

## Electronic Supporting Information:

### Truxene based Porous, Crystalline Covalent Organic Frameworks and it's Applications in Humidity Sensing

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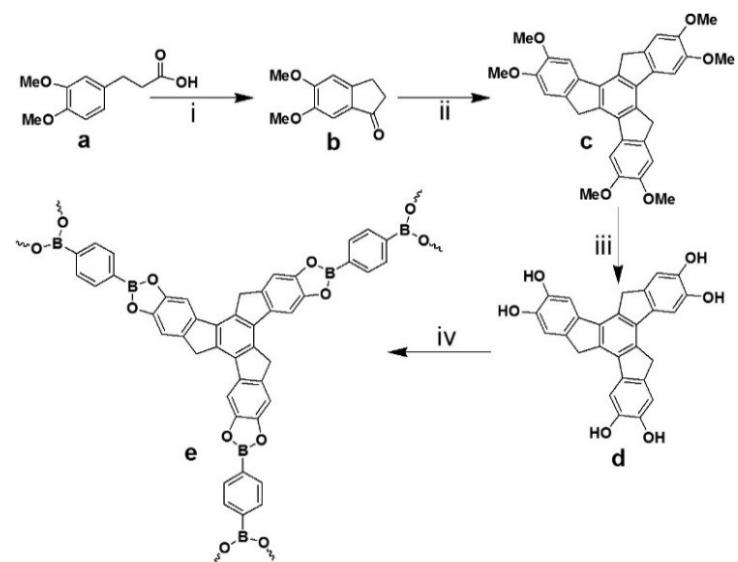
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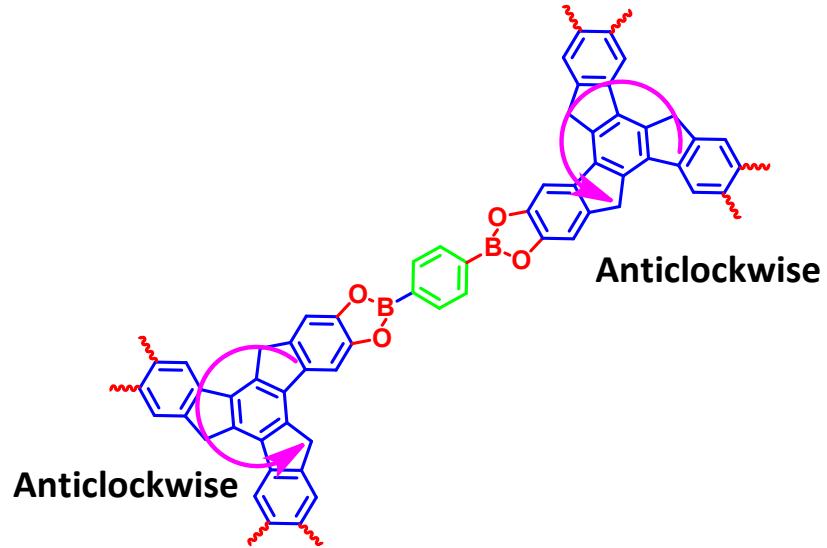
E-mail: [abirdesarkar@gmail.com](mailto:abirdesarkar@gmail.com) and [kamal@inst.ac.in](mailto:kamal@inst.ac.in)

**Synthesis Scheme:**

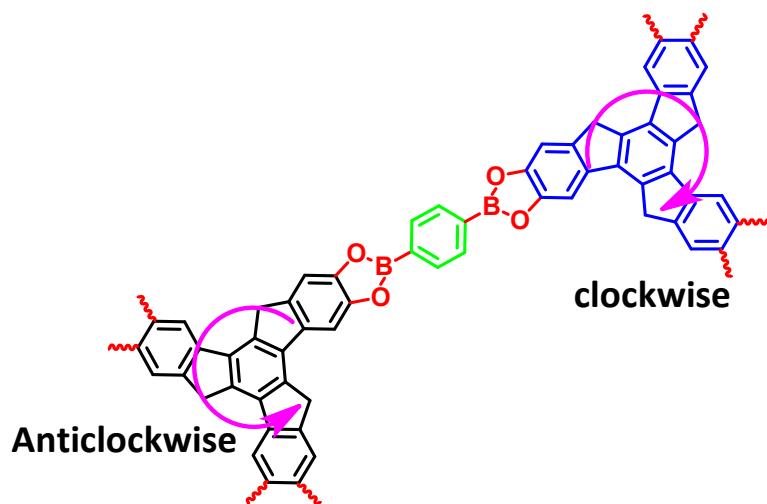


**Scheme S1** Reaction conditions:**(i)** PPA, 110 °C **(ii)** PPE, 140 °C **(iii)** BBr<sub>3</sub>, DCM **(iv)** 1,4 phenylenediboronic acid, dioxane/mesitylene/methanol (150:30:1), 110 °C.

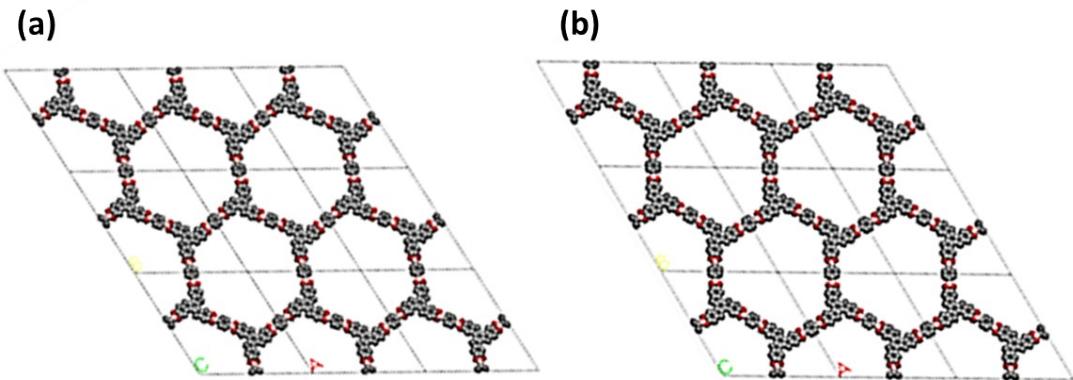
## Symmetric-COF-TXDBA (s-COF-TXDBA)



