Supporting Information

Topology modulation of 2D covalent organic frameworks *via* "two-in-one" strategy

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Section 1. Materials and Methods

Materials:

1,3,5-Tribromobenzene (98%), 4-formylphenylboronic acid (98%), 4-aminophenylboronic acidpinacolester (98%), bis(pinacolato)diboron (98%), $Pd(PPh_3)_4$ (99.9%) and $Pd(PPh_3)_2Cl_2$ (99.99%) were purchased from 3A Chemicals. Neopentyl glycol (98%), K_2CO_3, *p*-toluenesulfonic acid (98%), $MgSO_4$, KOAc, Dioxane, dichloromethane, mesitylene, n-BuOH, THF and 1,2-dichlorobenzene were purchased from Aladdin reagent. Phosphate buffer solution (PBS) (pH=7.4) was purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. All commercial available chemicals were directly used as received without further purification.

Methods:

Solution ^{1}H and ^{13}C NMR spectra of all monomers and intermediates were performed on a Bruker AVANCE III-400MHz NMR spectrometer at room temperature.

UV-VIS spectra were measured on a Lambda 20 spectrophotometer.

Powder X-ray diffraction (PXRD) patterns were recorded on X-ray diffractometer (RIGAKU SMARTLAB 9KW) with a Cu-target tube and a graphite monochromator.

BET surface areas were measured by nitrogen adsorption and desorption at 77 K using a Bel Japan Inc. model BELSOPR-max analyzer and the samples were degassed at 100 °C for 8 h under vacuum (10^{-5} bar) before analysis. Pore size distribution was calculated from the adsorption or desorption branch with the nonlocal density functional theory (NLDFT).

Fourier transform infrared (FT-IR) spectra were recorded in transmission mode on a Bruker Alpha spectrometer using KBr pellets in the range 400–4000 cm^{-1}.

The solid state ^{13}C cross-polarization magic angle spinning Nuclear Magnetic Resonance (ss CP/MAS NMR) spectra were recorded on Varian Infinityplus 300 (300 MHz) solid state NMR spectrometer with a 4 mm double resonance MAS probe and at a MAS rate of 10.0 kHz with a contact time of 2 ms (ramp 100) and a pulse delay of 3 s.

Thermogravimetric analysis (TGA) was evaluated with a differential thermal analysis instrument (TA Instruments TGA Q50-1918 analyzer) over the temperature range from 50 to 800 °C in N_2 atmosphere at a heating rate of 10 °C min^{-1} using an empty Al_2O_3 crucible as the reference. Transmission electron microscopies (TEM) were performed on a FEI model Tecani 20 microscope or a JEOL model JEM-2100F.

Field emission scanning electron microscopies (FE-SEM) were performed on a JEOL model JSM-6700 microscope operating at an accelerating voltage of 5.0 kV. Elemental analysis (C, H, N) was analyzed on a Perkin-Elmer 240C elemental analyzer.

The simulations of the possible structures were carried out in Accelrys Material Studio 7.0 software package. Simulated PXRD patterns were determined by the Reflex module. Pawley refinement of the experimental PXRD was conducted to optimize the lattice parameters iteratively until the R_{wp} value converges. The density-functional tight-binding (DFTB) method is applied to obtain the total energy and cohesive energy of optimized models. Standard DFTB parameters for X-Y element pairs (X, Y= C, H, O and N) interactions were selected.[S1, S2]

Chemical stabilities of BABN-DP COF were performed using 10 mg samples immersed in 5 mL acid or basic aqueous solutions for 24 h. The samples were separated by filter and washed thoroughly with H_2O, DMF, THF, DCM and Hexane. The samples were dried at 120 ^oC for 6 h under vaccum.

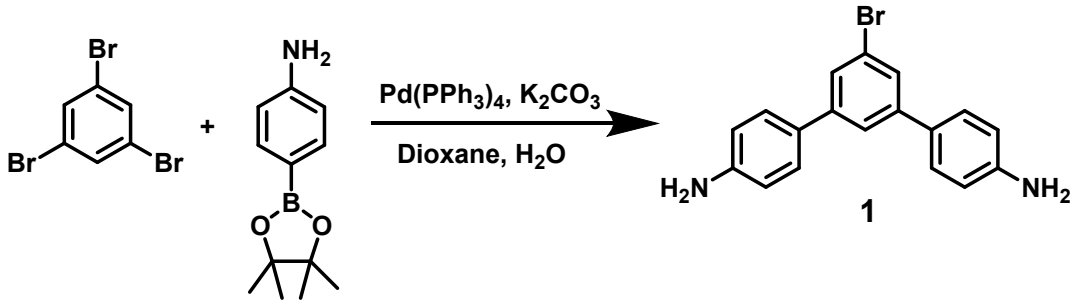
Drug loading and release:

Captopril loading was achieved by immersing solvent-free BABN-DP COF samples (95 mg) in 50 mL solution of CPT in acetone (0.25 M) with stirring for 12 h. The drug-loaded sample was separated from solution by vacuum filtration, washed with acetone, and dried at 50 ^oC under vaccum for 6 h in dark. The filtrate and washed solutions are collected and the residual Captopril content was determined by UV-vis spectroscopy to calculate the Captopril-loading capacity of BABN-DP COF. In vitro release of Captopril from CPT loaded BABN-DP COF@Captopril was performed as follow: 80 mg BABN-DP COF@Captopril was dispersed into a dialysis bag with 10 mL of phosphate buffer solution (PBS), then immersing the bag in 70 mL of PBS (pH=7.4) with stirring at 600 rpm, and sampling out 5 mL of released liquid at set intervals while a fresh PBS solution of 5 mL was added back. The concentration of the released Captopril was measured from

UV-vis absorbance at 202 nm with the help of a calibration curve. The release study was continued until no CPT was detectable in the withdrawn PBS. In the case of Ibuprofen loaded BABN COF, solvent-free BABN-DP COF samples (45 mg) in 50 mL solution of Ibuprofen in hexane (0.1 M), 40 mg BABN-DP COF@Ibuprofen was dispersed into a dialysis bag with 10 mL of phosphate buffer solution (PBS), then immersing the bag in 70 mL of PBS (pH=7.4). The concentration of the released Ibuprofen was measured from UV-vis absorbance at 364 nm with the help of a calibration curve.

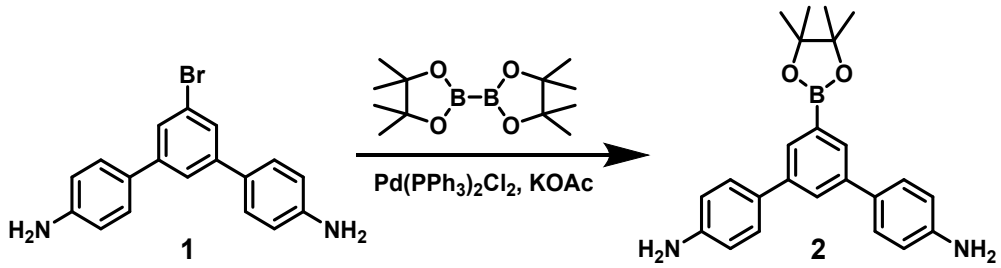
Section 2. Synthetic Procedures for Monomers and COFs

Preparation of monomers:



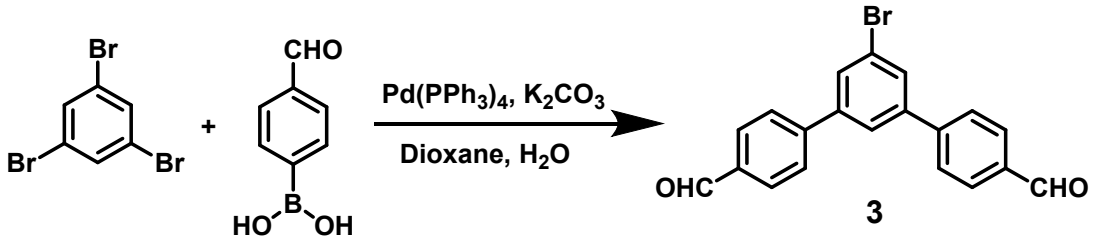
Scheme S1. Synthesis of 5'-bromo-[1,1':3',1"-terphenyl]-4,4"-diamine (**1**).

1,3,5−Tribromobenzene (3.14 g, 10 mmol), 4-aminophenylboronic acidpinacolester (4.4 g, 20 mmol), K_2CO_3 (5.6 g, 40 mmol) were mixed with $Pd(PPh_3)_4$ (1.15 g, 1 mmol) in a 250 mL three neck flask, then dioxane (100 mL) and H_2O (20 mL) were added in Ar. The mixture was heated at 100 ^oC for 12 h and then cooled to room temperature, quenched with H_2O, followed by extraction with dicholomethane. After the organic phase was washed with brine and dried over $MgSO_4$, the organic solvent was removed under reduced pressure. Compound 5'-bromo-[1,1':3',1"-terphenyl]-4,4"-diamine (**1**) was purified by column chromatography (EA/petroleum ether, 1/1, neutral alumina) and obtained as a white solid (1.32 g, yield: 39%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.59 (s, 1H), 7.56 (s, 2H), 7.42 (d, J = 8.4 Hz, 4H), 6.76 (d, J = 8.4 Hz, 4H), 3.12 (br-s, N-H, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.49, 143.55, 134.68, 130.23, 128.19, 127.20, 123.29, 115.46. MALDI TOF-MS: m/z Calc. 339.24, found 338.36.



Scheme S2. Synthesis of 5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1':3',1''-terphenyl]-4,4''-diamine (**2**).

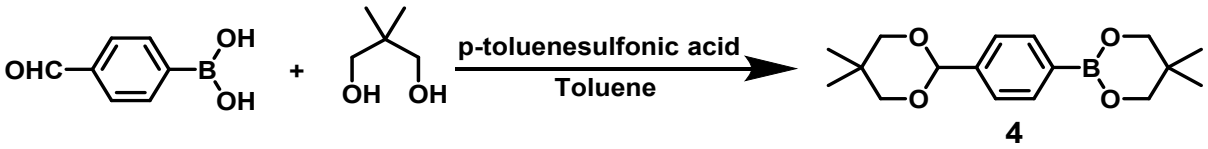
A 250 mL round flask was charged with **1** (1.7 g, 5 mmol), bis(pinacolato)diboron (3.0 g, 20 mmol), KOAc (4.0 g, 40 mmol) and $Pd(PPh_3)_2Cl_2$ (385 mg, 0.5 mmol), then dioxane (100 mL) was added in Ar. The mixture was refluxed at 100 °C for 12 h. After cooling to room temperature, H_2O was added. The reaction mixture was extracted with DCM and washed with brine, dried over $MgSO_4$. The organic solvent was removed under reduce pressure. Compound 5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1':3',1''-terphenyl]-4,4''-diamine (**2**) was isolated after column chromatography (EA/petroleum ether, 1/1, neutral alumina) as a white solid (1.06 g, yield: 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.90 (d, J = 1.6 Hz, 2H), 7.79 (s, 1H), 7.49 (d, J = 8.4 Hz, 4H), 6.76 (d, J = 8.4 Hz, 4H), 3.71 (br-s, N-H, 4H), 1.37 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.90, 141.04, 131.76, 130.96, 128.33, 127.65, 115.45, 83.93, 25.01. MALDI TOF-MS: m/z Calc. 386.30, found 385.60.



