# Supporting Information <br> Heteroporous bifluorenylidene-based covalent organic frameworks displaying exceptional dye adsorption behavior and high energy storage 

Ahmed F. M. EL-Mahdy, ${ }^{\text {a,b }}$ Mohamed Barakat Zakaria, ${ }^{\text {c,d,e }}$ Hao-Xin Wang, ${ }^{\text {a }}$ Tao Chen, ${ }^{\text {f }}$ Yusuke Yamauchi, ${ }^{\text {ce,eg }}$ and Shiao-Wei Kuo*a,h

${ }^{a}$ Department of Materials and Optoelectronic Science, Center of Crystal Research, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan.
b Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt.
c JST-ERATO Yamauchi Materials Space-Tectonics Project and International Research Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.
d Department of Chemistry, Faculty of Science,Tanta University, Tanta, Gharbeya 31527, Egypt.
e School of Chemical Engineering and Australian Institute for Bioengineering and Nanotechnology (AIBN), The University of Queensland, Brisbane, Queensland 4072, Australia.
$f$ Ningbo Institute of Material Technology and Engineering, Chinese Academy of Science, Zhongguan West Road 1219, 315201 Ningbo, China.
g JST-ERATO Yamauchi Materials Space-Tectonics Project, Kagami Memorial Research Institute for Materials Science and Technology, Waseda University, 2-8-26 Nishiwaseda, Shinjuku, Tokyo 169-0051, Japan.
${ }^{h} \quad$ Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 807, Taiwan.

Corresponding authors:
Shiao-Wei Kuo, +886-7-5252000 ext 4079, E-mail: kuosw@faculty.nsysu.edu.tw

## S1. Materials

Chemicals and solvents were obtained from commercial sources and used as received. Pyrene, tetrakis(triphenylphosphine)palladium(0), $n$-bromosuccinimide, and carbazole were purchased from Acros. Phenanthrene-9,10-dione, dibenzoyl peroxide, 4-bromoaniline, 4-formylphenylboronic acid, potassium permanganate, and Lawesson's reagent were obtained from Alfa Aesar. Bis(pinacolato)diboron, [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II), potassium hydroxide, sodium bisulfite, and potassium acetate were purchased from J. T. Baker. Bromine, nitrobenzene, sulfuric acid, and 4-aminophenylboronic acid pinacol ester were obtained from Sigma-Aldrich.

## S2. Characterization

${ }^{1} \mathbf{H}$ and ${ }^{13} \mathbf{C}$ NMR spectroscopy. NMR spectra were recorded using an INOVA 500 instrument, with DMSO- $d_{6}$ and $\mathrm{CDCl}_{3}$ as solvents and tetramethylsilane (TMS) as the external standard. Chemical shifts are provided in parts per million (ppm).
Fourier transform infrared (FTIR) spectroscopy. FTIR spectra were recorded using a Bruker Tensor 27 FTIR spectrophotometer and the conventional KBr plate method; 32 scans were collected at a resolution of $4 \mathrm{~cm}^{-1}$.
Solid state nuclear magnetic resonance (SSNMR) spectroscopy. SSNMR spectra were recorded at National Cheng Kung University using a Bruker Avance III HD solid state NMR spectrometer and a Bruker magic-angle-spinning (MAS) probe, running 32,000 scans.
Thermogravimetric analysis (TGA). TGA was performed using a TA Q-50 analyzer under a flow of $\mathrm{N}_{2}$. The samples were sealed in a Pt cell and heated from 40 to $800^{\circ} \mathrm{C}$ at a heating rate of $20^{\circ} \mathrm{C}$ $\min ^{-1}$ under $\mathrm{N}_{2}$ at a flow rate of $50 \mathrm{~mL} \mathrm{~min}^{-1}$.
Powder X-ray diffraction (PXRD). PXRD was performed using a Siemens D5000 and monochromated $C u / K \alpha(\lambda=0.1542 \mathrm{~nm})$. The sample was spread in a thin layer on the square recess of an XRD sample holder.
Surface area and porosimetry (ASAP/BET). The BET surface areas and porosimetry measurements of the prepared samples (ca. 20-100 mg) were performed using a Micromeritics ASAP 2020 surface area and porosity analyzer. Nitrogen isotherms were generated through incremental exposure to ultrahigh-purity $\mathrm{N}_{2}$ (up to ca. 1 atm ) in a liquid $\mathrm{N}_{2}(77 \mathrm{~K})$ bath.
Field-emission scanning electron microscopy (FE-SEM). FE-SEM was conducted using a JEOL JSM-7610F scanning electron microscope. Samples were subjected to Pt sputtering for 100 s prior to observation.
Transmission electron microscopy (TEM). TEM was performed using a JEOL-2100 scanning electron microscope, operated at 200 kV .
COF structural simulations. Molecular modeling was performed using Reflex, a software package for crystal determination from XRD patterns. Unit cell dimensions were first determined manually from the observed XRD peak positions using the coordinates.
UV-Vis-NIR spectroscopy. UV-Vis-NIR spectra were recorded at $25^{\circ} \mathrm{C}$ using a Jasco V-570 spectrometer, with deionized water as the solvent. Raman spectra were recorded at $25^{\circ} \mathrm{C}$ using a Jobin-Yvon T6400 micro Raman apparatus, with a He-Cd laser ( 325 nm line) as an excitation source.

## S3. Synthetic Procedures



Phenanthrene-9,10-dione
3,6-Dibromophenanthrene-9,10-dione
3,6-Dibromo-9H-fluoren-9-one
3,3',6,6'-Tetrabromo-9,9'-bifluorenylidene
(BF-4Br)

Scheme S1. Synthesis of 3,3',6,6'-tetrabromo-9,9'-bifluorenylidene (BF-4Br).
3,6-Dibromophenanthrene-9,10-dione: According to the reported method, ${ }^{\text {S1 }}$ phenanthrene-9,10dione ( $5 \mathrm{~g}, 24 \mathrm{mmol}$ ) and dibenzoyl peroxide $(0.2 \mathrm{~g}, 0.83 \mathrm{mmol})$ were dissolved at room temperature in nitrobenzene ( 30 mL ). Then, bromine $(1.4 \mathrm{~g}, 8.7 \mathrm{mmol})$ was added dropwise to the reaction mixture and then heated at $110^{\circ} \mathrm{C}$. Further amount of bromine ( $6.9 \mathrm{~g}, 43.3 \mathrm{mmol}$ ) was added dropwise to the reaction mixture. After two hours heating, the reaction mixture was cooled and diluted with ethanol ( 30 mL ) was added. The resultant solid was isolated by filtration and washed several times with ethanol. The product was then dried at $60^{\circ} \mathrm{C}$ to yield $8.3 \mathrm{~g}(91 \%$ yield $)$ 3,6-dibromophenanthrene-9,10-dione an orange powder. $1 \mathrm{H}-\mathrm{NMR}\left(500 \mathrm{MHz}\right.$, DMSO- $\left.d_{6}\right) \delta(\mathrm{ppm})$ : $8.19(\mathrm{~d}, J=1.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.93(\mathrm{~d}, J=6 \mathrm{~Hz}, 2 \mathrm{H}), 7.59(\mathrm{dd}, J=6,1.8 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 125 MHz , DMSO- $d_{6}$ ) $\delta(\mathrm{ppm}): 179.0,136.2,133.5,132.2,130.0,127.7$.

3,6-Dibromo-9H-fluoren-9-one: According to the reported method, ${ }^{\mathrm{S} 2}$ 3,6-dibromophenanthrene9,10 -dione ( $5 \mathrm{~g}, 13.6 \mathrm{mmol}$ ) was added to a solution of potassium hydroxide ( $8.15 \mathrm{~g}, 0.18 \mathrm{~mol}$ ) dissolved in water ( 60 mL ) and then heated to $130^{\circ} \mathrm{C}$. After two hours, potassium permanganate $(11.43 \mathrm{~g}, 72.3 \mathrm{mmol})$ was added and the reaction mixture further heated at $130^{\circ} \mathrm{C}$ for two hours. The mixture was cooled to room temperature and then neutralized with diluted sulfuric acid to $\mathrm{pH}=$ 7. Sodium bisulfite was added slowly until a complete precipitation of light-yellow solid. The resultant solid was filtered and washed several times with water. The product was then dried at 60 ${ }^{\circ} \mathrm{C}$ to yield 3.3 g ( $72 \%$ yield) 3,6-dibromo-9H-fluoren-9-one a light-yellow powder. $1 \mathrm{H}-\mathrm{NMR}$ ( 500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm}): 7.68(\mathrm{~d}, J=1.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.56(\mathrm{~d}, J=12 \mathrm{~Hz}, 2 \mathrm{H}), 7.51(\mathrm{dd}, J=12,1.8 \mathrm{~Hz}$, $2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 125 MHz, DMSO- $_{6}$ ) $\delta(\mathrm{ppm}): 193.8,146.2,133.4,132.0,130.1,125.8$.

3,3',6,6'-Tetrabromo-9,9'-bifluorenylidene (BF-4Br): A mixture of 3,6-dibromo-9H-fluoren-9one ( $1 \mathrm{~g}, 2.96 \mathrm{mmol}$ ) and Lawesson's reagent $(0.6 \mathrm{~g}, 1.483 \mathrm{mmol})$ in dry toluene ( 40 mL ) was refluxed at $110^{\circ} \mathrm{C}$ for 20 hours. After cooling, a precipitate was formed and isolated by filtration. The precipitate was heated in acetone for 10 minutes and then filtered again. The product was then dried at $60^{\circ} \mathrm{C}$ to yield 0.33 g ( $35 \%$ yield) $\mathrm{BF}-4 \mathrm{Br}$ as an orange powder. The product was partially soluble in common organic solvent, so we performed H NMR spectroscopy only. $1 \mathrm{H}-\mathrm{NMR}$ ( 500 MHz, DMSO- $d_{6}$ ) $\delta(\mathrm{ppm}): 8.66(\mathrm{~d}, J=1.8 \mathrm{~Hz}, 4 \mathrm{H}), 7.93(\mathrm{~d}, J=12 \mathrm{~Hz}, 4 \mathrm{H}), 7.77(\mathrm{dd}, J=6,1.8$ Hz, 4H).


