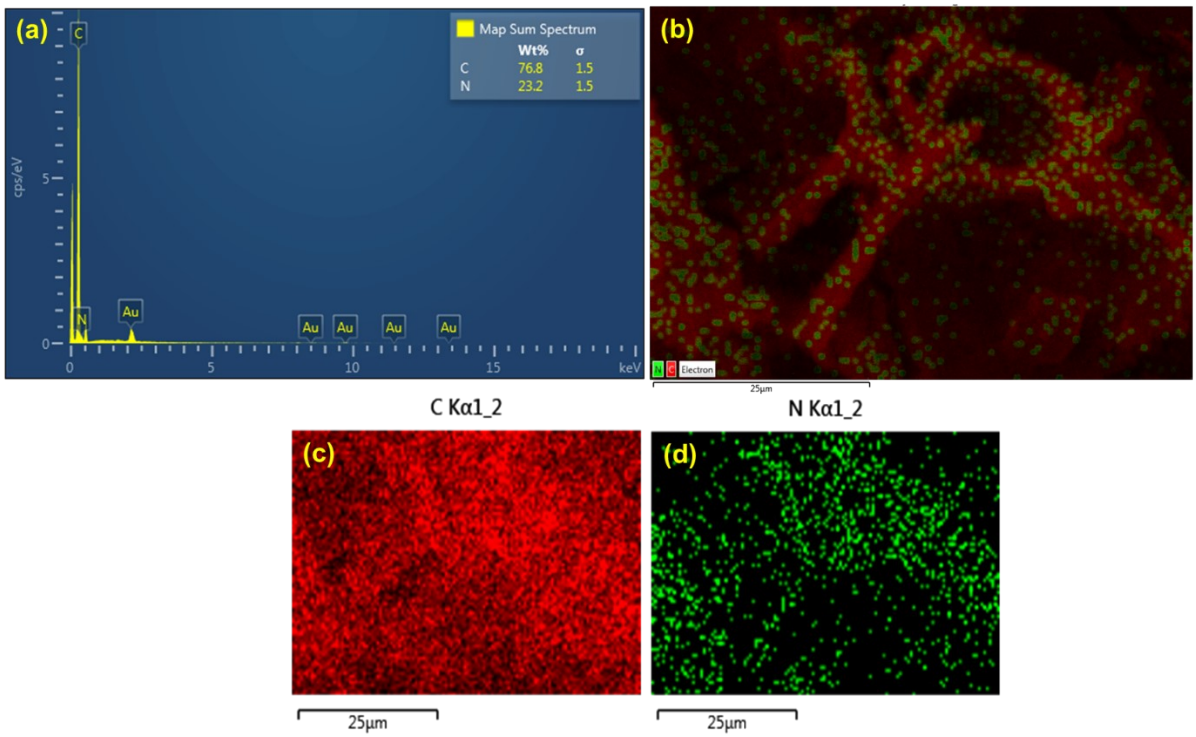

Fig. S10. (a) Elemental composition, and (b-d) elemental mapping of **TPT-COF**.