Scheme S3. Synthesis of 5'-bromo-[1,1':3',1''-terphenyl]-4,4''-dicarbaldehyde (**3**).

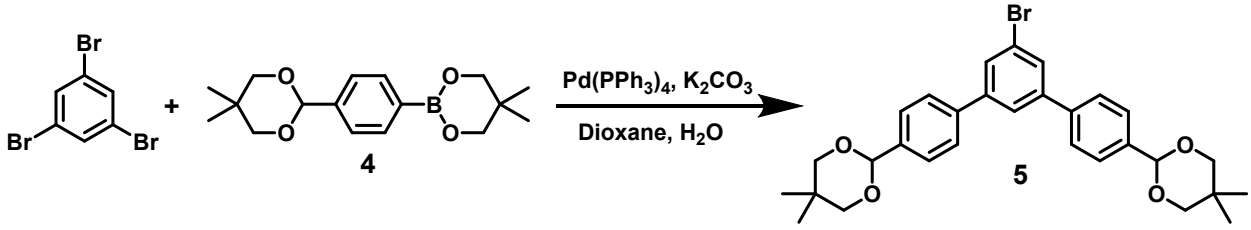
1,3,5–tribromobenzene (3.14 g, 10 mmol), 4-formylphenylboronic acid (3.0 g, 20 mmol,), K_2CO_3 (5.6 g, 40 mmol) were mixed with $Pd(PPh_3)_4$ (1.15 g, 1 mmol) in a 250 mL three neck flask, then dioxane (100 mL) and H_2O (20 mL) were added in Ar. The mixture was heated at 100 °C for 12 h and then cooled to room temperature, quenched with H_2O, followed by extraction with dicholomethane. After the organic phase was washed with brine and dried over $MgSO_4$, the organic solvent was removed under reduced pressure. Compound 5'-bromo-[1,1':3',1''-terphenyl]-

4,4"-dicarbaldehyde **(3)** was obtained by column chromatography (EA/petroleum ether, 1/2) as a white solid (1.53 g, yield: 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.09 (s, 2H), 8.01 (s, 2H), 7.99 (s, 2H), 7.68-7.83 (m, 7H).[S3] ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 191.80, 145.25, 142.58, 135.98, 130.51, 130.29, 127.97, 125.27, 123.85.



Scheme S4. Synthesis of 2-(4-(5,5-dimethyl-1,3-dioxan-2-yl)-phenyl)-5,5-dimethyl-1,3,2-dioxaborinane (**4**).

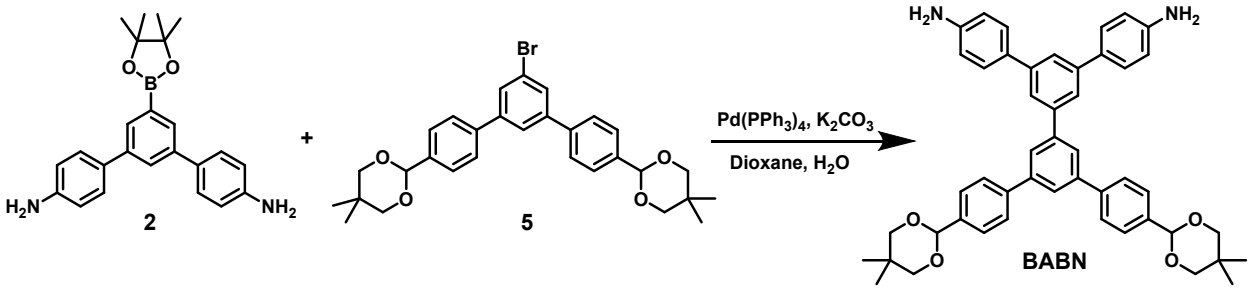
4-Formylphenylboronic acid (10.0 g, 66.7 mmol) and neopentyl glycol (15.3 g 147 mmol) were mixed in toluene (100 mL), then *p*-toluenesulfonic acid (230 mg, 1.33 mmol) was added. The mixture was heated at 115 ^{o}C for 24 h and then cooled to room temperature. Dichloromethane (100 mL) was added and the organic phase was washed with saturated aqueous $NaHCO_3$ solution. After dried over $MgSO_4$, the organic solvent was removed under reduce pressure. The resulted solid was collected by filtration and washed with methanol to afford compound 2-(4-(5,5-dimethyl-1,3-dioxan-2-yl)-phenyl)-5,5-dimethyl-1,3,2-dioxaborinane (**4)** as white solid (18.6 g, yield: 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (d, J = 8.0 Hz 2H), 7.48 (d, J = 8.0 Hz, 4H), 5.40 (s, 1H), 3.76 (s, 6H), 3.61 (s, 2H), 1.29 (s, 3H), 1.01 (s, 6H), 0.90 (s, 3H). ^{13} C NMR (100 MHz, $CDCl_3$) δ (ppm) 140.64, 133.89, 125.26, 101.81, 72.29, 31.89, 30.29, 23.09, 21.93. MALDI TOF-MS: m/z Calc. 304.19, found 303.19.



Scheme S5. Synthesis of 2,2'-(5'-bromo-[1,1':3',1"-terphenyl]-4,4"-diyl)-bis(5,5-dimethyl-1,3-dioxane) (**5**).

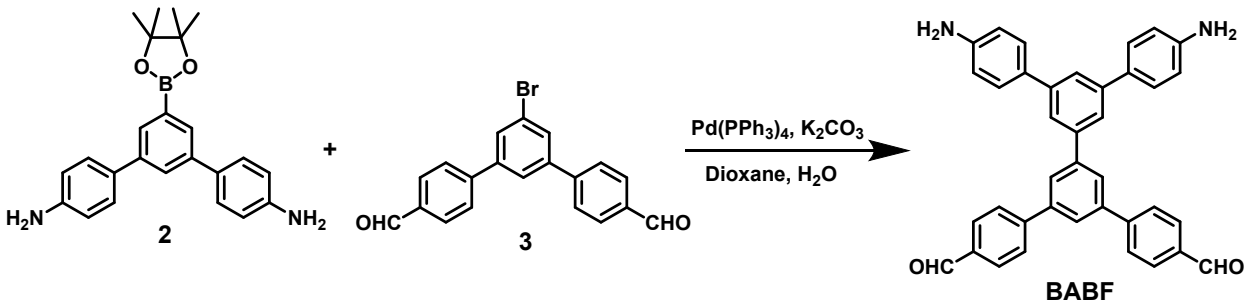
1,3,5–tribromobenzene (3.14 g, 10 mmol), **4** (6.6 g, 20 mmol), K_2CO_3 (5.6 g, 40 mmol) were mixed with $Pd(PPh_3)_4$ (1.15 g, 1 mmol,) in a 250 mL three neck flask, then dioxane (100 mL) and H_2O (20 mL) were added in Ar. The mixture was heated at 100 ^{o}C for 24 h and then cooled to

room temperature, quenched with H_2O, followed by extraction with dicholomethane. The organic phase was washed with brine and dried over $MgSO_4$, and removed under reduced pressure. Compound 2,2'-(5'-bromo-[1,1':3',1"-terphenyl]-4,4"-diyl)-bis(5,5-dimethyl-1,3-dioxane) **(5)** was purified by column chromatography (EA/petroleum ether, 1/3) to afford a white solid (2.6 g, yield: 52%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm) 7.76 (t, J = 1.6 Hz 1H), 7.74 (d, J = 1.6 Hz 2H), 7.64 (d, J = 8.4 Hz, 4H), 7.59 (d, J = 8.4 Hz, 4H), 5.44 (s, 2H), 3.77 (d, J = 11.2 Hz, 4H), 3.67 (d, J = 10.4 Hz, 4H), 1.28 (s, 6H), 0.80 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm) 143.69, 140.31, 139.18, 129.32, 127.34, 127.19, 125.24, 123.54, 101.60, 77.95, 30.49, 23.14, 21.97. MALDI TOF-MS: m/z Calc. 537.49, found 538.773.



Scheme S6. Synthesis of 5'-(4,4"-bis(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1':3',1"-terphenyl]-5'-yl)-[1,1':3',1"-terphenyl]-4,4"-diamine (**BABN**).

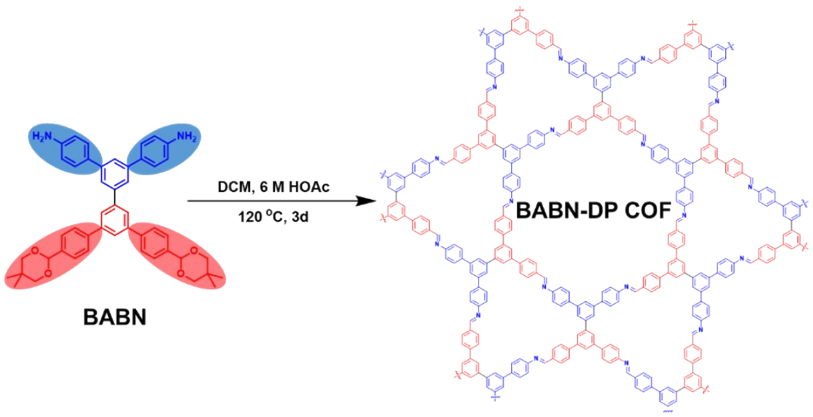
A 100 mL three neck flask was charged with **2** (680 mg, 2.0 mmol), **5** (730 mg, 2.0 mmol), K_2CO_3 (552 mg, 4.0 mmol) were mixed with $Pd(PPh_3)_4$ (230 mg, 0.2 mmol), then dioxane (20 mL) and H_2O (2 mL) were added in Ar. The mixture was heated at 100 ^{o}C for 48 h and cooled to room temperature, quenched with H_2O, followed by extraction with $CHCl_3$. The organic phase was washed with brine, dried over $MgSO_4$, and removed under reduced pressure. Compound 5'-(4,4"-bis(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1':3',1"-terphenyl]-5'-yl)-[1,1':3',1"-terphenyl]-4,4"-diamine (**BABN**) was purified by column chromatography (EA/petroleum ether, 1/1, neutral alumina) to afford a white solid (1.1 g, yield: 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.85 (d, J = 1.6 Hz, 2H), 7.77 (br-s, 1H), 7.72 (m, 6H), 7.62 (d, J = 8.0 Hz, 4H), 7.57 (s, 1H), 7.53 (d, J = 8.8 Hz, 4H), 6.80 (d, J = 8.4 Hz, 4H), 5.47 (s, 2H), 3.79 (t, J = 12 Hz, 8H), 3.69 (d, N-H, J = 10.4 Hz,4H), 1.32 (s, 6H), 0.82 (s, 6H). ^{13} C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.19, 142.92, 142.35, 142.18, 142.12, 141.75, 137.99, 131.62, 128.36, 127.46, 126.79, 125.61, 125.34, 124.13, 123.84, 115.54, 101.60, 77.80, 30.39, 23.20, 22.04. MALDI TOF-MS: m/z Calc. 716.92, found 716.396.



