Supplementary Materials for

Understanding Fragility and Engineering Activation Stability in Two-Dimensional Covalent Organic Frameworks

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Supplementary Text

Section 1. Materials, Instrumentation and Methods

Chemicals. All chemicals were purchased from commercial sources and used without further purification. 1,3,5-tris(4-aminophenyl)benzene (TAPB), 2,5-dibromoterephthalaldehyde (BrPDA), tetrafluoroterephthalaldehyde (FPDA) and 4,4'-diformylbiphenyl (DFBP) were purchased from Ambeed; [1,1'-biphenyl]-4,4'-diamine (BPDA) or benzidine (BZD), terephthaldehyde (PDA), 2,5-dimethoxyterephthalaldehyde (OMePDA) and tris(4-Formylphenyl)amine (TFPA) were purchased from Sigma Aldrich. 1,3,5-Tri(4-formylphenyl)benzene (TFPB), benzene-1,3,5-tricarbaldehyde (BTCA), 2,5-dihydroxy-1,4-benzenedicarboxaldehyde (OHPDA), 2,5-dichloroterephthalic dicarboxaldehyde (ClPDA), 1,3,6,8-tetrakis(4-aminophenyl)pyrene (Py), 2',5'-dimethoxy-[1,1':4',1"-terphenyl]-4,4"-dicarbaldehyde (OMe3P), [1,1':4',1"-terphenyl]-4,4"-dicarbaldehyde (3P), 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (TTAPP) and bis(octyloxy)terephthalaldehyde (C8PDA) were purchased from Jilin Chinese Academy of Sciences - Yanshen Technology Co., Ltd. Solvents including anhydrous 1-butanol, 1,4-diclorobenzene (o-DCB), dioxane and mesitylene were purchased from Sigma Aldrich. All other solvents used in this work were purchased from Fisher Scientific.
Section 2. Understanding fragility

2.1 Pore size series

2.1.1. TAPB-BTCA COF

Figure S1. Pore size distributions of TAPB-BTCA COF calculated using QSDFT model.
Figure S2. FTIR spectra of TAPB, BTCA monomers and TAPB-BTCA COF.
2.1.2. TAPB-TFPB COF

Figure S3. Pore size distributions of TAPB-TFPB COF calculated using QSDFT model.
Figure S4. FTIR spectra of TAPB, TFPB monomers and TAPB-TFPB COF.
2.1.3. TAPB-PDA COF

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Figure. S15. The ratio of BET surface areas after PFH and THF activation ($S_{\text{BET}}(\text{THF})/S_{\text{BET}}(\text{PFH})$) and those after MeOH and THF activation ($(S_{\text{BET}}(\text{THF})/S_{\text{BET}}(\text{MeOH}))$. 

2.2. Pore functionality series

2.2.1. TAPB-FPDA COF

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2.2.2. TAPB-OHPDA COF

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2.2.5. TAPB-OMePDA COF

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2.2.6. Comparison of fragility for COFs with different pore functionalities

Figure. S30. The ratio of BET surface areas after PFH and THF activation ($S_{BET}(THF)/S_{BET}(PFH)$) and those after MeOH and THF activation ($S_{BET}(THF)/S_{BET}(MeOH)$). The substituents are ordered in terms of their impact on activation stability, not in terms of size or polarity.
2.3. Pore architecture series

2.3.1. Py-1P COF

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2.3.2. Py-2P COF

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2.3.3. Py-OH1P COF

![Graph](image)

Figure. S35. Pore size distributions of Py-OH1P COF calculated using QSDFT model.
Figure. S36. FTIR spectra of Py, OHPDA monomers and Py-OH1P COF.
2.3.4. Py-OMe3P COF

Py-OMe3P COF has not been reported, so we did the Pawley refinement and simulated its structure. Structural modeling of COFs was generated using the Materials Studio program employing the Building (Crystal) module. The lattice model was geometrically optimized using force-field based method (Forcite, UFF, Qeq, Ewald summations) and SCC-DFTB (DFTB + module). The Pawley fitting (Reflex module) was performed to optimize the lattice parameters iteratively until the Rwp value converges and the overlay of the observed with refined profiles shows good agreement. We have deposited the crystallographic information file of the Py-OMe3P COF to the CCDC database with a deposition number: 2191120.