4,4',4",4"'-([9,9'-bifluorenylidene]-3,3',6,6'-tetrayl)tetrabenzaldehyde
(BFTB-4CHO)
Scheme S2. Synthesis of 4,4',4",4'"-([9,9'-bifluorenylidene]-3,3',6,6'-tetrayl)tetrabenzaldehyde (BFTB-4CHO).

4,4',4',4"'-([9,9'-bifluorenylidene]-3,3',6,6'-tetrayl)tetrabenzaldehyde (BFTB-4CHO): A 100 mL round-bottom flask was charged with $\mathrm{BF}-4 \mathrm{Br}(1 \mathrm{~g}, 1.55 \mathrm{mmol})$, 4-formylphenylboronic acid $(1.86 \mathrm{~g}, 12.4 \mathrm{mmol})$, tetrakis(triphenylphosphine)palladium(0)) $90 \mathrm{mg}, 0.077 \mathrm{mmol}$ ), and potassium carbonate ( $2.15 \mathrm{~g}, 15.55 \mathrm{mmol}$ ). The solids were evacuated under high pressure for 15 minutes. Then, dioxane $(50 \mathrm{~mL})$ and water $(10 \mathrm{~mL})$ were added and the reaction mixture allowed to heat at $100^{\circ} \mathrm{C}$ for 48 hours under $\mathrm{N}_{2}$. After the consummation of $\mathrm{BF}-4 \mathrm{Br}$, the reaction mixture was cooled to room-temperature and then poured into ice-water to produce a white precipitate. The precipitate was filtered and washed several times with water, methanol and dichloromethane. The product was then dried at $60^{\circ} \mathrm{C}$ to yield $0.70 \mathrm{~g}(60 \%$ yield) $\mathrm{BFTB}-4 \mathrm{CHO}$ as a red powder. The product was partially soluble in common organic solvent, so we performed H NMR spectroscopy only. 1 H-NMR ( 500 MHz, DMSO- $_{6}$ ) $\delta(\mathrm{ppm}): 10.10(\mathrm{~s}, 4 \mathrm{H}), 8.65(\mathrm{~s}, 4 \mathrm{H}), 8.43(\mathrm{~d}, J=6 \mathrm{~Hz}, 4 \mathrm{H})$, $8.14(\mathrm{~d}, J=6 \mathrm{~Hz}, 4 \mathrm{H}), 8.08(\mathrm{~d}, J=6 \mathrm{~Hz}, 4 \mathrm{H}), 7.78(\mathrm{~d}, J=6 \mathrm{~Hz}, 4 \mathrm{H})$.

(BFTB-4NH2)
Scheme S3. Synthesis of 4, $4^{\prime}, 4^{\prime \prime}, 4^{\prime \prime}$--([9,9'-bifluorenylidene]-3,3',6,6'-tetrayl)tetraaniline (BFTB$4 \mathrm{NH}_{2}$ ).

4,4',4',4"'-([9,9'-bifluorenylidene]-3,3',6,6'-tetrayl)tetraaniline (BFTB-4NH2): A 100 mL round-bottom flask was charged with $\mathrm{BF}-4 \mathrm{Br}(1 \mathrm{~g}, 1.55 \mathrm{mmol}), 4$-aminophenylboronic acid pinacol ester ( $2.70 \mathrm{~g}, 12.3 \mathrm{mmol}$ ), tetrakis(triphenylphosphine)palladium(0)) $90 \mathrm{mg}, 0.077 \mathrm{mmol}$ ), and potassium carbonate ( $2.15 \mathrm{~g}, 15.55 \mathrm{mmol}$ ). The solids were evacuated under high pressure for 15 minutes. Then, dioxane $(50 \mathrm{~mL})$ and water $(10 \mathrm{~mL})$ were added and the reaction mixture allowed to heat at $100^{\circ} \mathrm{C}$ for 48 hours under $\mathrm{N}_{2}$. After the consummation of $\mathrm{BF}-4 \mathrm{Br}$, the reaction mixture was cooled to room-temperature and then poured into ice-water to produce a white precipitate. The
precipitate was filtered and washed several times with water, methanol. The product was then dried at $60^{\circ} \mathrm{C}$ to yield $0.80 \mathrm{~g}\left(74 \%\right.$ yield) BFTB- $4 \mathrm{NH}_{2}$ as a blue powder. $1 \mathrm{H}-\mathrm{NMR}$ ( 500 MHz , DMSO$\left.d_{6}\right) \delta(\mathrm{ppm}): 8.32(\mathrm{~s}, 4 \mathrm{H}), 8.29(\mathrm{~d}, J=12 \mathrm{~Hz}, 4 \mathrm{H}), 7.66(\mathrm{~d}, J=12 \mathrm{~Hz}, 8 \mathrm{H}), 7.53(\mathrm{~d}, J=12 \mathrm{~Hz}, 4 \mathrm{H})$, $6.71(\mathrm{~d}, J=12 \mathrm{~Hz}, 8 \mathrm{H}), 5.40\left(\mathrm{~s}, \mathrm{br} ., 8 \mathrm{H}, 4 \mathrm{NH}_{2}\right) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{DMSO}-d_{6}$ ) $\delta(\mathrm{ppm}): 148.93$, $141.30,141.05,137,60,135.53,127.27,126.66,126.24,123.55,116.85,114.10$.


Scheme S4. Synthesis of 4,4',4",4"'-pyrene-1,3,6,8-tetrayl)tetraaniline (PyTA-4NH2).
1,3,6,8-tetrabromopyrene (Pyrene-4Br): was prepared as described in the literature with minor modifications. ${ }^{[53]}$ A 500 mL round-bottom flask was charged with pyrene ( $5.0 \mathrm{~g}, 24 \mathrm{mmol}$ ) and nitrobenzene ( 200 mL ) and then bromine ( $5.6 \mathrm{~mL}, 109 \mathrm{mmol}$ ) was added dropwise through a dropping funnel. The reaction mixture was allowed to reflux at $120^{\circ} \mathrm{C}$ for 15 hours. After the consummation of bromine, pale yellow crystallites of $1,3,6,8$-tetrabromopyrene were separated from the reaction mixture as precipitate. The suspension was filtrate and the pale-yellow product was washed several times with ethanol and dried under pressure for 12 hours to yield the product in $94 \%$. FTIR: $1592,1466,1450,1228,1052,988,871,812 \mathrm{~cm}^{-1}$.

4,4',4', $\mathbf{4}^{\prime \prime \prime}$-pyrene-1,3,6,8-tetrayl)tetraaniline (PyTA-4NH2): A 100 mL round-bottom flask was charged with pyrene- $4 \mathrm{Br}(2.0 \mathrm{~g}, 3.8 \mathrm{mmol})$, bis(pinacolato)diboron ( $5.98 \mathrm{~g}, 23.56 \mathrm{mmol})$, $\left[1,1^{\prime}-\right.$ Bis(diphenylphosphino)ferrocene]dichloro palladium(II) ( $241 \mathrm{mg}, 0.033 \mathrm{mmol}$ ), and potassium acetate $(2.33 \mathrm{~g}, 23.37 \mathrm{mmol})$. The solids were evacuated under high pressure for 15 minutes. Then, dioxane ( 40 mL ) was added and the reaction mixture allowed to reflux for 48 hours under $\mathrm{N}_{2}$. After the consummation of pyrene- 4 Br , the reaction mixture was cooled to room-temperature and then poured into ice-water to produce a yellow precipitate. The precipitate was filtered and washed several times with water and purified using flash column chromatography with THF/hexane as eluent. The isolate solid was finally recrystallized with methanol to give $1,3,6,8$-tetrakis( $4,4,5,5$ -tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (TTDBPy) as yellow crystals ( $70 \%$ yield).

A 100 mL round-bottom flask was charged with TTDBPy ( $1.0 \mathrm{~g}, 1.41 \mathrm{mmol}$ ), 4-bromoaniline $(1.95 \mathrm{~g}, 11.33 \mathrm{mmol})$, tetrakis(triphenylphosphine)palladium $(0)$ ( $80.88 \mathrm{mg}, 0.07 \mathrm{mmol}$ ), and potassium carbonate $(1.95 \mathrm{~g}, 14.1 \mathrm{mmol})$. The solids were evacuated under high pressure for 15 minutes. Then, dioxane $(40 \mathrm{~mL})$ and water $(7 \mathrm{~mL})$ were added and the reaction mixture allowed to heat at $100{ }^{\circ} \mathrm{C}$ for 48 hours under $\mathrm{N}_{2}$. After the consummation of TTDBPy, the reaction mixture was cooled to room-temperature and then poured into ice-water to produce a yellow-greenish precipitate. The precipitate was filtered and washed several times with water, methanol and dicholormethane. The isolate solid of 4,4',4",4"'-pyrene-1,3,6,8-tetrayl)tetraaniline (Py-TA-4NH2) was used without further purification ( $75 \%$ yield). ${ }^{1} \mathrm{H}$ NMR $(500 \mathrm{MHz}, \mathrm{DMSO}) \delta(\mathrm{ppm}): 8.12(\mathrm{~s}$, $4 \mathrm{H}), 7.79(\mathrm{~s}, 2 \mathrm{H}), 7.35(\mathrm{~d}, J=12 \mathrm{~Hz}, 8 \mathrm{H}), 6.78(\mathrm{~d}, J=12 \mathrm{~Hz}, 8 \mathrm{H}), 5.30\left(\mathrm{~s}, \mathrm{br} ., 8 \mathrm{H}, 4 \mathrm{NH}_{2}\right) .{ }^{13} \mathrm{C}$ 113.96.