Scheme S7. Synthesis of 5'-(4,4"-diamino-[1,1':3',1"-terphenyl]-5'-yl)-[1,1':3',1"-terphenyl]-4,4"-dicarbaldehyde (**BABF**).

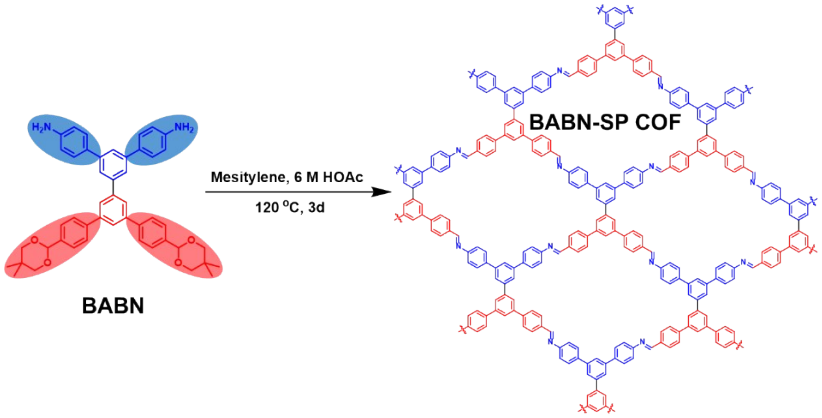
A 100 mL three neck flask was charged with **2** (680 mg, 2 mmol), **3** (1.08 mg, 2 mmol), K_2CO_3 (552 mg, 4 mmol) were mixed with $Pd(PPh_3)_4$ (230 mg, 0.2 mmol), then dioxane (20 mL) and H_2O (2 mL) were added in Ar. The mixture was heated at 100 °C for 48 h and then cooled to room temperature, quenched with H_2O, followed by extraction with $CHCl_3$. The organic phase was washed with brine, dried over $MgSO_4$ and concentrated under reduce pressure. Compound 5'-(4,4"-diamino-[1,1':3',1"-terphenyl]-5'-yl)-[1,1':3',1"-terphenyl]-4,4"-dicarbaldehyde (**BABF**) was obtained by precipitation from petroleum ether followed by filtration as a white solid (440 mg, yield: 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.10 (s, 2H), 8.01 (d, J = 8.4 Hz, 4H), 7.98 (s, 2H), 7.94-7.89 (m, 4H),7.88 (s, 1H) 7.70-7.75 (m, 3H), 7.53 (d, J = 8.8 Hz, 4H), 6.80 (d, J = 8.4 Hz, 4H), 3.78 (s, N-H, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.00, 146.83, 146.36, 142.59, 141.31, 135.68, 131.37, 130.52, 129.63, 128.36, 128.10, 126.68, 125.51, 124.52, 123.72, 121.70, 115.54. MALDI TOF-MS: m/z Calc. 544.65, found 543.97.

Preparation of COFs using BABN as monomer:



Scheme S8. Synthesis of BABN-DP COF.

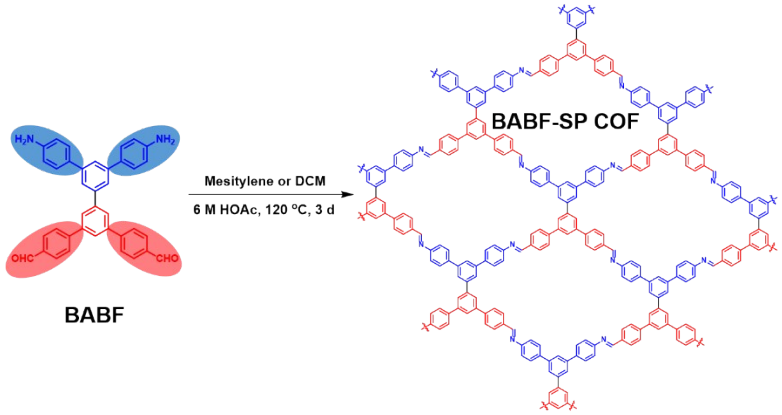
A 10 mL Pyrex tube was charged with **BABN** (53.7 mg, 0.075 mmol) and DCM (1mL). The mixture was sonicated for 2 minutes, followed by addition of acetic acid (6 M, 0.3 mL) and sonication for another 2 minutes. The mixture was degassed by three freeze–pump–thaw cycles, purged with Ar and heated at 120 °C for 3 days. After cooling, the precipitate was collected by filtration and washed by MeOH, THF and DCM, dried under vacuum to afford **BABN-DP COF** (28.8 mg, 75.5 %) as a bright yellow powder.



Scheme S9. Synthesis of BABN-SP COF.

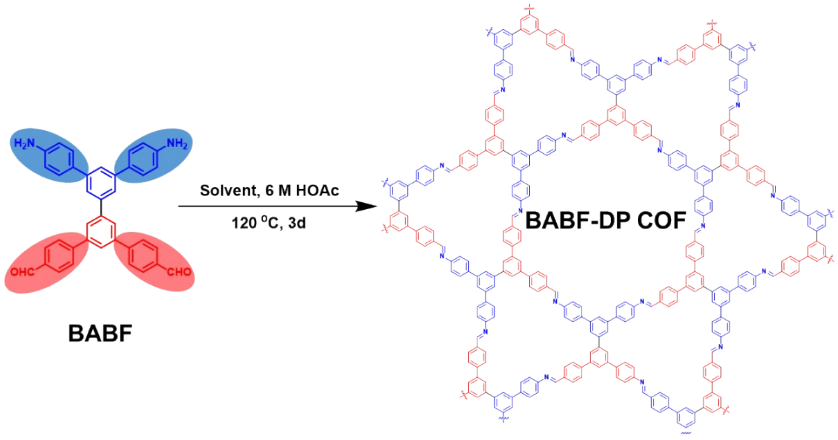
A 10 mL Pyrex tube was charged with **BABN** (53.7 mg, 0.075 mmol) and mesitylene (1mL). The mixture was sonicated for 2 minutes, followed by addition of acetic acid (6 M, 0.3 mL) and sonication for another 2 minutes. The mixture was degassed by three freeze–pump–thaw cycles, purged with Ar and heated at 120 °C for 3 days. After cooling, the precipitate was collected by filtration and washed by MeOH, THF and DCM, dried under vacuum to afford **BABN-SP COF** (17.9 mg, 47.2 %) as a light yellow powder.

Preparation of COFs using BABF as monomer:



Scheme S10. Synthesis of **BABF-SP COF**.

A 10 mL Pyrex tube was charged with BABF (40 mg, 0.075 mmol) and mesitylene or DCM (1mL). The mixture was sonicated for 2 minutes, followed by addition of acetic acid (6 M, 0.1 mL) and sonication for another 2 minutes. The mixture was degassed by three freeze–pump–thaw cycles, purged with Ar and heated at 120 °C for 3 days. After cooling, the precipitate was collected by filtration and washed by MeOH, THF and DCM, dried under vacuum to afford **BABF-SP COF** as a light yellow powder ((Mesitylene, 27.1 mg, 71.0%; DCM, 17.0 mg, 44.7%)).



Scheme S11. Synthesis of **BABF-DP COFs**.

A 10 mL Pyrex tube was charged with **BABF** (27 mg, 0.05 mmol) and different solvents (1 mL), such as THF, DCM, DCE and Benzyl alcohol. The mixture was sonicated for 2 minutes, followed by addition of acetic acid (6 M, 0.1 mL) and sonication for another 2 minutes. The mixture was degassed by three freeze–pump–thaw cycles, purged with Ar and heated at 120 °C for 3 days. After

cooling, the precipitate was collected by filtration and washed by MeOH, THF and DCM, dried under vacuum to afford **BABF-DP COFs** as a light yellow powder. (DCM, 25.3 mg yield: 99.5%; DCE, 25.1 mg, yield: 98.6%; THF, 17.5 mg, yield: 68.7%; Benzyl alcohol, yield: 48.8%) (*In these cases, the concentration of BABF (75 mM) is lower than that was used in preparation of* ***BABF-SP COF*** *with* ***BABF*** *as monomer (50 mM)*).

Section 3. NMR and IR spectra

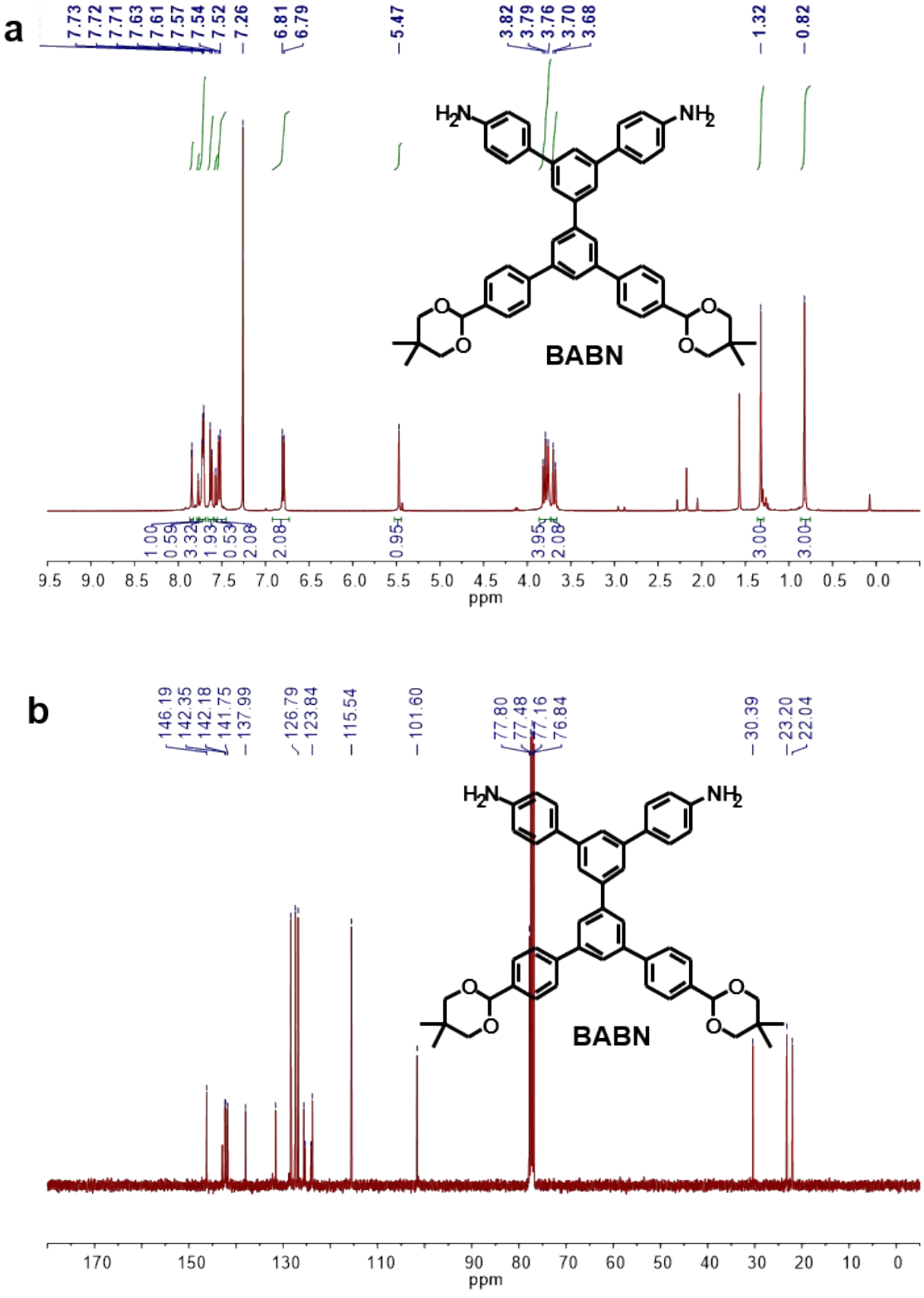


Figure S1. (a) ^{1}H and (b) ^{13}C NMR spectra of **BABN** in $CDCl_3$.