![Experimental, Pawley refined and simulated PXRD for Py-OMe3P COF.](image)

Figure. S37. Experimental, Pawley refined and simulated PXRD for Py-OMe3P COF.
Figure. S38. Simulated structure for Py-OMe3P COF.
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Figure. S42. FTIR spectra of Py, OMe3P monomers and Py-OMe3P COF.
2.3.5. Porphyrin COFs

In addition to hexagonal and rhombic topology, COFs with tetragonal topology are also widely investigated and represent the typical COF types with homogenous pore structures. We designed a series of COFs with tetragonal topology using the porphyrin nodes and different aldehyde linkers including linkers with different length and functionalities. However, possibly due to the low solubility of 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (TTAPP), highly crystalline and porous COFs with tetragonal topology could not be produced even after PFH activation. Therefore, it is difficult to compare the solvent activation effect on these samples. The synthesis trials and characterization results are shown below.

Synthesis of porphyrin-based COFs (COF-366, COF-367, COF-366-OMe). The synthesis conditions for porphyrin-based COFs follow a prior publication.6,7 The detailed synthesis of COF-366 is described here. 0.04 mmol 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (TTAPP) and 0.08 mmol terephthaldehyde (PDA) were weighed and placed in a Pyrex tube, then a solvent mixture of 0.34 mL benzyl alcohol and 0.66 mL mesitylene was added. To uniformly disperse the monomers, the Pyrex tube was sonicated for 5 minutes and followed by addition of 0.1 mL 6M acetic acid as the catalyst. Finally, the Pyrex tube was flame sealed and placed in oven to react at 120 °C for 5 days. To separate the dry COF-366 powders, the produced precipitates were thoroughly washed using THF and acetone thorough centrifugation. In the last washing step, perfluorohexane was used to avoid pore collapse. After vacuum dried at 80 °C under vacuum overnight, the samples were measured for PXRD, BET and FTIR analysis. However, all COF-366, COF-367 and COF-366-OMe showed limited crystallinity and limited porosity, which are not appropriate to be used as cases for pore collapse analysis. To note, we also tried to use solvent
system composed of ethanol and mesitylene as reported by Yaghi and coworker,7 and solvent mixture of dioxane/mesitylene or o-dichlorobenzene/1-butanol, but none of them could produce crystalline porphyrin-based COFs.
1. COF-366

Scheme S1. Scheme for synthesis of COF-366.
Figure. S43. PXRD pattern for COF-366 after PFH activation.
Figure. S44. Nitrogen sorption isotherms for COF-366 after PFH activation.
Figure. S45. Pore size distributions of COF-366 calculated using QSDFT model.
Figure. S46. FTIR spectra for TTAPP, PDA and COF-366.
Scheme S2. Scheme for the synthesis of COF-367.
Figure. S47. PXRD pattern for COF-367 after PFH activation.
Figure. S48. Nitrogen sorption isotherms for COF-367.
Figure. S49. Pore size distributions of COF-367 calculated using QSDFT model.
Figure S50. FTIR spectra for TTAPP, DFBP and COF-367.
3. COF-366-OMe

Scheme S3. Scheme for the synthesis of COF-366-OMe.
Figure. S51. PXRD for COF-366-OMe after PFH activation.
Figure. S52. Nitrogen sorption isotherms for COF-366-OMe.
Figure. S53. Pore size distributions of COF-366-OMe calculated using QSDFT model.
Figure. S54. FTIR spectra for TTAPP, OMePDA and COF-366-OMe.
2.4. DFT calculation