Scheme S5. Synthesis of 3,3'6,6'-Tetrabromo-9,9'-bicarbazole (BC-4Br).

3,6-Dibromo-9H-carbazole (Cz-2Br). Cz-2Br was prepared as previously reported with slight modification. ${ }^{[54]}$ To a suspension of carbazole ( $5 \mathrm{~g}, 30 \mathrm{mmol}$ ) in dichloromethane ( 300 mL ), a solution of $N$-Bromosuccinimide (NBS) ( $10.68 \mathrm{~g}, 60 \mathrm{mmol}$ ) in 50 mL DMF was added slowly. The reaction mixture was stirred at room temperature overnight. The solution was washed with water (3 $\times 150 \mathrm{~mL}$ ), then the organic layer was separated, and the solvent was evaporated. The solid was washed with DCM, then collected and dried under vacuum to yield 3,6-dibromocarbazole ( 7.7 g , yield: $82 \%$ ) of the product. ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , DMSO) $\delta(\mathrm{ppm}): 11.58(\mathrm{NH}, 1 \mathrm{H}), 8.41(\mathrm{~S}, 2 \mathrm{H})$, $7.52(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.42(\mathrm{~d}, J=2 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{DMSO}$ ) $\delta(\mathrm{ppm}): 139.42$, 129.42, 124.34, 123.47, 112.97, 112.32.

3,3'6,6'-Tetrabromo-9,9'-bicarbazole (BC-4Br). $\mathbf{B C}-4 \mathbf{B r}$ was prepared as previously reported with slight modification. ${ }^{[54]}$ Potassium permanganate ( $2.92 \mathrm{~g}, 90 \mathrm{mmol}$ ) was added to a solution of 3,6-dibromocarbazole ( $2 \mathrm{~g}, 30 \mathrm{mmol}$ ) in 40 mL acetone at $50^{\circ} \mathrm{C}$. Then the solution was hydrolyzed with 100 mL distilled water. The mixture was extracted with dichloromethane and the solvent was evaporated. The residue was washed with methanol to yield 3,3'6,6'-tetrabromo-9,9'-bicarbazole ( 6.92 g, yield: $71 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta(\mathrm{ppm}): 8.27$ (d, 4 H ), 7.47 (dd, $J=8.5 \mathrm{~Hz}, 4 \mathrm{H}$ ), $6.75(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta(\mathrm{ppm}): 139.31,131.19,124.81,123.30$, 115.41, 110.59 .


Scheme S6. Synthesis of 4,4',4",4'"-([9,9'-bicarbazole]-3,3',6,6'-tetrayl)tetraaniline (BCTA-4NH2).

4,4',4',4"'-([9,9'-bicarbazole]-3,3',6,6'-tetrayl)tetraaniline (BCTA-4NH2): Take a pair of two neck flask, add $\mathrm{BC}-4 \mathrm{Br}(1 \mathrm{~g}, 1.54 \mathrm{mmol})$, 4-aminophenylboronic acid pinacol ester ( $2.7 \mathrm{~g}, 12.34$ $\mathrm{mmol}), \mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(90 \mathrm{mg}, 0.078 \mathrm{mmol}), \mathrm{k}_{2} \mathrm{CO}_{3}(2.13 \mathrm{~g}, 15.41 \mathrm{mmol})$ in order and vacuum for 15 minutes. Add 50 mL dioxane and $8 \mathrm{ml} \mathrm{H}_{2} \mathrm{O}$, then heat to $100^{\circ} \mathrm{C}$ in an oil pot and the mixture was stirred at $100^{\circ} \mathrm{C}$ for 48 h . Pour the solution into a beaker filled with ice cubes and $\mathrm{H}_{2} \mathrm{O}$ and stir, then suction filter. The crude product was purified over a chromatographic silica gel column (hexane/AcOEt, 3:1) to give the pure BCTA-4NH2. FTIR (powder): ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (DMSO-d6, $25^{\circ} \mathrm{C}$, 500 MHz ): $\delta=8.63(\mathrm{~s}, 4 \mathrm{H}), 7.56(\mathrm{~s}, 4 \mathrm{H}), 7.50(\mathrm{~s}, 8 \mathrm{H}), 6.86(\mathrm{~s}, 4 \mathrm{H}), 6.70(\mathrm{~d}, J=10 \mathrm{~Hz}, 8 \mathrm{H}), 5.18(\mathrm{~s}$, 8 H ). ${ }^{13} \mathrm{C}-\mathrm{NMR}$ (DMSO- $d_{6}, 25^{\circ} \mathrm{C}, 125 \mathrm{MHz}$ ):149.14, 139.72, 135.8, 129.3, 128.52. 125.95, 123.63, 119.06, 115.32, 109.85 ppm .


Scheme S7. Synthesis of BFTB-PyTA COF.

In a $25-\mathrm{mL}$ Schlenk storage tube, PyTA- $4 \mathrm{NH}_{2}(53 \mathrm{mg}, 0.094 \mathrm{mmol})$ and BFTB-4CHO ( 70 mg , $0.140 .094 \mathrm{mmol})$ was dissolved in n -butanol $(3.5 \mathrm{~mL})$ and $o$-dichlorobenzene $(3.5 \mathrm{~mL})$ in the presence of acetic acid ( $6 \mathrm{M}, 0.7 \mathrm{~mL}$ ). The tube was sealed and degassed through three freeze-pump-thaw cycles. The tube was sealed off by flame and heated at $120^{\circ} \mathrm{C}$ for 3 days. After cooling to room temperature, the tube was opened and the precipitate filtered and washed two times with nbutanol, THF, and acetone respectively. The solid was dried under vacuum at $120^{\circ} \mathrm{C}$ overnight to afford BFTB-PyTA COF as a red powder, ( $90 \%$ yield).


Scheme S8. Synthesis of BFTB-BFTB COF.

In a $25-\mathrm{mL}$ Schlenk storage tube, BFTB-4NH2 $(65 \mathrm{mg}, 0.094 \mathrm{mmol})$ and BFTB-4CHO ( 70 mg , $0.140 .094 \mathrm{mmol})$ was dissolved in n -butanol $(3.5 \mathrm{~mL})$ and $o$-dichlorobenzene ( 3.5 mL ) in the presence of acetic acid ( $6 \mathrm{M}, 0.7 \mathrm{~mL}$ ). The tube was sealed and degassed through three freeze-pump-thaw cycles. The tube was sealed off by flame and heated at $120^{\circ} \mathrm{C}$ for 3 days. After cooling to room temperature, the tube was opened and the precipitate filtered and washed two times with nbutanol, THF, and acetone respectively. The solid was dried under vacuum at $120^{\circ} \mathrm{C}$ overnight to afford BFTB-BFTB COF as a red powder, ( $91 \%$ yield).


Scheme S9. Synthesis of BFTB-BCTA COF.

In a $25-\mathrm{mL}$ Schlenk storage tube, BCTB-4NH $(38 \mathrm{mg}, 0.055 \mathrm{mmol})$ and BFTB-4CHO ( 40 mg , 0.055 mmol ) was dissolved in n-butanol ( 2 mL ) and o-dichlorobenzene $(2 \mathrm{~mL})$ in the presence of acetic acid ( $6 \mathrm{M}, 0.4 \mathrm{~mL}$ ). The tube was sealed and degassed through three freeze-pump-thaw
cycles. The tube was sealed off by flame and heated at $120^{\circ} \mathrm{C}$ for 3 days. After cooling to room temperature, the tube was opened and the precipitate filtered and washed two times with n-butanol, THF, and acetone respectively. The solid was dried under vacuum at $120^{\circ} \mathrm{C}$ overnight to afford BFTB-BCTA COF as a red powder. ( $91 \%$ yield).

## S4. FTIR Spectral Profiles of COFs



Figure S1. FT-IR spectra of (a) BFTB-4CHO, (b) PyTA-4NH2, and (c) BFTB-PyTA COF.


Figure S2. FT-IR spectra of (a) BFTB-4CHO, (b) BFTB $-4 \mathrm{NH}_{2}$, and (c) BFTB- BFTB COF.


Figure S3. FT-IR spectra of (a) BFTB-4CHO, (b) BCTA-4NH ${ }_{2}$, and (c) BFTB- BCTA COF.

## S5. Thermal Gravimetric Analysis



Figure S4. Thermogravimetric analysis trace of BFTB-PyTA, BFTB- BFTB, and BFTB- BCTA COFs under nitrogen atmosphere with heating rate of $20^{\circ} \mathrm{C} \mathrm{min}{ }^{-1}$.

Table S1. Values of $T_{d 10 \%}$ and Char yield of COFs.

|  | $\boldsymbol{T}_{\mathrm{d} 10 \%}\left({ }^{\circ} \mathrm{C}\right)$ | Char yield (\%) |
| :--- | :---: | :---: |
| BFTB-PyTA COF | 433 | 70 |
| BFTB-BFTB COF | 416 | 69 |
| BFTB-BCTA COF | 449 | 71 |

S6. Field Emission Scanning Electron Microscopy (FE-SEM)


Figure S5. FE-SEM images of (a,b) BFTB-PyTA, (c,d) BFTB-BFTB, and (e,f) BFTB-BCTA COFs at different magnification scales.

## S7. Transmission Electron Microscopy (TEM)



Figure S6. TEM images of (a-c) BFTB-PyTA, (d-f) BFTB-BFTB, and (g-i) BFTB-BCTA COFs at different magnification scales.

## S8. Experimental and Simulation X-ray Diffraction Patterns for COFs Structures



Figure S7. PXRD pattern of the as-synthesized BFTB-PyTA COF (black), compared with the simulated PXRD pattern of the eclipsed AA-stacking model (purple).