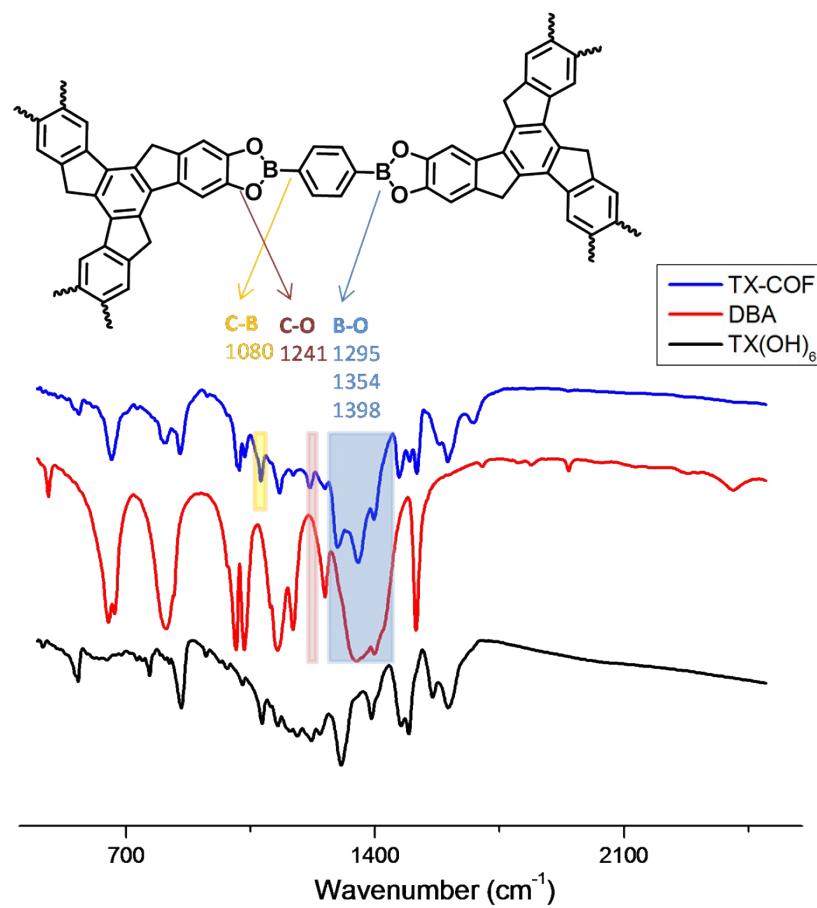
## Asymmetric-COF-TXDBA (a-COF-TXDBA)



**Scheme S2** Two possible structural arrangement of the precursors to build the periodic crystal lattices, Symmetric-COF-TXDBA (s-COF-TXDBA) and Asymmetric-COF-TXDBA (a-COF-TXDBA).

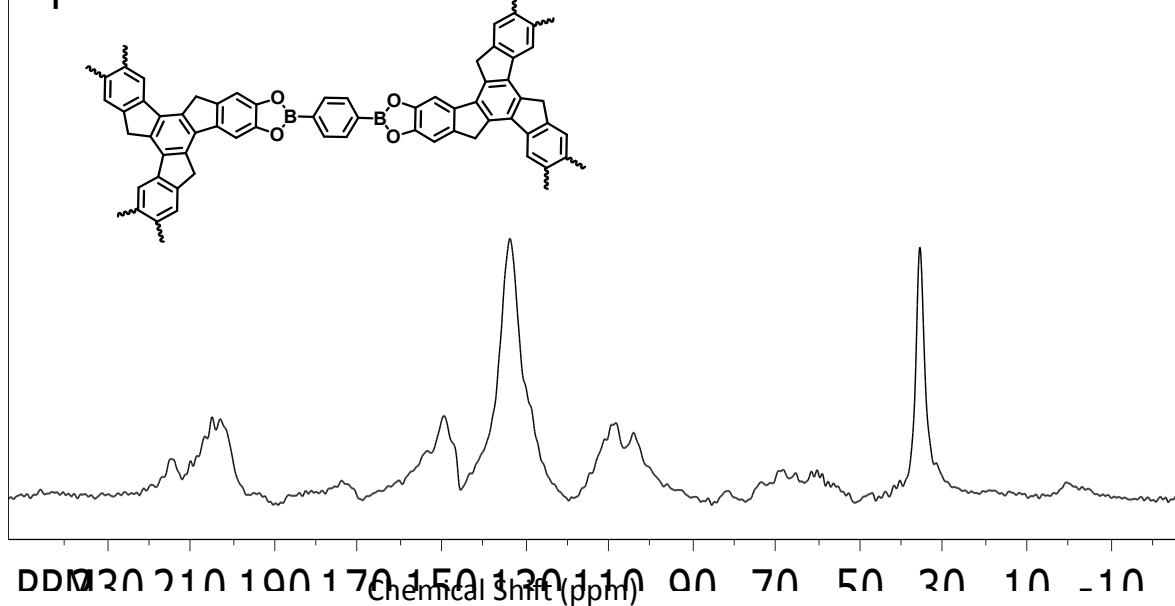


**Scheme S3** (a) Symmetric-COF-TXDBA (s-COF-TXDBA) with symmetric honeycomb like pore produced by symmetric building block; (b) Asymmetric-COF-TXDBA (a-COF-TXDBA) with asymmetric pore shape produced by asymmetric building blocks.

