materials

MDPI

Supplementary Materials

Catalytically Active Imine-based Covalent Organic Frameworks for Detoxification of Nerve Agent Simulants in Aqueous Media

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FTIR spectra of COFs

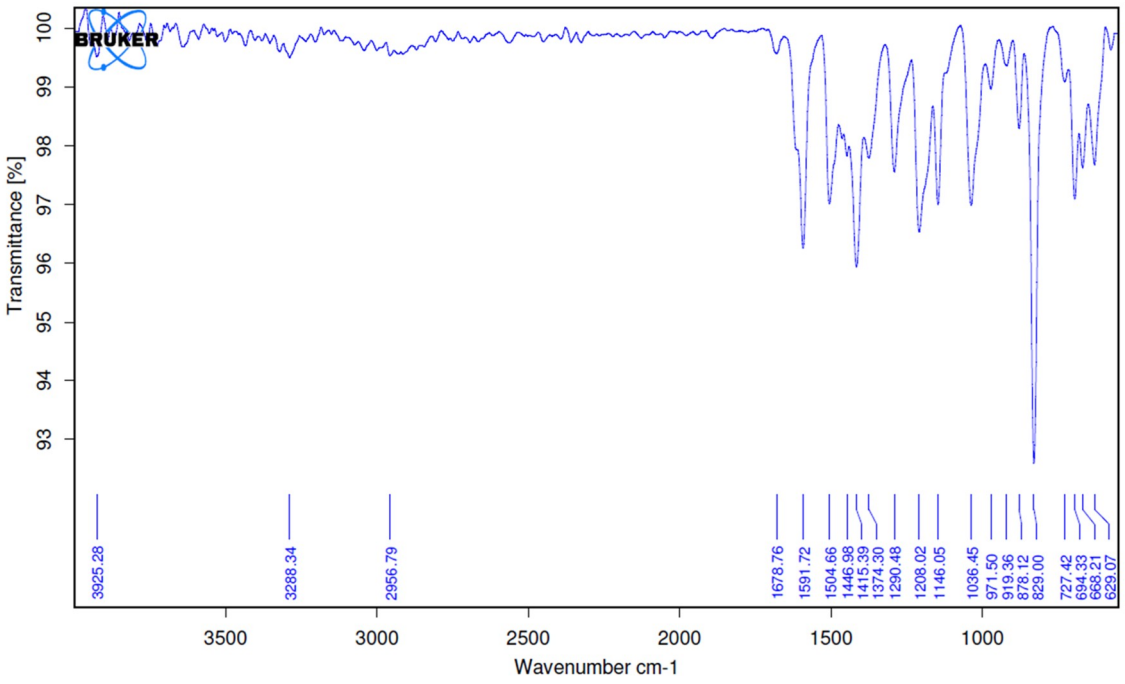

Figure S1. FTIR (ATR) spectrum of **[HC≡C]$_{0.5}$-TPB-DMTP-COF**.

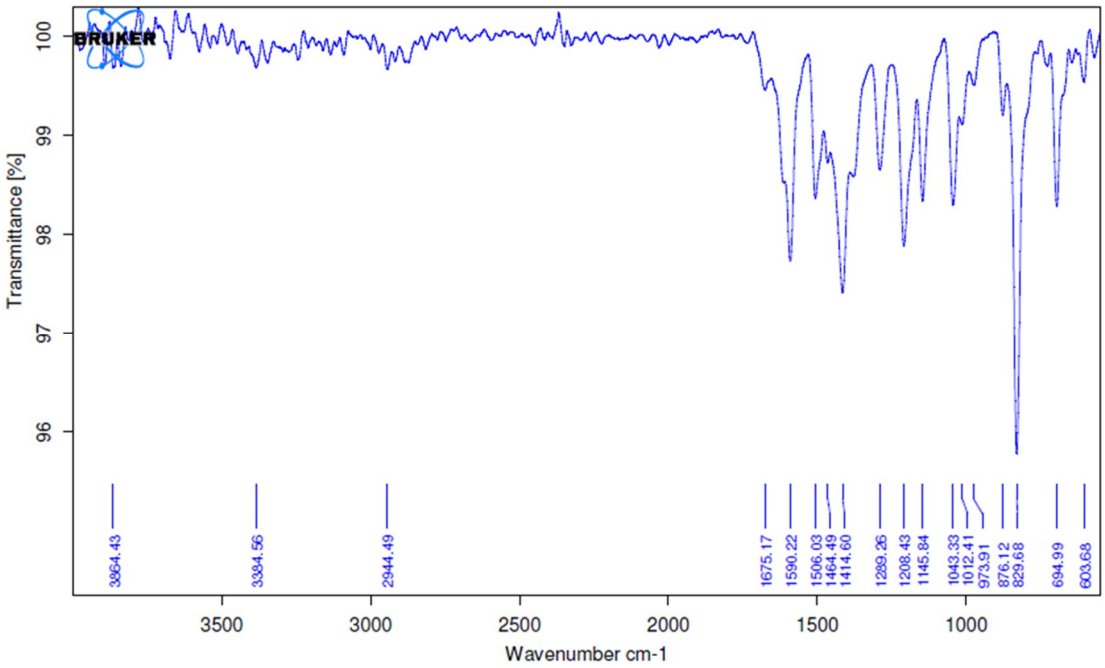

Figure S2. FTIR (ATR) spectrum of **[(*S*)-Py]$_{0.5}$-TPB-DMTP-COF**.

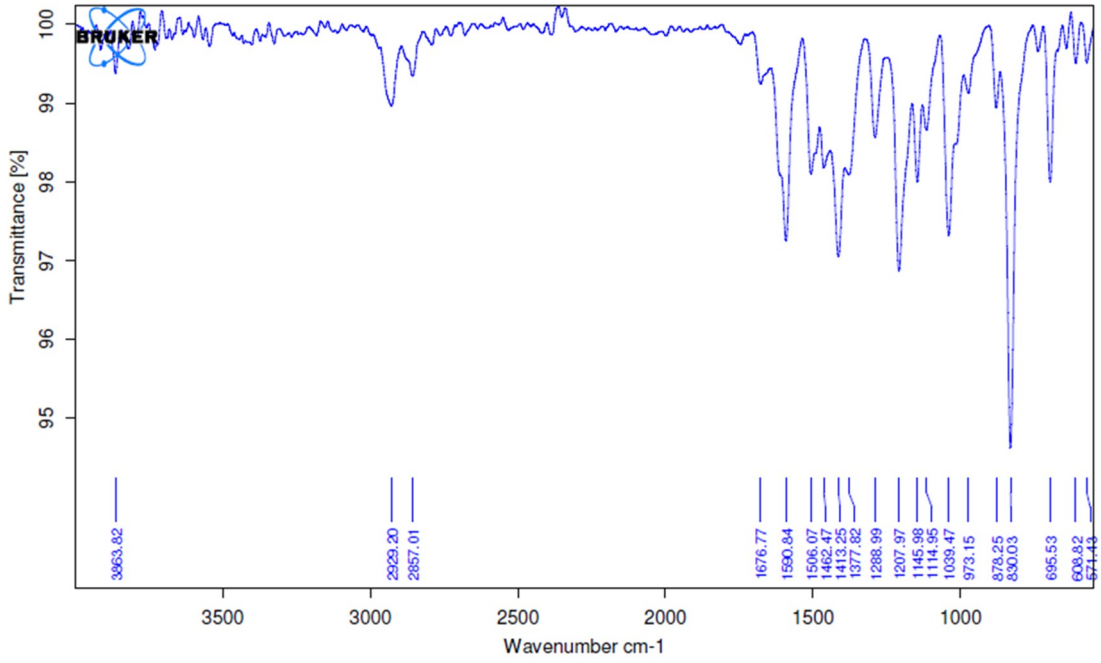

Figure S3. FTIR (ATR) spectrum of **2-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF**.

