# Supporting Information

# Fluorinated 2D Covalent Organic Frameworks with hcb Topology for Selective $C_2H_4/C_3H_6$ Separation

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### 1. Materials and methods

1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene,2,4,6-Trihydroxybenzene-1,3,5tricarbaldehyde, 4-bromo-2,6-difluoroaniline and 4-bromo-2,3,5,6-tetrafluoroaniline were purchased from Shanghai Tensus Biotech Co., Ltd. Pd(dppf)Cl<sub>2</sub>, CsF, Tetrahydrofuran, 1,4-Dioxane, dichloromethane, N, N-dimethylformamide, N, N-dimethylacetamide (DMA, 99%), Dimethyl sulfoxide, 1,2-dichlorobenzene and Acetic Acid were purchased from Tokyo Chemical Industry Co., Ltd., All the materials were used as received without further purification.

**Solution nuclear magnetic resonance (NMR):** Liquid state <sup>1</sup>H nuclear magnetic resonance spectroscopy was collected on a Varian Mercury Plus 400 NMR Spectrometer.

**Solid-state nuclear magnetic resonance (ssNMR):** Solid-state nuclear magnetic resonance (NMR) data were performed on a Bruker AVANCE III 600 spectrometer with cross-polarization magic-angle-spinning (CP/MAS) at a resonance frequency of 150.9 MHz. <sup>13</sup>C CP/MAS NMR spectra were recorded using a 4 mm MAS probe and a spinning rate of 14 kHz. A contact time of 4 ms and a recycle delay of 2 s were used for the 13C CP/MAS NMR measurement. The chemical shifts of 13C were externally referenced to tetramethylsilane (TMS).

**Fourier transform infrared (FT-IR):** IR spectrum was measured on an IR spectrometer (Nicolet 6700) between the ranges of 4000 to 400 cm<sup>-1</sup>.

**Power X-ray diffraction (PXRD):** PXRD patterns were collected on an X-ray diffraction (XRD) system (DX-27mini, China) using Cu Kα radiation.

**Scanning electron microscopy (SEM):** SEM images were collected using a GeminiSEM 500 system. **Transmission electron microscope (TEM):** TEM images were obtained with a Tecnai G2 F30 STwin.

**Thermogravimetric analysis (TGA):** TGA was performed using a TA Q600. When under flowing N<sub>2</sub> atmosphere, the samples were heated in a Platinum pan (800 °C, 10 °C min<sup>-1</sup>) under a N<sub>2</sub> flux (60 mL min<sup>-1</sup>).

**Sorption isotherm for N<sub>2</sub>:** Micrometrics ASAP2040 system were used to measure the specific surface area and pore structure using nitrogen as the adsorbate at 77 K, after outgassing the samples overnight at 120 °C.

**Gas sorption:** The samples were activated under vacuum for 12 hours at 120 °C. Gas adsorption experiments at 298 K were performed by using JW-BK200 surface area analyzer. A circulation constant temperature water bath was used to stabilize the temperature at 298 K during the test.

**Crystal structure modeling**: Crystal structure modeling: The unit cell parameters of the COFs were obtained from the indexing of the PXRD peaks using the Dicvol (Reflex module in the Materials

Studio program) <sup>1</sup>, the structural modeling of COFs was generated using the Building (Crystal) module, the lattice model was geometrically optimized using force-filed based method (Forcite molecular dynamics module). The Pawley fitting (Reflex module) was performed to optimize the lattice parameters iteratively until the *R*wp value converges and the overlay of the observed with refined profiles shows good agreement.

### Calculation of selectivity via ideal adsorption solution theory (IAST):

The gas adsorption isotherms were first fitted to a dual-site Langmuir-Freundlich (DSLF) model (eqn (3)), where is the amount of adsorbed gas q (mmol g<sup>-1</sup>), P is the bulk gas phase pressure (atm), qsat is the saturation amount (mmol g<sup>-1</sup>), b is the Langmuir-Freundlich parameter (atm<sup>- $\alpha$ </sup>), and  $\alpha$  is the Langmuir-Freundlich exponent (dimensionless) for two adsorption sites A and B indicating the presence of weak and strong adsorption sites.

$$q = q_{A,sat} \frac{b_A p}{1 + b_A p} + q_{B,sat} \frac{b_B p}{1 + b_B p}$$
(3)

IAST starts from the Raoult's Law type of relationship between the fluid and adsorbed phase (4) and (5), where  $P_i$  is the partial pressure of component i (atm), P is the total pressure (atm), and  $y_i$  and  $x_i$  represent mole fractions of component i in gas and the adsorbed phase (dimensionless).  $P_i^0$  is the equilibrium vapour pressure (atm).

$$P_{i} = Py_{i} = P_{i}^{0}x_{i}$$

$$\sum_{i=1}^{n} x_{i} = \sum_{i=1}^{n} \frac{P_{i}}{P_{i}^{0}} = 1$$
(5)