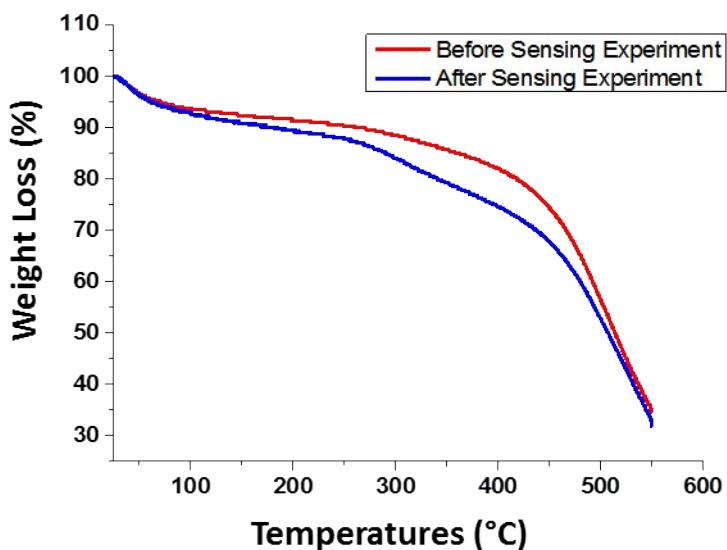


**Fig. S1** The IR spectrum of COF-TXDBA (Blue); Compound (d) (Black); 1,4-phenylenediboronic acid (Red).

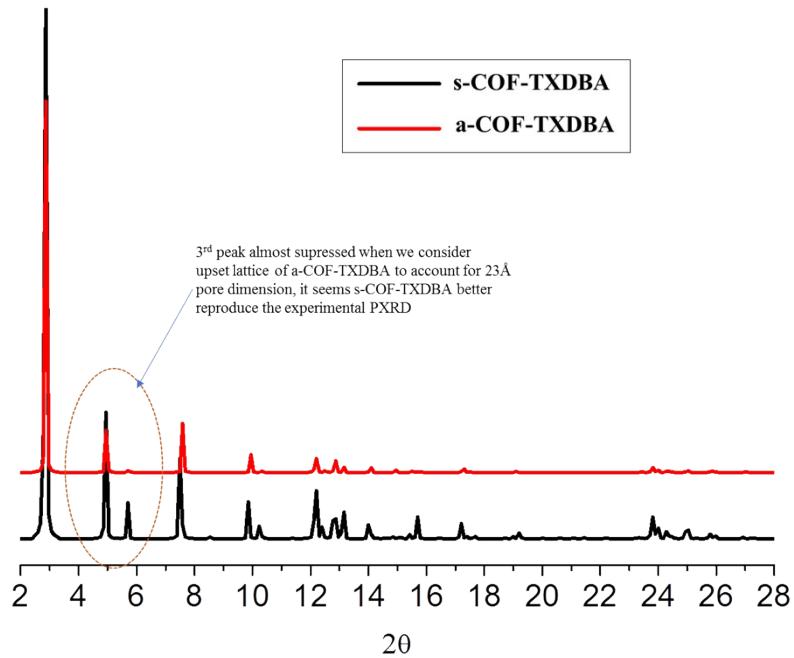
## SpinWorks 3: COF-TXDBA



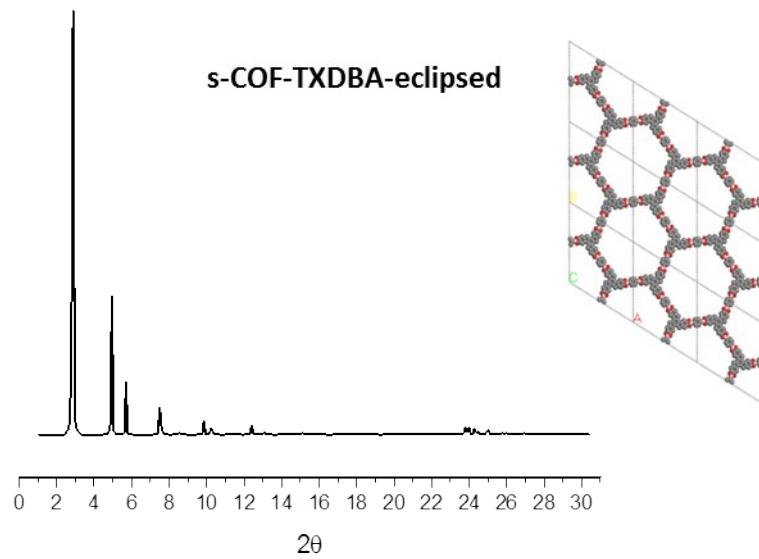
**Fig. S2** | Solid state  $^{13}\text{C}\{^1\text{H}\}$  CPMAS NMR of COF-TXDBA.



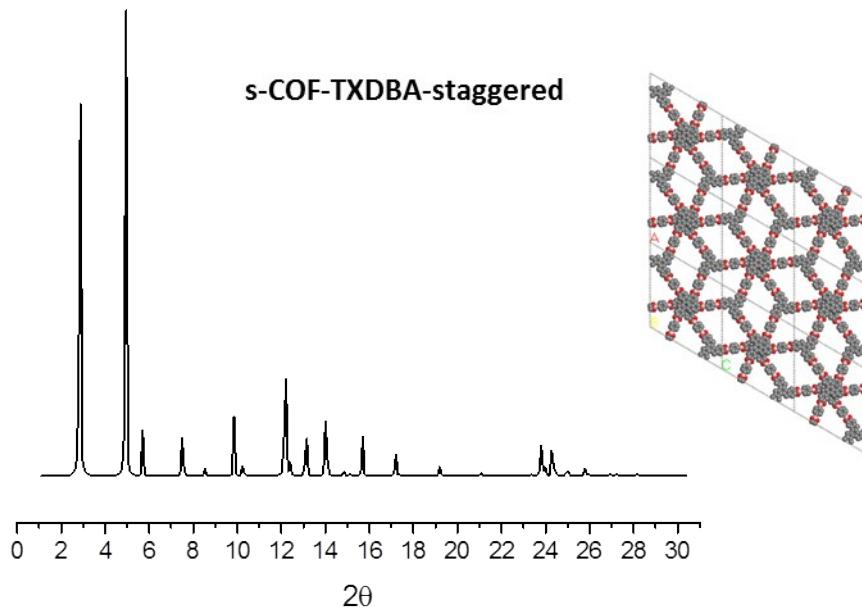
**Fig. S3** | Thermogravimetric analyses (TGA) of as synthesized COF-TXDBA shows minimal weight loss upto 410 °C. The weight loss at lower temperatures < 200 °C is attributed to the evaporation of solvent molecules present in the nano-channels of COF-TXDBA. Further, TGA analysis of sample after the sensing experiment shows nearly 10% weight loss after 250 °C as compare to as synthesized COF-TXDBA, which can be attributed to formation of small amount of oligomers during interaction of water molecule and COF-TXDBA.



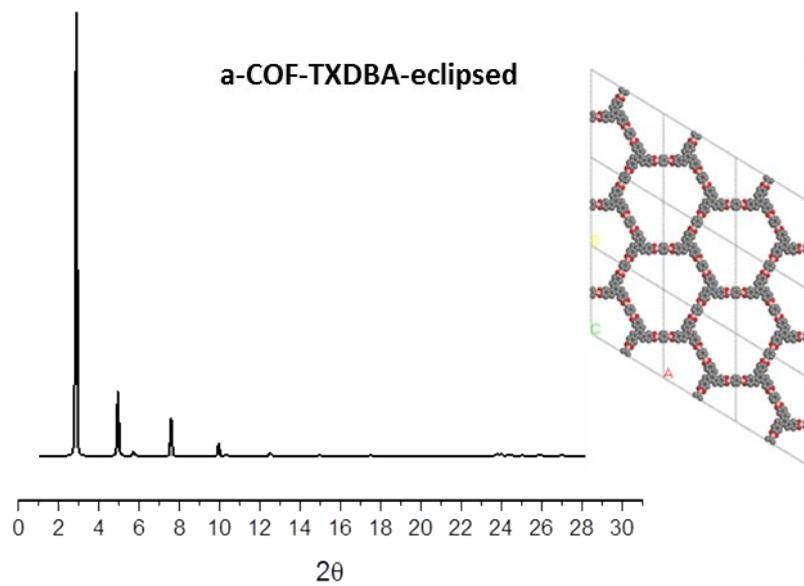
**Fig.S4** Comparisons between simulated PXRD pattern of s-COF-TXDBA and a-COF-TXDBA shows appearance of sharp intense peaks at low angle regime for s-COF-TXDBA better reproduce the experimental PXRD.