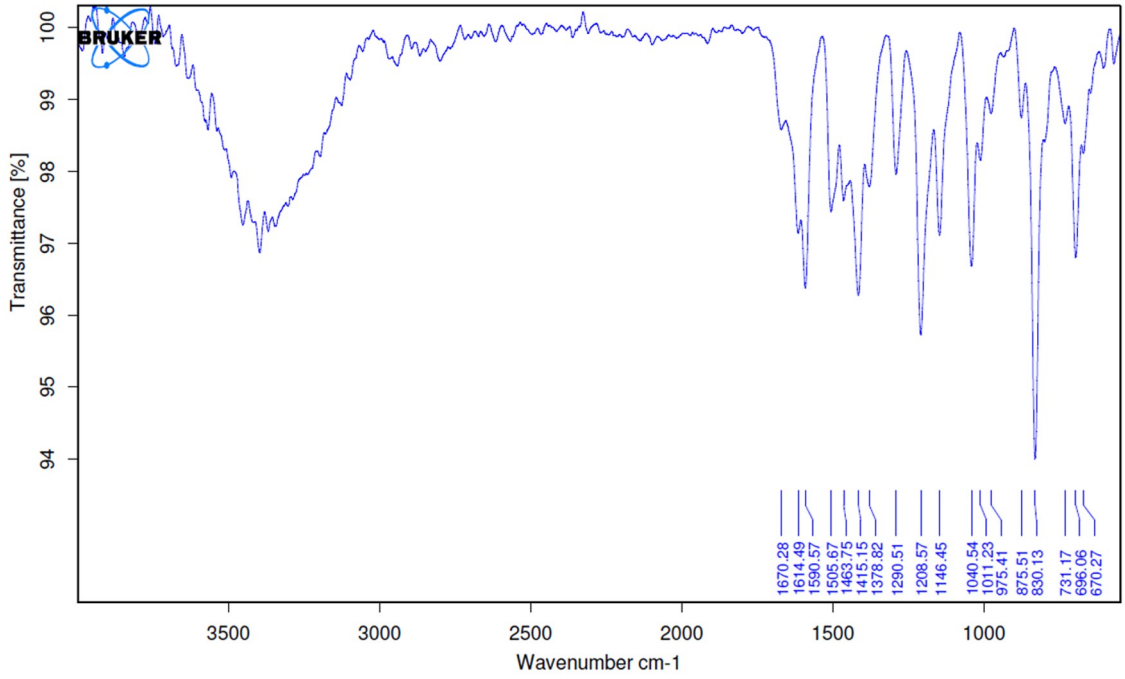

Figure S4. FTIR (ATR) spectrum of **2-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF**.

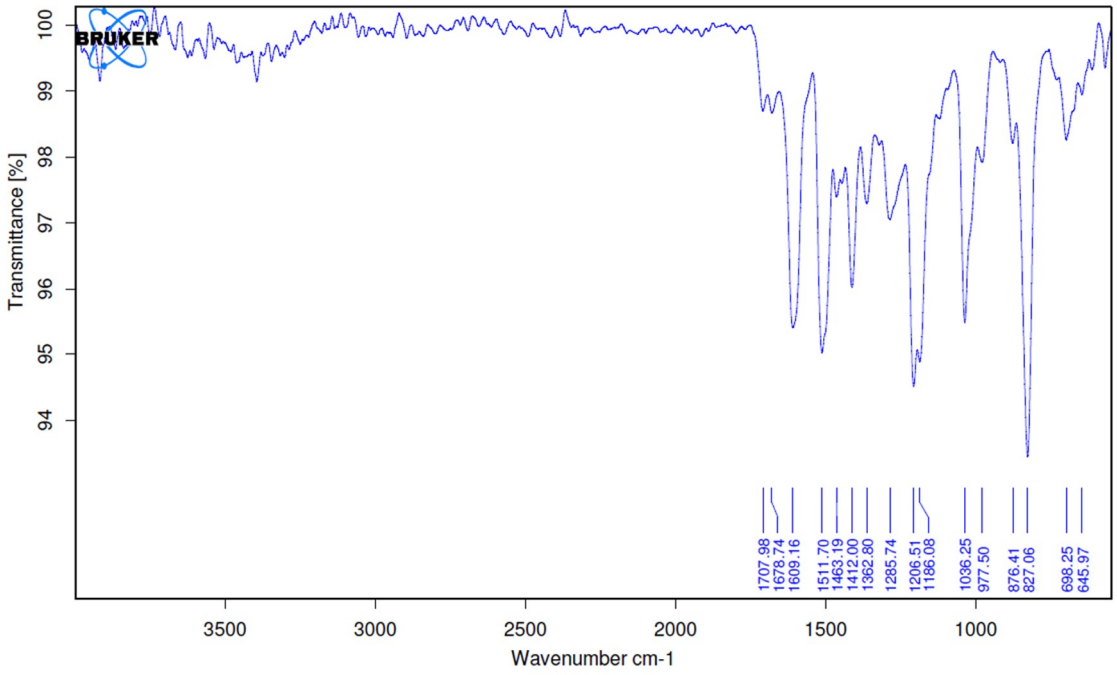

Figure S5. FTIR (ATR) spectrum of **[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-Polym**.