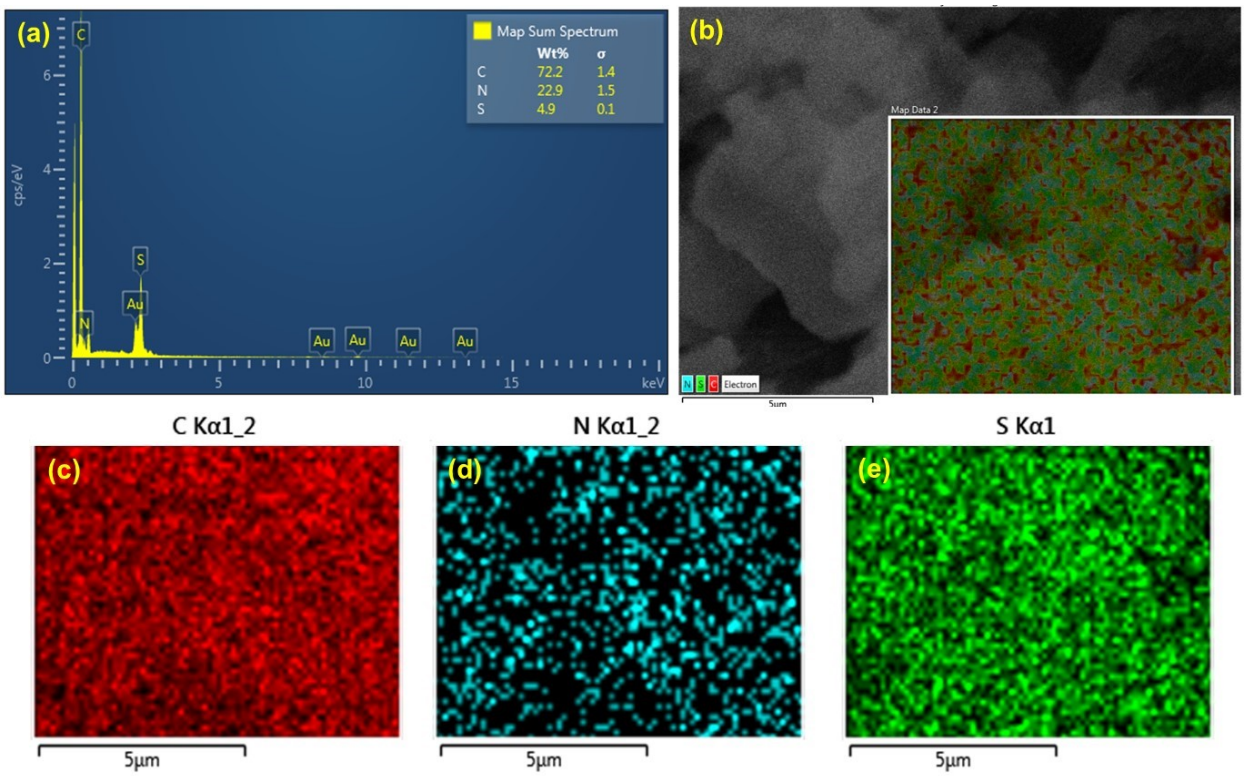

Fig. S11. (a) Elemental composition, and (b-e) elemental mapping of **BTT-TPT-COF**.

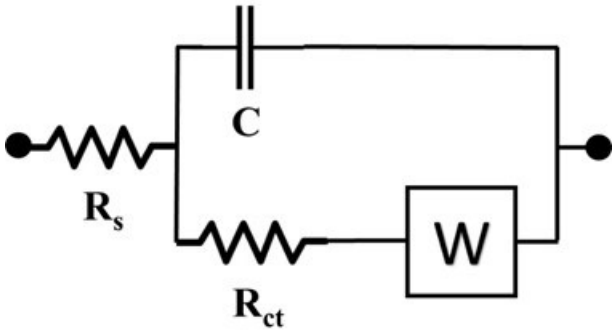

Fig. S12: Circuit for a three-electrode system.

Table S5: Circuit fitting parameter of a three-electrode system.

Elements	**BTT-TPT COF**	**TPT-COF**
R_S (Ω)	1.11	1.58
R_{CT} (Ω)	4.11	7.04
C (μF)	286	329
W (mMho*S^(1/2))	26.8	69.2

Fig. S13: Circuit for two electrode system **BTT-TPT-COF//AC**.

Table S6: Circuit fitting parameter for two electrode system **BTT-TPT-COF//AC**.

Elements	**BTT-TPT COF**
R_S (Ω)	3.82
R_{CT} (nΩ)	284
C (μF)	614
W (μMho*S^(1/2))	846

