

Electronic supplementary information (ESI)

**Room-temperature fabrication of superhydrophobic covalent organic frameworks (COFs) decorated cotton fabric for high-flux water-in-oil emulsions separation**

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## **Experimental**

### **1. Materials**

Anhydrous methanol, methylene blue, dichloromethane, chlorobenzene, xylene, *o*-dichlorobenzene, *n*-hexane, isooctane, cyclohexane, petroleum ether and acetic acid (36%) were obtained from Cologne Chemical Co., Ltd. (Chengdu, China). Mesitylene, Span 80, ethanol (95%) and safranin T were purchased from Aladdin biochemical Technology Co., Ltd. (Shanghai, China). 1,3,5-benzenetricarboxaldehyde (TFB) and 3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diamine (BD(Me)<sub>2</sub>) were purchased from Chinese Academy of Sciences - Yanshen Technology Co., Ltd. (Changchun, China). Gasoline (92#) was purchased from SINOPEC (Beijing, China). All chemicals were commercial products and used directly without further purification. Cotton fabric nonwoven fabric, filter paper and nickel foam were bought from a local shop.

### **2. Preparation of TFB-BD(Me)<sub>2</sub> COFs coated cotton fabric**

Cotton fabric was cut into small pieces ( $5.5 \times 5.5 \text{ cm}^2$ ) and immersed in distilled water and 95% ethanol to wash 3 times for each 10 min under ultrasonic. After dried, the cotton fabric was slightly wetted with 36% acetic acid until the dripping appeared.

Solution A (95.5 mg BD(Me)<sub>2</sub> in 20 mL mesitylene) and solution B (48.1 mg TFB and 10.0 mg Span-80 in 20 mL mesitylene) were mixed together with gentle stirring. Subsequently, the wetted cotton fabrics clamped by a special tool was placed into the above mixed solution. After 72 h of room-temperature reaction, the fabric was taken out, washed with anhydrous methanol and dried at 60 °C.

Meanwhile, some COFs powder in the reaction solution was collected, rinsed with anhydrous methanol and dried at 60 °C in N<sub>2</sub> atmosphere for the later characterization.

### **3. Preparation and separation of water-in-oil emulsions**

For preparation of surfactant-stabilized water-in-oil emulsions, 0.5 mL water was added into 50 mL oil (including chlorobenzene, dichloromethane, *o*-dichlorobenzene, xylene, gasoline, *n*-hexane, isooctane, cyclohexane and petroleum ether) and treated under violent sonication and stirring to ensure uniform emulsification.

The separation experiment was performed by fixing the COFs coated cotton fabric into a dead-end filtration system. 50 mL emulsion feed was then poured into the upper cell and the filtrate was collected by the bottom vessel. The separation was operated under gravity. During the water-in-oil emulsion separation experiments, all the tests were repeated more than three times.

#### 4. Characterization

Powder X-ray diffraction (PXRD) patterns of the TFB-BD(Me)<sub>2</sub> were analyzed on the SHIMADZU XRD-6000 Advance X-ray diffractometer at 40 kV and 40 mA using Cu K $\alpha$  radiation. Thermogravimetric analysis (TGA) was conducted on a Netzsch DTG-60H system in air condition with a heating rate of 10 °C/min from 25 to 900 °C. The surface morphologies of samples were observed by a field-emission scanning electron microscope (SEM, Hitachi S-4800) and a transmission emission microscopy (TEM, Thermo Fisher Scientific Talos F200S). N<sub>2</sub> adsorption/desorption measurements were conducted by a Micrometrics ASAP 2020 Plus specific surface area tester. Fourier-transform infrared (FTIR) spectra was measured on a Thermo Scientific Nicolet TM iSTM 10 spectrometer. The liquid-state <sup>1</sup>H nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker Avance-400 (400 MHz) spectrometer. The static contact angle of water on the fabric surface and on the flat COFs powder that was impacted by a glass slide, was investigated using a contact angle analyzer (Defnuo ZR-SDJ-QH6). The particle size of water droplets in oil were observed by an Olympus BX51TRF optical microscopy. The moisture content in feed and filtrate was measured by the Karl-Fischer method on an Anting ZSD-2 moisture meter.