- **^{13}C CP/MAS NMR spectra of COFs**

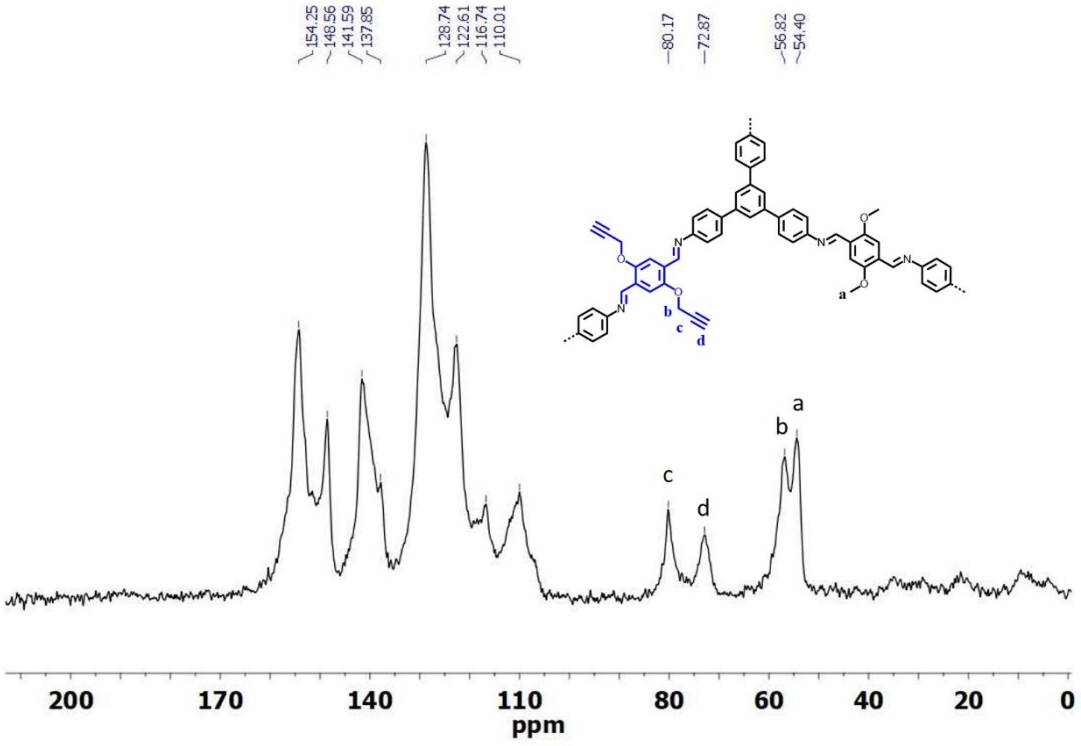

Figure S6. ^{13}C CP/MAS NMR of **[HC≡C]$_{0.5}$-TPB-DMTP-COF**.

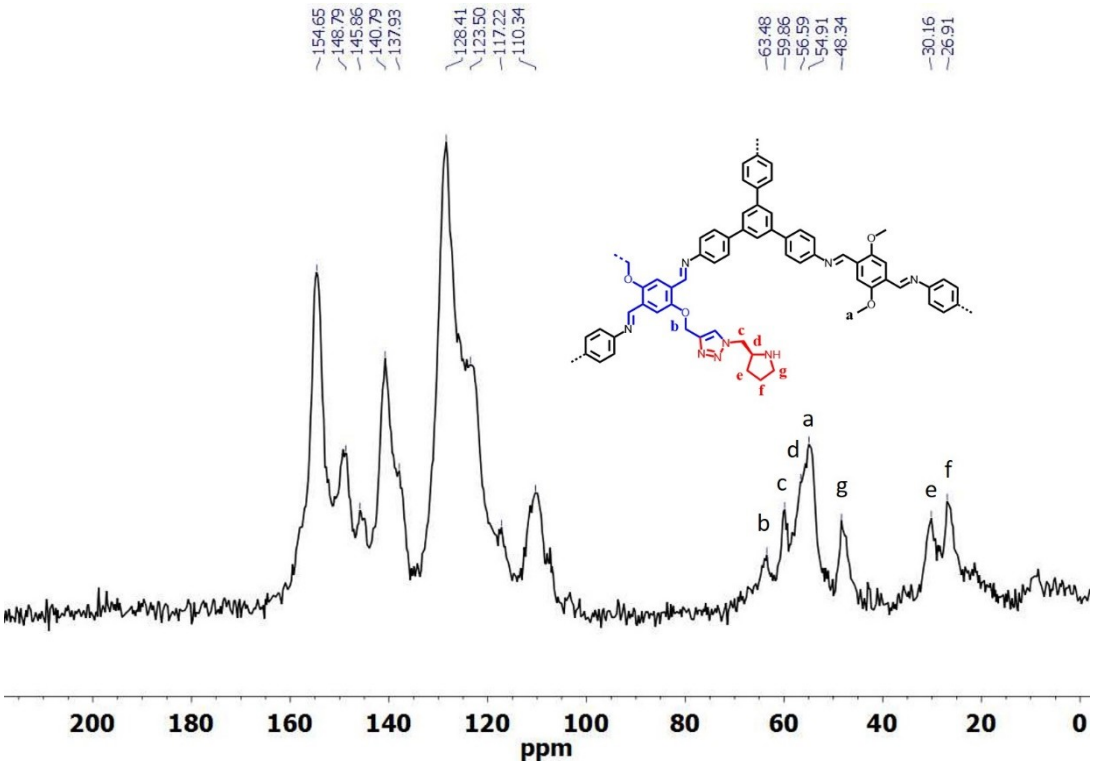

Figure S7. ^{13}C CP/MAS NMR of **[(*S*)-Py]$_{0.5}$-TPB-DMTP-COF**.

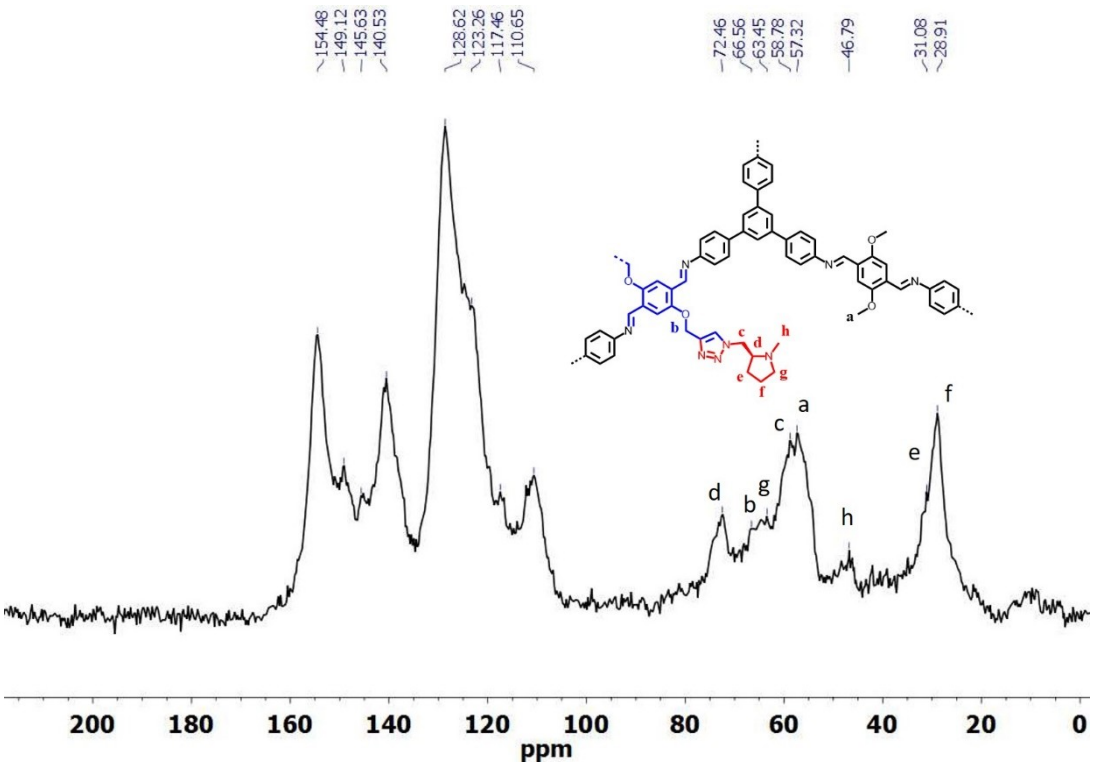

Figure S8. ^{13}C CP/MAS NMR of **2-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF**.