In IAST, *P* is defined by relating to spreading pressure  $\pi$  (6), where  $\pi$  is the spreading pressure, S is the specific surface area of the adsorbent (m<sup>2</sup> g<sup>-1</sup>), R is the gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>), T is the temperature (K), and  $q_i(P_i)$  is the single component equilibrium obtained from isotherms (mmol g<sup>-1</sup>).

$$\frac{\pi S}{RT} = \int_{0}^{p_{0}^{0}} i \frac{q_{i}(P_{i})}{P_{i}} dp_{i} = \Pi(condtant)$$

For a DSLF model, we have an analytical expression for the integral (7). The isotherm parameters are derived from the previous fitting. For a binary component system, the unknowns will be  $\Pi$ , *P*, and which can be obtained by simultaneously solving eqn (5) and (7).

$$\int_{0}^{p_{0}^{0}} i \frac{q_{i}(P_{i})}{P_{i}} dP_{i} = \Pi(condtant) = \frac{q_{sat,A}}{a_{A}} \ln\left[1 + b_{A}(P_{i}^{0})^{a_{A}}\right] + \frac{q_{sat,B}}{a_{B}} \ln\left[1 + b_{B}(P_{i}^{0})^{a_{B}}\right]$$
(7)

(6)

The adsorbed amount of each compound in a mixture is (8) and (9), where q is the adsorbed amount of component (mmol g<sup>-1</sup>), and is the total adsorbed amount (mmol g<sup>-1</sup>).

(8)

$$q_{i}^{mix} = x_{i}q_{t}$$

$$\frac{1}{q_{T}} = \sum_{i=1}^{n} \frac{x_{i}}{q_{i}(P_{i}^{0})}$$
(9)

The adsorption selectivities  $S_{ads}$  were calculated using eqn (10). In this study, IAST calculations were carried out assuming a binary mixed gas with a molar ratio of 50:50 at 298 K and pressures up to 1 atm.

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$
(10)

## 2. Synthesis and characterization

## 2.1. Synthesis of monomers



**Scheme S1.** 1,3,5-tris(3,5-difluoro-4-aminophenyl)benzene (**Df-TAPB**). 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**A**, 2.3 g, 5.0 mmol), 4-bromo-2,6-difluoroaniline (**B**, 3.6 g, 17.0 mmol), CsF (7.6 g,50.0 mmol), and Pd(dppf)Cl<sub>2</sub> (0.20 g, 0.25 mmol) were mixed in a 250 mL single neck flask, then 1,4-Dioxane (120 mL) and H<sub>2</sub>O (30 mL) were added. The mixture was heated at 110 °C for 24 hours under nitrogen atmosphere and then cooled to room temperature, followed by extraction with dichloromethane. After the organic phase was washed with brine and dried over MgSO<sub>4</sub>, the organic solvent was removed under reduced pressure. Df-TAPB was purified by column chromatography (EA/petroleum ether, 1/5) and obtained as a white solid (1.9 g, yield: 83 %). <sup>1</sup>H NMR (400 MHz, *d*-DMSO, δ) 7.75(s, 3 H), 7.63(d, 6 H), 5.38(s, 6 H).



**Figure S1**. <sup>1</sup>H NMR spectrum of Df-TAPB, Solvent peaks of *d*-DMSO (a), H<sub>2</sub>O (b).



**Scheme S2.** 1,3,5-tris(2,3,5,6-tetrafluoro-4-aminophenyl)benzene (**Tf-TAPB**). 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**A**, 2.3 g, 5.0 mmol), 4-bromo-2,3,5,6-tetrafluoroaniline (**B**, 4.1 g, 17.0 mmol),CsF (7.6 g,50.0 mmol), and Pd(dppf)Cl<sub>2</sub> (0.20 g, 0.25 mmol) were mixed in a 250 mL single neck flask, then 1,4-Dioxane (120 mL) and H<sub>2</sub>O (30 mL) were added. The mixture was heated at 110 °C for 24 hours under nitrogen atmosphere and then cooled to room temperature, followed by extraction with dichloromethane. After the organic phase was washed with brine and dried over MgSO<sub>4</sub>, the organic solvent was removed under reduced pressure. Tf-TAPB was purified by column chromatography (EA/petroleum ether, 1/6) and obtained as a white solid (2.1 g, yield: 75 %).<sup>1</sup>H NMR (400 MHz, *d*-DMSO,  $\delta$ ) 7.54(s, 3 H), 6.23(d, 6 H).