The separation efficiency of the fabric was calculated by Eq. s1:

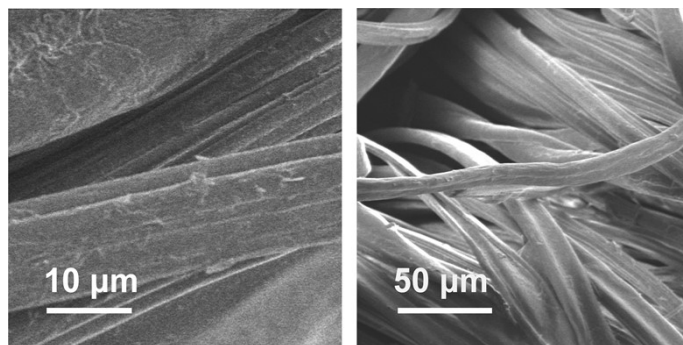
$$R = (1 - V_{\text{KF}} \frac{f}{W}) \times 100\% \quad (\text{s1})$$

where  $R$  is the separation efficiency,  $V_{\text{KF}}$  is the volume (mL) of Karl-Fischer reagent consumed by the filtrate;  $f=a/b$ ,  $a$  and  $b$  are the weight (mg) of water and the volume (mL) of Karl-Fischer reagent consumed by water, respectively.  $W$  is the weight of collected filtrate.

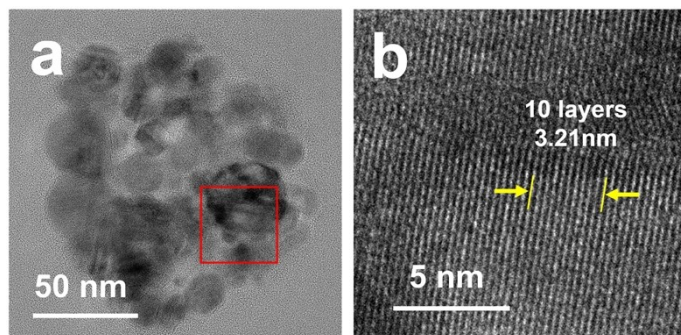
The separation flux was calculated using Eq. s2:

$$F = \frac{V}{A \times t} \quad (\text{s2})$$

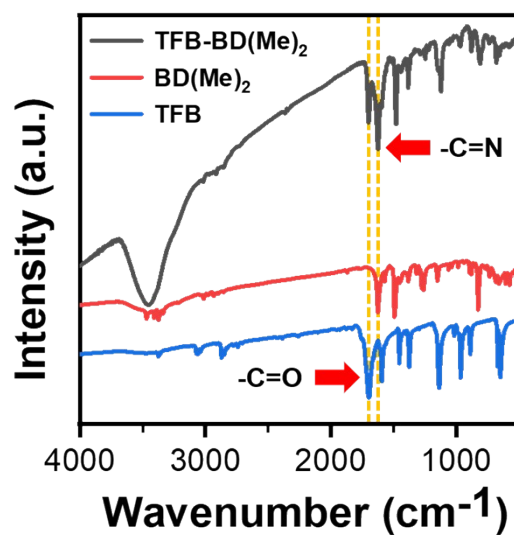
where  $F$  is the flux ( $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ),  $V$ ,  $A$  and  $t$  are the separation volume (L), effective separation area ( $\text{m}^2$ ) and filtration time (h), respectively.