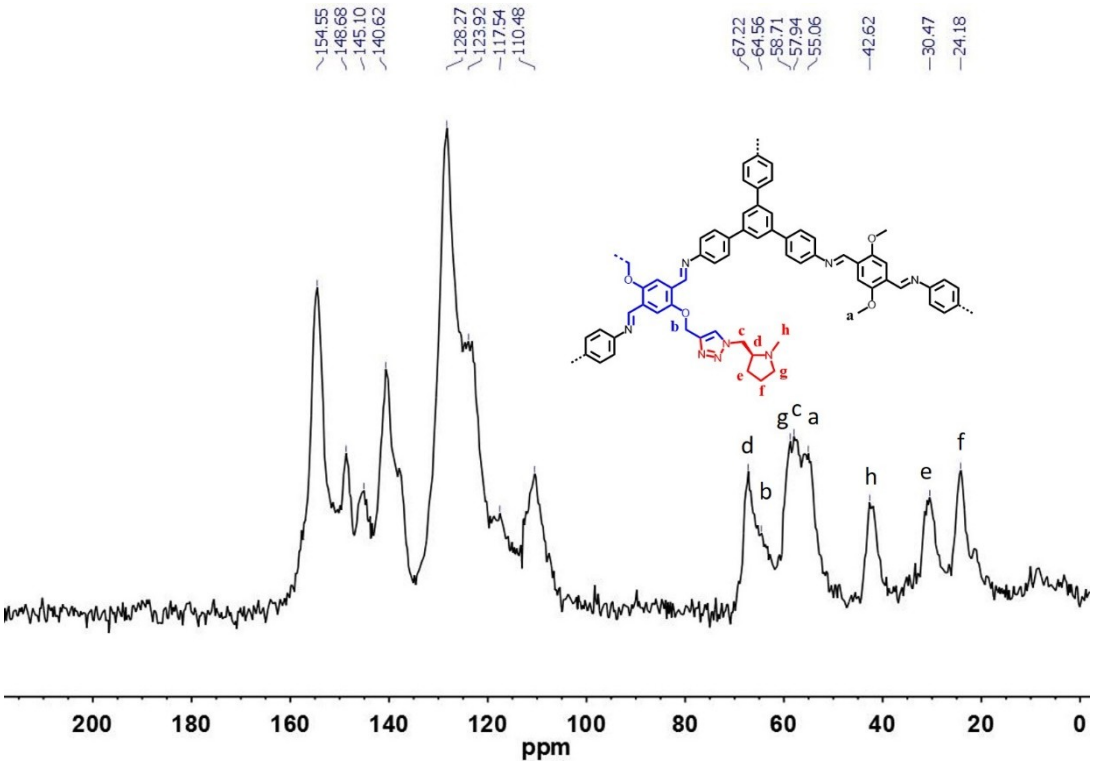

Figure S9. ^{13}C CP/MAS NMR of **1-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF**.

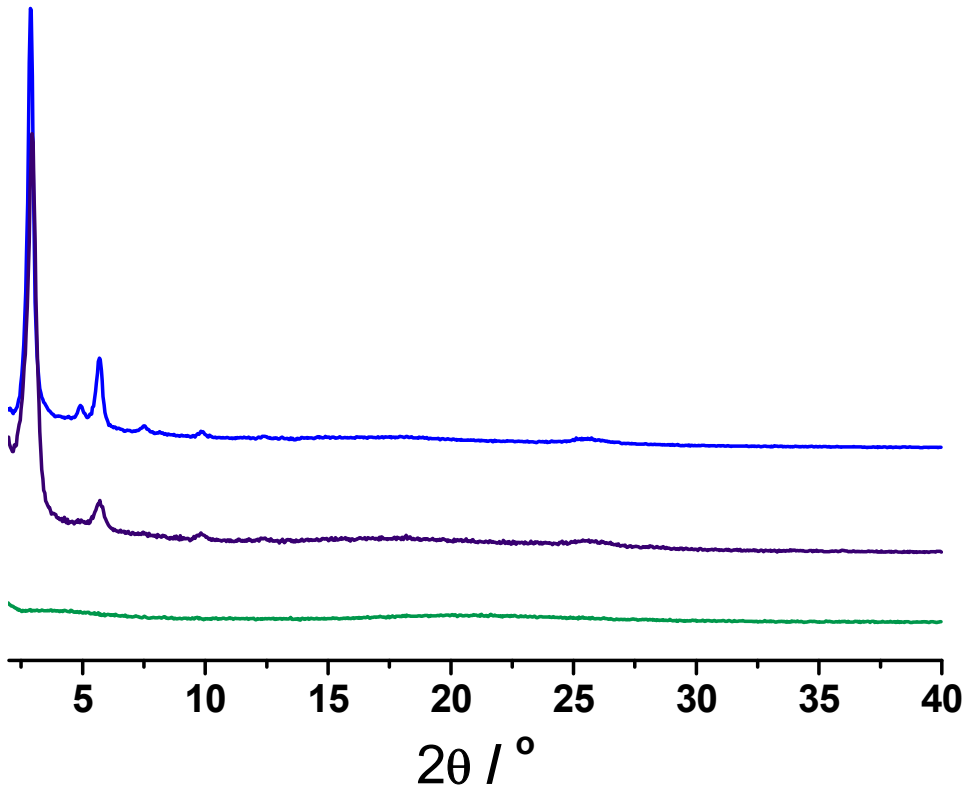

Figure S10. PXRD of **1-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF** (blue), **2-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF** (purple) and **[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-Polym** (green).

Table S1. Lattice parameters of the synthesized COFs.

	a = b (Å)	**c (Å)**	**α = β (º)**	**γ (º)**
[HC≡C]$_{0.5}$-TPB-DMTP-COF	35.3	3.50	90	120
[(*S*)-Py]$_{0.5}$-TPB-DMTP-COF	34.7	3.51	90	120
2-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF	35.5	3.50	90	120
1-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF	35.7	3.50	90	120

- **Characterization of materials by N_2 (77 K) and CO_2 (273 K) adsorption**

Table S2. Summary of textural properties of COF materials from N_2 adsorption measurements at 77 K.