Figure S8. PXRD pattern of the as-synthesized BFTB-BFTB COF (black), compared with the simulated PXRD pattern of the eclipsed AA-stacking model (purple).


Figure S9. PXRD pattern of the as-synthesized BFTB-BCTA COF (black), compared with the simulated PXRD pattern of the eclipsed AA-stacking model (purple).

## S9. PXRD data and BET parameters

Table S2. PXRD and BET parameters of the synthesized COFs.

| COF | $\mathrm{S}_{\text {BET }}$ <br> $\left(\mathrm{m}^{2} \mathrm{~g}^{-1}\right)$ | $\mathbf{d}_{110}$ <br> $(\mathrm{~nm})$ | Pore size <br> $(\mathrm{nm})$ | Pore volume <br> $\left(\mathrm{cm}^{3} \mathrm{~g}^{-1}\right)$ | Interlayer <br> Distance $(\AA)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| BFTB-PyTA | 1133 | 1.94 | 1.63 | 0.41 | 3.71 |
| BFTB-BFTB | 1040 | 2.19 | $1.78,1.11$ | 0.69 | 3.79 |
| BFTB-BCTA | 834 | 2.11 | $1.75,1.07$ | 0.67 | 3.87 |

S10. Structural Modeling and Fractional atomic coordinates for COF Structures


Figure S10. Crystalline structure for BFTB-PyTA COF based on (a) AA-eclipsed stacking models (b) AB-staggered stacking models.
(a)

(b)


Figure S11. Crystalline structure for BFTB-BFTB COF based on (a) AA-eclipsed stacking models (b) AB-staggered stacking models.
(a)

(b)


Figure S12. Crystalline structure for BFTB-BCTA COF based on (a) AA-eclipsed stacking models (b) AB-staggered stacking models.

Table S3. Fractional atomic coordinates for the unit cell of BFTB-PyTA COF with AA-stacking.

| Sample Name : BFTB-PyTA COF |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Space Group : P 1 |  |  |  |  |  |  |  |
| $\mathrm{a}=24.918, \mathrm{~b}=31.042, \mathrm{c}=3.528 \quad \alpha=\beta=\gamma=90^{\circ}$ |  |  |  |  |  |  |  |
| $\mathrm{R}_{\mathrm{wp}}=8.70 \% \quad \mathrm{R}_{\mathrm{p}}=6.12 \%$ |  |  |  |  |  |  |  |
| Atom | $x / a$ | $y / b$ | $z / c$ | Atom | $x / a$ | $y / b$ | $z / c$ |
| C1 | 0.49862 | 0.91631 | 0.51787 | C30 | 0.00055 | 0.43426 | 0.51787 |
| C2 | 0.54956 | 0.91631 | 0.51787 | C31 | 0.04873 | 0.43426 | 0.51787 |
| C3 | 0.56557 | 0.96263 | 0.51787 | C32 | 0.07461 | 0.47652 | 0.51787 |
| C4 | 0.52409 | 0.99586 | 0.51787 | C33 | 0.12499 | 0.47643 | 0.51787 |
| C5 | 0.48262 | 0.96263 | 0.51787 | C34 | 0.14831 | 0.52016 | 0.51787 |
| C6 | 0.43377 | 0.97109 | 0.51786 | C35 | 0.12499 | 0.56389 | 0.51787 |
| C7 | 0.40199 | 0.93269 | 0.51787 | C36 | 0.15571 | 0.60742 | 0.51787 |
| C8 | 0.41886 | 0.88556 | 0.51787 | C37 | 0.15571 | 0.4329 | 0.51787 |
| C9 | 0.46812 | 0.87752 | 0.51787 | C38 | 0.20541 | 0.60226 | 0.51787 |
| C10 | 0.58007 | 0.87752 | 0.51787 | C39 | 0.2353 | 0.64165 | 0.51787 |
| C11 | 0.62933 | 0.88556 | 0.51787 | C40 | 0.21624 | 0.68759 | 0.51787 |
| C12 | 0.64619 | 0.93269 | 0.51787 | C41 | 0.16694 | 0.69334 | 0.51787 |
| C13 | 0.61442 | 0.97109 | 0.51787 | C42 | 0.13708 | 0.65368 | 0.51787 |
| C14 | 0.38558 | 0.84489 | 0.51787 | C43 | 0.13708 | 0.38665 | 0.51787 |
| C15 | 0.66261 | 0.84489 | 0.51787 | C44 | 0.16694 | 0.34698 | 0.51787 |
| C16 | 0.33618 | 0.85195 | 0.51787 | C45 | 0.21624 | 0.35273 | 0.51786 |
| C17 | 0.30514 | 0.81317 | 0.51787 | C46 | 0.2353 | 0.39867 | 0.51786 |
| C18 | 0.32325 | 0.76686 | 0.51787 | C47 | 0.20541 | 0.43807 | 0.51787 |
| C19 | 0.37229 | 0.75967 | 0.51787 | C48 | 0.54956 | 0.12401 | 0.51787 |
| C20 | 0.4032 | 0.79832 | 0.51787 | C49 | 0.49862 | 0.12401 | 0.51787 |
| C21 | 0.64498 | 0.79832 | 0.51787 | C50 | 0.48262 | 0.07769 | 0.51787 |
| C22 | 0.67589 | 0.75967 | 0.51787 | C51 | 0.52409 | 0.04446 | 0.51787 |
| C23 | 0.72493 | 0.76686 | 0.51787 | C52 | 0.56557 | 0.07769 | 0.51787 |
| C24 | 0.74304 | 0.81317 | 0.51787 | C53 | 0.61442 | 0.06923 | 0.51787 |
| C25 | 0.71201 | 0.85195 | 0.51787 | C54 | 0.64619 | 0.10763 | 0.51787 |
| C26 | 0.04941 | 0.52016 | 0.51787 | C55 | 0.62933 | 0.15476 | 0.51787 |
| C27 | 0.07461 | 0.56381 | 0.51787 | C56 | 0.58007 | 0.16281 | 0.51787 |
| C28 | 0.04873 | 0.60606 | 0.51787 | C57 | 0.46812 | 0.16281 | 0.51787 |
| C29 | 0.00055 | 0.60606 | 0.51787 | C58 | 0.41886 | 0.15476 | 0.51787 |

Continuous (Table S3)

| Atom | $x / a$ | $y / b$ | $z / c$ | Atom | $x / a$ | $y / b$ | $z / c$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C59 | 0.41886 | 0.15476 | 0.51787 | C94 | 0.29221 | 0.3151 | 0.51787 |
| C60 | 0.40199 | 0.10763 | 0.51787 | N95 | 0.24629 | 0.72861 | 0.51787 |
| C61 | 0.43377 | 0.06923 | 0.51787 | N96 | 0.24629 | 0.31171 | 0.51786 |
| C62 | 0.66261 | 0.19544 | 0.51787 | N97 | 0.33618 | 0.18838 | 0.51787 |
| C63 | 0.38558 | 0.19544 | 0.51787 | N98 | 0.8019 | 0.31171 | 0.51787 |
| C64 | 0.71201 | 0.18838 | 0.51787 | H99 | 0.41981 | 1.00904 | 0.51786 |
| C65 | 0.74304 | 0.22715 | 0.51787 | H100 | 0.36206 | 0.93941 | 0.51787 |
| C66 | 0.72493 | 0.27346 | 0.51786 | H101 | 0.48244 | 0.83969 | 0.51787 |
| C67 | 0.67589 | 0.28065 | 0.51787 | H102 | 0.56499 | 0.83999 | 0.51786 |
| C68 | 0.64498 | 0.24201 | 0.51787 | H103 | 0.68603 | 0.93995 | 0.51787 |
| C69 | 0.4032 | 0.24201 | 0.51787 | H104 | 0.62855 | 1.00898 | 0.51787 |
| C70 | 0.37229 | 0.28065 | 0.51787 | H105 | 0.3211 | 0.88948 | 0.51787 |
| C71 | 0.32325 | 0.27346 | 0.51787 | H106 | 0.26511 | 0.81923 | 0.51787 |
| C72 | 0.30514 | 0.22715 | 0.51787 | H107 | 0.38723 | 0.72208 | 0.51787 |
| C73 | 0.8019 | 0.72861 | 0.51787 | H108 | 0.44324 | 0.79226 | 0.51787 |
| C74 | 0.84278 | 0.43807 | 0.51787 | H109 | 0.60502 | 0.79178 | 0.51787 |
| C75 | 0.81288 | 0.39867 | 0.51787 | H110 | 0.66112 | 0.72202 | 0.51787 |
| C76 | 0.83195 | 0.35273 | 0.51787 | H111 | 0.78307 | 0.81926 | 0.51787 |
| C77 | 0.88124 | 0.34698 | 0.51787 | H112 | 0.72677 | 0.8896 | 0.51786 |
| C78 | 0.9111 | 0.65368 | 0.51787 | H113 | 0.06809 | 0.64158 | 0.51787 |
| C79 | 0.88124 | 0.69334 | 0.51787 | H114 | 0.02079 | 0.64108 | 0.51786 |
| C80 | 0.83195 | 0.68759 | 0.51787 | H115 | 0.02079 | 0.39925 | 0.51786 |
| C81 | 0.81288 | 0.64165 | 0.51787 | H116 | 0.06898 | 0.39925 | 0.51787 |
| C82 | 0.84278 | 0.60226 | 0.51787 | H117 | 0.18878 | 0.52154 | 0.51787 |
| C83 | 0.89247 | 0.4329 | 0.51787 | H118 | 0.22192 | 0.56533 | 0.51787 |
| C84 | 0.89247 | 0.60742 | 0.51787 | H119 | 0.27548 | 0.63661 | 0.51787 |
| C85 | 0.9232 | 0.56389 | 0.51787 | H120 | 0.15091 | 0.73047 | 0.51787 |
| C86 | 0.89987 | 0.52016 | 0.51787 | H121 | 0.09688 | 0.65855 | 0.51787 |
| C87 | 0.9232 | 0.47643 | 0.51787 | H122 | 0.09699 | 0.38095 | 0.51787 |
| C88 | 0.97357 | 0.47652 | 0.51787 | H123 | 0.15108 | 0.30978 | 0.51787 |
| C89 | 0.97357 | 0.56381 | 0.51787 | H124 | 0.27545 | 0.40395 | 0.51786 |
| C90 | 0.99877 | 0.52016 | 0.51787 | H125 | 0.22113 | 0.47533 | 0.51787 |
| C91 | 0.75598 | 0.72522 | 0.51787 | H126 | 0.62837 | 0.03128 | 0.51787 |
| C92 | 0.75598 | 0.3151 | 0.51786 | H127 | 0.68612 | 0.10091 | 0.51787 |
| C93 | 0.29221 | 0.72522 | 0.51786 | H128 | 0.56575 | 0.20063 | 0.51787 |