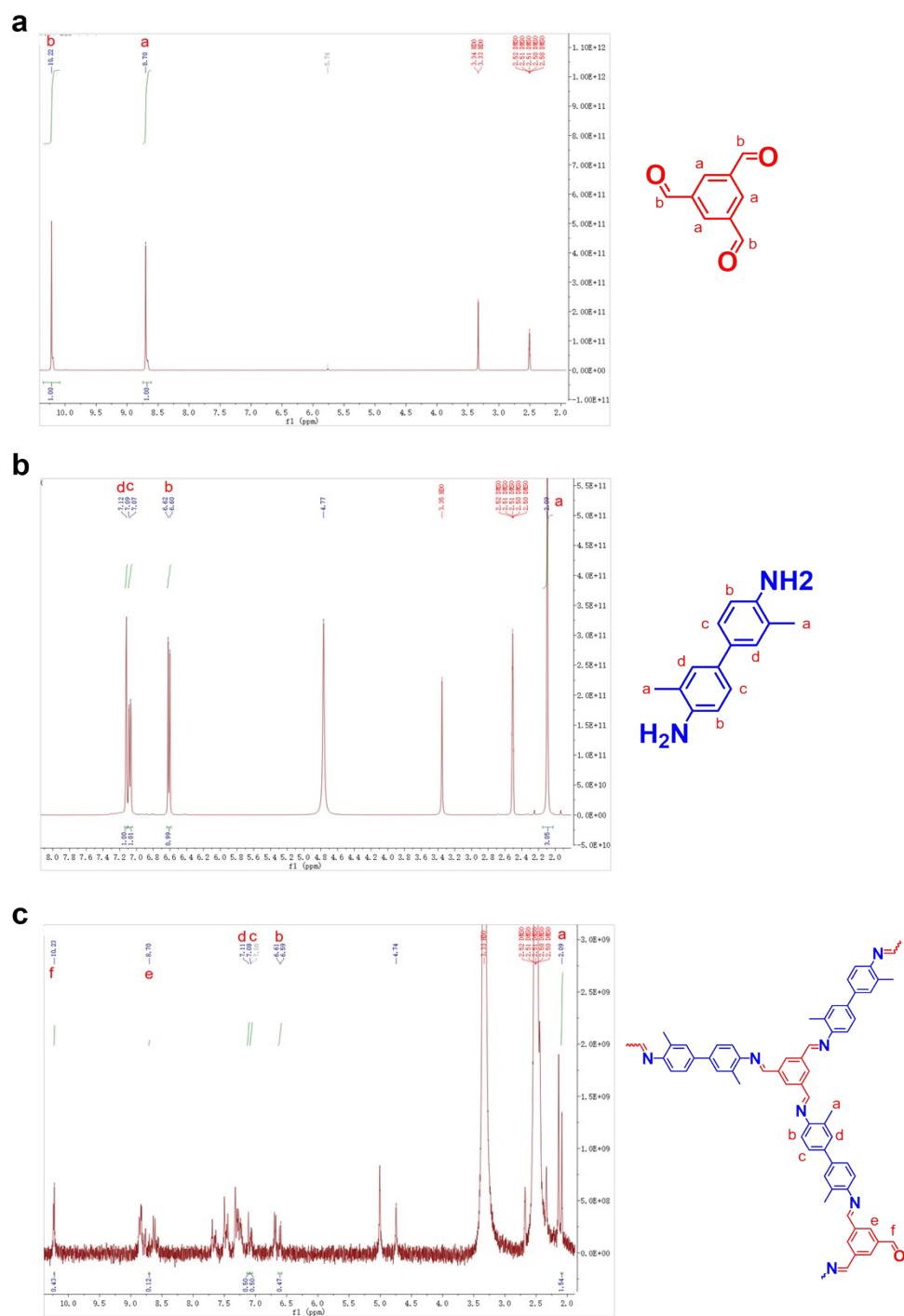
**Fig. S1** SEM images of the pristine cotton fabric with different magnifications.