	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore size (nm)
[HC≡C]$_{0.5}$-TPB-DMTP-COF	3440	3.0	3.6
[(*S*)-Py]$_{0.5}$-TPB-DMTP-COF	1030	0.40	3.3
2-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF	95	0.06	2.9
1-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF	318	0.20	3.0
[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-Polym	7.5	-	-

N_2 adsorption isotherms

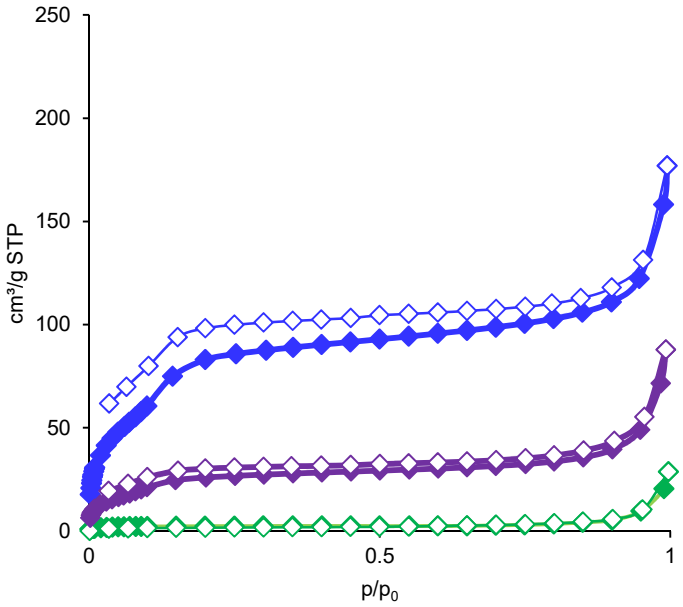

Figure S11. N_2 (77 K) adsorption isotherms for **1-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF** (blue), **2-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF** (purple) and **[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-Polym** (green).

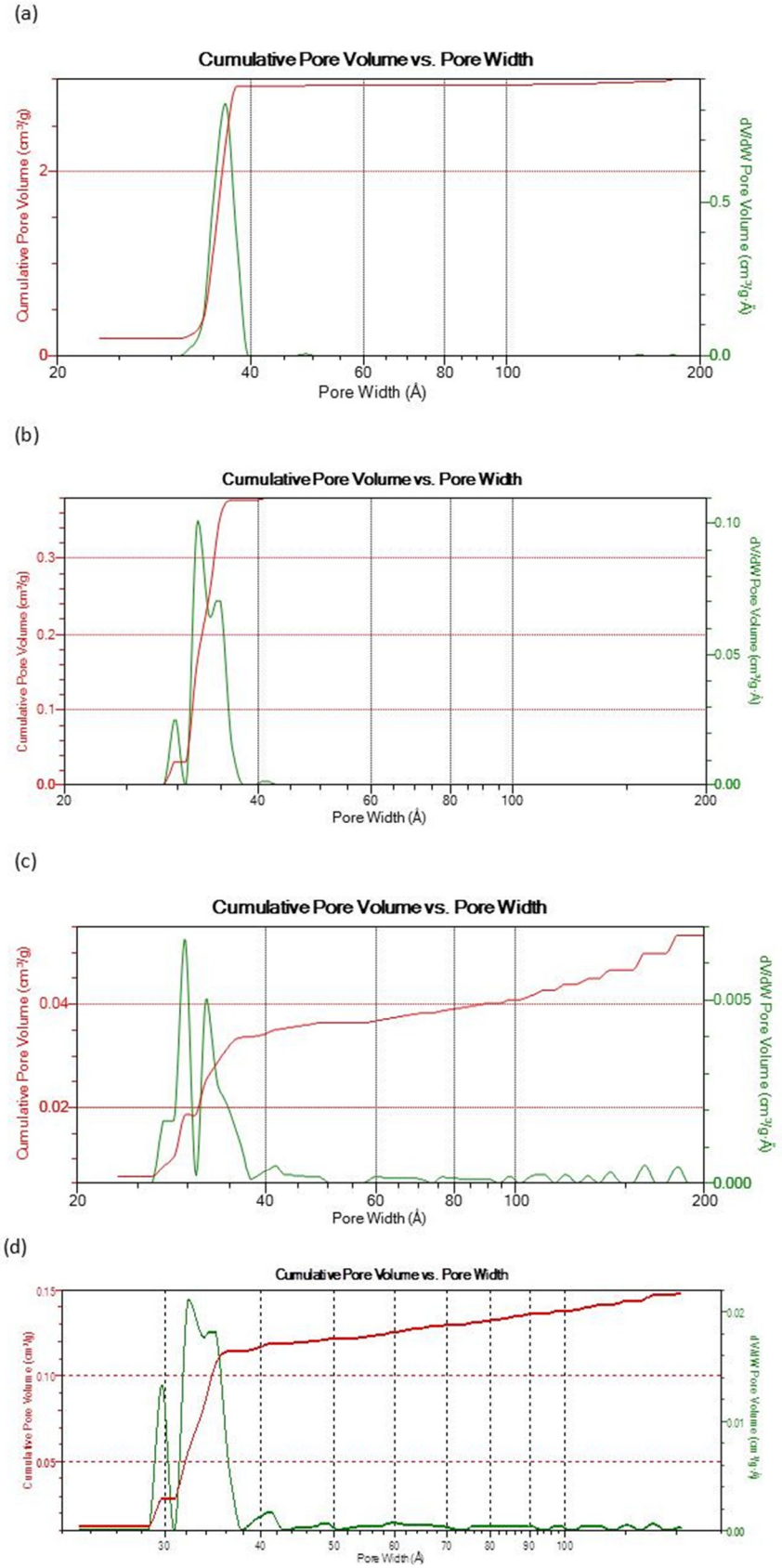

Figure S12. NLDFT pore size distribution for the essayed COF materials **[HC≡C]$_{0.5}$-TPB-DMTP-COF** (a), **[(*S*)-Py]$_{0.5}$-TPB-DMTP-COF** (b), **2-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF** (c) and **1-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF** (d).