The crystal model was performed using the plane wave basis Vienna ab initio simulation package (VASP) code. [1-2] The generalized gradient approximation in the Perdew-Burke-Ernzerhof (GGA-PBE) formulation are used with a cutoff energy of 600 eV. The vacuum space of \(\sim 20 \, \text{Å} \) is intercalated into interlamination to eliminate the interaction between layers. A 6×6 2D
grid uniform k-points is applied for Density-functional theatrical (DFT) calculations. The van der Waals (vdW) corrections were employed (DFT-D3) to calculate the interlayer distance in bulk phases.
To focus on the local interlayer interactions caused by side functionalities, we simplified the COF models by using molecular models and reduced the calculation working load. The molecular model was carried out with the Gaussian 16 code based on DFT. [3] The Becke exchange functional (B) and the Lee–Yang–Parr (LYP) correlation functional within a generalized gradient approximation (GGA) was used to describe the interaction between the ionic cores and electrons. [4-5] The hybrid basic set b3lyp/6-311+g(d,p) was employed to optimize all structures and calculate total energy.
Figure. S57. (a) Two types of dihedral angles $U$ and $Z$ between two benzenes along the $C=N$ linkage. (b) Calculated energy surface as functions of $U$ and $Z$ for the model in (a).
The moieties linked at both sides of -C=N- bonds have two types of dihedral angles $U$ and $Z$ as shown in Figure. S57A. We first calculated the energy surface as functions of $U$ and $Z$ for the model in Figure. S57A, and the results were shown in Figure. S57B. Observed from the energy surface plot, the lowest conformation energy located at the dihedral angles $(U, Z) = (\pm 40^\circ, 180^\circ)$. When $Z$ is fixed, the distortion along $U$ direction from $-90^\circ$ to $90^\circ$ resulted in minor energy change. However, when $U$ is fixed, the distortion along $Z$ direction from $90^\circ$ to $270^\circ$ result in significant energy change. Therefore, the distortion energy along dihedral angles $Z$ was significantly higher than that along $U$ direction, indicating that $Z$-direction distortion is not preferred.
Section 3. Engineering robustness through multivariate approach

3.1. Extra data for TAPB-PDAs-C8PDAs COFs

Figure. S59. FTIR spectra for TAPB-PDAs-C8PDAs COFs after PFH activation.
Figure. S60. Nitrogen sorption isotherms for TAPB-PDAx-C8PDAy COFs after PHF activation.
Figure. S61. Pore size distributions of TAPB-PDAx-C8PDAy COFs after PFH activation calculated using QSDFT model.
Figure. S62. Nitrogen sorption isotherms for TAPB-PDAx-C8PDAy COFs after THF activation.
Figure. S63. Pore size distributions of TAPB-PDAx-C8PDAy COFs after THF activation calculated using QSDFT model.
3.2. Extra data for TAPB-PDAX-OMePDAy COFs

Figure S64. Reaction scheme and schematic for tailoring COF robustness through systematic variations in pore functionality. The schematic shows that increasing the number of pore functionalities improves robustness.
Figure. S65. FTIR spectra for TAPB-PDAx-OMePDAy COFs.
Figure. S66. PXRD patterns for TAPB-PDAx-OMePDAy COFs after activation using PFH.
Figure S67. PXRD patterns for TAPB-PDAx-OMePDAy COFs after activation using THF.
Figure. S68. Nitrogen sorption isotherms for TAPB-PDAX-OMePDAy COFs after activation using PFH.
Figure. S69. Pore size distributions of TAPB-PDAx-OMePDAy COFs after PFH activation calculated using QSDFT model.
Figure S70. Nitrogen sorption isotherms for TAPB-PDAx-OMePDAy COFs after activation using THF.
Figure. S71. Pore size distributions of TAPB-PDax-OMePDAy COFs after THF activation calculated using QSDFT model.
Figure. S72. BET surface area of COFs activated by THF relative to the surface area measured after PFH activation. COFs with a higher methoxyl pore functionality content are more robust, as measured by the percentage of BET surface area retained after THF activation relative to that after PFH activation.
Table S1. Synthesis conditions for each COF