**Fig. S2** (a) TEM and (b) high-resolution TEM images of the TFB-BD(Me)<sub>2</sub>.

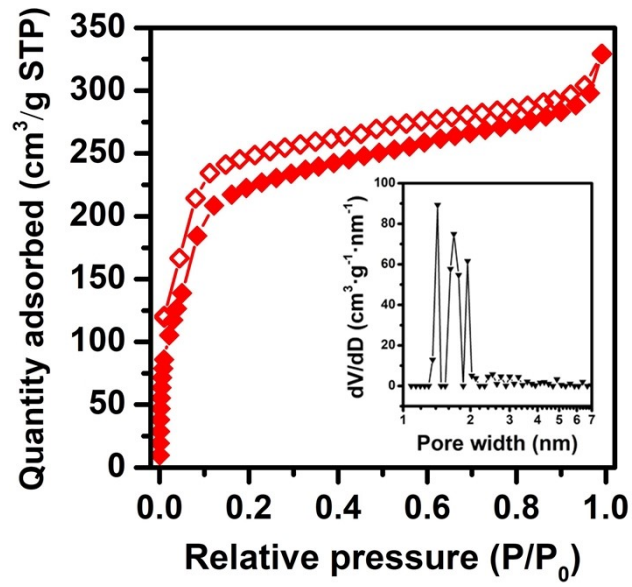


**Fig. S3** FTIR spectrum of TFB, BD(Me)<sub>2</sub> and TFB-BD(Me)<sub>2</sub> COFs. In the FTIR spectrum of TFB-BD(Me)<sub>2</sub>, the stretching band observed at 1625 cm<sup>-1</sup> corresponds to the C=N Schiff bonds. Compared with TFB-BD(Me)<sub>2</sub>, the monomer TFB shows a loss of free aldehyde stretch at wavenumber of 1700 cm<sup>-1</sup>.

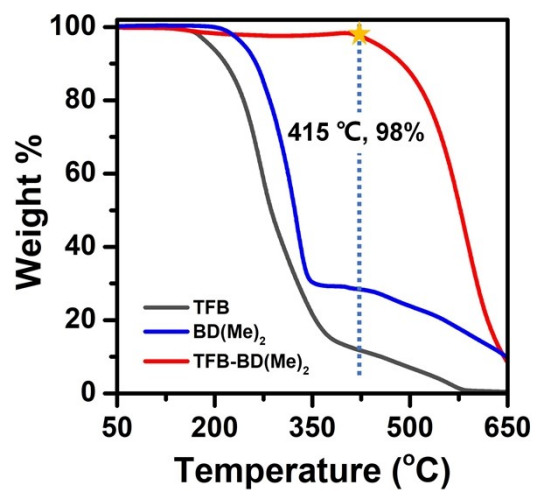


**Fig. S4**  $^1\text{H}$  NMR spectra of (a) TFB, (b)  $\text{BD}(\text{Me})_2$  and (c) TFB- $\text{BD}(\text{Me})_2$  COFs. The  $^1\text{H}$  NMR signal of H ratio (e: f) changes from 1:1 to 2:7, indicating that the privileged reaction between aldehyde and the amino groups.

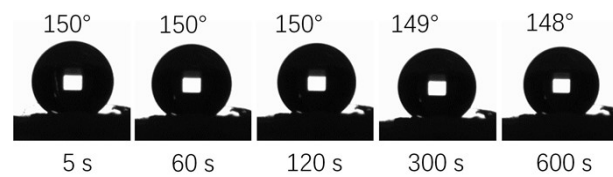




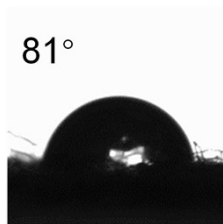
**Fig. S5** N<sub>2</sub> adsorption-desorption isotherm of the TFB-BD(Me)<sub>2</sub> COFs powder, the inset is the pore size distribution.



