Supporting Information for:

One-pot furfural production from sustainable biomass-derived sugars using a functionalized covalent organic framework as a heterogeneous catalyst

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1. Materials and methods

1.1 Materials

1,3,5-Tris-(4-aminophenyl)-triazine (TAPT), o-dichlorobenzene (o-DCB), n-butanol (n-BuOH), acetic acid (AcOH), tetrahydrofuran (THF), dioxane (DIO), toluene (TOL), γ-valerolactone (GVL), methyl isobutyl ketone (MIBK), furfural, D-xylose, L-arabinose, xylan, L-lyxose, D-xylulose were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). 2,5-dihydroxyterephthalaldehyde (DHPA) was obtained from Macklin Chemical Co., Ltd. (Shanghai, China). Nitrogen (N_2, 99.999%) was supplied by Deyang Lab Gas Co., Ltd. (Jinan, China).

1.2 Preparation and characterization of TAPT-DHPA-COF

The synthesis of TAPT-DHPA-COF was prepared by amine-aldehyde condensation referring to the previous procedure. TAPT (170.13 mg), n-butanol (3 ml), DHPA (119.61 mg), and o-dichlorobenzene (3 ml) were placed into a Pyrex tube successively, the mixture was ultrasonically treated for 20 min, then acetic acid (6 M, 0.6 ml) was added dropwise into the mixture with vigorous stirring. After quickly frozen with liquid N_2 bath and degassed through a vacuum pump for three cycles. The Pyrex tube was sealed and placed in an oven at 120 °C for 72 h. After the reaction, the precipitate was washed three times with tetrahydrofuran, acetone, and hot water (50 °C), respectively. TAPT-DHPA-COF was obtained after drying at 80 °C under vacuum for 12 h.

The crystal structure of TAPT-DHPA-COF was measured by an X-ray diffractometer (XRD, Smartlab) with a scanning speed of 4 °/min and a step size of 0.01° in the range of 2−40° [1]. A Fourier-transform infrared (FTIR, ALPHA) spectrometer was used to measure the vibrational spectra of TAPT-DHPA-COF in the region of 400-4000cm^{-1}. The thermal stability of TAPT-DHPA-COF was tested by a thermal gravimetric analyzer (TGA, Q50/DSAQ20) at a heating rate of 10 °C/min in a nitrogen atmosphere ranging from 40 to 800 °C. The microstructure and element distribution of TAPT-DHPA-COF were observed by scanning electron microscope (SEM, Regulus8220) and transmission electron microscope (TEM, Thermo Fisher Talos F200S G2). The concentration and strength of acid sites of TAPT-DHPA-COF were detected using NH_3 temperature programmed desorption (NH_3-TPD, MicrotracBEL, Corp). Briefly, the sample was activated with the He flow at 500 °C for 1 h. After cooling to 100 °C, the sample was exposed to a flowing 5% NH_3 balanced with He for 30 min. Finally, the signal of desorbed NH_3 was recorded by the TCD

detector in the range of 100-550 °C with a 10 °C/min heating rate.

1.3 Catalytic conversion of biomass-derived sugars into furfural

Catalytic conversion reactions were processed in a Parr reactor with high temperature and high pressure (Series 5100 HP Compact Reactors). Briefly, the biomass-derived sugars, TAPT-DHPA-COF, and solvent were transferred into the reactor in turn. The reactor was purged with nitrogen to remove the air. The mixture was heated up to the preset temperature and maintained for a certain time at a constant stirring rate of 500 rpm. In this study, the concentration of biomass-derived sugars was 40 g/l, except for D-xylulose (1 g/l). The total solvent volume was 30 ml. The specific experimental parameters were shown in **Table S1**.

Table S1. Experimental setting of furfural production from biomass-derived sugars catalyzed by TAPT-DHPA-COF