| Pore size   | Solvents, reaction conditions                                      |
|------------|-------------------------------------------------------------------|
| TAPB-BTCA  | dioxane=1.5 ml; mesitylene=1.5 ml; 6M AcOH=0.3 ml; 120 °C, 3 days |
| TAPB-TFPA  | dioxane/mesitylene/6M AcOH=5:5:1, v/v/v; 120 °C, 3 days           |
| TAPB-TFPB  | dioxane/mesitylene/6M AcOH=8:2:1, v/v/v; 120 °C, 3 days           |
| PI-2       | o-dichlorobenzene/1-butanol/6M AcOH=19:1:2, v/v/v; 120 °C, 3 days |
| Pore functiona   |                                                             |
| TAPB-FPDA  | dioxane/mesitylene/6M AcOH=8:2:1, v/v/v; 120 °C, 3 days           |
| TAPB-OHPDA  | dioxane/mesitylene/6M AcOH=8:2:1, v/v/v; 120 °C, 3 days           |
| TAPB-ClPDA  | dioxane/mesitylene/6M AcOH=8:2:1, v/v/v; 120 °C, 3 days           |
| TAPB-BrPDA  | dioxane/mesitylene/6M AcOH=8:2:1, v/v/v; 120 °C, 3 days           |
| TAPB-OMePDA | dioxane/mesitylene/6M AcOH=8:2:1, v/v/v; 120 °C, 3 days           |
| Pore architecture   |                                                             |
| Py-1P      | dioxane/mesitylene/6M AcOH=10:20:3, v/v/v; 120 °C, 7 days         |
| Py-OH1P    | o-dichlorobenzene/1-butanol/6M AcOH=5:5:2, v/v/v; 120 °C, 3 days  |
| Py-2P      | o-dichlorobenzene/1-butanol/6M AcOH=5:5:2, v/v/v; 120 °C, 3 days  |
| Py-OMe3P   | o-dichlorobenzene/1-butanol/6M AcOH=19:1:2, v/v/v; 120 °C, 3 days  |
| COFs       | $S_{\text{BET}}$(PFH) m$^2$ g$^{-1}$ | $S_{\text{BET}}$(MeOH) m$^2$ g$^{-1}$ | $S_{\text{BET}}$(THF) m$^2$ g$^{-1}$ |
|------------|----------------------------------|---------------------------------|----------------------------------|
| TAPB-BTCA  | 1022                             | 1001                            | 956                              |
| TAPB-TFPA  | 1125                             | 1140                            | 841                              |
| TAPB-TFPB  | 687                              | 651                             | 108                              |
| PI-2       | 780                              | 215                             | 224                              |
| TAPB-PDA   | 1919                             | 45                              | 30                               |
Table S3. BET surface areas for COFs with different pore functionalities

| COFs     | $S_{\text{BET}}$(PFH) m² g⁻¹ | $S_{\text{BET}}$(MeOH) m² g⁻¹ | $S_{\text{BET}}$(THF) m² g⁻¹ |
|----------|-------------------------------|-------------------------------|-------------------------------|
| TAPB-PDA | 1919                          | 45                            | 30                            |
| TAPB-FPDA | 653                          | 75                            | 55                            |
| TAPB-OHPDA | 1452                        | 1190                          | 155                           |
| TAPB-CIPDA | 1996                        | 1952                          | 1873                          |
| TAPB-BrPDA | 1689                        | 1555                          | 1559                          |
| TAPB-OMePDA | 2205                       | 2213                          | 2194                          |
Table S4. BET surface areas for COFs with rhombic topology

| COFs      | $S_{\text{BET}}$(PFH), m$^2$ g$^{-1}$ | $S_{\text{BET}}$(MeOH), m$^2$ g$^{-1}$ | $S_{\text{BET}}$(THF), m$^2$ g$^{-1}$ |
|-----------|--------------------------------------|----------------------------------------|--------------------------------------|
| Py-OH1P   | 901                                  | 938                                    | 763                                  |
| Py-1P     | 2598                                 | 2321                                   | 1504                                 |
| Py-2P     | 3312                                 | 3121                                   | 91                                   |
| Py-OMe3P  | 1786                                 | 1580                                   | 77                                   |
Table S5. Fractional atomic coordinates for Py-OMe3P COF.