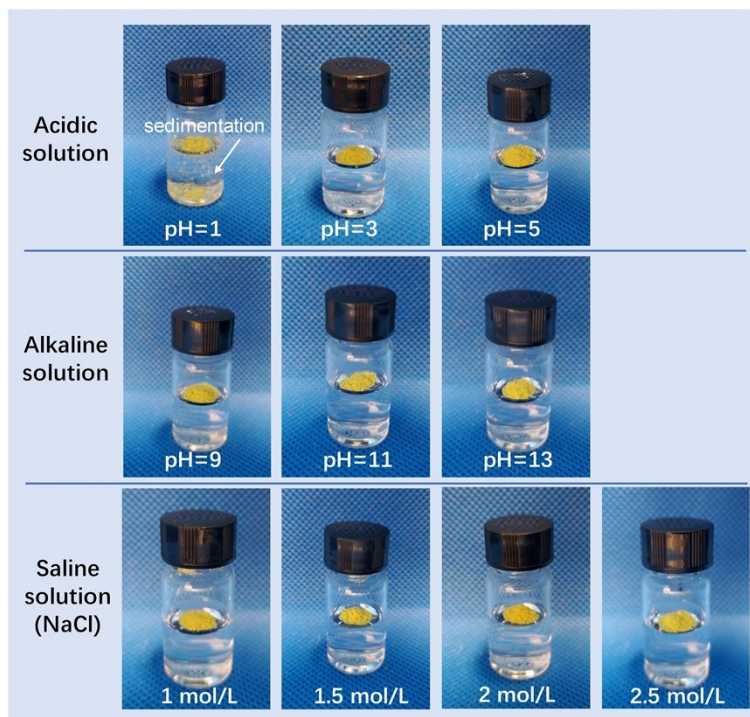
**Fig. S6** TGA curves of TFB, BD(Me)<sub>2</sub>, and TFB-BD(Me)<sub>2</sub> COFs powder.