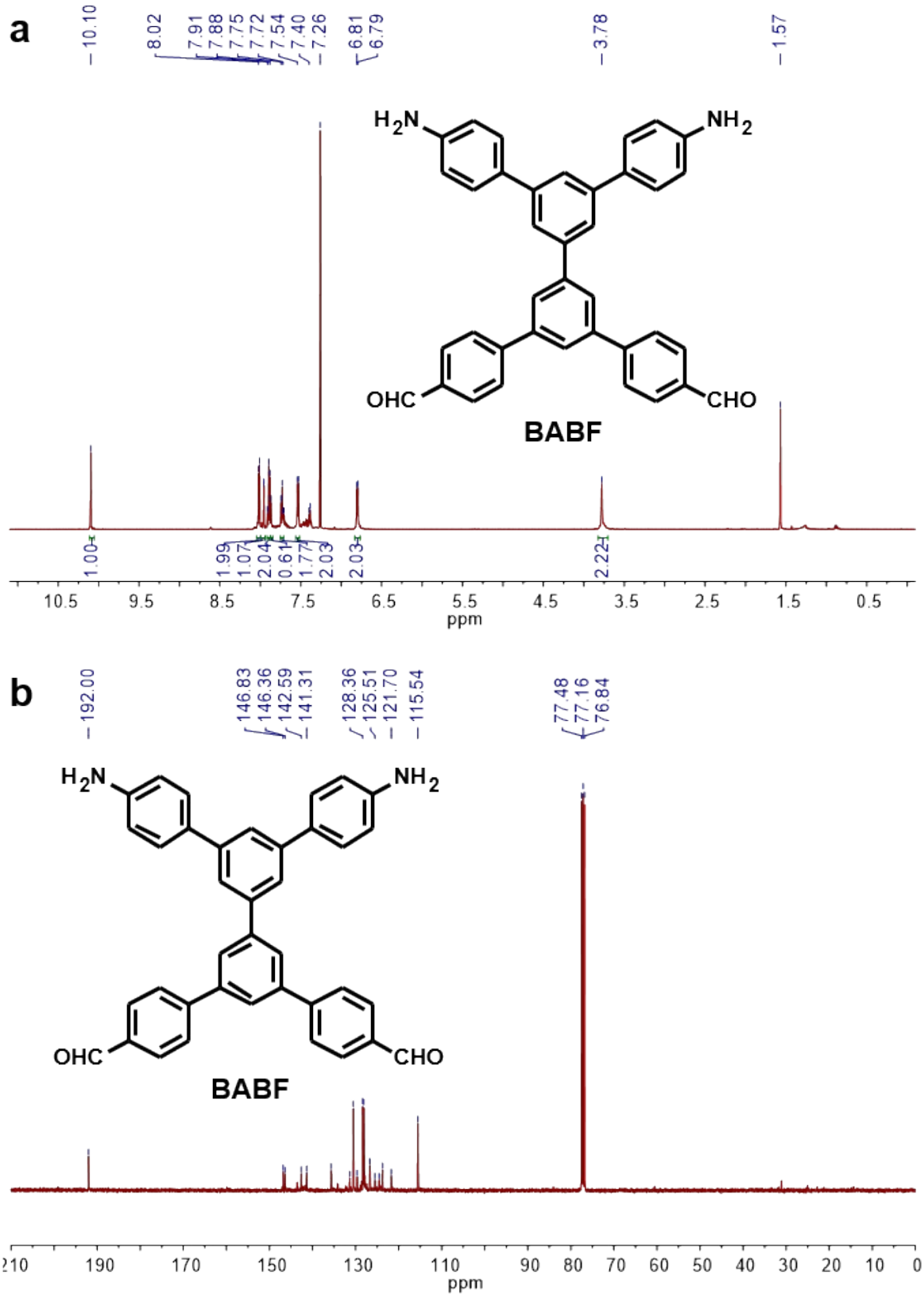


Figure S2. (a) ^{1}H and (b) ^{13}C NMR spectra of **BABF** in $CDCl_3$.

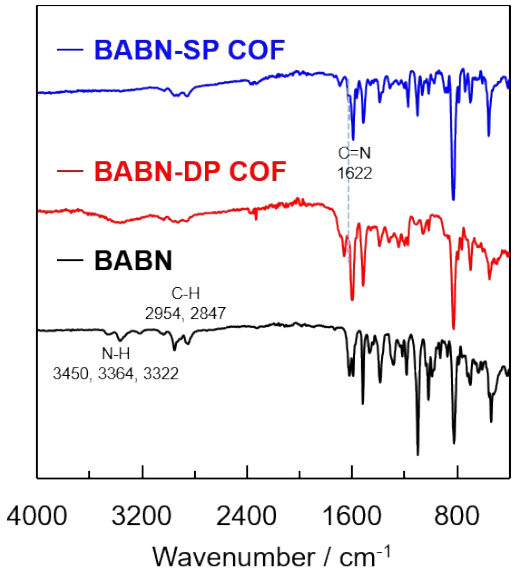
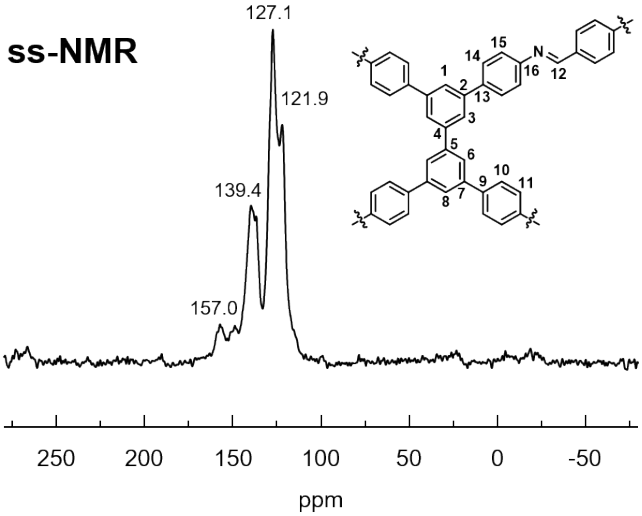


Figure S3. IR spectra of monomer **BABN** (black), **BABN-DP COF** (red) and **BABN-SP COF** (blue) from 4000 to 400 cm^{-1}. Unreacted neopentyl acetal groups (reflected as peaks around 2847-2954 cm^{-1} assigned to C-H vibration from neopentyl acetal group in the FT-IR spectra of **BABN-DP COF** and **BABN-SP COF**) or impurities blocked in pores are supposed to lower the porosity of the **BABN-DP COF**.



Chemical shifts (ppm)	Assignments
157.0	**12, 16**
139.4	**2, 4, 5, 7, 9, 13**
127.1	**6, 10, 11, 14**
121.0	**1, 3, 8, 15**

Figure S4. Solid-State ^{13}C CP-MAS NMR spectra of **BABN COFs** (**BABN** as monomer). No peak belongs to 5,5-dimethyl-1,3-dioxane groups carbons exists.

Table S1. Elemental analysis of **BABN COFs** (**BABN** as the monomer).

Elemental analysis			
	C (wt%)	**H (wt%)**	**N (wt%)**
Calculated	**90.09**	**4.38**	**5.53**
Found	**79.24**	**5.13**	**4.19**

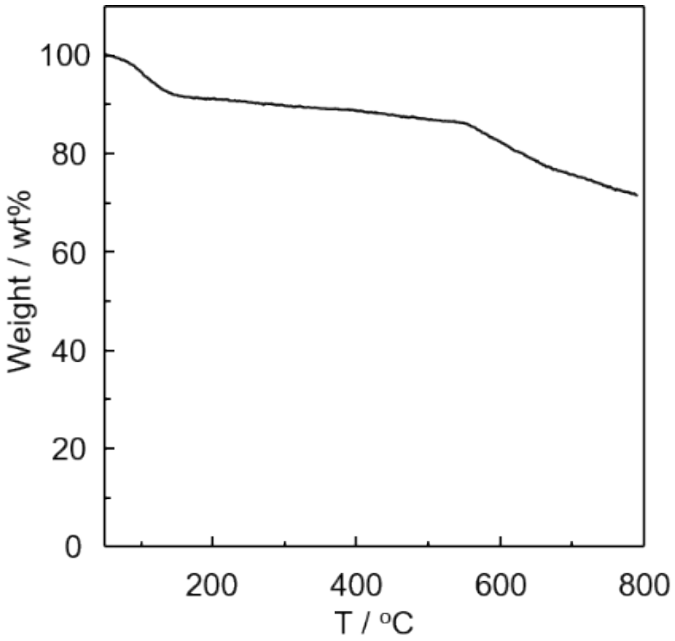


Figure S5. TGA profile of **BABN COFs** in N_2 atmosphere. Weight loss below 200 °C should attributed to volatile solvent inside the pores. Weight loss 5.14% from 170 °C to 540 °C.