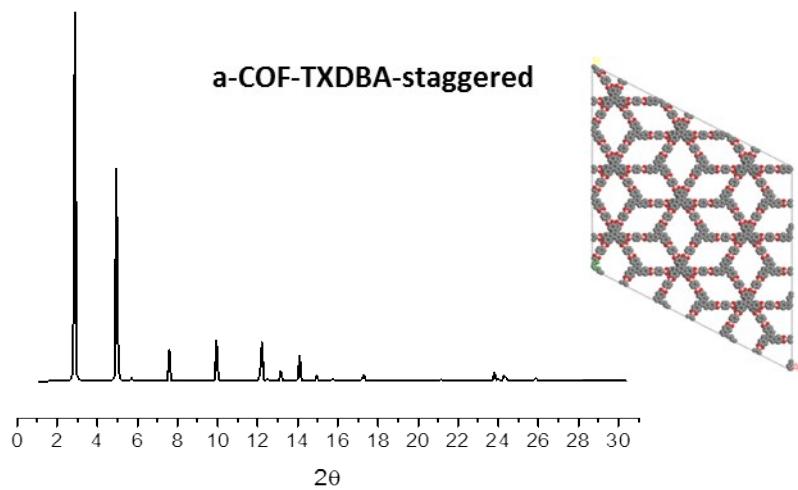
**Fig.S5** Simulated PXRD of Symmetric-COF-TXDBA in eclipsed geometry (symmetric hexagonal pore).



**Fig.S6** | Simulated PXRD of Symmetric-COF-TXDBA in staggered geometry.

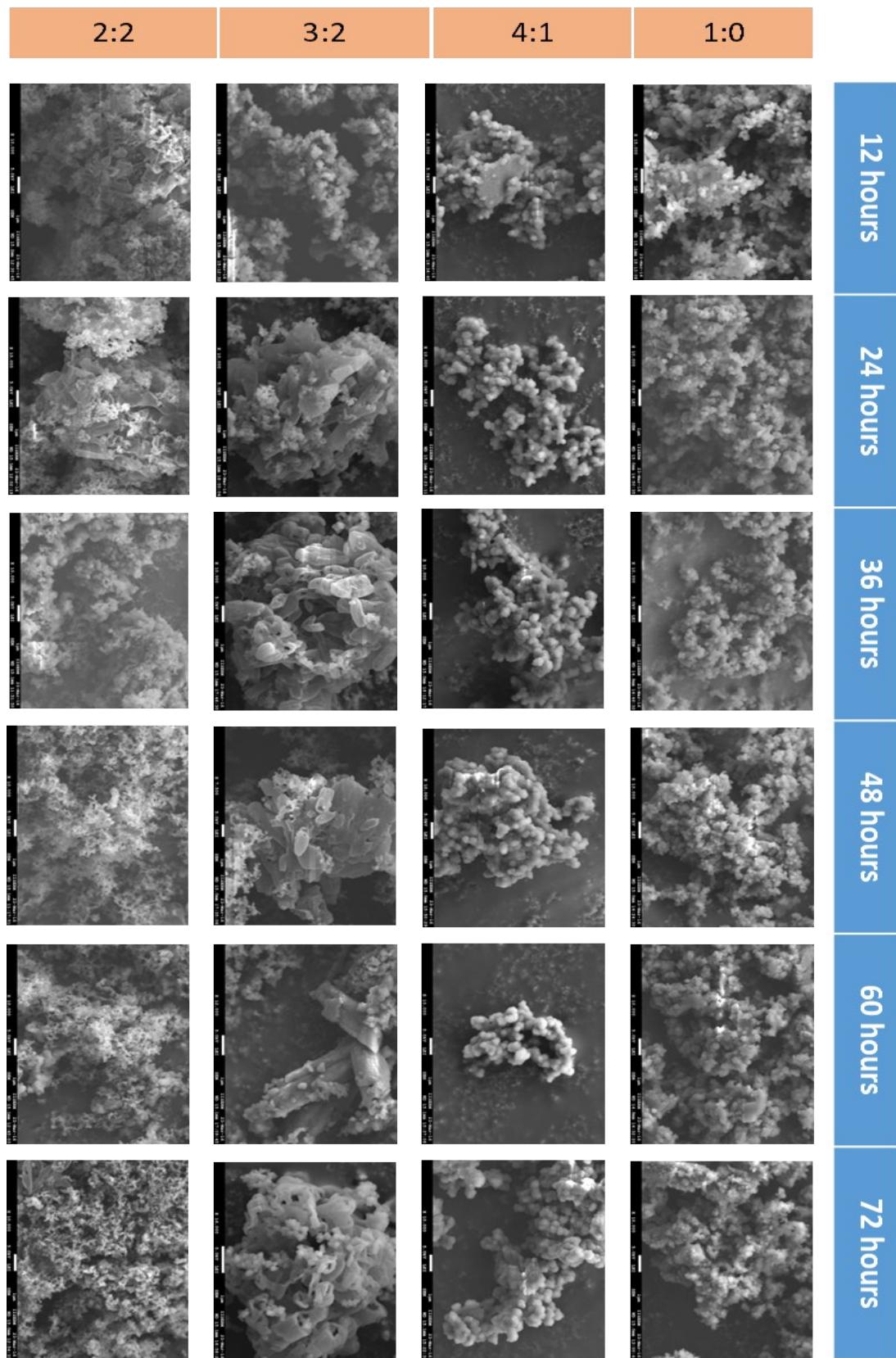


**Fig.S7** | Simulated PXRD of Asymmetric-COF-TXDBA in eclipsed geometry (asymmetric hexagonal pore).



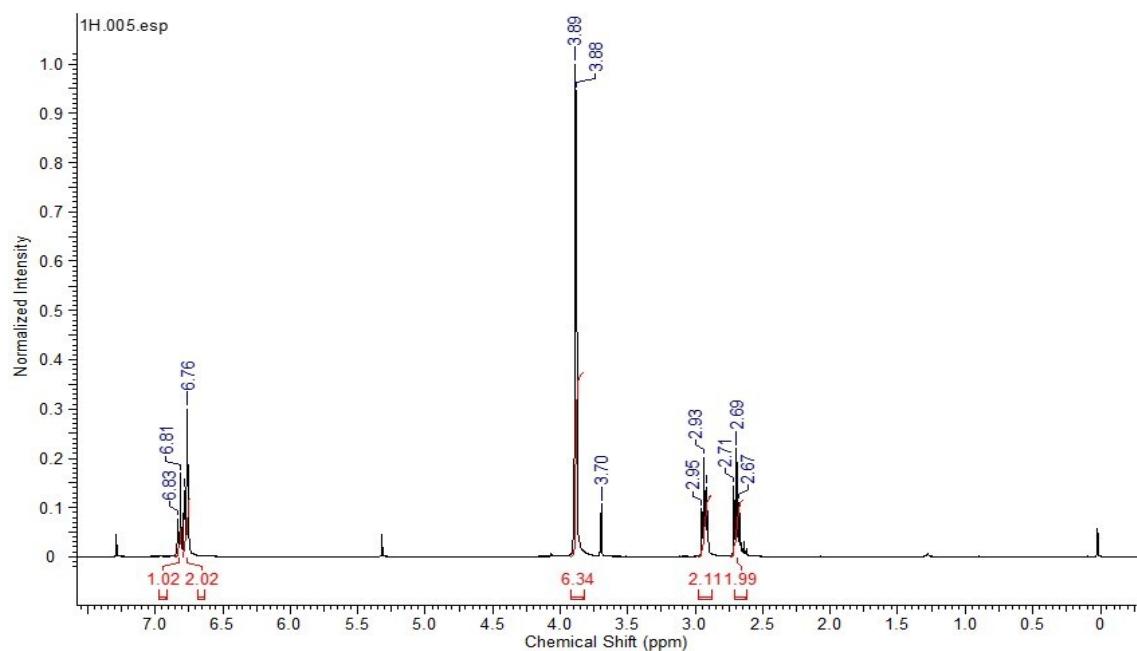
**Fig.S8** | Simulated PXRD of Asymmetric-COF-TXDBA in staggered geometry.