CO_2 adsorption isotherms

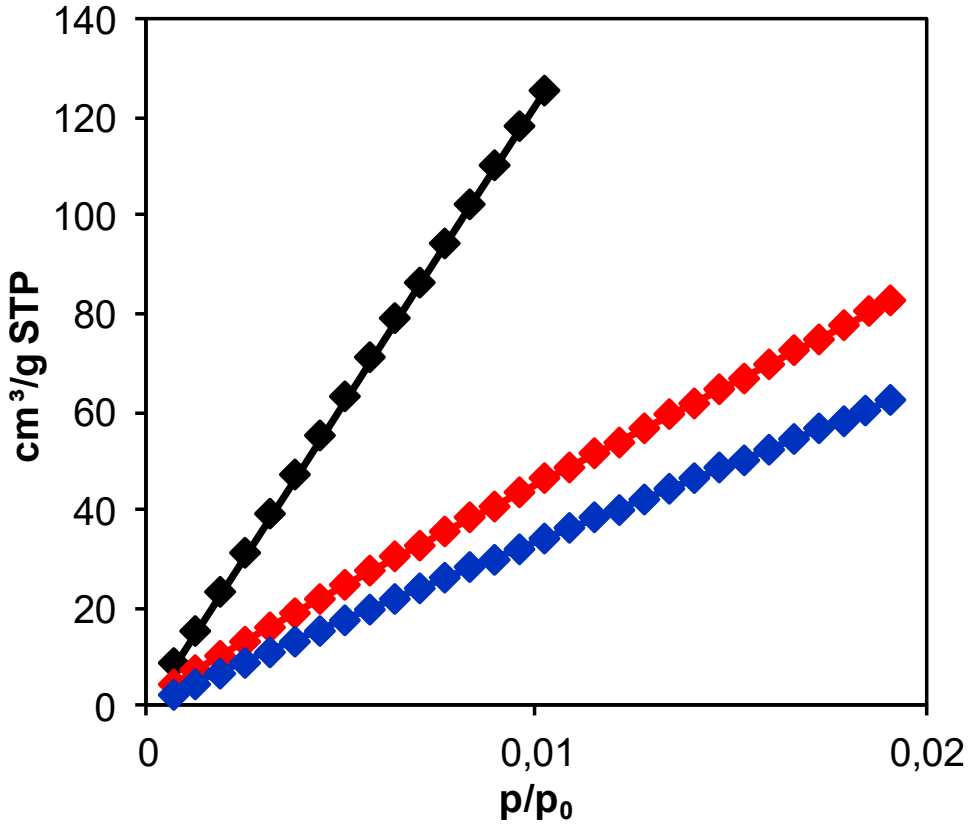

Figure S13. CO_2 (298 K) adsorption isotherms for **[HC≡C]$_{0.5}$-TPB-DMTP-COF** (black), **[(*S*)-Py]$_{0.5}$-TPB-DMTP-COF** (red) and **[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF** (blue).

- **SEM images**

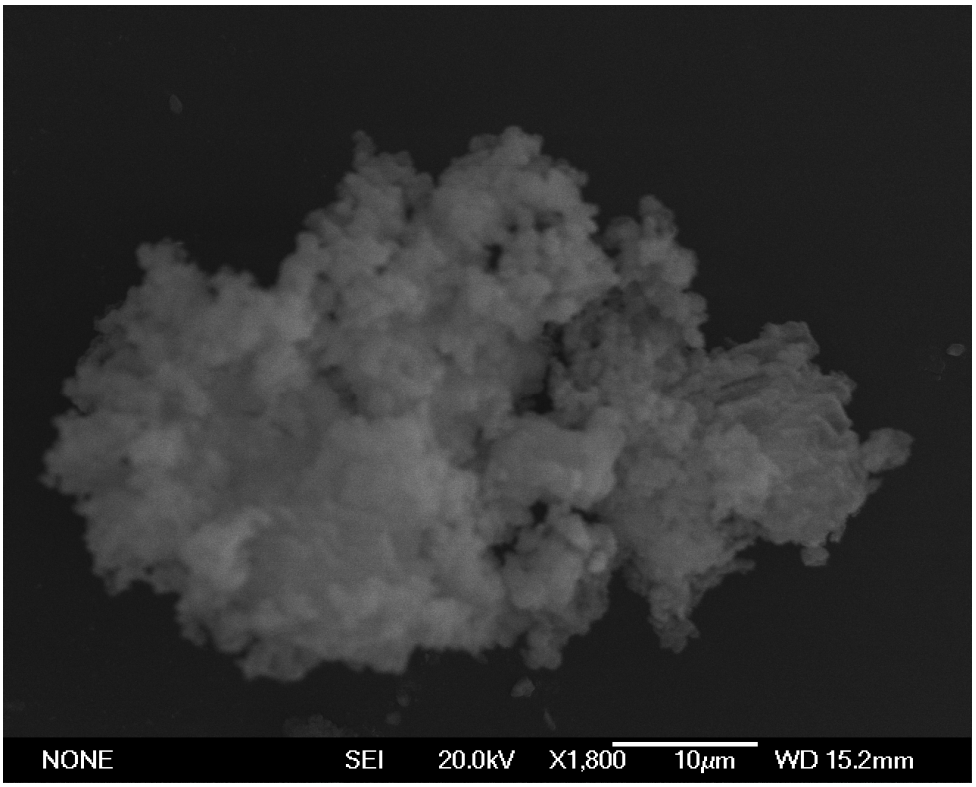

Figure S14. SEM image of **[(*S*)-Py]$_{0.5}$-TPB-DMTP-COF**.

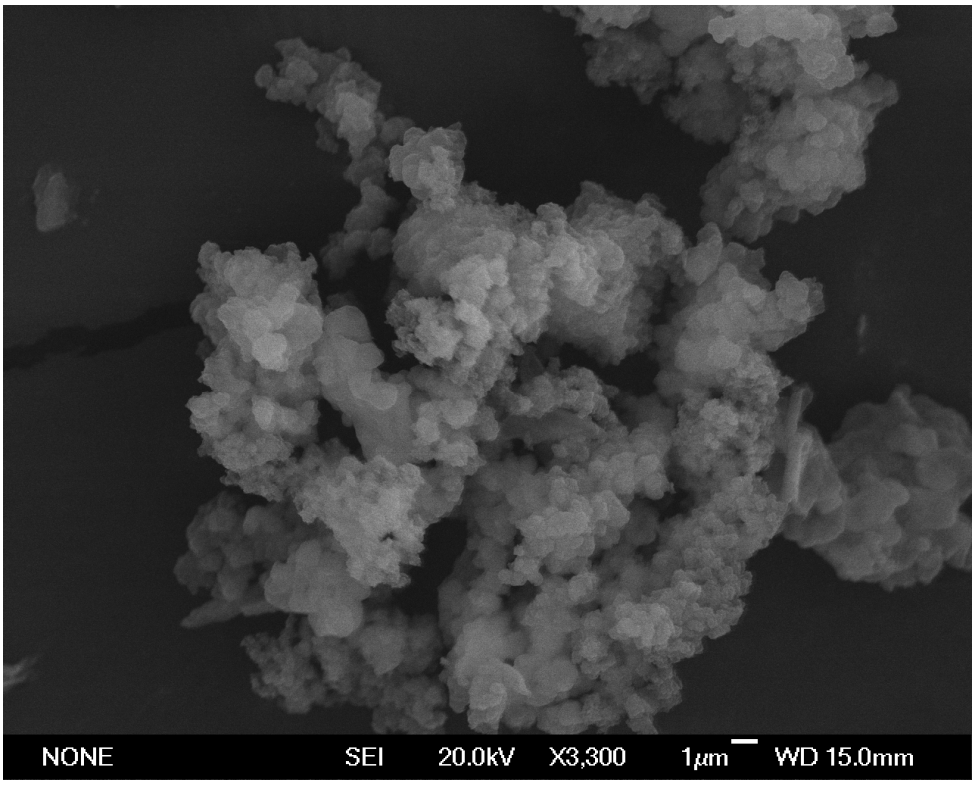

Figure S15. SEM image of **2-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF**.