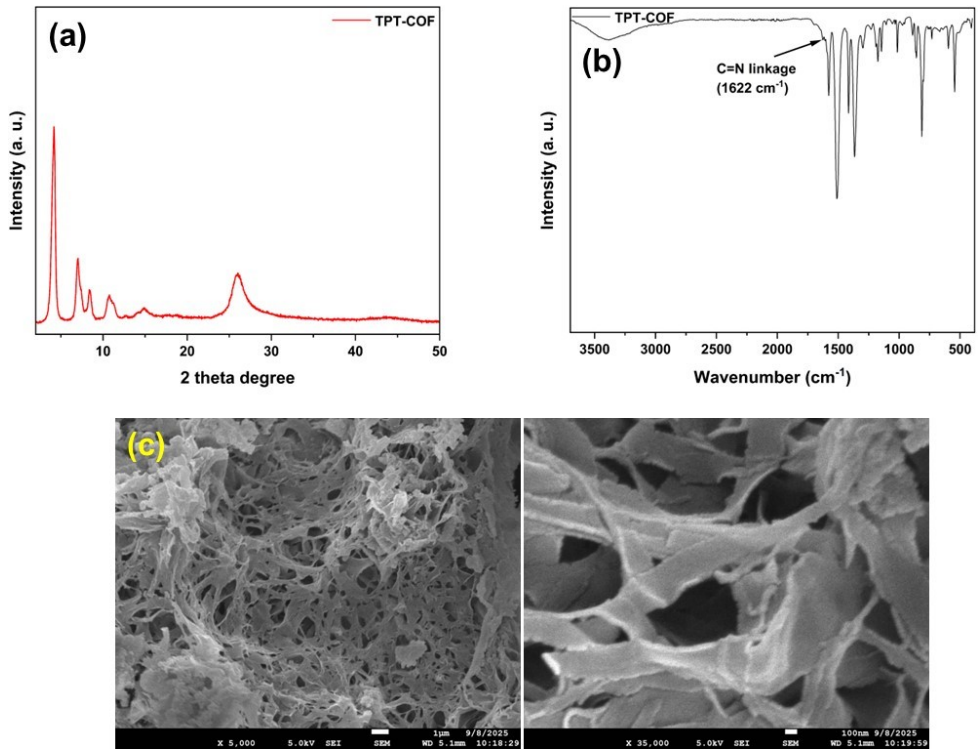

Fig. S14: (a) PXRD; (b) FTIR, (c) SEM images of **TPT-COF** after electrochemical study

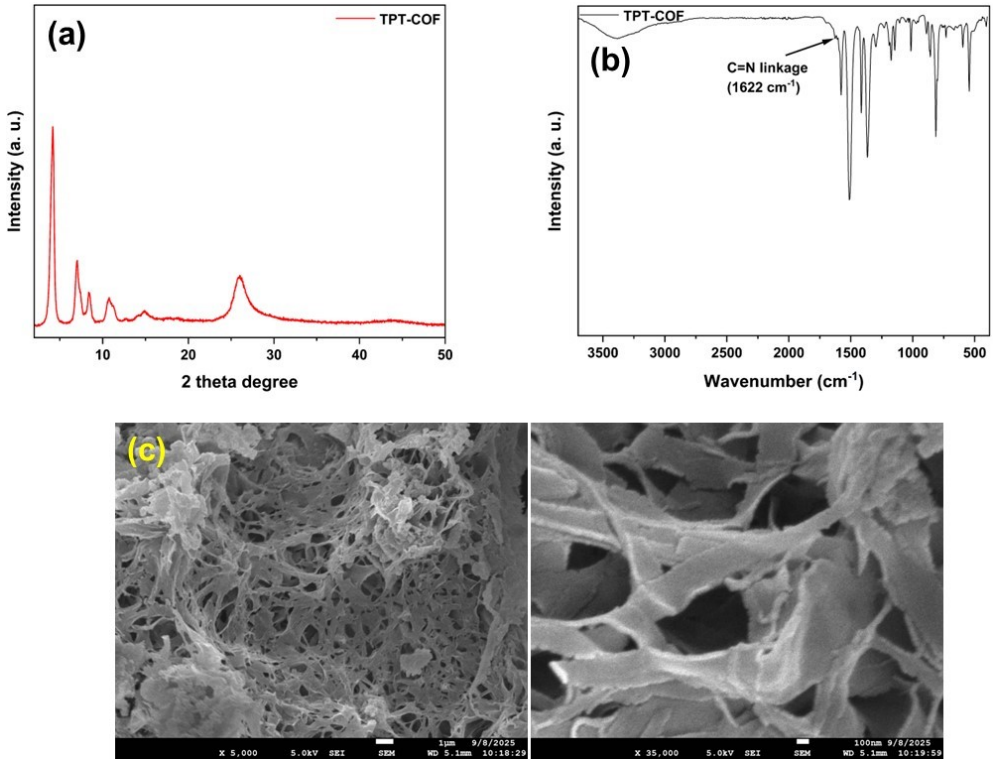

Fig. S15: (a) PXRD; (b) FTIR, (c) SEM images of **BTT-TPT-COF** after electrochemical study