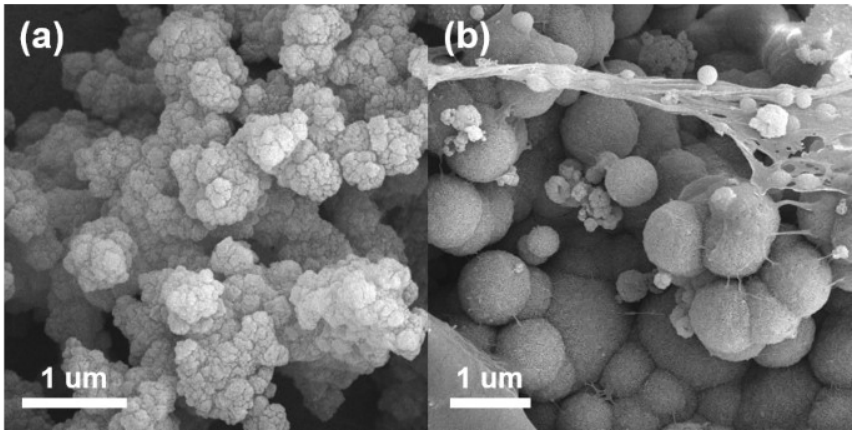


Figure S6. SEM images of (a) **BABN-DP COF** and (b) **BABN-SP COF**.

Section 4. Simulated Structural Models for COFs.

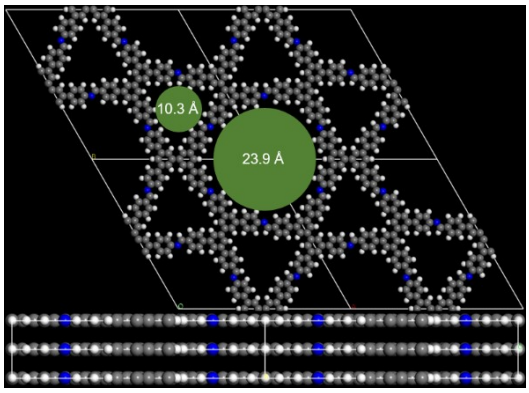


Figure S7. (up) Top-view and (bottom) Side view of Simulated AA-stacked model for dual-pore **BABN-DP COF** (gray, carbon; blue, nitrogen; white, hydrogen). Insert shows the pore width presentation for simulated AA-stacked dual-pore models of **BABN-DP COF**.

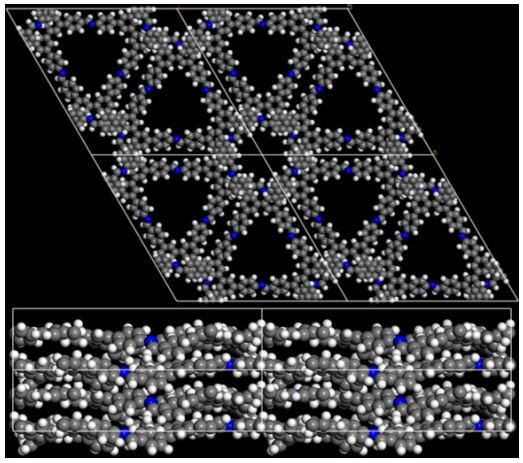


Figure S8. (up) Top-view and (bottom) Side view of Simulated AB-staggered model with space group of P*63* (no. 173) for dual-pore **BABN-DP COF** (gray, carbon; blue, nitrogen; white, hydrogen).

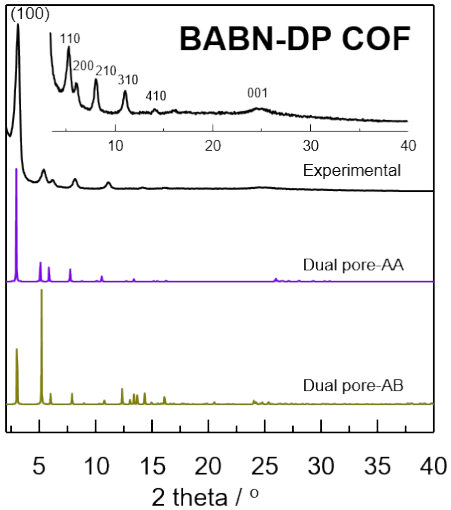


Figure S9. Comparison of experimental PXRD pattern (black) for **BABN-DP COF** with simulated dual-pore AA-stacked (purple) and AB-staggered (brown) models.

Table S2. Refined unit cell parameters and fractional atomic coordinates of the AA-stacked Model for **BABN-DP COF**.

BABN-DP COF			
Space group		*P*-6	
a = b = 33.5003 Å, c= 3.5608 Å			
α, β = 90 °, γ = 120 °			
R_{wp} = 4.20 %, R_p = 3.18 %			
Atom name	x	y	z
C1	0.45556	0.28633	0.00000
C2	0.49384	0.32722	0.00000
C3	0.49201	0.36589	0.00000
C4	0.45140	0.36560	0.00000
C5	0.41280	0.32343	0.00000
C6	0.41494	0.28463	0.00000
C7	0.44989	0.40847	0.00000
C8	0.48907	0.44958	0.00000
C9	0.45965	0.24654	0.00000
N10	0.42548	0.20718	0.00000
C11	0.16660	0.42645	0.00000
C12	0.16518	0.46566	0.00000
C13	0.12692	0.38669	0.00000
C14	0.12520	0.46497	0.00000
C15	0.08438	0.42503	0.00000
C16	0.08658	0.38576	0.00000
C17	0.04068	0.42461	0.00000
C18	0.03941	0.46416	0.00000
H19	0.52574	0.32943	0.00000
H20	0.52366	0.39518	0.00000
H21	0.38014	0.31864	0.00000
H22	0.38467	0.25328	0.00000

H23	0.51905	0.44968	0.00000
H24	0.49254	0.25157	0.00000
H25	0.19454	0.49751	0.00000
H26	0.12720	0.35600	0.00000
H27	0.12820	0.49692	0.00000
H28	0.05787	0.35357	0.00000
H29	0.06958	0.49394	0.00000
H30	0.37802	0.37802	0.00000
C31	0.40927	0.40927	0.00000
C32	0.49041	0.49041	0.00000
C33	0.00000	0.38495	0.00000
C34	0.00000	0.46571	0.00000
H35	0.00000	0.35470	0.00000

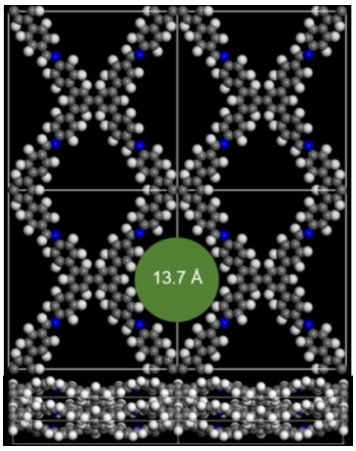


Figure S10. (up) Top-view and (bottom) Side view of Simulated AA-stacked model for single-pore **BABN-SP COF** (gray, carbon; blue, nitrogen; white, hydrogen). Insert shows the pore width presentation for simulated AA-stacked single-pore models of **BABN-SP COF**.

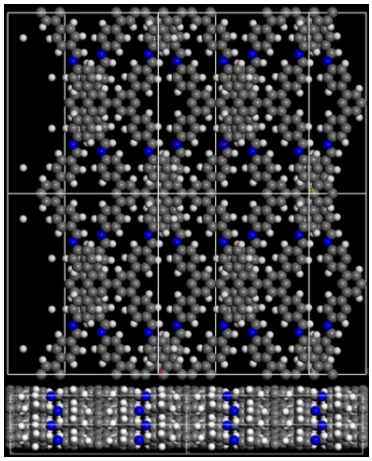


Figure S11. (up) Top-view and (bottom) Side view of Simulated AB-staggered model for single-pore **BABN-SP COF** with space group of C*m* (no. 8) (gray, carbon; blue, nitrogen; white, hydrogen).

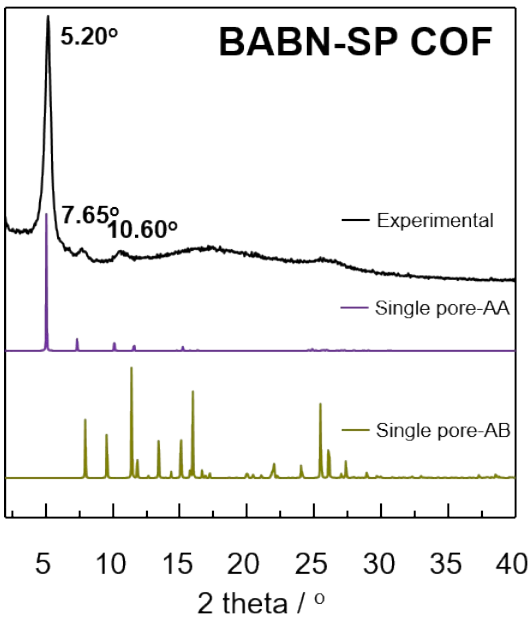


Figure S12. Comparison of experimental PXRD pattern (black) for **BABN-SP COF** with simulated dual-pore AA-stacked (purple) and AB-staggered (brown) models.

Table S3 Refined unit cell parameters and fractional atomic coordinates of the AA-stacked Model for **BABN-SP COF**.

BABN-SP COF			
Space group		*P*M	
a = 23.9922 Å, b= 25.7933 Å, c = 3.1318 Å			
α= 90 °, β= 87.36 °, γ= 90 °			
R_{wp} = 4.06 %, R_p = 3.23 %			
Atom name	X	y	z
C1	0.88882	0.95218	0.76786
C2	0.94274	0.95258	0.91724
C3	0.80145	0.89813	0.78088
C4	0.85879	0.90172	0.70739
C5	0.88720	0.85641	0.58802
C6	0.85887	0.80874	0.54562
C7	0.80178	0.80557	0.61431
C8	0.77321	0.85061	0.73431
C9	0.64013	0.69158	0.41262
C10	0.69631	0.69682	0.50962

C11	0.72585	0.65231	0.62852
C12	0.61350	0.64299	0.44166
C13	0.64247	0.59854	0.56997
C14	0.69917	0.60366	0.65903
C15	0.61301	0.54779	0.62908
C16	0.55872	0.45266	0.77277
C17	0.22234	0.24931	1.49727
N18	0.27462	0.25556	1.41695
C19	0.11302	0.04779	1.37087
C20	0.05872	0.04734	1.22718
C21	0.19918	0.10366	1.34091
C22	0.14248	0.09854	1.42998
C23	0.11351	0.14299	1.55830
C24	0.14014	0.19158	1.58734
C25	0.19631	0.19681	1.49034
C26	0.22585	0.15231	1.37142
C27	0.35888	0.30874	1.45438
C28	0.30179	0.30557	1.38567
C29	0.27322	0.35061	1.26565
C30	0.38721	0.35641	1.41198
C31	0.35880	0.40172	1.29259
C32	0.30146	0.39812	1.21908
C33	0.38882	0.45218	1.23211
C34	0.44274	0.54742	1.08273
N35	0.77462	0.75556	0.58302
C36	0.72233	0.74931	0.50270
H37	0.96033	0.91508	0.98432
H38	0.77873	0.93164	0.88647
H39	0.93117	0.85782	0.52489
H40	0.88112	0.77409	0.45553
H41	0.72962	0.84865	0.80583

H42	0.61668	0.72529	0.31729
H43	0.76908	0.65568	0.70905
H44	0.57012	0.64025	0.36445
H45	0.72233	0.57055	0.76671
H46	0.54078	0.41518	0.83610
H47	0.19667	0.28285	1.56713
H48	0.04079	0.08482	1.16386
H49	0.22233	0.07055	1.23321
H50	0.07013	0.14025	1.63551
H51	0.11669	0.22529	1.68269
H52	0.26908	0.15567	1.29088
H53	0.38113	0.27409	1.54448
H54	0.22962	0.34865	1.19412
H55	0.43118	0.35783	1.47511
H56	0.27874	0.43163	1.11348
H57	0.46033	0.58492	1.01567
H58	0.69666	0.78286	0.43284
C59	0.63956	0.50000	0.55460
C60	0.47146	0.50000	1.00778
C61	0.36280	0.50000	1.31239
C62	0.52996	0.50000	0.84686
H63	0.68070	0.50000	0.43321
H64	0.32223	0.50000	1.44193
C65	0.13956	0.00000	1.44535
C66	0.02996	0.00000	1.15310
C67	0.86280	0.00000	0.68757
C68	0.97146	0.00000	0.99219
H69	0.18071	0.00000	1.56674
H70	0.82223	0.00000	0.55802

Table S4. Calculated Total Energy Values (E_c) for **BABN-DP COF** and **BABN-SP COF**.