**Figure S2**. <sup>1</sup>H NMR spectrum of Tf-TAPB, Solvent peaks of *d*-DMSO (a),  $H_2O$  (b).

#### 2.2 Synthesis of TpDf-COF and TpTf-COF





Scheme S3. Synthesis of TpDf-COF: A 10-mL Pyrex tube was charged with Tp (8.5 mg, 0.04 mmol), Df-TAPB (18.4 mg, 0.04 mmol) with 1,4-Dioxane (0.5 mL) and mesitylene (0.5 mL). The mixture was sonicated for 5 minutes to obtain a yellow turbid solution. To this, 9 M acetic acid (0.1 mL) were added as a catalyst. The tube was subsequently cooled to 77 K using a liquid nitrogen bath and subjected to three freeze-pump-thaw cycles for degassing. After sealing under vacuum, the tube was heated at 120 °C for 3 days. Upon cooling to room temperature, a yellow precipitate isolated by centrifugation at 40 g (6000 rpm) for 2 minutes, washed with anhydrous acetone, and subjected to solvent exchange with anhydrous tetrahydrofuran three times. The sample was dried under vacuum at 80 °C 12 hours to yield a yellow powder (18.7 mg, 78.5% isolated yield).





Scheme S4. Synthesis of TpTf-COF: A 10-mL Pyrex tube was charged with Tp (8.5 mg, 0.04 mmol), Tf-TAPB (22.7 mg, 0.04 mmol) with 1,4-Dioxane (0.5 mL) and 1,2-Dichlorobenzene (0.5 mL). The mixture was sonicated for 5 minutes to obtain a yellow turbid solution. To this, 9 M acetic acid (0.1 mL) were added as a catalyst. The tube was subsequently cooled to 77 K using a liquid nitrogen bath and subjected to three freeze-pump-thaw cycles for degassing. After sealing under vacuum, the tube was heated at 120 °C for 3 days. Upon cooling to room temperature, a yellow precipitate was isolated through centrifugation at 40 g (6000 rpm) for 2 minutes, washed with anhydrous acetone, and subjected to solvent exchange with anhydrous tetrahydrofuran three times. The sample was dried under vacuum at 80 °C 12 hours to yield a yellow powder (25.1 mg, 86.2% isolated yield).

## 2.3. Characterization of TpDf-COF and TpTf-COF



Figure S3. FT-IR spectra of Tp, Df-TAPB, and TpDf-COF.



Figure S4. FT-IR spectra of Tp, TF-TAPB, and TpTf-COF.



Figure S5. Solid-state <sup>13</sup>C CP/MAS NMR spectrum of TpDf-COF.



Figure S6. Solid-state <sup>13</sup>C CP/MAS NMR spectrum of TpTf-COF.



Figure S7. TGA curves of TpDf-COF and TpTf-COF under  $N_2$  atmosphere conditions.



**Figure S8.** PXRD patterns of TpDf-COF after immersion in various solvents for 72 hours, demonstrating its structural stability.



**Figure S9.** PXRD patterns of TpTf-COF after immersion in various solvents for 72 hours, demonstrating its structural stability.







**Figure S12**. (a) PXRD patterns of TpDf-COF: comparison of the experimental profile with simulated patterns based on AA, AB, and ABC stacking models. (b) Structural models of TpDf-COF illustrating the AA, AB, and ABC stacking arrangements.



Figure S13. (a) PXRD patterns of TpTf-COF: comparison of the experimental profile with simulatedpatterns based on AA, AB, and ABC stacking models. (b) Structural models of TpTf-COF illustratingtheAA,AB,andABCstackingarrangements.

| Spa                  | ace group | ŀ  | 23      |  |
|----------------------|-----------|--|---------|--|
| Calculated unit cell |           | a = 18.4498 Å, b = 18.4498 Å,                    |         |  |
|                      |           | <i>c</i> = 3.5013 Å                              |         |  |
|                      |           | $\alpha = 90.0000^\circ, \beta = 90.0000^\circ,$ |         |  |
|                      |           | γ = 120.0000°                                    |         |  |
| Atoms                | X         | Y  | Z       |  |
| C1                   | 0.75221   | 0.36807  | 0.55117 |  |
| C2                   | 0.71786   | 0.4192   | 0.55052 |  |
| 03                   | 0.83585   | 0.40274  | 0.55438 |  |
| C4                   | 0.77424   | 0.50878  | 0.55162 |  |
| N5                   | 0.74914   | 0.56109  | 0.51778 |  |
| C6                   | 0.81516   | 0.78258  | 0.4299  |  |
| C7                   | 0.76725   | 0.6972   | 0.43342 |  |
| C8                   | 0.80167   | 0.6485   | 0.5207  |  |
| C9                   | 0.88568   | 0.68668  | 0.61059 |  |
| C10                  | 0.93386   | 0.77212  | 0.61224 |  |
| C11                  | 0.89964   | 0.82192  | 0.52037 |  |
| C12                  | 0.95124   | 0.91348  | 0.51979 |  |
| F13                  | 0.92141   | 0.64188  | 0.70457 |  |
| F14                  | 0.68641   | 0.66128  | 0.34537 |  |
| C15                  | 0.91534   | 0.96305  | 0.51977 |  |
| H16                  | 0.71789   | 0.41925  | 0.22493 |  |
| H17                  | 0.84449   | 0.53497  | 0.58389 |  |
| H18                  | 0.78499   | 0.82147  | 0.35156 |  |
| H19                  | 1.00304   | 0.80325  | 0.68977 |  |
| H20                  | 0.84429   | 0.93321  | 0.51974 |  |