Table S7. Comparative table for synthesized COFs with previously reported metal-free COFs for their supercapacitor applications

COF as electrode material	Electrolyte	Specific capacitance ($F.g^{-1}$)	Current density ($A.g^{-1}$)	Reference
Pent-TRUX-DAB	1 M H_2SO_4	634	1	*ACS Appl. Energy Mater.* **2023**, *6*, 11890−11896
TAPA-TPTCOF	1 M H_2SO_4	205	0.5	*ACS Appl. Energy Mater.* **2024**, *7*, 1723−1734
SLD-COF	1 M H_2SO_4 1 M KOH	31.5 41.7	0.5	*ACS Appl. Mater. Interfaces* **2025**, *17*, 11027−11035
TPT@BDA-COF	1 M $NaClO_4$	47.7	0.2	*Chem Asian J.* **2025**, *20*, e202401149
TDMTA-TFP-COF	1 M KCl	327.29	2.86	*Chem. Commun.* **2025**, *61*, 7831–7834
PPDA-TFPT-COF	0.5 M H_2SO_4	250	1	*Chem. Eur. J.* **2025**, *31*, e202501252
a-COF	1 M H_2SO_4	115	0.1	*Chem. Select* **2023**, *8*, e202301774
TFPAZO-COF	1 M H_2SO_4	178	0.5	*Polymer* **2025**, *329*, 128484
TFPB-AZO-COF	1 M KOH	450	1	*J of Mol Struct* **2023**, *1286*, 135647
DPP-TBB COF	1 M KOH	384	0.3	*Small* **2024**, *20*, 2402993
PDC−MA−COF	6M KOH	335	1	*ACS Appl. Mater. Interfaces* **2019**, *11*, 26355−26363
TDFP-1	0.1 M H_2SO_4	354	0.5	*ChemSusChem* **2017**, *10*,921–929
PT-COF	0.5 M H_2SO_4	1443	0.5	*Chem.Mater.* **2021**, *33*, 8512−8523
TpPa-$(OH)_2$	1 M phosphate buffer (pH 7.2)	416	0.5	*Chem. Mater.* **2017**, *29*, 2074−2080
ACOF1	6 M KOH	234	1	*Chem. Eur. J.* **2017**, *23*,17504–17510
TTF-COF1	3 M KOH	752	1	*Chem. Commun.* **2020**, *56*, 14187-14190
TPPDA-TPTPE COF	1 M KOH	237.1	2	*Chem. Commun.* **2019**, *55*, 14890-14893
TPT-DAHQCOF	1 M KOH	256	0.5	*Chem. Asian J.* **2019**, *14*,1429-1435
BIBDZ	1 M H_3PO_4	88.4	0.5	*Eur. Polym J.* **2017**, *93*, 448-

				457
TPA-COF	1 M H_2SO_4	263.1	0.1	*J Appl Polym Sci.* **2022**, *139*, e51510.
TaPa-Py COF	1 M H_2SO_4	209	0.5	*J. Mater. Chem. A* **2016**, *4*, 16312–16317
DBT-MA-COF	6 M KOH	407	1	*Micropor. Mesopor. Mat.* **2021**, *312*, 110766
HADQ COF	ionic liquid	174	0.5	*Mater. Chem. Front.* **2023**, *7*, 2464-2474
DAT-COF	1 M H_2SO_4	235	0.5	*J. Power Sources* **2023**, *564*, 232873
TFP-NDA-COF	1 M H_2SO_4	348	0.5	*Micropor. Mesopor. Mat.* **2018**, *266*, 109-166
PG-BBT	3 M KOH	724	1	*Polym. Chem.* **2020**, *11*, 47–52
TAPT-2,3-NA$(OH)_2$	1 M KOH	271	0.5	*Polymers* **2022**, *14*, 3428
TPT-COF	**1 M KOH**	**466**	**1**	**This work**
BTT-TPT-COF	**1 M KOH**	**916**	**1**	**This work**