COF	Stacking model	Total Energy (kcal mol $^{-1}$)	Relative Total Energy (kcal mol $^{-1}$)
BABN-DP COF	AA	961.1098	-27.4696
BABN-SP COF	AA	988.5794	0

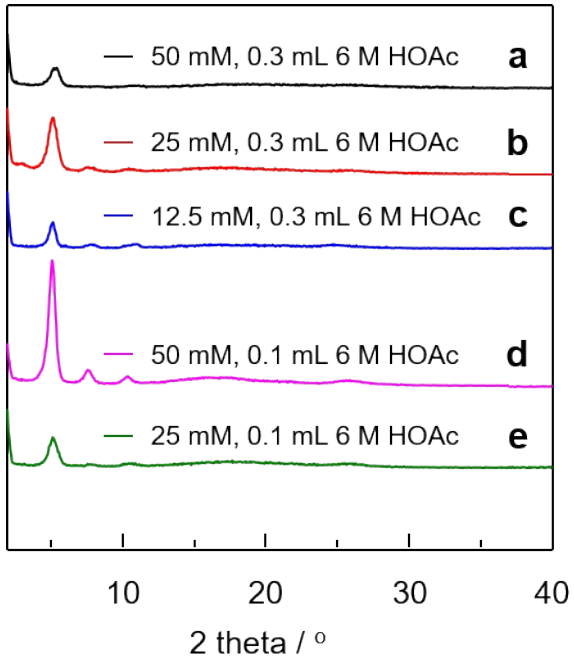


Figure S13. PXRD patterns of BABN COFs synthesized under various BABN monomer concentration with acid catalyst of 0.3 mL 6 M HOAc (a,b,c) and 0.1 mL 6 M HOAc (d,e) in 1 mL mesitylene.

Section S5. General Procedure for the Synthesis of BABN and BABF COFs.

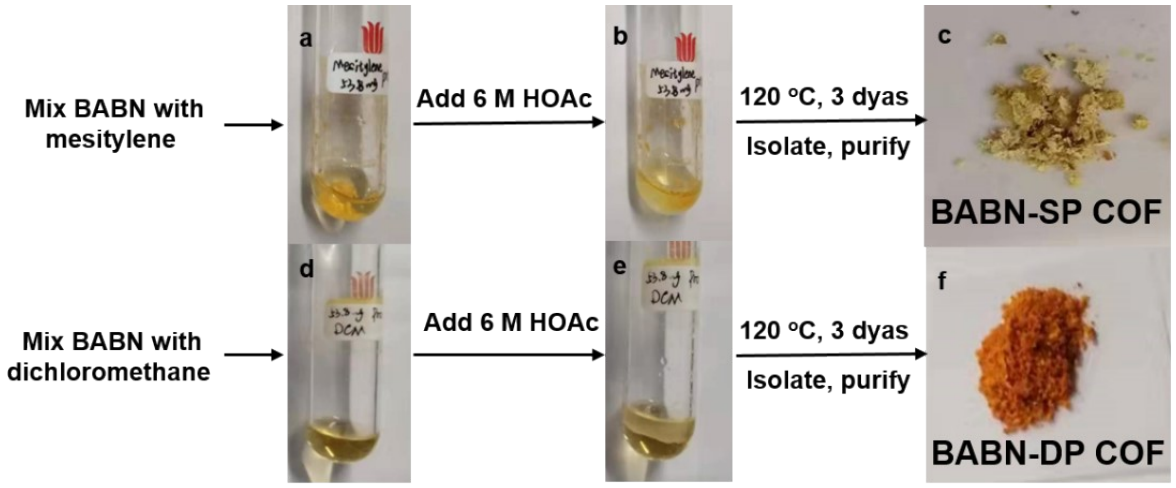


Figure S14. Pictorial illustration of **BABN-DP COFs** (a, b and c) and **BABN-SP COF** (d, e and f) synthesis in dichloromethane and mesitylene, respectively. The BABN monomer show better solubility in dichloromethane than mesitylene.

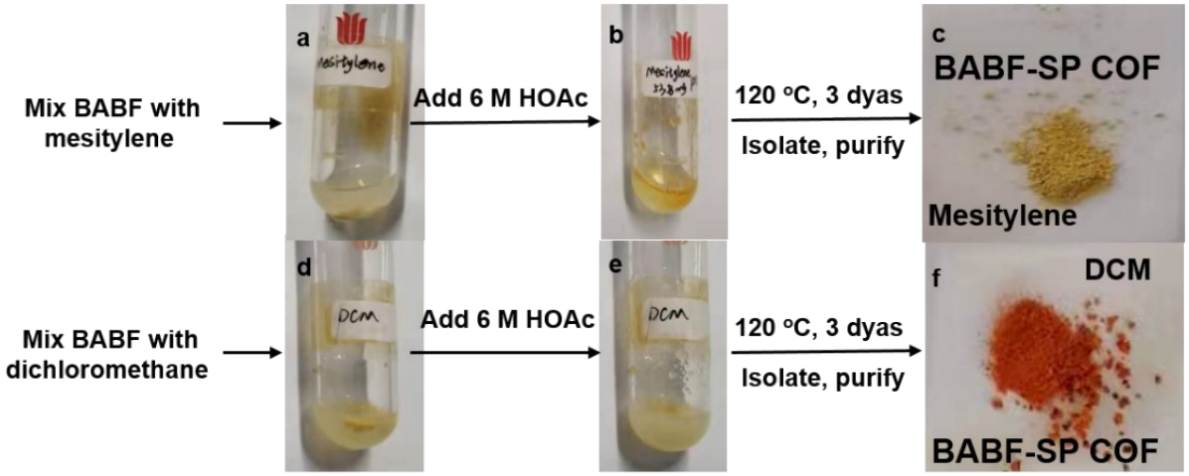


Figure S15. Pictorial illustration for synthesis of **BABF-SP COFs** (a, b and c) in Mesitylene and **BABN-SP COF** (d, e and f) in dichloromethane, respectively. The BABF monomer show better solubility in dichloromethane than mesitylene.

Section 6. Characterization of BABF COFs.

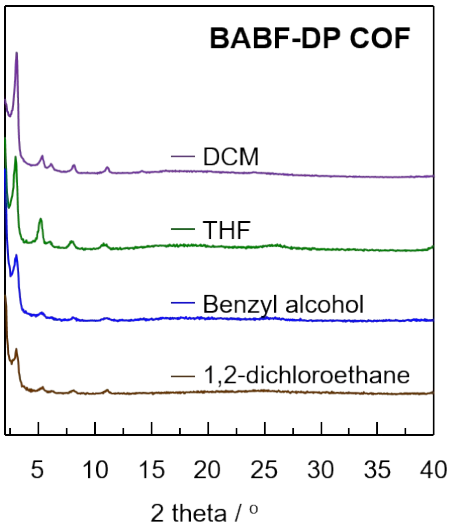


Figure S16. Comparison of PXRD patterns for BABF-DP COF and BABN-DP COF.

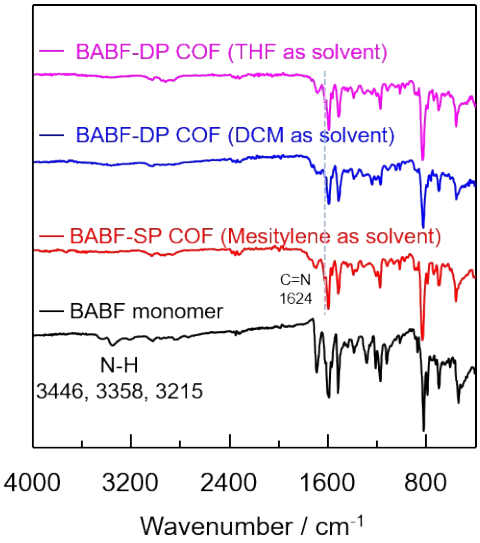
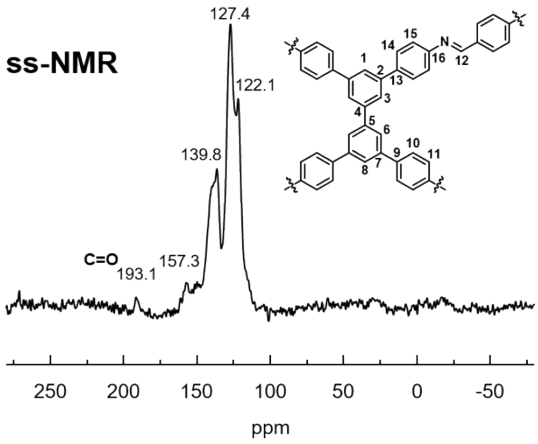


Figure S17. Comparison of FT-IR spectra for **BABF-DP COF** prepared in various solvent with BABF monomer.



Chemical shifts (ppm)	Assignments
193.1	unreacted C=O
157.3	12, 16
139.8	2, 4, 5, 7, 9, 13
127.1	6, 10, 11, 14
122.1	1, 3, 8, 15

Figure S18. Solid-State ^{13}C CP-MAS NMR spectra of **BABF COFs** (**BABF** as the monomer). Signal at 193.1 ppm contribute to unreacted C=O is observed.

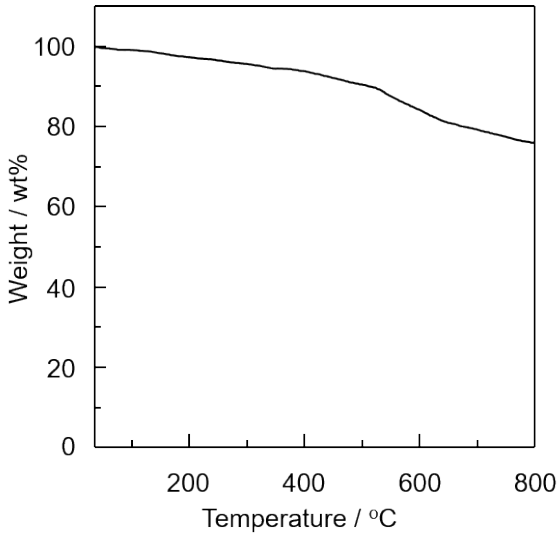


Figure S19. TGA profile of **BABF COFs** (**BABF** as the monomer) in N_2 atmosphere.