Entry※	Catalyst	Sugar type	Solvent	Solvent ratio	Temperature (°C)	Time (h)	Catalyst dosage (wt%)
Solvent system							
1	TAPT-DHPA-COF	D-xylose	H_2O	-	200	1.0	0.33
2	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.0	0.33
3	TAPT-DHPA-COF	D-xylose	H_2O-GVL	5-5	200	1.0	0.33
4	TAPT-DHPA-COF	D-xylose	H_2O-DIO	5-5	200	1.0	0.33
5	TAPT-DHPA-COF	D-xylose	H_2O-TOL	5-5	200	1.0	0.33
6	TAPT-DHPA-COF	D-xylose	H_2O-MIBK	5-5	200	1.0	0.33
H_2O/THF							
1	TAPT-DHPA-COF	D-xylose	H_2O-THF	10-0	200	1.0	0.33
2	TAPT-DHPA-COF	D-xylose	H_2O-THF	8-2	200	1.0	0.33
3	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.0	0.33
4	TAPT-DHPA-COF	D-xylose	H_2O-THF	2-8	200	1.0	0.33
5	TAPT-DHPA-COF	D-xylose	H_2O-THF	0-10	200	1.0	0.33
Reaction time							
1	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	0.5	0.33
2	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.0	0.33
3	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.5	0.33

| 4 | TAPT-DHPA-COF | D-xylose | H_2O-THF | 5-5 | 200 | 2.0 | 0.33 |
| 5 | TAPT-DHPA-COF | D-xylose | H_2O-THF | 5-5 | 200 | 2.5 | 0.33 |

Reaction temperature

1	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	170	1.5	0.33
2	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	180	1.5	0.33
3	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	190	1.5	0.33
4	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.5	0.33
5	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	210	1.5	0.33

Catalyst dosage

1	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.5	0.0
2	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.5	0.17
3	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.5	0.33
4	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.5	0.50
5	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.5	0.67

Cyclic experiment

1	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.5	0.33
2	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.5	0.33
3	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.5	0.33

4	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.5	0.33
5	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.5	0.33
6	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.5	0.33

Catalyst type

1	TAPT	D-xylose	H_2O-THF	5-5	200	1.5	0.33
2	DHPA	D-xylose	H_2O-THF	5-5	200	1.5	0.33
3	TAPT-DHPA	D-xylose	H_2O-THF	5-5	200	1.5	0.33
4	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.5	0.33

Biomass-derived sugars

1	TAPT-DHPA-COF	D-xylose	H_2O-THF	5-5	200	1.5	0.33
2	TAPT-DHPA-COF	Xylan	H_2O-THF	5-5	200	1.5	0.33
3	TAPT-DHPA-COF	L-arabinose	H_2O-THF	5-5	200	1.5	0.33
4	TAPT-DHPA-COF	D-xylulose	H_2O-THF	5-5	190	1.0	0.01
5	TAPT-DHPA-COF	L-lyxose	H_2O-THF	5-5	190	1.0	0.33

※ Each set of experiments was performed 3 times to reduce the error.

After the reaction, liquid products and catalysts were severally separated and collected through filtration for product analysis and circulation experiments. The concentrations of biomass-derived sugars and furfural were analyzed by using high-performance liquid chromatography (HPLC, LC-20AT) equipped with a Shodex SC1011 packed column. The sugar conversion, furfural yield, and furfural selectivity were calculated according to the following formula.

$$\text{Sugar conversion} = \frac{\text{Moles of reacted sugar}}{\text{Moles of initial sugar}} \times 100\%$$

$$\text{Furfural yield} = \frac{\text{Moles of furfural produced}}{\text{Moles of initial sugar}} \times 100\%$$

$$\text{Furfural selectivity} = \frac{\text{Moles of furfural produced}}{\text{Moles of reacted sugar}} \times 100\%$$

1.4 Separation of furfural from the product

The furfural was extracted and purified using an organic solvent, specifically by mixing the reaction solution with ethyl acetate in a volume ratio of 1:2. The resulting mixture was stirred at room temperature for 10 min, followed by a one-hour settling period to separate the organic phase from the aqueous phase. To obtain a pure aqueous solution of furfural, an equal volume of water was added to the organic phase and subsequently removing the ethyl acetate by reduced pressure distillation.

1.5 Nuclear magnetic resonance (NMR) analysis of furfural

To confirm the identity of furfural in the initial liquid product, purified liquid product, and furfural standard sample obtained during catalytic experiments, we employed a Bruker 400MHz nuclear magnetic resonance (NMR) spectrometer. Deuterated reagent heavy water was chosen for mixing with the samples prior to scanning using the same instrument. The acquired data was subsequently analyzed utilizing Bruker Topspin 3.1 software.