### Dioxane : Mesitylene

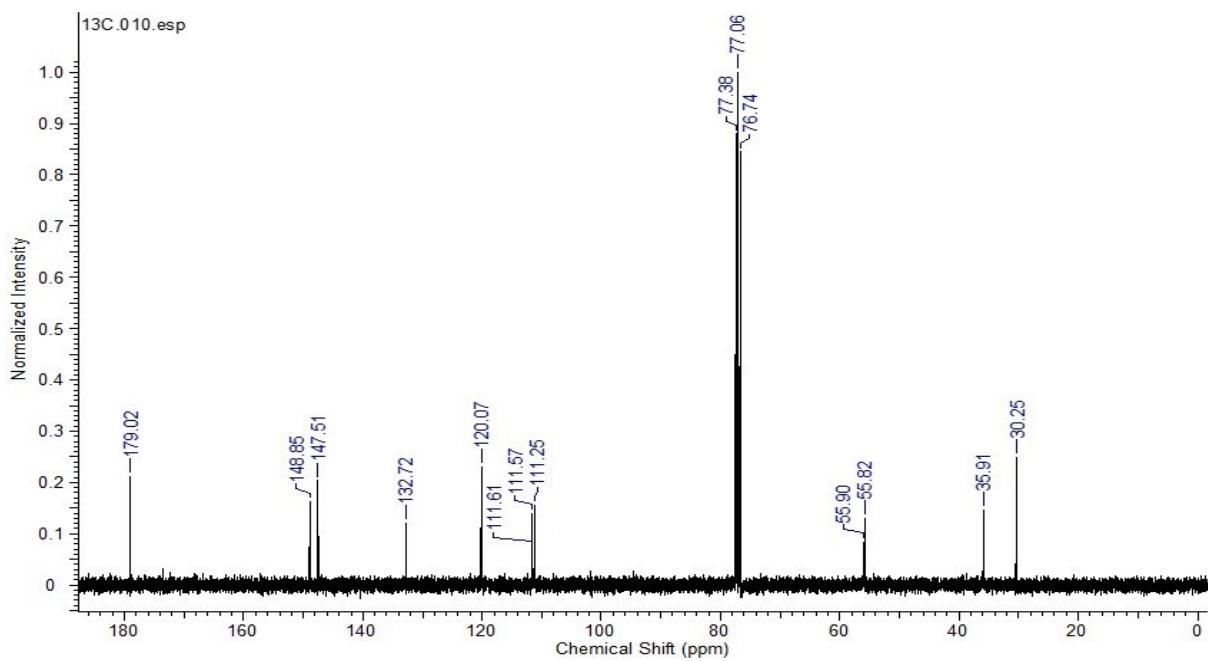


**Fig. S9** | SEM images of Truxene COF at different Mesitylene and dioxane ratio at different times shows the formation of capsules at Dioxane: Mesitylene ratio 3:2.

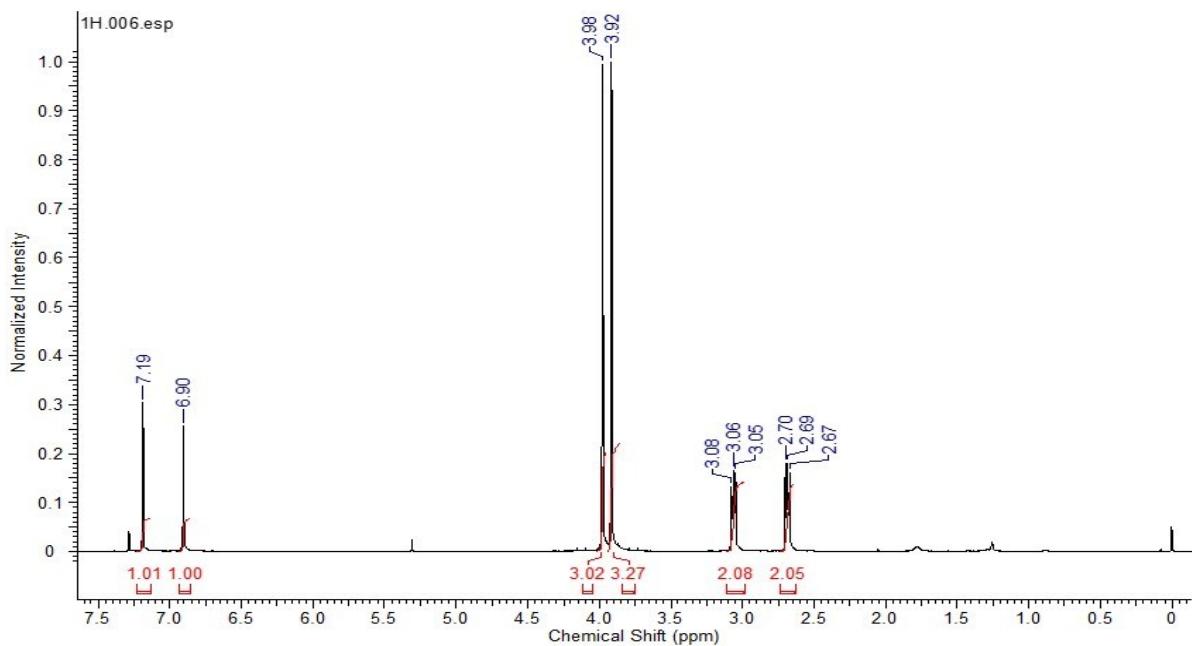
**<sup>1</sup>H NMR spectra of compound (a).**