Continuous (Table S3)

| Atom | $x / a$ | $y / b$ | $z / c$ | Atom | $x / a$ | $y / b$ | $z / c$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| H129 | 0.4832 | 0.20033 | 0.51787 |  |  |  |  |
| H130 | 0.36216 | 0.10037 | 0.51787 |  |  |  |  |
| H131 | 0.41963 | 0.03134 | 0.51787 |  |  |  |  |
| H132 | 0.72708 | 0.15085 | 0.51787 |  |  |  |  |
| H133 | 0.78308 | 0.22109 | 0.51787 |  |  |  |  |
| H134 | 0.66096 | 0.31824 | 0.51786 |  |  |  |  |
| H135 | 0.60494 | 0.24806 | 0.51787 |  |  |  |  |
| H136 | 0.44317 | 0.24854 | 0.51787 |  |  |  |  |
| H137 | 0.38706 | 0.3183 | 0.51787 |  |  |  |  |
| H138 | 0.26511 | 0.22106 | 0.51787 |  |  |  |  |
| H139 | 0.32142 | 0.15072 | 0.51787 |  |  |  |  |
| H140 | 0.82627 | 0.47499 | 0.51786 |  |  |  |  |
| H141 | 0.7727 | 0.40371 | 0.51787 |  |  |  |  |
| H142 | 0.89728 | 0.30985 | 0.51787 |  |  |  |  |
| H143 | 0.9513 | 0.38177 | 0.51787 |  |  |  |  |
| H144 | 0.9512 | 0.65937 | 0.51787 |  |  |  |  |
| H145 | 0.89711 | 0.73055 | 0.51787 |  |  |  |  |
| H146 | 0.77273 | 0.63638 | 0.51787 |  |  |  |  |
| H147 | 0.82705 | 0.56499 | 0.51787 |  |  |  |  |
| H148 | 0.8594 | 0.51878 | 0.51787 |  |  |  |  |
| H149 | 0.73993 | 0.68809 | 0.51787 |  |  |  |  |
| H150 | 0.73993 | 0.35223 | 0.51786 |  |  |  |  |
| H151 | 0.30825 | 0.68809 | 0.51786 |  |  |  |  |
| H152 | 0.30825 | 0.35223 | 0.51787 |  |  |  |  |

Table S4. Fractional atomic coordinates for the unit cell of BFTB-BFTB COF with AA-stacking.

| Sample Name: BFTB-BFTB COF |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Space Group: P 1 |  |  |  |  |  |  |  |
| $\mathrm{a}=24.664, \mathrm{~b}=31.454, \mathrm{c}=3.291 \quad \alpha=\beta=\gamma=90^{\circ}$ |  |  |  |  |  |  |  |
| $\mathrm{R}_{\mathrm{wp}}=7.69 \% \quad \mathrm{R}_{\mathrm{p}}=6.09 \%$ |  |  |  |  |  |  |  |
| Atom | $x / a$ | $y / b$ | $z / \mathrm{c}$ | Atom | $x / a$ | $y / b$ | $z / c$ |
| C1 | 0.4817 | 0.90038 | 0.59817 | C29 | 0.47147 | 0.0823 | 0.68205 |
| C2 | 0.52902 | 0.90244 | 0.66519 | C30 | 0.45678 | 0.0405 | 0.67104 |
| C3 | 0.5431 | 0.94435 | 0.66394 | C31 | 0.4983 | 0.01393 | 0.59733 |
| C4 | 0.50209 | 0.97115 | 0.59388 | C32 | 0.53384 | 0.04489 | 0.54378 |
| C5 | 0.46634 | 0.94021 | 0.53419 | C33 | 0.57416 | 0.0399 | 0.37364 |
| C6 | 0.42644 | 0.94528 | 0.35501 | C34 | 0.60311 | 0.07478 | 0.34562 |
| C7 | 0.39785 | 0.91003 | 0.31267 | C35 | 0.59 | 0.11532 | 0.4672 |
| C8 | 0.41125 | 0.86927 | 0.42816 | C36 | 0.54634 | 0.12013 | 0.59326 |
| C9 | 0.45483 | 0.86467 | 0.56168 | C37 | 0.44271 | 0.11639 | 0.71584 |
| C10 | 0.55809 | 0.86849 | 0.68861 | C38 | 0.39697 | 0.10963 | 0.759 |
| C11 | 0.60368 | 0.8759 | 0.73402 | C39 | 0.38166 | 0.06744 | 0.77294 |
| C12 | 0.61863 | 0.91799 | 0.7625 | C40 | 0.4102 | 0.03248 | 0.72941 |
| C13 | 0.58935 | 0.95271 | 0.72622 | C41 | 0.62004 | 0.15291 | 0.44627 |
| C14 | 0.38094 | 0.8318 | 0.4047 | C42 | 0.3661 | 0.14676 | 0.78278 |
| C15 | 0.63494 | 0.83936 | 0.73191 | C43 | 0.66553 | 0.14966 | 0.52706 |
| C16 | 0.33516 | 0.83564 | 0.4701 | C44 | 0.6927 | 0.1856 | 0.53578 |
| C17 | 0.30754 | 0.79991 | 0.48049 | C45 | 0.67544 | 0.22575 | 0.45726 |
| C18 | 0.32494 | 0.75931 | 0.42123 | C46 | 0.63041 | 0.22862 | 0.36596 |
| C19 | 0.37034 | 0.7556 | 0.34924 | C47 | 0.60332 | 0.1928 | 0.35639 |
| C20 | 0.39787 | 0.79108 | 0.33938 | C48 | 0.38195 | 0.1863 | 0.90272 |
| C21 | 0.62226 | 0.8 | 0.87668 | C49 | 0.356 | 0.22251 | 0.8774 |
| C22 | 0.64868 | 0.76424 | 0.83148 | C50 | 0.31234 | 0.22028 | 0.74733 |
| C23 | 0.68911 | 0.76667 | 0.64837 | C51 | 0.29553 | 0.18077 | 0.6416 |
| C24 | 0.70279 | 0.80599 | 0.51773 | C52 | 0.32203 | 0.1445 | 0.65903 |
| C25 | 0.67602 | 0.84198 | 0.55855 | C53 | 0.09487 | 0.47022 | 0.53114 |
| C26 | 0.29663 | 0.72061 | 0.43247 | C54 | 0.09535 | 0.51622 | 0.54856 |
| C27 | 0.28672 | 0.25983 | 0.70592 | C55 | 0.05169 | 0.53017 | 0.56254 |
| C28 | 0.51877 | 0.08467 | 0.61697 | C56 | 0.02007 | 0.49353 | 0.53304 |

Continuous (Table S4)

| Atom | $x / a$ | $y / b$ | $z / \mathrm{c}$ | Atom | $x / a$ | $y / b$ | z/c |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C57 | 0.05105 | 0.45665 | 0.50906 | C92 | 0.94897 | 0.42134 | 0.781 |
| C58 | 0.0427 | 0.41423 | 0.43332 | C93 | 0.84416 | 0.62384 | 0.34288 |
| C59 | 0.07735 | 0.38532 | 0.43718 | C94 | 0.83702 | 0.36731 | 0.64548 |
| C60 | 0.12107 | 0.39769 | 0.51268 | C95 | 0.85964 | 0.66485 | 0.41395 |
| C61 | 0.13027 | 0.44131 | 0.54194 | C96 | 0.83043 | 0.6986 | 0.45389 |
| C62 | 0.13148 | 0.54441 | 0.54479 | C97 | 0.78474 | 0.69256 | 0.4351 |
| C63 | 0.1233 | 0.58844 | 0.57463 | C98 | 0.76869 | 0.65174 | 0.36462 |
| C64 | 0.07921 | 0.60142 | 0.64191 | C99 | 0.7981 | 0.61772 | 0.32136 |
| C65 | 0.044 | 0.57292 | 0.63536 | C100 | 0.7911 | 0.37503 | 0.66356 |
| C66 | 0.15528 | 0.36404 | 0.57232 | C101 | 0.76033 | 0.34178 | 0.63108 |
| C67 | 0.15895 | 0.6216 | 0.53401 | C102 | 0.77458 | 0.29991 | 0.5796 |
| C68 | 0.14215 | 0.32523 | 0.72625 | C103 | 0.82019 | 0.29216 | 0.55792 |
| C69 | 0.17179 | 0.29166 | 0.75606 | C104 | 0.85082 | 0.32513 | 0.5864 |
| C70 | 0.2158 | 0.29606 | 0.64943 | N105 | 0.24358 | 0.2595 | 0.67553 |
| C71 | 0.22984 | 0.33484 | 0.50526 | N106 | 0.25381 | 0.72275 | 0.46603 |
| C72 | 0.19987 | 0.36865 | 0.46723 | N107 | 0.75627 | 0.7287 | 0.48423 |
| C73 | 0.20338 | 0.61449 | 0.63145 | N108 | 0.74464 | 0.26432 | 0.55764 |
| C74 | 0.23518 | 0.6471 | 0.60771 | H109 | 0.4186 | 0.97611 | 0.24586 |
| C75 | 0.22321 | 0.68765 | 0.48204 | H110 | 0.36664 | 0.91451 | 0.176 |
| C76 | 0.17915 | 0.69453 | 0.38633 | H111 | 0.46718 | 0.83423 | 0.64201 |
| C77 | 0.14801 | 0.66204 | 0.40271 | H112 | 0.5454 | 0.83686 | 0.6564 |
| C78 | 0.7028 | 0.26509 | 0.47495 | H113 | 0.65341 | 0.92421 | 0.81655 |
| C79 | 0.71546 | 0.72774 | 0.59811 | H114 | 0.60658 | 0.98385 | 0.76751 |
| C80 | 0.90018 | 0.51647 | 0.44513 | H115 | 0.32077 | 0.86613 | 0.52521 |
| C81 | 0.89881 | 0.47235 | 0.5497 | H116 | 0.27272 | 0.80366 | 0.53844 |
| C82 | 0.94202 | 0.45967 | 0.61191 | H117 | 0.38443 | 0.72485 | 0.30064 |
| C83 | 0.97435 | 0.49377 | 0.52231 | H118 | 0.43256 | 0.78667 | 0.27898 |
| C84 | 0.94403 | 0.52825 | 0.40775 | H119 | 0.59196 | 0.79719 | 1.0311 |
| C85 | 0.95376 | 0.5663 | 0.2458 | H120 | 0.63774 | 0.73464 | 0.94528 |
| C86 | 0.92047 | 0.59624 | 0.1999 | H121 | 0.73384 | 0.80863 | 0.37622 |
| C87 | 0.8765 | 0.58806 | 0.31246 | H122 | 0.68663 | 0.87134 | 0.44103 |
| C88 | 0.86581 | 0.54611 | 0.41449 | H123 | 0.31244 | 0.69026 | 0.39276 |
| C89 | 0.8631 | 0.44392 | 0.56591 | H124 | 0.3041 | 0.28983 | 0.73116 |
| C90 | 0.87116 | 0.40178 | 0.67739 | H125 | 0.58245 | 0.0094 | 0.26126 |
| C91 | 0.91405 | 0.39227 | 0.8097 | H126 | 0.63452 | 0.07045 | 0.21669 |