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| N1   | -0.35894 | -0.38042 | 2.63619 |
| C2   | -0.43782 | -0.47476 | 3.06097 |
| C3   | -0.46893 | -0.47466 | 3.27774 |
| C4   | -0.48486 | -0.45007 | 3.39447 |
| C5   | -0.41846 | -0.4495  | 2.95891 |
| C6   | -0.42769 | -0.42683 | 2.79566 |
| C7   | -0.40889 | -0.40371 | 2.6943  |
| C8   | -0.37979 | -0.40315 | 2.74415 |
| C9   | -0.37019 | -0.42597 | 2.89833 |
| C10  | -0.38928 | -0.44884 | 3.00653 |
| C11  | -0.36413 | -0.35701 | 2.50468 |
| C12  | -0.34018 | -0.33561 | 2.4048  |
| C13  | -0.31074 | -0.34046 | 2.42846 |
| C14  | -0.34692 | -0.3099  | 2.28398 |
| C15  | -0.71257 | -0.31863 | 4.67476 |
| C16  | -0.70482 | -0.29312 | 4.7887  |
| C17  | -0.67514 | -0.28903 | 4.80993 |
| C18  | -0.75636 | -0.7236  | 5.14351 |
| C19  | -0.77871 | -0.74432 | 5.25482 |
| C20  | -0.72787 | -0.72913 | 4.8925  |
| O21  | -0.80717 | -0.73995 | 5.51837 |
| C22  | -0.81517 | -0.71286 | 5.65747 |
| H23  | -0.47433 | -0.43019 | 3.32791 |
| H24  | -0.44935 | -0.42706 | 2.74285 |
| H25  | -0.41704 | -0.38696 | 2.56782 |
| H26  | -0.34791 | -0.42571 | 2.93926 |
| H27  | -0.38144 | -0.46592 | 3.13273 |
| H28  | -0.38603 | -0.3525  | 2.4681  |
| H29  | -0.30496 | -0.35999 | 2.52379 |
| H30  | -0.36949 | -0.30592 | 2.26152 |
| H31  | -0.73525 | -0.32234 | 4.65483 |
| H32  | -0.66919 | -0.26943 | 4.90345 |
| H33  | -0.7606  | -0.70314 | 5.25402 |
|   |      |      |      |
|---|------|------|------|
| H34 | -0.81646 | -0.69842 | 5.44359 |
| H35 | -0.79873 | -0.7052 | 5.79208 |
| H36 | -0.8381 | -0.7136 | 5.86022 |
| C37 | -0.57661 | -0.5 | 4.05005 |
| C38 | -0.51552 | -0.5 | 3.61296 |
| H39 | 0.39999 | 0.5 | 2.22477 |
Table S6. Elemental analysis results for TAPB-PD\textsubscript{A}x-C8PDA\textsubscript{y} COFs

| Sample            | C wt.% | N wt.% | H wt.% |
|-------------------|--------|--------|--------|
| TAPB-PDA\textsubscript{10}-C8PDA\textsubscript{90} | 78.2   | 6.5    | 4.0    |
| TAPB-PDA\textsubscript{25}-C8PDA\textsubscript{75} | 84.5   | 6.6    | 5.3    |
| TAPB-PDA\textsubscript{30}-C8PDA\textsubscript{70} | 84.0   | 6.4    | 5.4    |
| TAPB-PDA\textsubscript{50}-C8PDA\textsubscript{50} | 83.1   | 5.6    | 6.3    |
| TAPB-PDA\textsubscript{75}-C8PDA\textsubscript{25} | 83.1   | 5.3    | 6.8    |
Table S7. BET surface areas for TAPB-PDAx-C8PDAy COFs after PFH and THF activation.

| COFs        | 90%PDA+10%C8PDA | 75%PDA+25%C8PDA | 70%PDA+30%C8PDA | 50%PDA+50%C8PDA | 25%PDA+75%C8PDA |
|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $S_{\text{BET}}$(PFH) (m² g⁻¹) | 1539            | 1904            | 1979            | 1903            | 1534            |
| $S_{\text{BET}}$(THF) (m² g⁻¹) | 28              | 534             | 822             | 1584            | 1422            |
Table S8. Elemental analysis results for TAPB-PDA$_x$-OMePDA$_y$ COFs

| Sample               | C w.t.% | N w.t.% | H w.t.% |
|----------------------|---------|---------|---------|
| TAPB-PDA$_{10}$-OMePDA$_{90}$ | 85.6    | 8.0     | 4.3     |
| TAPB-PDA$_{25}$-OMePDA$_{75}$ | 81.4    | 7.8     | 3.8     |
| TAPB-PDA$_{30}$-OMePDA$_{70}$ | 83.3    | 7.8     | 4.0     |
| TAPB-PDA$_{50}$-OMePDA$_{50}$ | 81.8    | 7.4     | 4.2     |
| TAPB-PDA$_{75}$-OMePDA$_{25}$ | 80.3    | 7.0     | 4.4     |
Table S9. BET surface areas for TAPB-PDA\textsubscript{x}-OMePDA\textsubscript{y} COFs after PFH and THF activation.

| COFs                  | 90\%PDA+10\%OMePDA | 75\%PDA+25\%OMePDA | 70\%PDA+30\%OMePDA | 50\%PDA+50\%OMePDA | 25\%PDA+75\%OMePDA |
|-----------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| \( S_{\text{BET}} \) (PFH) (m\(^2\) g\(^{-1}\)) | 1956               | 2197               | 2170               | 2391               | 2173               |
| \( S_{\text{BET}} \) (THF) (m\(^2\) g\(^{-1}\)) | 69                 | 53                 | 298                | 1611               | 2031               |
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