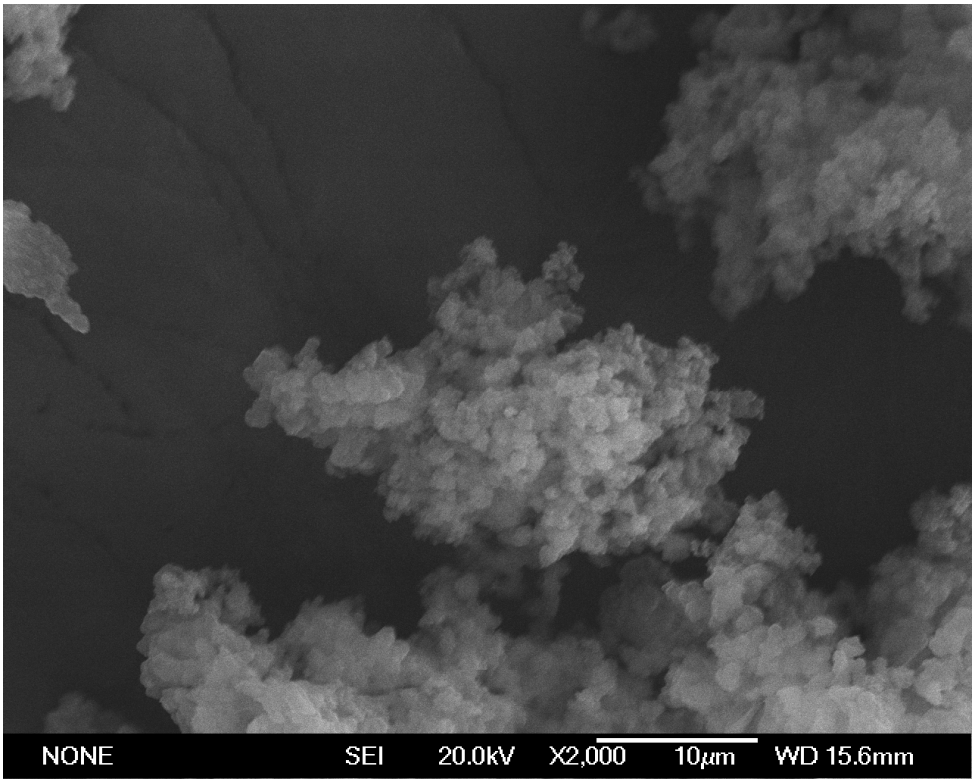

Figure S16. SEM image of **1-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF**.

- **TGA of COFs**

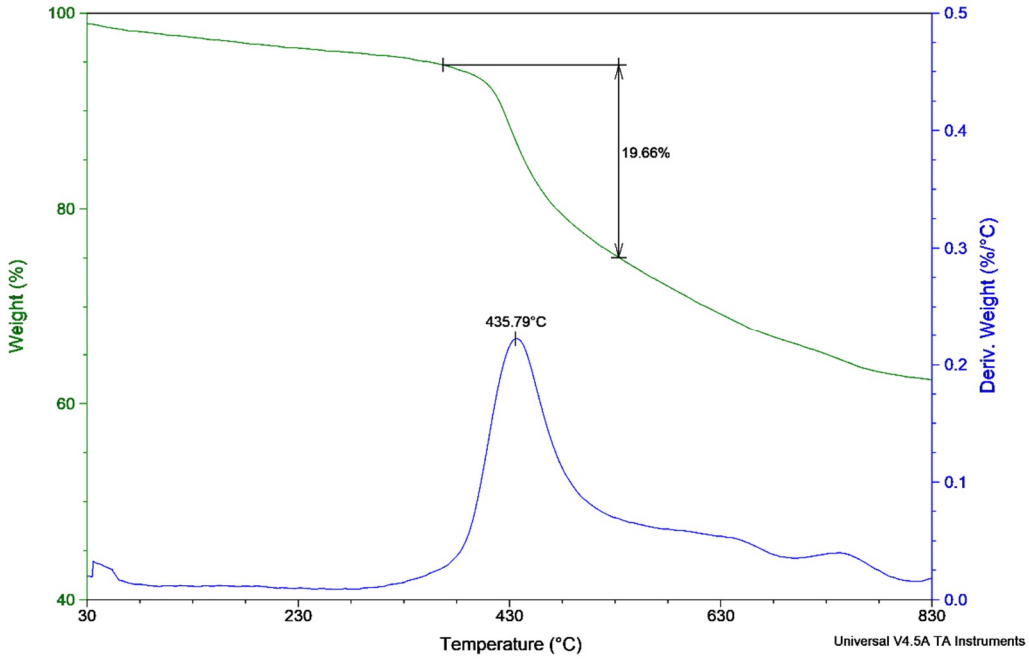

Figure S17. TGA profile of **[HC≡C]$_{0.5}$-TPB-DMTP-COF**.

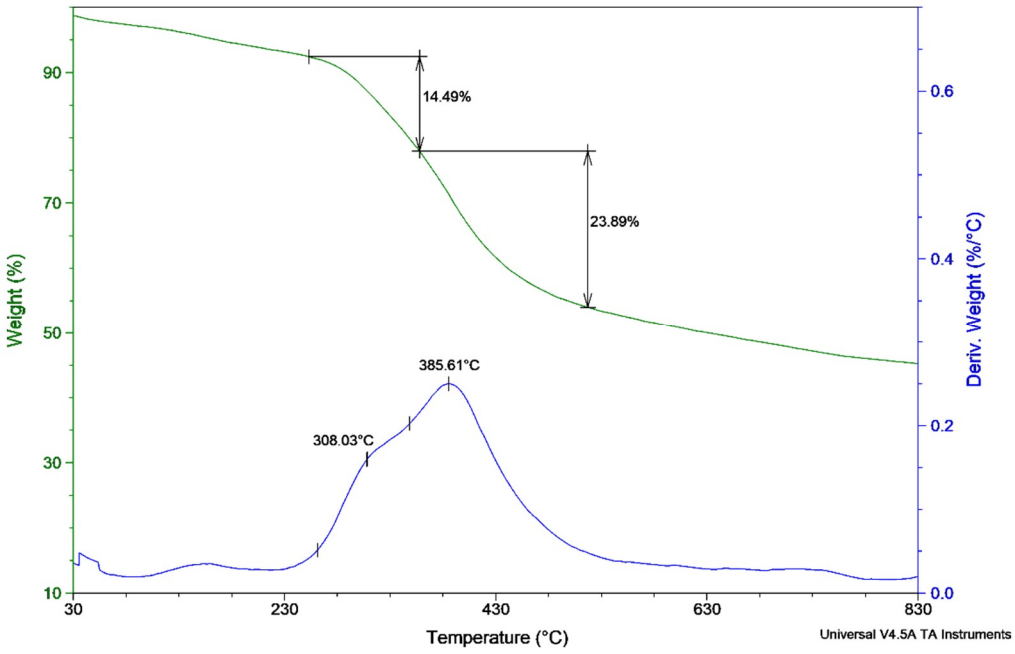

Figure S18. TGA profile of **[(*S*)-Py]$_{0.5}$-TPB-DMTP-COF**.