Continuous (Table S4)

| H127 | 0.53346 | 0.15059 | 0.66837 | H163 | 0.73359 | 0.64624 | 0.33671 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| H128 | 0.45612 | 0.14796 | 0.69321 | H164 | 0.78463 | 0.587 | 0.26857 |
| H129 | 0.34722 | 0.06115 | 0.81442 | H165 | 0.77901 | 0.40661 | 0.71084 |
| H130 | 0.39212 | 0.00132 | 0.74058 | H166 | 0.72569 | 0.34881 | 0.65517 |
| H131 | 0.6795 | 0.11938 | 0.59662 | H167 | 0.83206 | 0.26029 | 0.51082 |
| H132 | 0.72705 | 0.18229 | 0.61039 | H168 | 0.88563 | 0.31732 | 0.55087 |
| H133 | 0.61628 | 0.25915 | 0.30198 |  |  |  |  |
| H134 | 0.56905 | 0.19643 | 0.27979 |  |  |  |  |
| H135 | 0.41451 | 0.18952 | 1.01514 |  |  |  |  |
| H136 | 0.36991 | 0.25224 | 0.96365 |  |  |  |  |
| H137 | 0.26199 | 0.17838 | 0.53429 |  |  |  |  |
| H138 | 0.30837 | 0.11502 | 0.56079 |  |  |  |  |
| H139 | 0.01018 | 0.40186 | 0.37651 |  |  |  |  |
| H140 | 0.06938 | 0.35289 | 0.3861 |  |  |  |  |
| H141 | 0.16352 | 0.45211 | 0.58794 |  |  |  |  |
| H142 | 0.16464 | 0.53256 | 0.51203 |  |  |  |  |
| H143 | 0.07151 | 0.63416 | 0.6954 |  |  |  |  |
| H144 | 0.01133 | 0.58538 | 0.67976 |  |  |  |  |
| H145 | 0.10883 | 0.32088 | 0.82792 |  |  |  |  |
| H146 | 0.16086 | 0.2622 | 0.87285 |  |  |  |  |
| H147 | 0.26305 | 0.33846 | 0.40494 |  |  |  |  |
| H148 | 0.211 | 0.3974 | 0.34077 |  |  |  |  |
| H149 | 0.21319 | 0.58428 | 0.73895 |  |  |  |  |
| H150 | 0.2685 | 0.64118 | 0.69928 |  |  |  |  |
| H151 | 0.1694 | 0.72512 | 0.28721 |  |  |  |  |
| H152 | 0.11504 | 0.66864 | 0.3093 |  |  |  |  |
| H153 | 0.68694 | 0.2945 | 0.40803 |  |  |  |  |
| H154 | 0.70078 | 0.698 | 0.67275 |  |  |  |  |
| H155 | 0.98707 | 0.57316 | 0.16822 |  |  |  |  |
| H156 | 0.92953 | 0.62626 | 0.08139 |  |  |  |  |
| H157 | 0.83254 | 0.53741 | 0.48742 |  |  |  |  |
| H158 | 0.83107 | 0.45395 | 0.47169 |  |  |  |  |
| H159 | 0.92067 | 0.36213 | 0.93634 |  |  |  |  |
| H160 | 0.98114 | 0.41435 | 0.88524 |  |  |  |  |
| H161 | 0.89447 | 0.6712 | 0.44733 |  |  |  |  |
| H162 | 0.84316 | 0.73002 | 0.5045 |  |  |  |  |
|  |  |  |  |  |  |  |  |

Table S5. Fractional atomic coordinates for the unit cell of BFTB-BCTA COF with AA-stacking.

| Sample Name: BFTB-BCTA COF |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Space Group: P 222 |  |  |  |  |  |  |  |
| $\mathrm{a}=31.909, \mathrm{~b}=28.274, \mathrm{c}=4.073 \quad \alpha=\beta=\gamma=90^{\circ}$ |  |  |  |  |  |  |  |
| $\mathrm{R}_{\mathrm{wp}}=5.82 \% \quad \mathrm{R}_{\mathrm{p}}=4.32 \%$ |  |  |  |  |  |  |  |
| Atom | $x / a$ | $y / b$ | $z / \mathrm{c}$ | Atom | $x / a$ | $y / b$ | z/c |
| C1 | 0.4782 | 0.89691 | 0.4509 | H30 | 0.36647 | 0.92309 | 0.14984 |
| C2 | 0.53531 | 0.9432 | 0.57575 | H31 | 0.46553 | 0.82325 | 0.38283 |
| C3 | 0.42502 | 0.95225 | 0.29495 | H32 | 0.34053 | 0.86489 | 0.13417 |
| C4 | 0.3979 | 0.91449 | 0.22772 | H33 | 0.28831 | 0.80253 | 0.17692 |
| C5 | 0.41115 | 0.86689 | 0.2644 | H34 | 0.36325 | 0.71273 | 0.44166 |
| C6 | 0.45273 | 0.85852 | 0.36943 | H35 | 0.41362 | 0.77603 | 0.51659 |
| C7 | 0.38155 | 0.82667 | 0.20129 | H36 | 0.29727 | 0.6809 | 0.20463 |
| C8 | 0.34574 | 0.83266 | 0.00219 | H37 | 0.1742 | 0.74701 | 0.26064 |
| C9 | 0.31592 | 0.79669 | 0.02749 | H38 | 0.11561 | 0.69178 | 0.34041 |
| C10 | 0.32178 | 0.75324 | 0.13142 | H39 | 0.19155 | 0.57867 | 0.05205 |
| C11 | 0.35837 | 0.74587 | 0.31382 | H40 | 0.25016 | 0.63417 | 0.11907 |
| C12 | 0.38758 | 0.78228 | 0.35279 | H41 | 0.06446 | 0.64425 | 0.07522 |
| C13 | 0.28925 | 0.71625 | 0.12291 | H42 | 0.00795 | 0.59087 | 0.24475 |
| C14 | 0.21634 | 0.69439 | 0.07324 | H43 | 0.1558 | 0.54053 | 0.39398 |
| C15 | 0.17771 | 0.71036 | 0.18956 |  |  |  |  |
| C16 | 0.14441 | 0.67886 | 0.23242 |  |  |  |  |
| C17 | 0.14905 | 0.63076 | 0.15192 |  |  |  |  |
| C18 | 0.18743 | 0.61522 | 0.02015 |  |  |  |  |
| C19 | 0.22088 | 0.64677 | 0.01802 |  |  |  |  |
| C20 | 0.1147 | 0.59676 | 0.22132 |  |  |  |  |
| C21 | 0.07227 | 0.61 | 0.1771 |  |  |  |  |
| C22 | 0.03958 | 0.57927 | 0.26653 |  |  |  |  |
| C23 | 0.04907 | 0.53503 | 0.39677 |  |  |  |  |
| C24 | 0.09053 | 0.52215 | 0.43382 |  |  |  |  |
| C25 | 0.12386 | 0.55166 | 0.35021 |  |  |  |  |
| C26 | 0.5 | 0.9759 | 0.5 |  |  |  |  |
| N27 | 0.25055 | 0.27284 | 0.94092 |  |  |  |  |
| N28 | 0.02248 | 0.5 | 0.5 |  |  |  |  |
| H29 | 0.41459 | 0.9876 | 0.24765 |  |  |  |  |