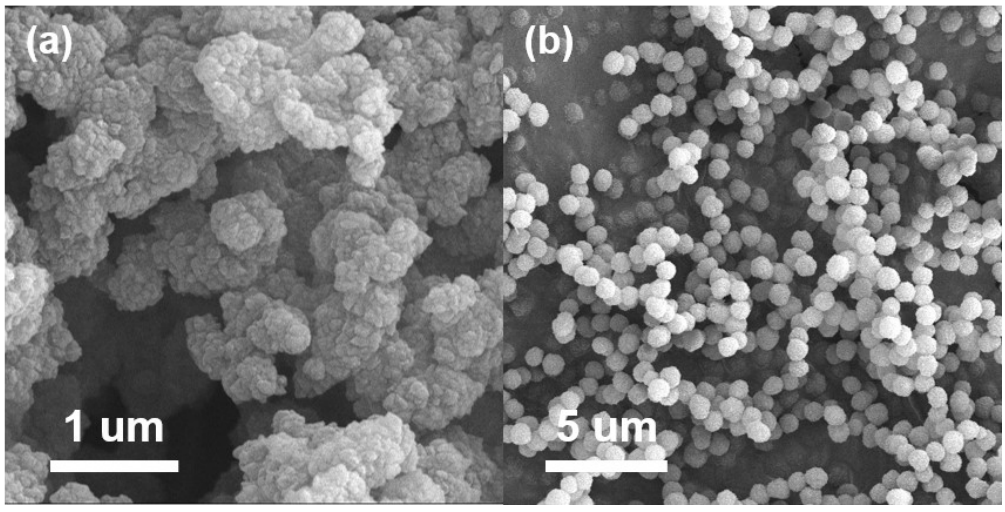


Figure S20. SEM image of **BABF-DP COF** (prepared in DCM).

Table S5. Elemental analysis of **BABF COFs** (BABF as the monomer).

Elemental analysis			
	C (wt%)	H (wt%)	N (wt%)
Calculated	90.09	4.38	5.53
Found	81.06	4.75	4.06

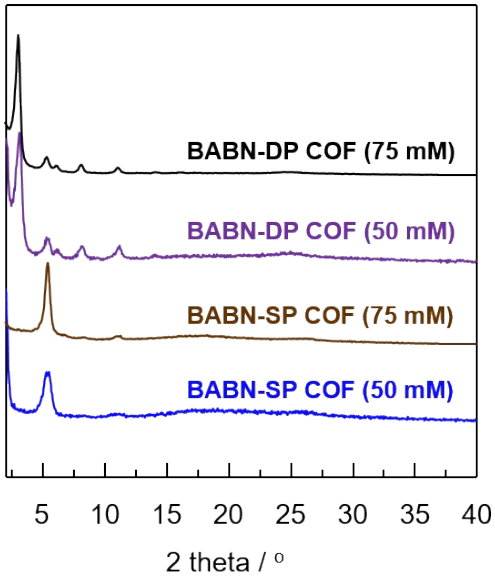


Figure S21. PXRD patterns of the BABN-DP COFs synthesized in DCM (black and purple lines) and BABN-SP COFs (brown and blue lines) synthesized in Mesitylene with different monomer concentrations.

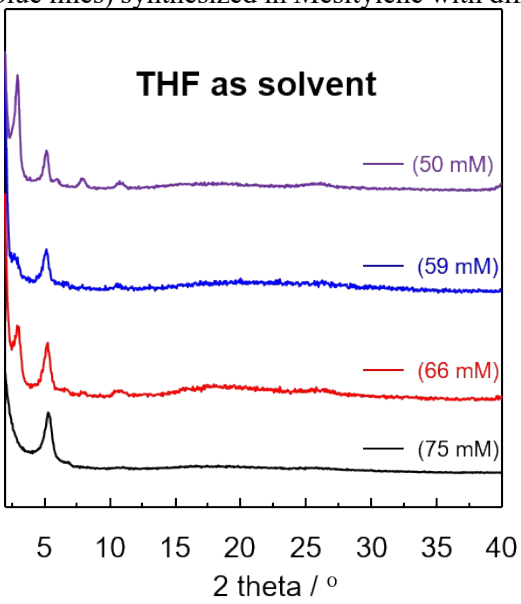


Figure S22. PXRD patterns of BABF COFs synthesized under various BABF monomer concentration with acid catalyst of 0.1 mL 6 M in 1 mL THF.

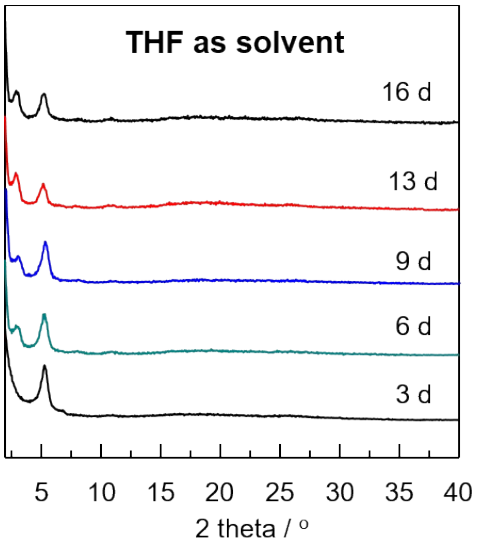


Figure S23. PXRD patterns of BABF COFs synthesized for various reaction time with acid catalyst of 0.1 mL 6 M in 1 mL THF under monomer concentration of 75 mM.

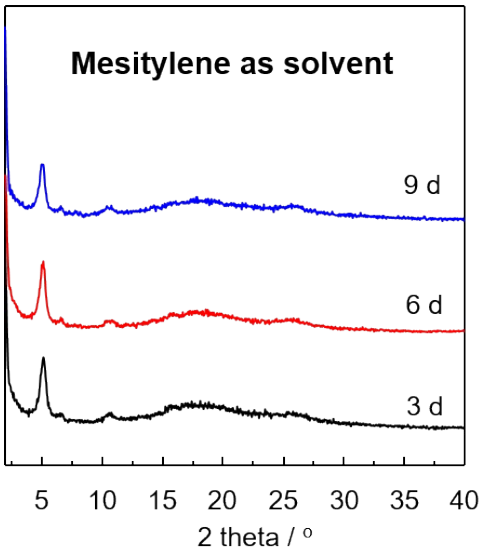


Figure S24. PXRD patterns of BABF COFs synthesized for various reaction time with acid catalyst of 0.1 mL 6 M in 1 mL mesitylene under monomer concentration (75 mM).

Section 8. Drug load and release of BABN-DP COFs

Chemical stabilities of BABN-DP COF in acid and basic aqueous solutions.

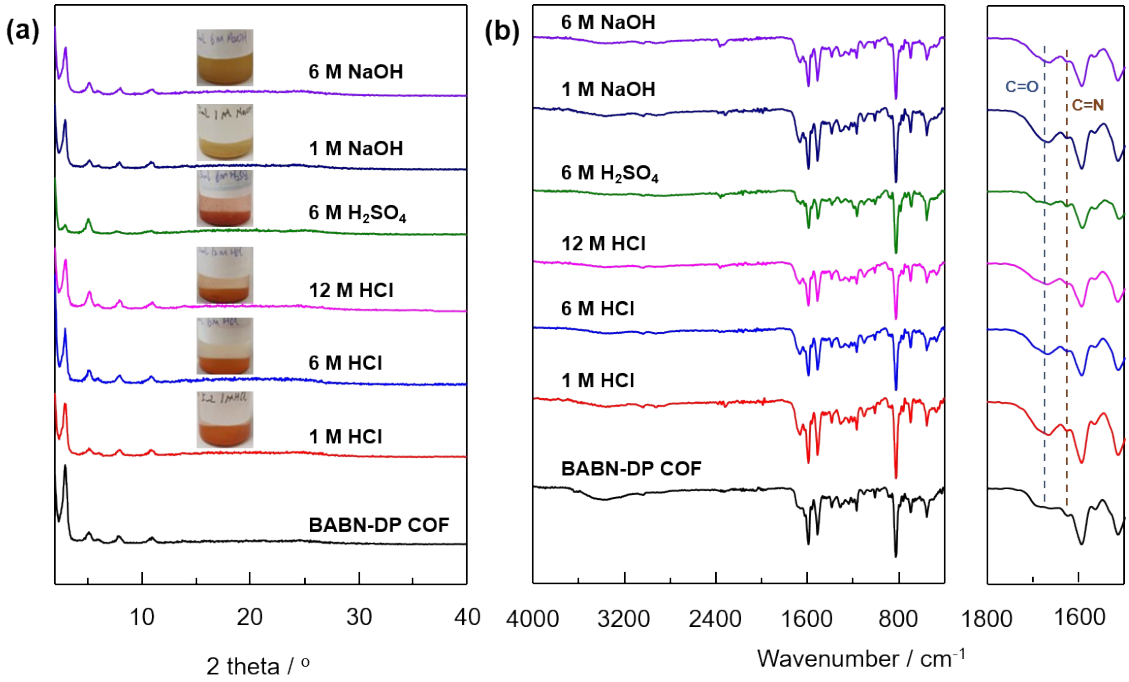


Figure S25. (a) Comparison of PXRD patterns and (b) FT-IR spectra of BABN-DP COF after immersed in 1 M, 6 M, 12 M HCl, 1 M, 6 M NaOH and 6 M H_2SO_4 for 24 h.

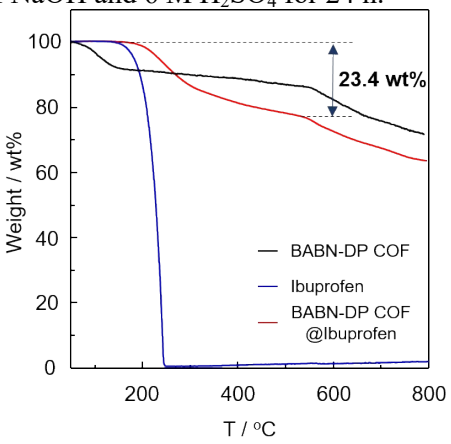


Figure S26. TGA of Ibuprofen (blue), BABN-DP COF (black) and BABN-DP COF @ Ibuprofen (red). The loading amount of Ibuprofen is calculated to be 23.4 wt% based on the weight loss from 200 to 540 °C.