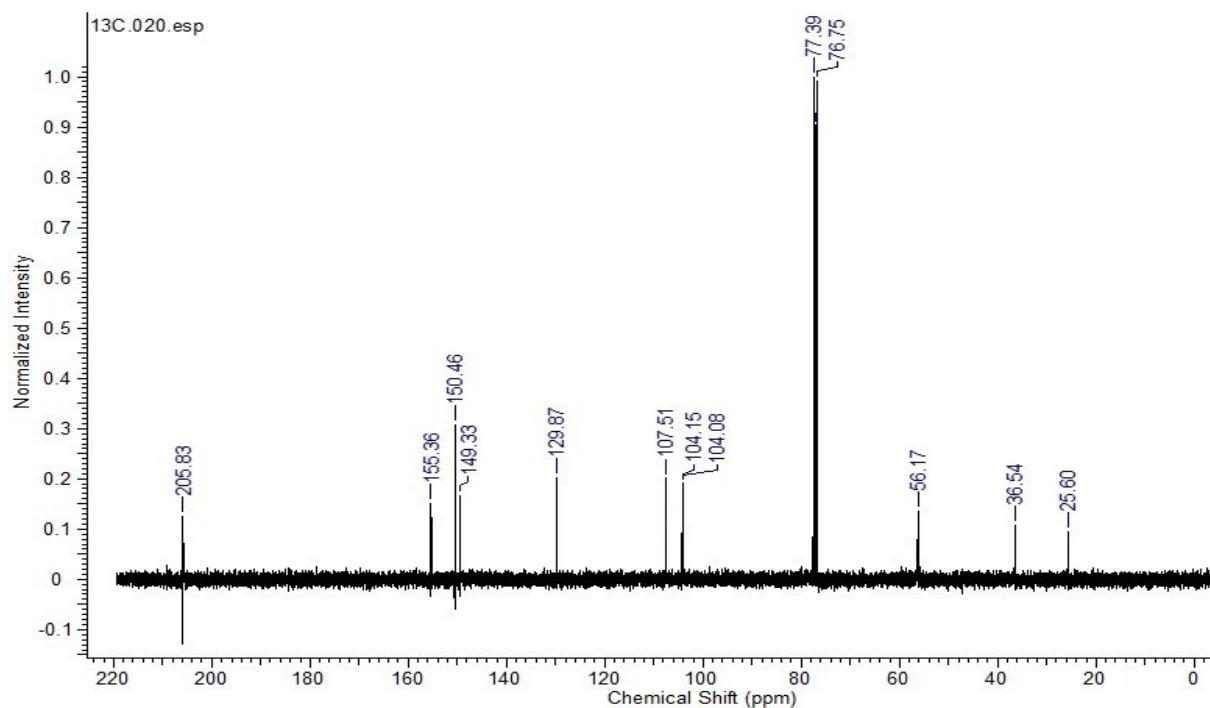
**$^{13}\text{C}$  NMR spectra of compound (a).**



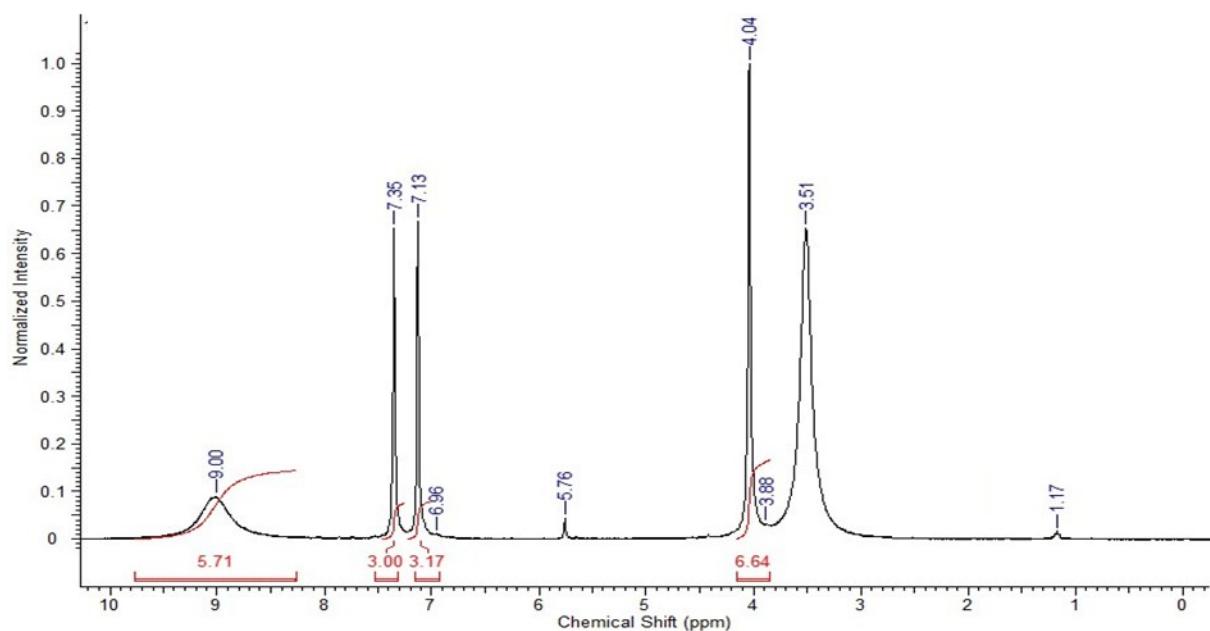
**$^1\text{H}$  NMR spectra of compound (b).**



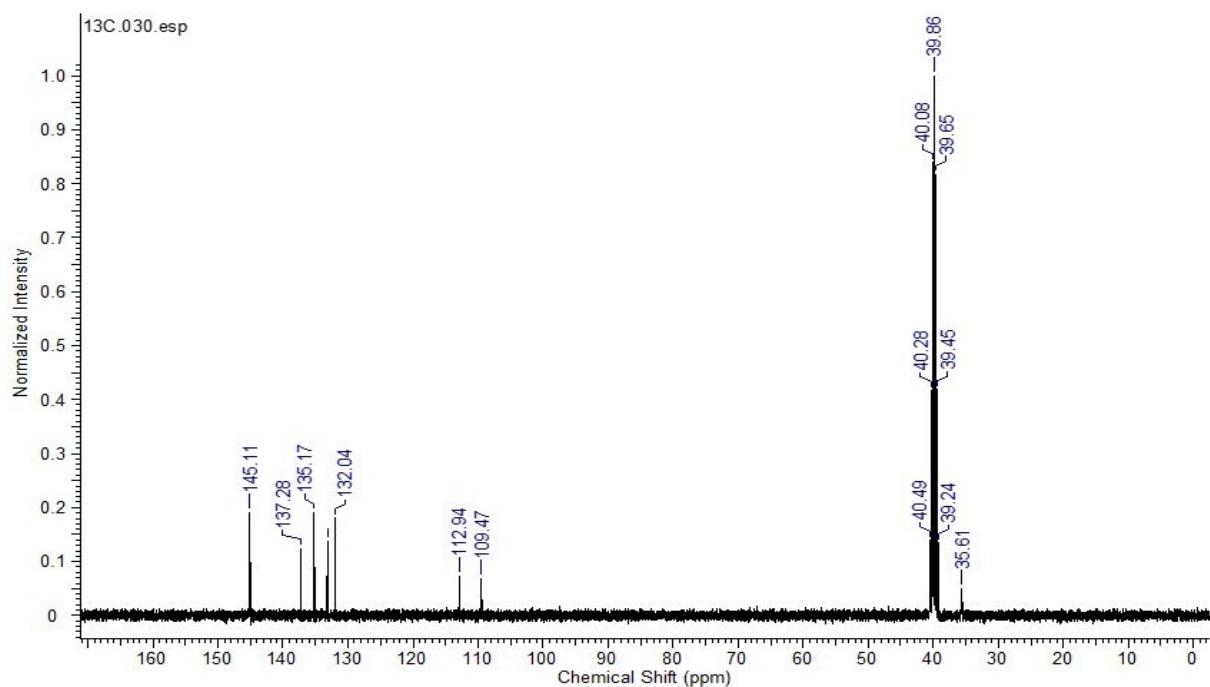
**$^{13}\text{C}$  NMR spectra of compound (b).**