## S11. Organic Pollutant Treatment in Water

## Dye adsorption experiments

The organic dye RhB was selected to study the efficiency of the BFTB-PyTA, BFTB-BFTB, and BFTB-BCTA COFs for the removal of dyes from water. In a typical experiment, a BFTB-PyTA, BFTB-BFTB, or BFTB-BCTA COF ( 4 mg ) was added to an aqueous solution of RhB ( 10 mL ) in a glass vial and then the mixture was stirred (for $0,5,10,15,20$, or 30 min ) at a rate of 500 rpm . The supernatant was then isolated through centrifugation ( $6000 \mathrm{rpm}, 10 \mathrm{~min}$ ). The UV-Vis spectrum of the isolated supernatant was measured. To obtain adsorption isothermal curves, various concentrations of the aqueous dye (from 25 to $200 \mathrm{mg} \mathrm{L}^{-1}$ ) were used. For each test, a FTB-PyTA, BFTB-BFTB, or BFTB-BCTA COF ( 2 mg ) was added to an aqueous solution of RhB ( 10 mL ) in a glass vial and then the mixture was stirred ( 500 rpm ) for 24 h . The supernatant was isolated through centrifugation and its UV-Vis spectrum recorded, to construct the isothermal curve. Adsorption reusability tests were performed by adding a BFTB-PyTA, BFTB-BFTB, or BFTB-BCTA COF (3 $\mathrm{mg})$ to an aqueous solution of the dye $\left(25 \mathrm{mg} \mathrm{L}^{-1}, 10 \mathrm{~mL}\right)$ and then stirring for 1 h . The supernatant was isolated and its UV-Vis spectrum recorded. The BFTB-PyTA, BFTB-BFTB, and BFTBBCTA COFs were washed several times with $\mathrm{H}_{2} \mathrm{O}$, EtOH , THF, and acetone to remove the adsorbed dye. After drying the BFTB-PyTA, BFTB-BFTB, and BFTB-BCTA COFs overnight at $100^{\circ} \mathrm{C}$, they were used in the next dye removal test. The adsorption isothermals of RhB was fitted using the Langmuir isothermal model (linear form), expressed as follows:
$\frac{C_{e}}{Q_{e}}=\frac{1}{K_{L} Q_{m}}+\frac{C_{e}}{Q_{m}}$
where $C_{\mathrm{e}}\left(\mathrm{mg} \mathrm{L}^{-1}\right)$ is the equilibrium dye concentration in the liquid phase; $Q_{\mathrm{e}}\left(\mathrm{mg} \mathrm{g}^{-1}\right)$ is the equilibrium adsorption of dye per unit mass of the adsorbent carbon; $Q_{\mathrm{m}}\left(\mathrm{mg} \mathrm{g}^{-1}\right)$ is the maximum equilibrium adsorption of dye per unit mass of the adsorbent carbon; and $K_{\mathrm{L}}\left(\mathrm{L} \mathrm{mg}^{-1}\right)$ is the Langmuir constant.


Figure S13. FT-IR spectra of (a) BFTB-PyTA COF, (b) rhodamine B (RhB), and (c) BFTB-PyTA COF after adsorbed rhodamine B. (d) Adsorption mechanism of rhodamine B on BFTB-PyTA COF.



Figure S14. FT-IR spectra of (a) BFTB-BFTB COF, (b) rhodamine B (RhB), and (c) BFTB-PyTA COF after adsorbed rhodamine B. (d) Adsorption mechanism of rhodamine B on BFTB- BFTB COF.



Figure S15. FT-IR spectra of (a) BFTB-BCTA COF, (b) rhodamine B (RhB), and (c) BFTB-PyTA COF after adsorbed rhodamine B. (d) Adsorption mechanism of rhodamine B on BFTB- BCTA COF.

igure S16. (a) Langmuir isothermal models and (b) adsorption isothermal curves for RhB on the BFTB-PyTA, BFTB-BFTB, and BFTB-BCTA COFs.


Fig
ure S17. Reusability of the (a) BFTB-PyTA, (b) BFTB-BFTB, and (c) BFTB-BCTA COFs for the removal of RhB within 10 min .

Table S6. Fitted parameters for the adsorptions of RhB on the BFTB-PyTA, BFTB-BFTB, and BFTB-BCTA COFs, calculated using the Langmuir adsorption isothermal model.

|  | $\boldsymbol{Q}_{\mathbf{m}}\left(\mathbf{m g ~ g}^{\mathbf{- 1}} \mathbf{)}\right.$ | $\boldsymbol{K}_{\mathbf{L}}$ | $\boldsymbol{R}_{\mathbf{L}}{ }^{\mathbf{2}}$ |
| :--- | :---: | :---: | :---: |
| BFTB-PyTA COF | 2127 | 0.7580 | 0.9903 |
| BFTB-BFTB COF | 1854 | 0.6227 | 0.9891 |
| BFTB-BCTA COF | 1605 | 0.4127 | 0.9949 |

Table S7. Maximum adsorption capacities of RhB on the BFTB-PyTA, BFTB-BFTB, and BFTBBCTA COFs, compared with those of other reported materials.

| Adsorbent | Dye | $\mathrm{Q}_{\mathrm{m}}\left(\mathrm{mg} \mathrm{g}^{-1}\right)$ | Ref. |
| :---: | :---: | :---: | :---: |
| Graphene sponge | RhB | 72 | S 5 |
| Nanoporous PDVB-VI-0.2 | RhB | 260 | S 6 |
| S1 | RhB | 200 | S 7 |
| activated carbon (OAC) | RhB | 321 | S 8 |
| Mesoporous carbon (ST-A) | RhB | 83 | S 9 |
| N-doped mesoporous gyroid carbon | RhB | 204.08 | S 10 |
| PDVB-VI nanoporous polymer | RhB | 260 | S 11 |
| CMP-YA | RhB | 535 | S 12 |
| Py-BF-CMP | RhB | 1905 | S 13 |
| TPE-BF-CMP | RhB | 1024 | S 13 |
| TPA-BF-CMP | RhB | 926 | S 13 |
| Ttba-TPDA-COF | RhB | 833 | S 14 |
| CuP-DMNDA-COF/Fe | RhB | 424 | S 15 |
| BFTB-PyTA | RhB | 2127 | This work |
| BFTB-BFTB | RhB | 1854 | This work |
| BFTB-BCTA | RhB | 1605 | This work |

## S12. Chemical stability of COFs



Figure S18. FTIR spectra of BFTB-PyTA COF (a) as-synthesized, (b) after recyclability from dye experiments and (a) after immersing 3 days in 1.0 M KOH .


Figure S19. FTIR spectra of BFTB-BFTB COF (a) as-synthesized, (b) after recyclability from dye experiments and (a) after immersing 3 days in 1.0 M KOH .


Figure S20. FTIR spectra of BFTB-BCTA COF (a) as-synthesized, (b) after recyclability from dye experiments and (a) after immersing 3 days in 1.0 M KOH .


Figure S21. PXRD patterns of BFTB-PyTA COF (a) as-synthesized, (b) after recyclability from dye experiments and (a) after immersing 3 days in 1.0 M KOH .


Figure S22. PXRD patterns of BFTB-BFTB COF (a) as-synthesized, (b) after recyclability from dye experiments and (a) after immersing 3 days in 1.0 M KOH .


Figure S23. PXRD patterns of BFTB-BCTA COF (a) as-synthesized, (b) after recyclability from dye experiments and (a) after immersing 3 days in 1.0 M KOH .

## S13. Electrochemical measurements

All electrochemical measurements were performed using an Autolab potentiostat (PGSTAT204) in a three-electrode electrochemical cell. The performance of the electrodes was investigated through cyclic voltammetry (CV) and the galvanostatic charge-discharge (GCD) method in 1.0 M KOH as the electrolyte. A Pt wire was used as the counter electrode; $\mathrm{Ag} / \mathrm{AgCl}$ was used as the reference electrode; a glassy carbon electrode (GCE) was used as the working electrode (diameter: 5.61 mm ; $0.2475 \mathrm{~cm}^{2}$ ). Prior to use, the GCE was polished several times sequentially with $0.1-$ and $0.05-\mu \mathrm{m}$ alumina powder, washed with distilled water and EtOH after each polishing step, cleaned via sonication ( 5 min ) in a water bath, washed with EtOH , and finally dried under a stream of $\mathrm{N}_{2}$.

The working electrode was prepared by coating a slurry containing the active material. The slurry was prepared by dispersing the active material ( 2.0 mg ), carbon black ( 2.0 mg ), and Nafion $(0.4 \mathrm{mg})$ in $\mathrm{EtOH}(1.0 \mathrm{~mL})$, which had undergone sonication for 1 h . A portion of the freshly prepared slurry $(10 \mu \mathrm{~L})$ was coated onto the tip of the electrode, then dried in air for 30 min prior to use. The electrochemical performance was studied through CV at various sweep rates (from 5 to $200 \mathrm{mV} \mathrm{s}^{-1}$ ) and through the GCD method in the potential range from -1.0 to $0.0 \mathrm{~V}(\mathrm{vs} . \mathrm{Ag} / \mathrm{AgCl})$ at various current densities (from 0.5 to $20 \mathrm{~A} \mathrm{~g}^{-1}$ ) in 1 M KOH as the aqueous electrolyte. The specific gravimetric capacitance of each electrode was calculated from the CV curves by using the following equation (1):

$$
\begin{equation*}
C_{g}=\frac{1}{m s(V f-V I)} \int_{V i}^{V f} I(V) d v \tag{1}
\end{equation*}
$$

where $C_{\mathrm{g}}$ is the gravimetric capacitance $\left(\mathrm{F} \mathrm{g}^{-1}\right), s$ is the potential scan rate, $V$ is the potential window, $I$ is the current (A), $t$ is the discharge time (s), and $m$ is the mass of the active material $(\mathrm{g})$.

Based on the GCD data, the gravimetric specific capacitance ( $C_{\mathrm{g}}, \mathrm{Fg}^{-1}$ ) was calculated using the following equation (2):
$C_{g}=\frac{I \times t}{m \times \Delta V}$
where $I$ is the discharge current (A), $t$ is the discharge time (s), $m$ is the mass of the active material $(\mathrm{g})$, and $\Delta V$ is the potential change during the discharge process $(\mathrm{V})$.