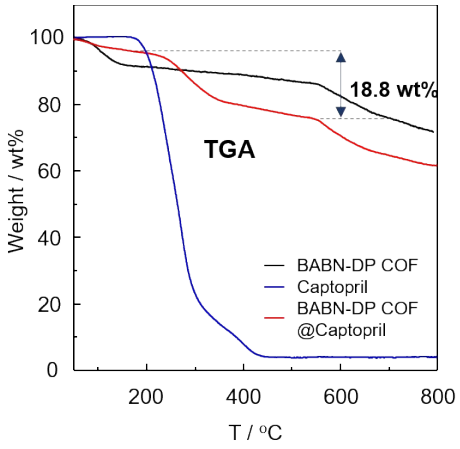


Figure S27. TGA of Captopril (blue), BABN-DP COF (black) and BABN-DP COF @ Captopril (red). The loading amount of Ibuprofen is calculated to be 18.8 wt% based on the weight loss from 200 to 540 °C.

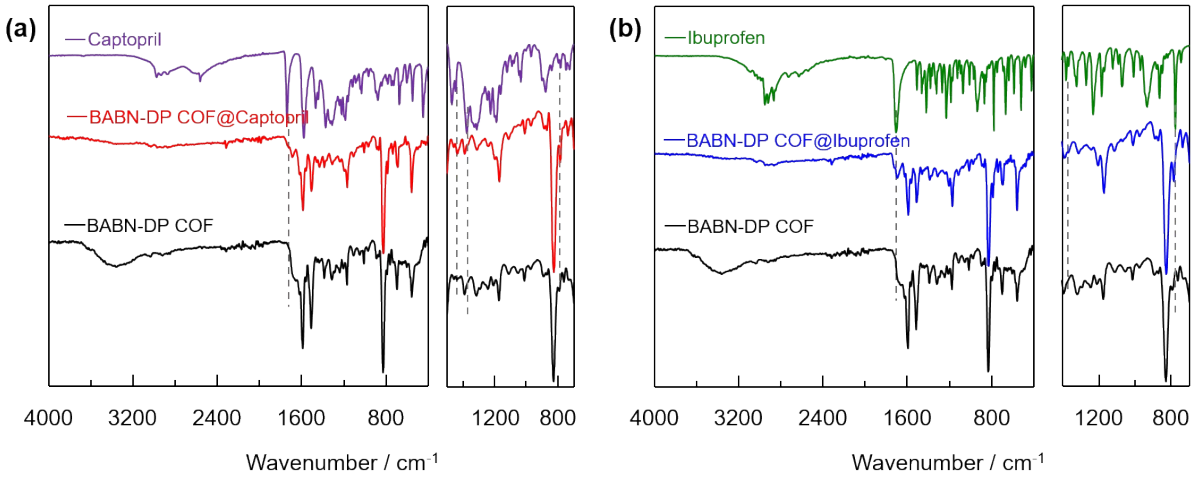


Figure S28. (a) Comparison of FT-IR spectra of Captopril (purple), Captopril loaded BABN-DP COF (red), with BABN-DP COF (black) from 4000 to 400 cm^{-1} and the extended spectra from 1500-700 cm^{-1}; (b) Comparison of FT-IR spectra of Ibuprofen (green), Ibuprofen loaded BABN-DP COF (blue) with BABN-DP COF (black) from 4000 to 400 cm^{-1} and the extended spectra from 1400-700 cm^{-1}.

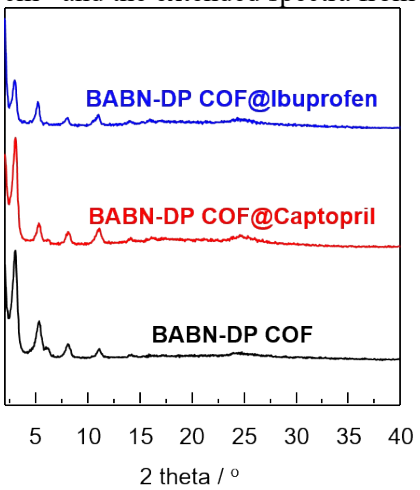


Figure S29. PXRD patterns of BABN-DP COF @ Ibuprofen (blue) and BABN-DP COF @ Captopril (red) compared with BABN-DP COF (black).

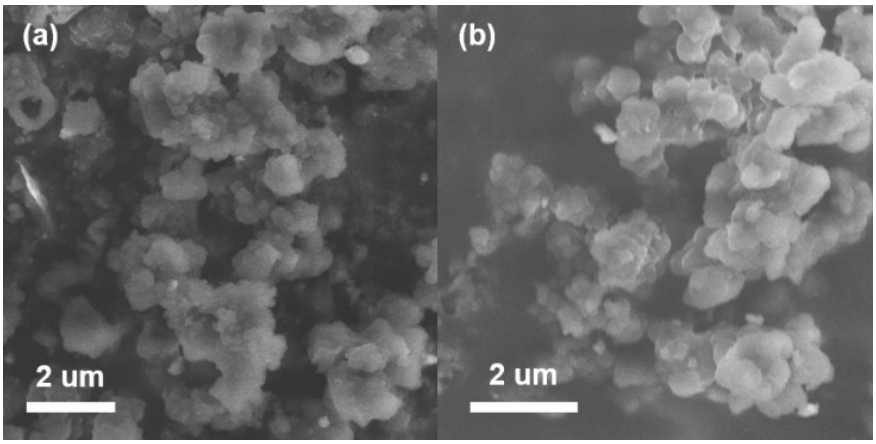


Figure S30. SEM images of BABN-DP COF @ Captopril (a) and BABN-DP COF @ Ibuprofen (b).

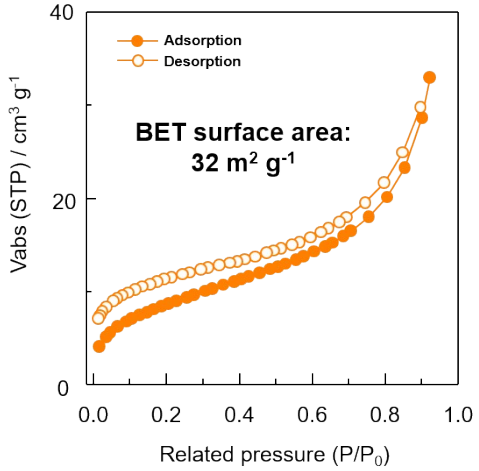


Figure S31. N_2 adsorption isotherms of Captopril loaded BABN-DP COFs.

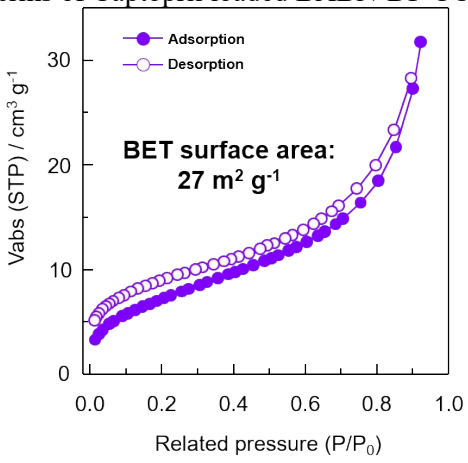


Figure S32. N_2 adsorption isotherms of Ibuprofen loaded BABN-DP COFs.

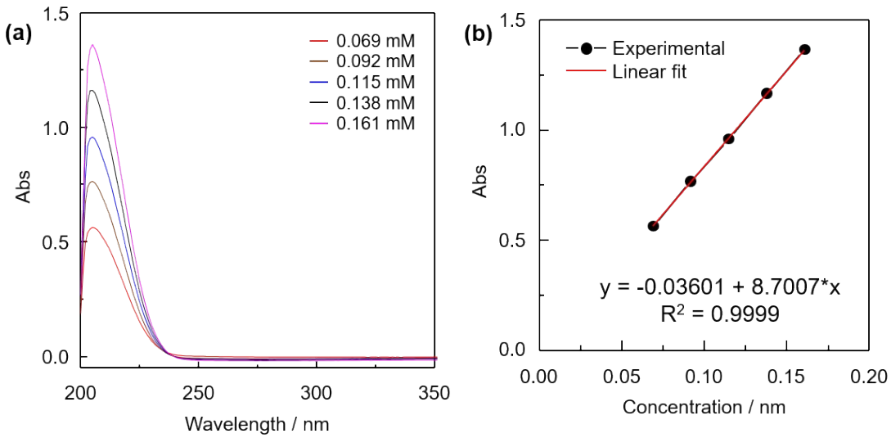


Figure S33. (a) UV−vis spectra of Captopril in simulated body fluid (SBF) (pH 7.4, buffer solution) at different concentrations. (b) Captopril calibration curve.

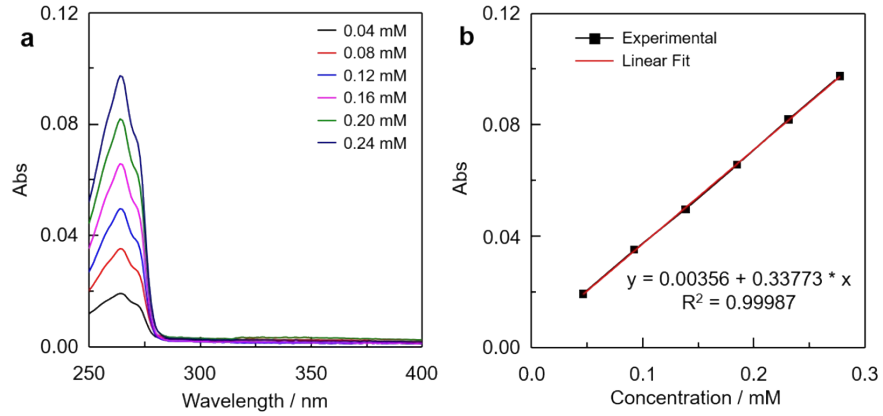


Figure S34. (a) UV−vis spectra of Ibuprofen in simulated body fluid (SBF) (pH 7.4, buffer solution) at different concentrations. (b) Ibuprofen calibration curve.

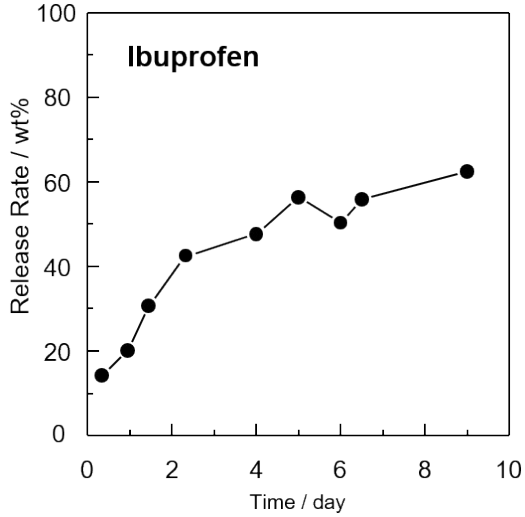


Figure S35. Release profiles of Ibuprofen from the BABN-DP COF@Ibuprofen. Release rate of 62.4 wt% was detected after 9 days.

Section 9. References

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