**Fig. S7** States of water on the TFB-BD(Me)<sub>2</sub> COFs powder for different time.

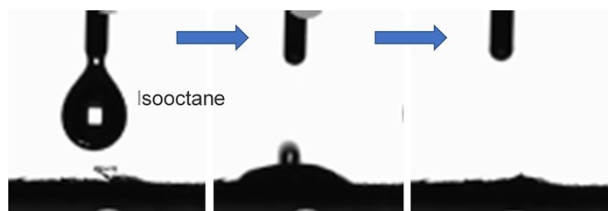


**Fig. S8** Water contact angle of pristine cotton fabric.

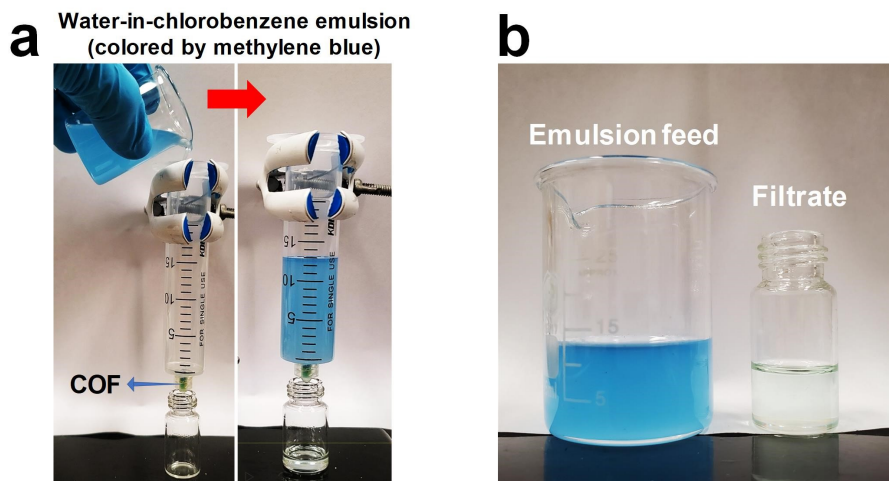


**Fig. S9** States of TFB-BD(Me)<sub>2</sub> COFs powder in different corrosive solutions.

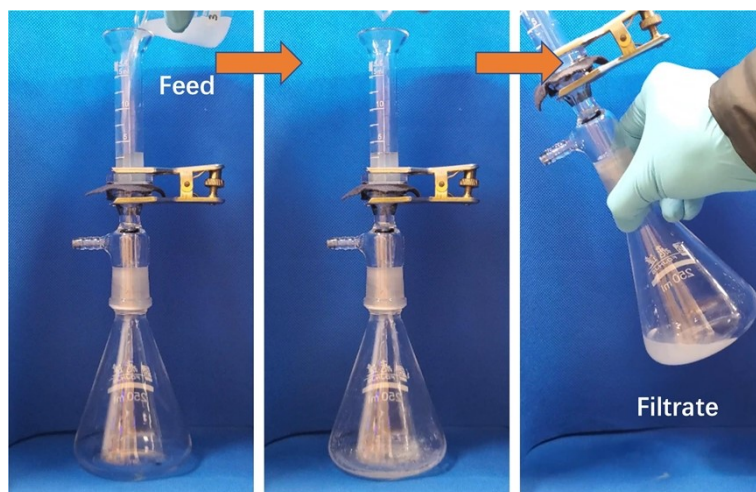
(Temperature:  $25 \pm 2$  °C; Time: 48 h; COFs weight:  $3.0 \pm 0.2$  mg)



**Fig. S10** Photographs of an isooctane droplet dripping on the COFs coated fabric.

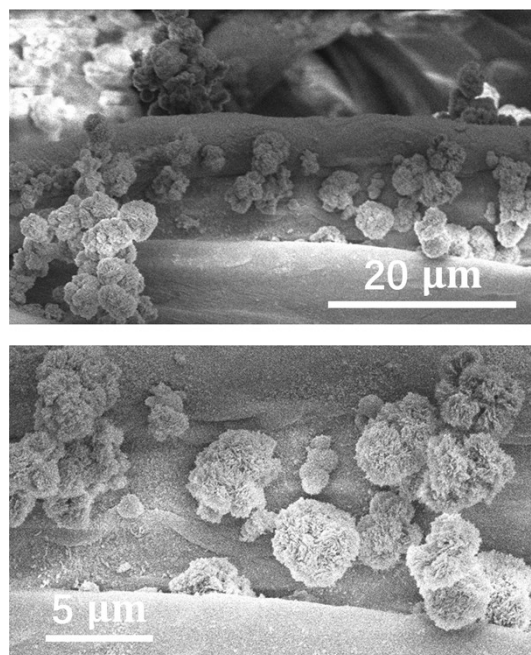


**Fig. S11** Separation of water-in-chlorobenzene emulsion (colored with methylene blue) by TFB-BD(Me)<sub>2</sub> COFs powder which was fixed into the cusp of a syringe: (a) during separation and (b) after separation. It can be clearly seen that the filtrate is clear and colorless. The separation flux and separation efficiency were about 1698 L·m<sup>-2</sup>·h<sup>-1</sup> and 97.2%, respectively.