Figure S24. Cycling performances of a) BFTB-PyTA, b) BFTB-BFTB and c) BFTB-BCTA electrodes at $10 \mathrm{~A} \mathrm{~g}^{-1}$.


Figure S25. (a) CV curves and (b) GCD curves of black carbon.

Table S8. Gravimetric specific capacitance values calculated at different scan rates and retention.

|  | Scan rate $\left(\mathrm{mV} \mathrm{~s}^{-1}\right)$ | Discharge area ( $\mathrm{cm}^{2}$ ) | $\begin{gathered} \mathrm{Cg} \\ \left(\mathrm{Fg}^{-1}\right) \end{gathered}$ | Retention <br> (\%) |
| :---: | :---: | :---: | :---: | :---: |
| BFTB-PyTA | 5 | 0.068 | 68.0 |  |
|  | 10 | 0.119 | 59.5 |  |
|  | 30 | 0.295 | 49.1 |  |
|  | 50 | 0.451 | 45.1 | 52.9 |
|  | 70 | 0.598 | 42.7 |  |
|  | 100 | 0.805 | 40.3 |  |
|  | 200 | 1.410 | 35.3 |  |
| BFTB- BFTB | 5 | 0.084 | 84.5 |  |
|  | 10 | 0.148 | 74.2 |  |
|  | 30 | 0.377 | 62.8 |  |
|  | 50 | 0.574 | 57.5 | 47.7 |
|  | 70 | 0.754 | 53.8 |  |
|  | 100 | 0.992 | 49.5 |  |
|  | 200 | 1.613 | 40.3 |  |
| BFTB-BCTA | 5 | 0.089 | 89.9 |  |
|  | 10 | 0.145 | 72.6 |  |
|  | 30 | 0.339 | 56.5 |  |
|  | 50 | 0.523 | 52.3 | 47.4 |
|  | 70 | 0.697 | 49.7 |  |
|  | 100 | 0.943 | 47.1 |  |
|  | 200 | 1.707 | 42.6 |  |

Table S9. Comparison between the specific surface area/specific capacitance of BFTB-PyTA, BFTB-BFTB, and BFTB-BCTA COFs with those of previously reported COFs for supercapacitor application.

| COFs | $\mathrm{S}_{\text {BET }}\left(\mathrm{m}^{2} \mathrm{~g}^{-1}\right)$ | Capacitance | Ref. |
| :---: | :---: | :---: | :---: |
| Car-TPA COF | 1334 | $13.6 \mathrm{~F} \mathrm{~g}^{-1}$ at $0.2 \mathrm{~A} \mathrm{~g}^{-1}$ | S 16 |
| Car-TPP COF | 743 | $14.5 \mathrm{~F} \mathrm{~g}^{-1}$ at $0.2 \mathrm{~A} \mathrm{~g} \mathrm{~g}^{-1}$ | S 16 |
| Car-TPT COF | 721 | $17.4 \mathrm{~F} \mathrm{~g}^{-1}$ at $0.2 \mathrm{~A} \mathrm{~g}^{-1}$ | S 16 |
| DAAQ-TFP COF | 1280 | $48 \pm 10 \mathrm{~F} \mathrm{~g}^{-1}$ at $0.1 \mathrm{~A} \mathrm{~g} \mathrm{~g}^{-1}$ | S 17 |
| TPA-COF-1 | 714 | $51.3 \mathrm{~F} \mathrm{~g}^{-1}$ at $0.2 \mathrm{~A} \mathrm{~g}^{-1}$ | S 18 |
| TPA-COF-2 | 478 | $14.4 \mathrm{~F} \mathrm{~g}^{-1}$ at $0.2 \mathrm{~A} \mathrm{~g} \mathrm{~g}^{-1}$ | S 18 |
| TPA-COF-3 | 557 | $5.1 \mathrm{~F} \mathrm{~g}^{-1}$ at $0.2 \mathrm{~A} \mathrm{~g}^{-1}$ | S 18 |
| TPT-COF-4 | 1132 | $2.4 \mathrm{~F} \mathrm{~g}^{-1}$ at $0.2 \mathrm{~A} \mathrm{~g}^{-1}$ | S 18 |
| TPT-COF-5 | 1747 | $0.34 \mathrm{~F} \mathrm{~g}^{-1}$ at $0.2 \mathrm{~A} \mathrm{~g}^{-1}$ | S 18 |
| TPT-COF-6 | 1535 | $0.24 \mathrm{~F} \mathrm{~g}^{-1}$ at $0.2 \mathrm{~A} \mathrm{~g} \mathrm{~g}^{-1}$ | S 18 |
| TaPay-Py COF | 687 | $209 \mathrm{~F} \mathrm{~g}^{-1}$ at $0.5 \mathrm{~A} \mathrm{~g}^{-1}$ | S 19 |
| DAB-TFP COF | 385 | $98 \mathrm{~F} \mathrm{~g}^{-1}$ at $0.5 \mathrm{~A} \mathrm{~g}^{-1}$ | S 19 |
| TPT-DAHQ COF | 1855 | $256 \mathrm{~F} \mathrm{~g}^{-1}$ at $0.5 \mathrm{~A} \mathrm{~g}^{-1}$ | S 20 |
| PDC-MA COF | 748 | $335 \mathrm{~F} \mathrm{~g}^{-1}$ at $1.0 \mathrm{~A} \mathrm{~g}^{-1}$ | S 21 |
| TpPa-(OH) ${ }_{2}$ COF | 369 | $416 \mathrm{~F} \mathrm{~g}^{-1}$ at $1.0 \mathrm{~A} \mathrm{~g}^{-1}$ | S 22 |
| BFTB-PyTA COF | 1133 | $71 \mathrm{~F} \mathrm{~g}^{-1}$ at $1 \mathrm{~A} \mathrm{~g}^{-1}$ | This work |

## S14. Reference

[S1] K. Brunner, A. V. Dijken, H. Borner, J. J. A. M. Bastiaansen, N. M. M. Kiggen and B. M. W. Langeveld, J. Am. Chem. Soc., 2004, 126, 6035-6042.
[S2] J. Ipaktschi, R. Hosseinzadeh, P. Schlaf and E. Dreiseidler, Helv. Chim. Acta., 1998, 81, 18211834.
[S3] P. Rios, T. S. Carter, T. J. Mooibroek, M. P. Crump, M. Lisbjerg, M. Pittelkow, N. T. Supekar, G. J. Boons and A. P. Davis, Angew. Chem. Int. Ed., 2016, 55, 3387-3392.
[S4] H. R. Abuzeid, A. F. M. EL-Mahdy and S. W. Kuo, Microporous Mesoporous Mater., 2020, 300, 110151.
[S5] J. Zhao, W. Ren and H. M. Cheng, J. Mater. Chem., 2012, 22, 20197-20202.
[S6] Y. Han, W. Li, J. Zhang, H. Meng, Y. Xu and X. Zhang, RSC Adv., 2015, 5, 104915-104922.
[S7] S. Wang, B. Yang and Y. Liu, J. Colloid Interface Sci., 2017, 507, 225-233.
[S8] O. Üner, Ü. Geçgel, H. Kolancilar and Y. Bayrak, Chem. Eng. Commun., 2017, 204, 772-783.
[S9] K. Jedynak, D. Wideł and N. Redzia, Colloids Interfaces, 2019, 3, 30.
[S10] A. F. M. EL-Mahdy, T. E. Liu and S. W. Kuo, J. Hazard. Mater., 2020, 391, 122163.
[S11] Y. Han, W. Li, J. Zhang, H. Meng, Y. Xu and X. Zhang, RSC Adv., 2015, 5, 104915-104922.
[S12] Y. Yuan, H. Huang, L. Chen and Y. Chen, Macromolecules, 2017, 50, 4993-5003.
[S13] B. Wang, Z. Xie, Y. Li, Z. Yang and L. Chen, Macromolecules, 2018, 51, 3443-3449.
[S14] T. Xu, S. An, C. Peng, J. Hu and H. Liu, Ind. Eng. Chem. Res., 2020, 59, 8315-8322.
[S15] Y. Hou, X. Zhang, C. Wang, D. Qi, Y. Gu, Z. Wang, and J. Jiang, New J. Chem., 2017, 41, 6145-6151.
[S16] A. F. M. El-Mahdy, C. Young, J. Kim, J. You, Y. Yamauchi and S. W. Kuo, ACS Appl. Mater. Interfaces, 2019, 11, 9343-9354.
[S17] C. R. DeBlase, K. E. Silberstein, T. T. Truong, H. D. Abruña and W. R. Dichtel, J. Am. Chem. Soc., 2013, 135, 16821-16824.
[S18] A. F. M. El-Mahdy, C. H. Kuo, A. Alshehri, C. Young, Y. Yamauchi, J. Kim and S. W. Kuo, J. Mater. Chem. A, 2018, 6, 19532-19541.
[S19] A. M. Khattak, Z. A. Ghazi, B. Liang, N. A. Khan, A. Iqbal, L. Li and Z. Tang, J. Mater. Chem. A, 2016, 4, 16312-16317.
[S20] A. F. M. EL-Mahdy, Y. -H. Hung, T. H. Mansoure, H. -H. Yu, T. Chen, and S. W. Kuo, Chem. Asian J., 2019, 14, 1429-1435.
[S21] L. Li, F. Lu, R. Xue, B. Ma, Q. Li, N. Wu, H. Liu, W. Yao, H. Guo, and W. Yang, ACS Appl. Mater. Interfaces 2019, 11, 26355-26363.
[S22] S. Chandra, D. R. Chowdhury, M. Addicoat, T. Heine, A. Paul, and R. Banerjee, Chem. Mater. 2017, 29, 2074-2080.