**Table S1.** Unit cell parameters and fractional atomic coordinates of TpDf-COF derived fromstructural optimization based on AA stacking with hcb topology.

**Table S2.** Unit cell parameters and fractional atomic coordinates of TpTf-COF derived fromstructural optimization based on AA stacking with hcb topology.

| Space group          |         | P3   |         |  |
|----------------------|---------|--|---------|--|
| Calculated unit cell |         | a = 18.8987 Å, b = 18.8987 Å,                    |         |  |
|                      |         | <i>c</i> = 3.4925 Å                              |         |  |
|                      |         | $\alpha = 90.0000^\circ, \beta = 90.0000^\circ,$ |         |  |
|                      |         | γ = 120.0000°                                    |         |  |
| Atoms                | X       | Y  | Z       |  |
| C1                   | 0.72035 | 0.42371  | 0.50583 |  |
| C2                   | 0.62996 | 0.38651  | 0.50761 |  |
| O3                   | 0.59911 | 0.42993  | 0.51081 |  |
| C4                   | 0.7714  | 0.50481  | 0.50207 |  |
| C5                   | 0.0355  | 0.9512   | 0.50549 |  |
| C6                   | 0.95012 | 0.91383  | 0.50554 |  |
| C7                   | 0.89733 | 0.82263  | 0.50467 |  |
| C8                   | 0.81288 | 0.78475  | 0.41977 |  |
| C9                   | 0.76395 | 0.69971  | 0.42066 |  |
| C10                  | 0.79739 | 0.65004  | 0.49921 |  |
| C11                  | 0.88112 | 0.68656  | 0.58428 |  |
| C12                  | 0.93037 | 0.77163  | 0.58896 |  |
| N13                  | 0.74441 | 0.56314  | 0.49156 |  |
| F14                  | 0.91559 | 0.64053  | 0.67158 |  |
| F15                  | 0.68323 | 0.66516  | 0.33743 |  |
| F16                  | 0.77693 | 0.82923  | 0.32803 |  |
| F17                  | 0.01019 | 0.80333  | 0.68464 |  |
| H18                  | 0.84028 | 0.53036  | 0.50736 |  |
| H19                  | 0.05336 | 0.92665  | 0.76378 |  |
| H20                  | 0.04821 | 0.92453  | 0.23893 |  |
| H21                  | 0.95007 | 0.91374  | 0.83195 |  |
| H22                  | 0.67813 | 0.54214  | 0.47634 |  |



Figure S14. SEM image and TEM elemental mapping of TpDf-COF.



Figure S15. SEM image and TEM elemental mapping of TpTf-COF.



Figure S16. TEM image of TpDf-COF.



Figure S17. TEM image of TpTf-COF.

**Table S3.** Summary of  $C_2H_4$  and  $C_3H_6$  adsorption capacities and  $C_2H_4/C_3H_6$  (50/50, v/v) IAST selectivities for various porous materials at 298 K and 100 kPa.

| Porous materials | q, C₂H₄<br>(mmol·g⁻¹) | q <i>,</i> C₃H <sub>6</sub><br>(mmol·g⁻¹) | C <sub>3</sub> H <sub>6</sub> /C <sub>2</sub> H <sub>4</sub><br>selectivity | Refs.        |
|------------------|-----------------------|---|---|--------------|
| TpDf-COF         | 1.39                  | 3.32                                      | 6.1   | This<br>work |
| TpTf-COF         | 0.81                  | 4.25                                      | 9.2   | This<br>work |
| Mn-dtzip         | 3.4                   | 9.6                                       | 8.6   | 2            |
| Zn-BPZ-SA        | 2.8                   | 3.0                                       | 4.8   | 3            |
| Zn-BPZ-TATB      | 4.1                   | 5.1                                       | 7.4   | 4            |
| spe-MOF          | 2.2                   | 10.5                                      | 7.7   | 5            |
| UPC-33           | 1.4                   | 4.2                                       | 5.7   | 6            |
| NEM-7-Cu         | 1.3                   | 3.4                                       | 8.6   | 7            |
| iso-MOF-4        | 3.3                   | 11.4                                      | 7.7   | 8            |
| MFM-202a         | 2.9                   | 7.2                                       | 8.4   | 9            |

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