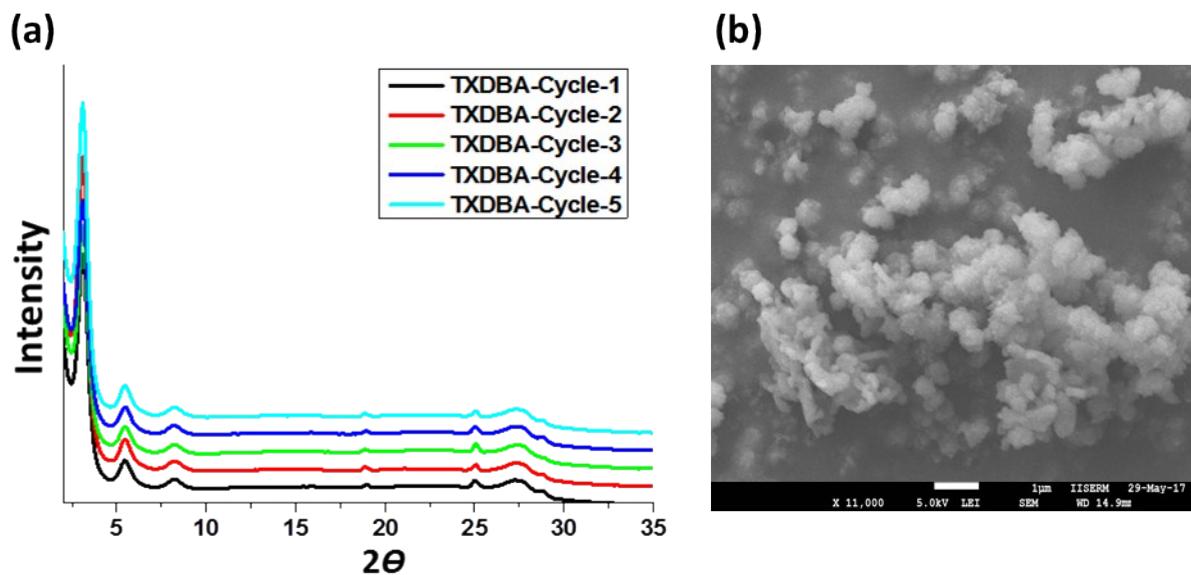


**$^1\text{H}$  NMR spectra of compound (d).**

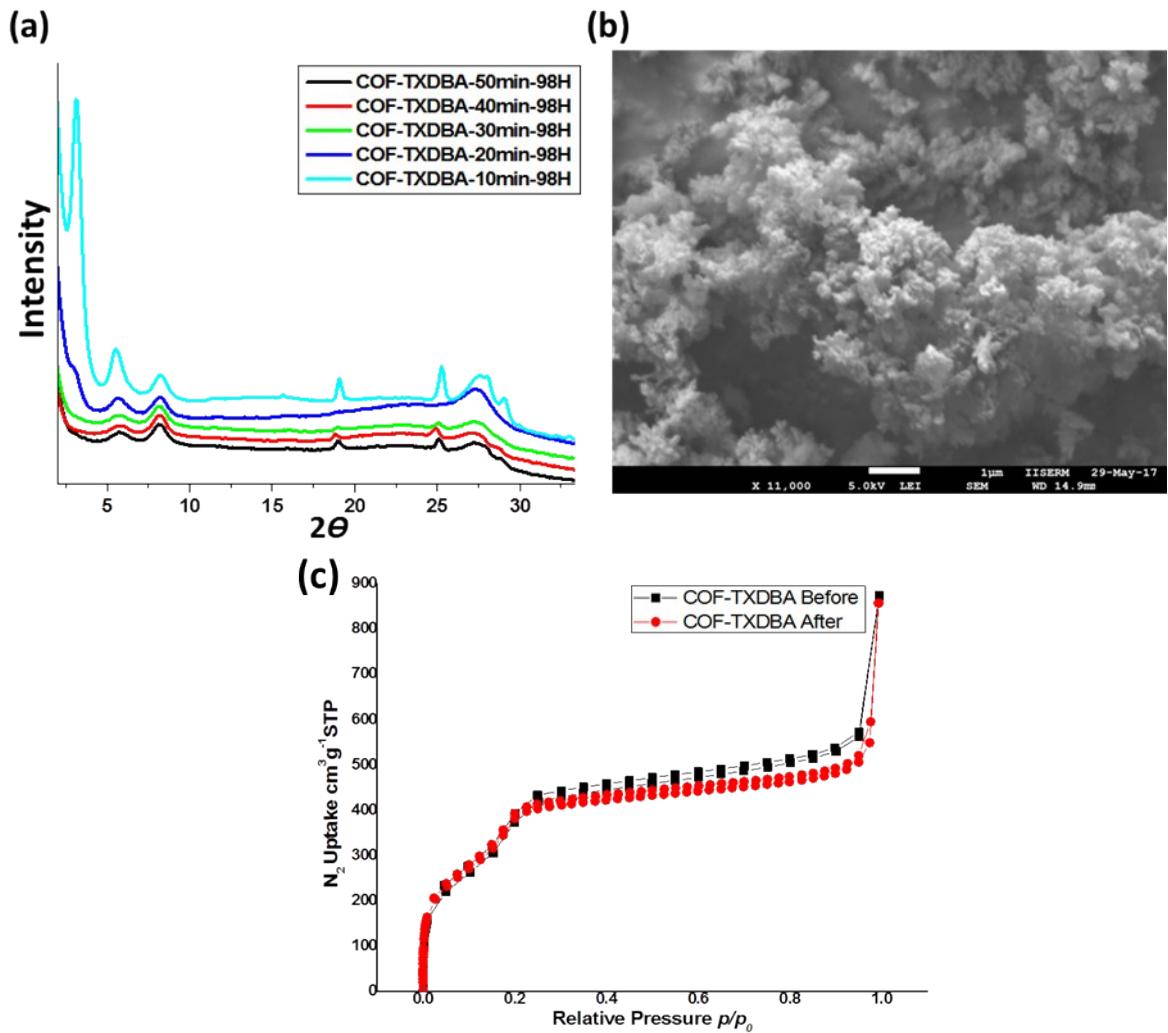


**<sup>13</sup>C NMR spectra of compound (d).**

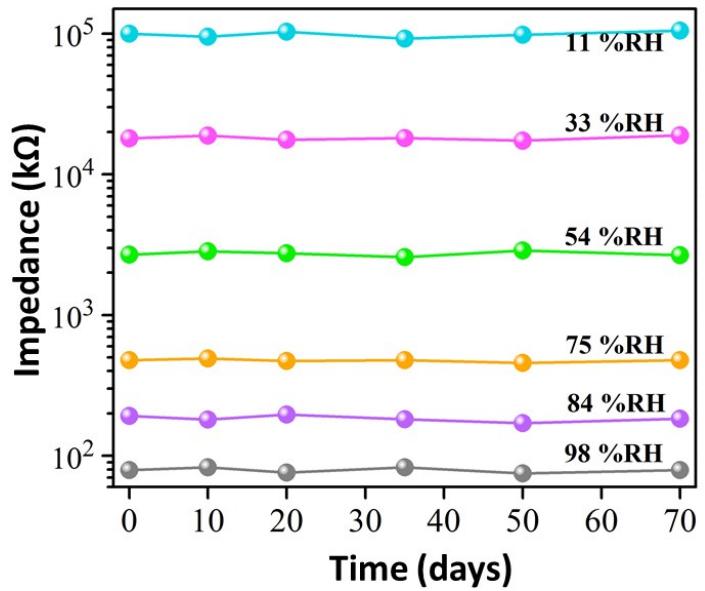




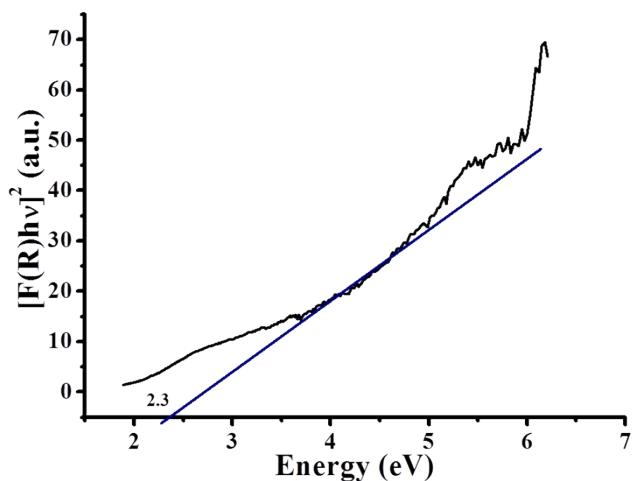
**Fig S10:** (a) %RH dependent stability test of COF-TXDBA is performed by checking its PXRD after each cycle of experiment from 11-98% RH. Sample was vacuum dried at 100 °C after each cycle. PXRD of COF shows that crystallinity of COF-TXDBA remains intact after five cycles of measurements; (b) SEM images of COF-TXDBA after fifth cycle of humidity sensing experiments.



**Fig S11:** (a) Time-dependent stability test of COF-TXDBA by keeping the sample in 98% RH humidity chamber for 50 min. PXRD was measured after each 10 min intervals shows that long range order of COF-TXDBA reduces with time. (b) SEM images of COF-TXDBA after keeping the sample in 98% RH for long 50 min. (c) Nitrogen isotherm at 77 K for COF-TXDBA Before and After 98% RH for 50 min followed by overnight vacuum drying at 120 °C.



**Fig S12:** The response of COF-TXDBA monitored at different humidity conditions for 70 days.



**Fig. S13** Band gap measurement of COF-TXDBA.

**Table T1:** A comparison of humidity sensing performance of previously published works.

| Sr. No. | Material   | Order of magnitude change in impedance in complete %RH range | Response time (S) | Recovery time (S) | Hysteresis (%) | Ref       |
|---------|--|--|-------------------|-------------------|----------------|-----------|
| 1       | NiO-PPY/SBA-15   | 3.5  | 45                | 90                | --             | 1         |
| 2       | SnO <sub>2</sub> /SBA-15   | 4.5  | 33                | 50                | 2.9            | 2         |
| 3       | Fe/SiO <sub>2</sub>  | 3.5  | 20                | 50                | --             | 3         |
| 4       | Li doped mesoporous silica   | 3  | 21                | 51                | 6              | 4         |