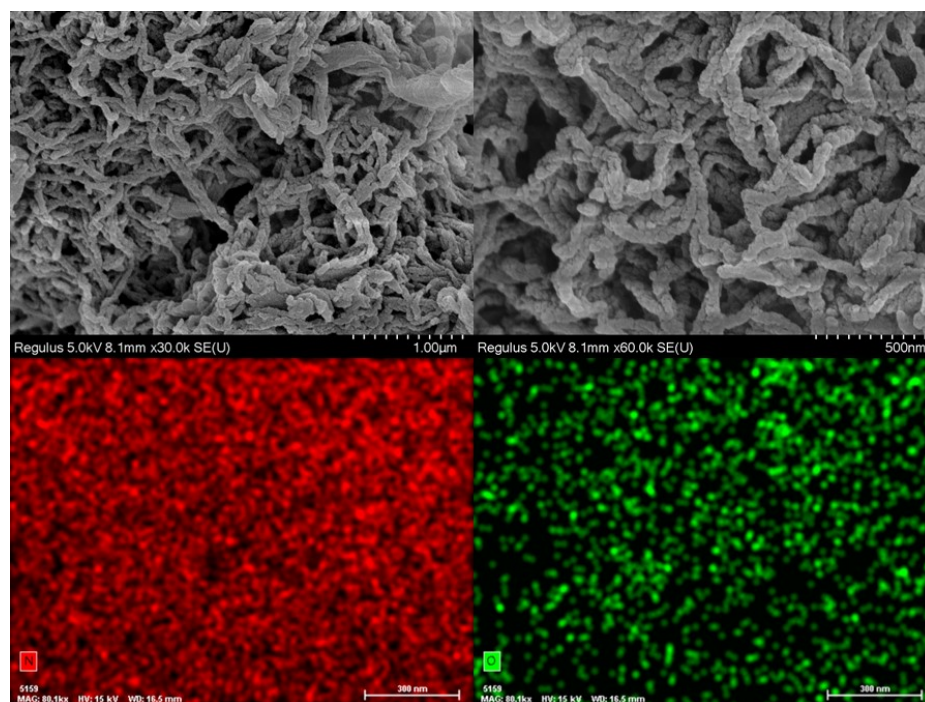# 2. Results and discussion

2.1 Characterization of TAPT-DHPA-COF
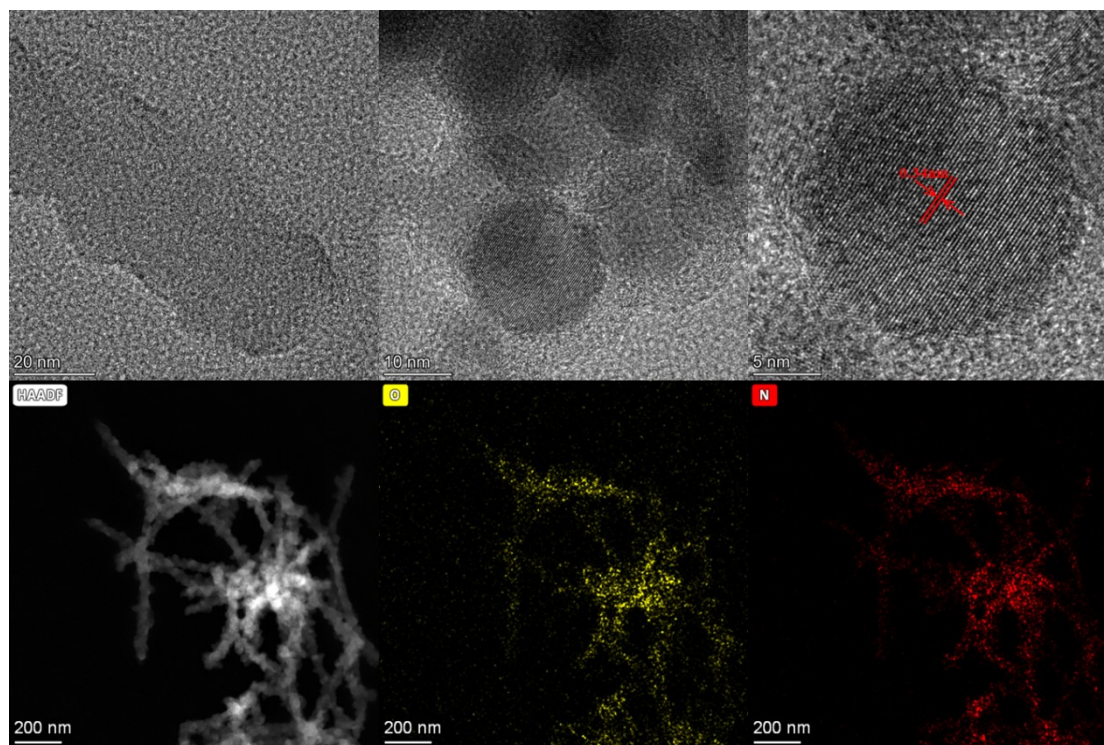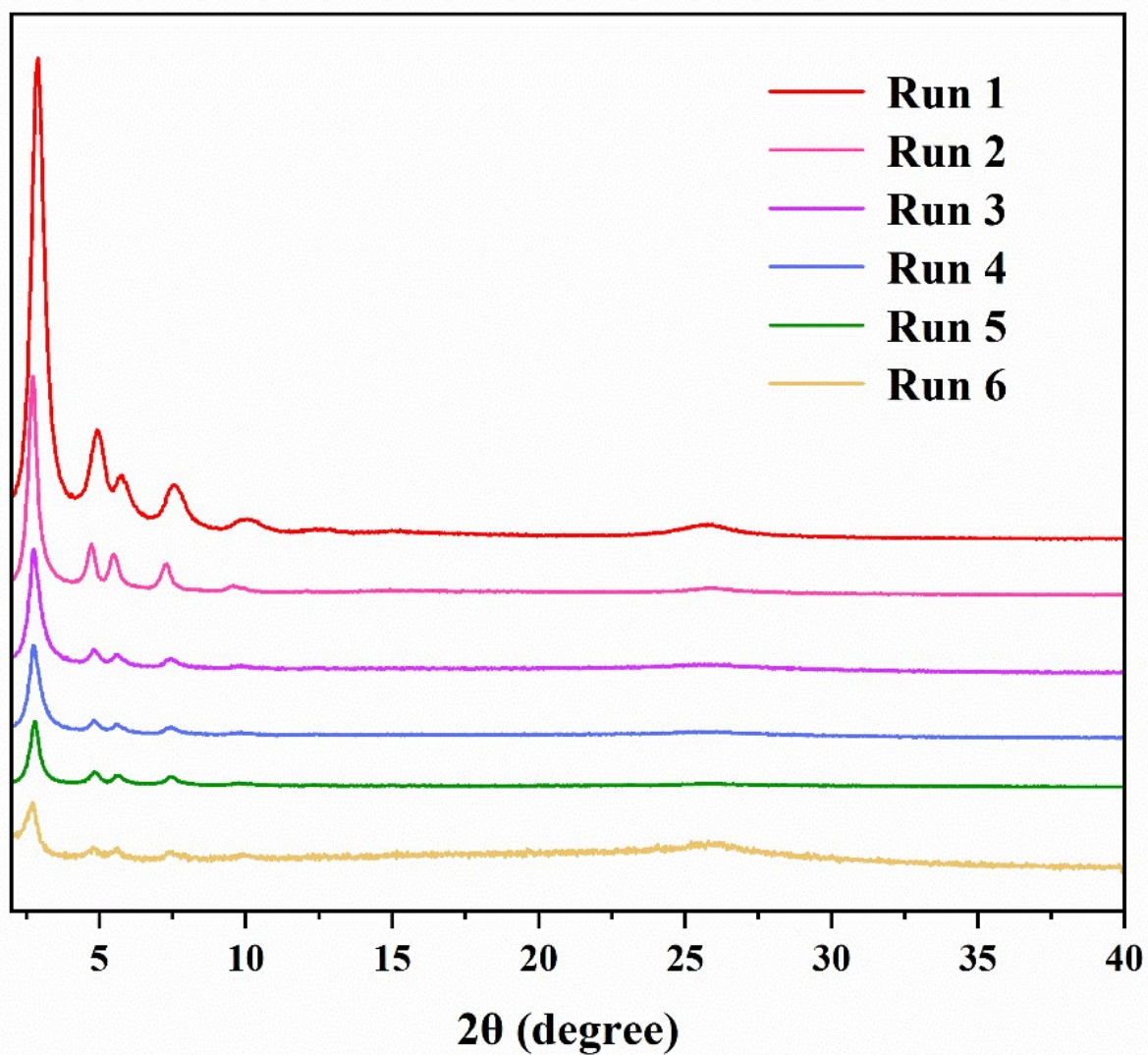

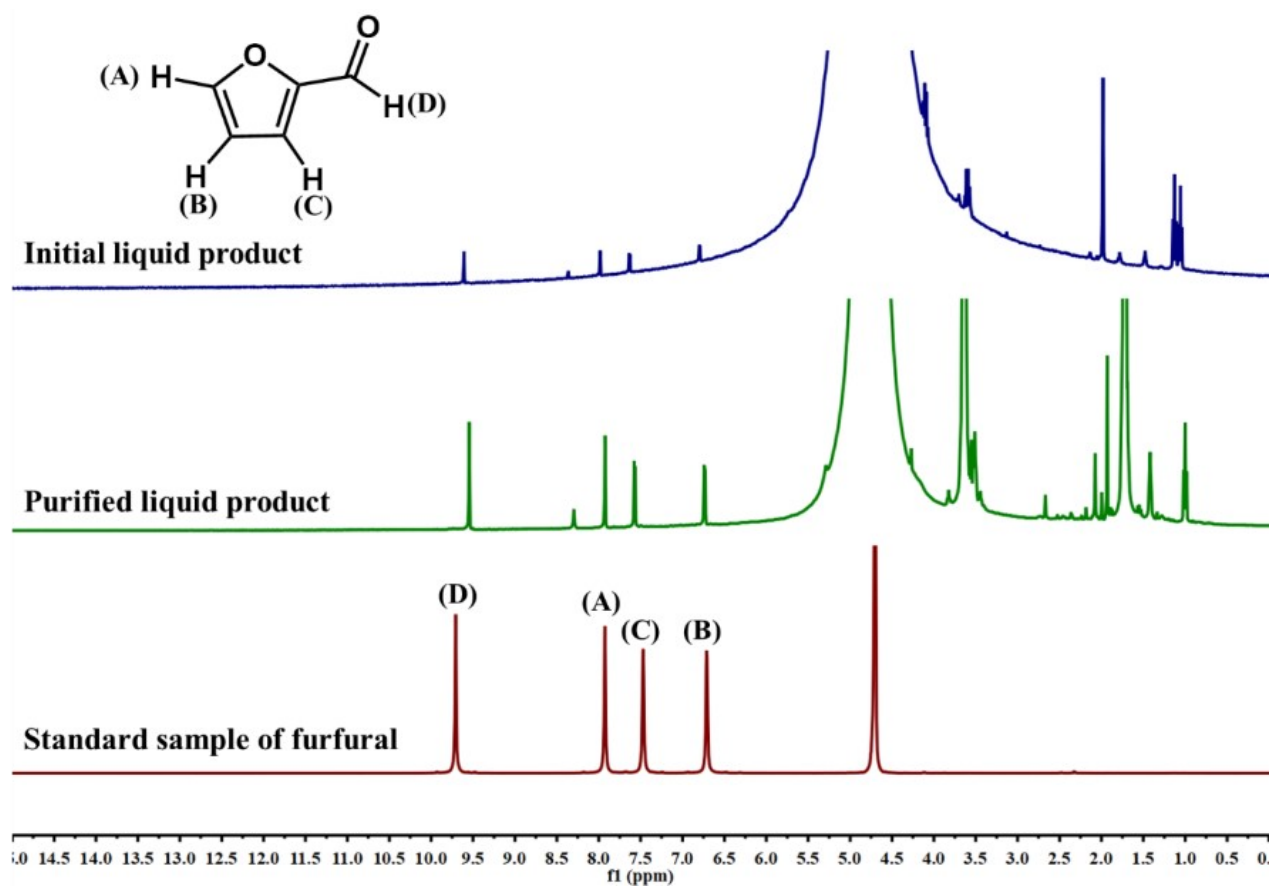**Figure S1.** SEM image of TAPT-DHPA-COF.

Figure S2. TEM image of TAPT-DHPA-COF.

Figure S3. The XRD of recycled TAPT-DHPA-COF

2.2 Structural characterization of furfural in the product

Figure S4. ^{1}H-NMR spectrum of initial liquid product, purified liquid product and standard sample of furfural

2.3 Catalytic conversion of L-lyxose and D-xylulose into furfural

Table S2. TAPT-DHPA-COF catalyzed production of furfural from L-lyxose and D-xylulose

Sugar type	Sugar conversion (%)	Furfural yield (%)	Furfural selectivity (%)
D-xylose	95.6	86.7	90.7
L-lyxose	98.9	88.1	89.1
D-xylulose	99.1	89.1	89.9