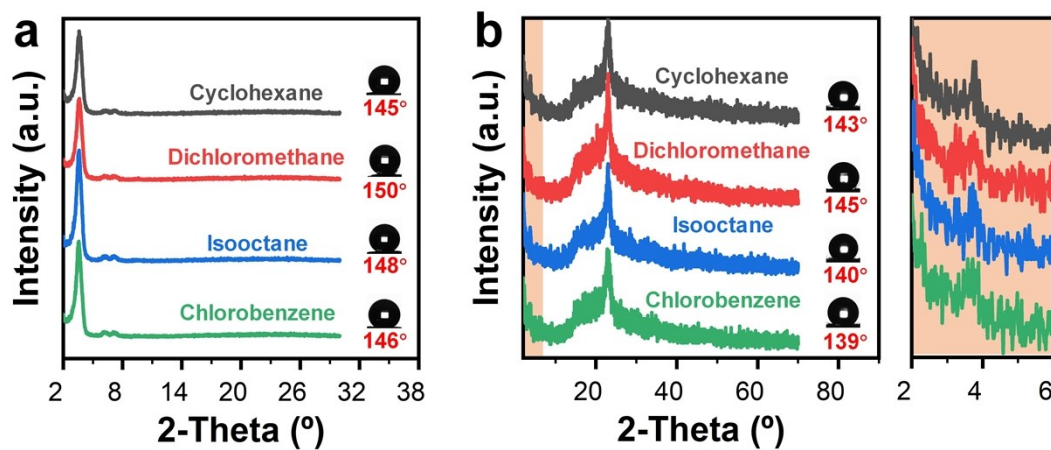


**Fig. S12** Separation of water-in-chlorobenzene emulsion by pristine cotton fabric.





**Fig. S13** SEM images of the TFB-BD(Me)<sub>2</sub> COFs coated fabric after undergone 500 mL of water-in-chlorobenzene emulsion separation.



**Fig. S14** (a) PXRD patterns of the TFB-BD(Me)<sub>2</sub> COFs and (b) XRD patterns of the TFB-BD(Me)<sub>2</sub> COFs coated fabric after soaked in different organic solvents (cyclohexane, dichloromethane, isooctane and chlorobenzene) for 48 h. The corresponding water contact angles are inserted.

**Table S1.** Fractional atomistic coordinates for the unit cell of TFB-BD(Me)<sub>2</sub> with AA stacking mode optimized by the Forcite module.

TFB-BD(Me) <sub>2</sub> with eclipsed (AA) stacking mode			
P6/m; a=b=30.3 Å; c=3.4 Å; α=β=90°; γ=120°			
Atom	x (Å)	y (Å)	z (Å)
N1	2.8076	-2.58866	0.500
C2	2.76901	-2.58131	0.500
C3	2.67532	-2.61696	0.500
C4	2.71675	-2.62526	0.500
C5	2.55761	-2.57993	0.500
C6	2.50322	-2.60308	0.500
C7	2.48226	-2.57042	0.500
C8	2.51202	-2.51681	0.500
C9	2.56503	-2.49611	0.500
C10	2.58664	-2.52700	0.500
C11	2.53456	-2.33978	0.500

**Table S2.** Fractional atomistic coordinates for the unit cell of TFB-BD(Me)<sub>2</sub> with AB stacking mode optimized by the Forcite module.

TFB-BD(Me) <sub>2</sub> with eclipsed (AB) stacking mode			
P63/m; a=b=30.1 Å; c=6.7 Å; $\alpha=\beta=90^\circ$ ; $\gamma=120^\circ$			
Atom	x (Å)	y (Å)	z (Å)
N1	-1.72450	0.75127	0.250
C2	-1.73895	0.70286	0.250
C3	-1.71923	0.63249	0.250
C4	-1.70156	0.68519	0.250
C5	-1.77173	0.47067	0.250
C6	-1.74206	0.44590	0.250
C7	-1.76676	0.39231	0.250
C8	-1.82042	0.36236	0.250
C9	-1.84941	0.38707	0.250
C10	-1.82526	0.44051	0.250
C11	-1.84599	0.30562	0.250
C12	-1.81700	0.28091	0.250
C13	-1.84115	0.22748	0.250
C14	-1.89468	0.19731	0.250
C15	-1.92435	0.22208	0.250
C16	-1.89966	0.27566	0.250
N17	-1.91594	0.14258	0.250
C18	-1.96435	0.10862	0.250
C19	-1.98156	0.19389	0.250
C20	-1.68485	0.47408	0.250
C21	-1.98201	0.05356	0.250
C22	-2.03470	0.01853	0.250