| 5       | ZnO nanosheets   | 2  | 600               | 3                 | 5              | 5         |
| 6       | Feather like ZnO   | 2  | 40                | 80                | --             | 6         |
| 7       | ZnO cauliflowers   | --   | 20                | 3                 | 4.16           | 7         |
| 8       | ZnO nanotetrapods  | --   | 36                | 17                | --             | 8         |
| 9       | La <sup>3+</sup> and K <sup>+</sup> doped TiO <sub>2</sub> -10 mol% SnO <sub>2</sub> | 5  | 11                | 18                | --             | 9         |
| 10      | SnWO <sub>4</sub> -SnO <sub>2</sub>  | 3  | 30                | 100               | --             | 10        |
| 11      | K <sup>+</sup> -doped SnO <sub>2</sub> -LiZnVO <sub>4</sub>                          | 3  | 80                | 100               | --             | 11        |
| 12      | MgO-KCl/SiO <sub>2</sub>   | 4  | 6                 | 26                | 4              | 12        |
| 13      | WO <sub>3</sub> -SnO <sub>2</sub>  | 3  | 117               | 411               | 3              | 13        |
| 14      | NaCl-KIT-6   | 5  | 47                | 150               | --             | 14        |
| 15      | MCM-48 fiber   | 2  | 15                | 18                | 5              | 15        |
| 16      | Fe/SnO <sub>2</sub>  | 4  | 1                 | 4                 | --             | 16        |
| 17      | Nanoporous polymers based on 1,4-divinylbenzene                                      | 3  | 3                 | 75                | 4              | 17        |
| 18      | Graphene/TiO <sub>2</sub>  | 3  | 128               | 68                | 0.39           | 18        |
| 19      | LiCl-PEBAX nanofiber   | 4  | 30                | 80                | negligible     | 19        |
| 20      | CeO <sub>2</sub>   | 3  | 2-3               | 9-10              | <1             | 20        |
| 21      | COF-TXDBA  | 3  | 37                | 42                | 2.5            | This work |

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