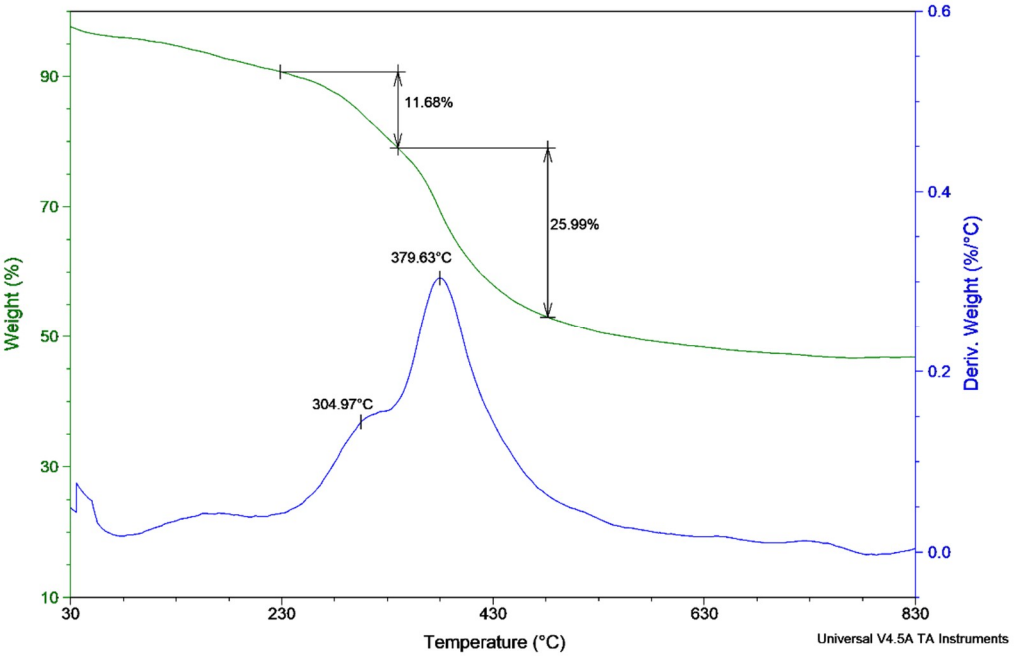

Figure S19. TGA profile of **2-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF**.

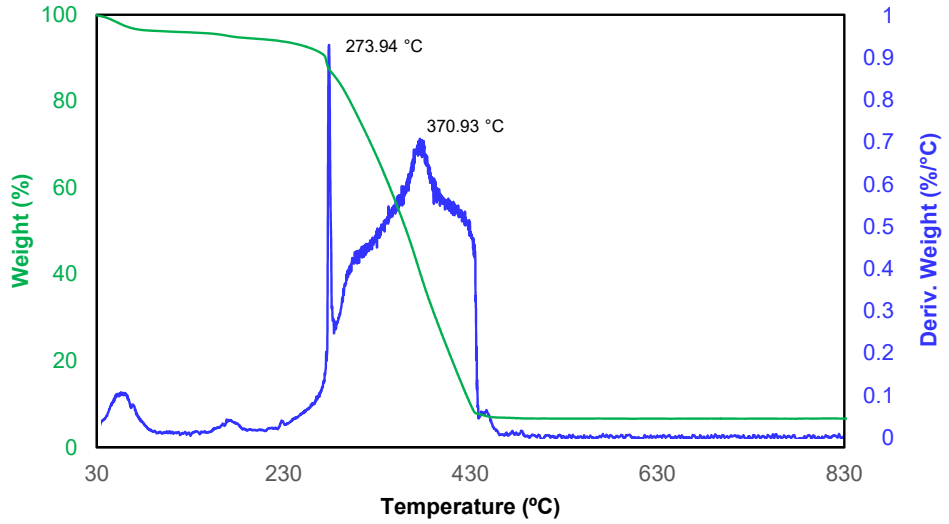

Figure S20. TGA profile of **1-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF**.

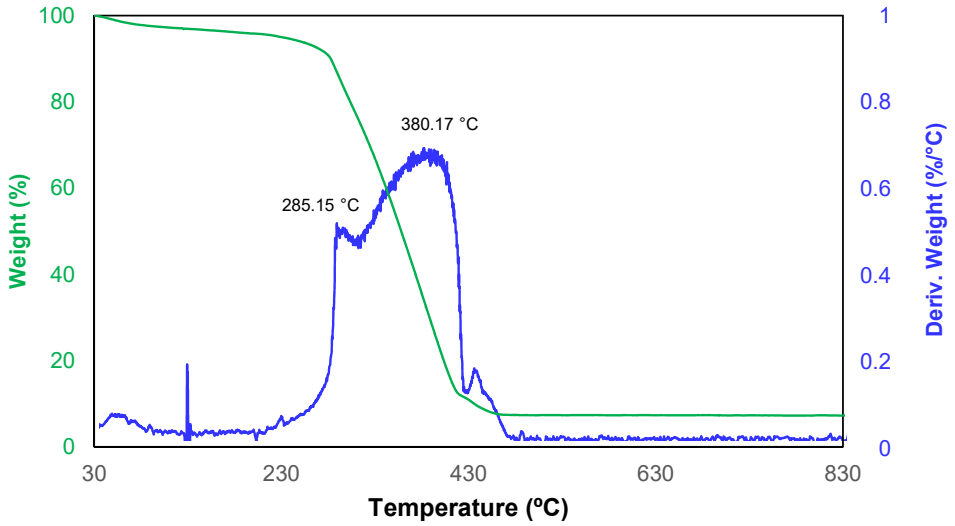

Figure S21. TGA profile of **[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-Polym**.

- **Elemental Analysis**

  - **[HC≡C]$_{0.5}$-TPB-DMTP-COF**

    Calculated - C: 80.75 %, H: 4.84 %, N: 6.73 %
    Experimental - C: 78.73 %, H: 5.06 %, N: 6.46 %
    Experimental - C: 79.20 %, H: 4.99 %, N: 6.48 %
    Experimental - C: 79.04 %, H: 5.05 %, N: 6.47 %

  - **[(*S*)-Py]$_{0.5}$-TPB-DMTP-COF**

    Calculated - C: 73.04 %, H: 5.57 %, N: 15.49 %
    Experimental - C: 69.47 %, H: 5.48 %, N: 13.75 %
    Experimental - C: 69.93 %, H: 5.52 %, N: 13.81 %
    Experimental - C: 69.65 %, H: 5.53 %, N: 13.80 %

  - **2-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF**

    Calculated - C: 73.36 %, H: 5.79 %, N: 15.10 %
    Experimental - C: 70.11 %, H: 5.50 %, N: 13.17 %
    Experimental - C: 69.69 %, H: 5.40 %, N: 13.17 %
    Experimental - C: 70.41 %, H: 5.47 %, N: 13.21 %

  - **1-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF**

    Calculated - C: 73.36 %, H: 5.79 %, N: 15.10 %
    Experimental - C: 70.38 %, H: 5.64 %, N: 13.12 %
    Experimental - C: 70.47 %, H: 5.52 %, N: 13.08 %

- **Catalysis heterogeneity test**

Table S3. Catalytic degradation of diisopropylfluorophosphate (DIFP) nerve agent simulant.

	No buffer	Buffer
[HC≡C]$_{0.5}$-TPB-DMTP-COF	83.8	100
[(*S*)-Py]$_{0.5}$-TPB-DMTP-COF	89.4	100
2-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF	99.0	100
1-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF	100	100
[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-Polym	84.1	100

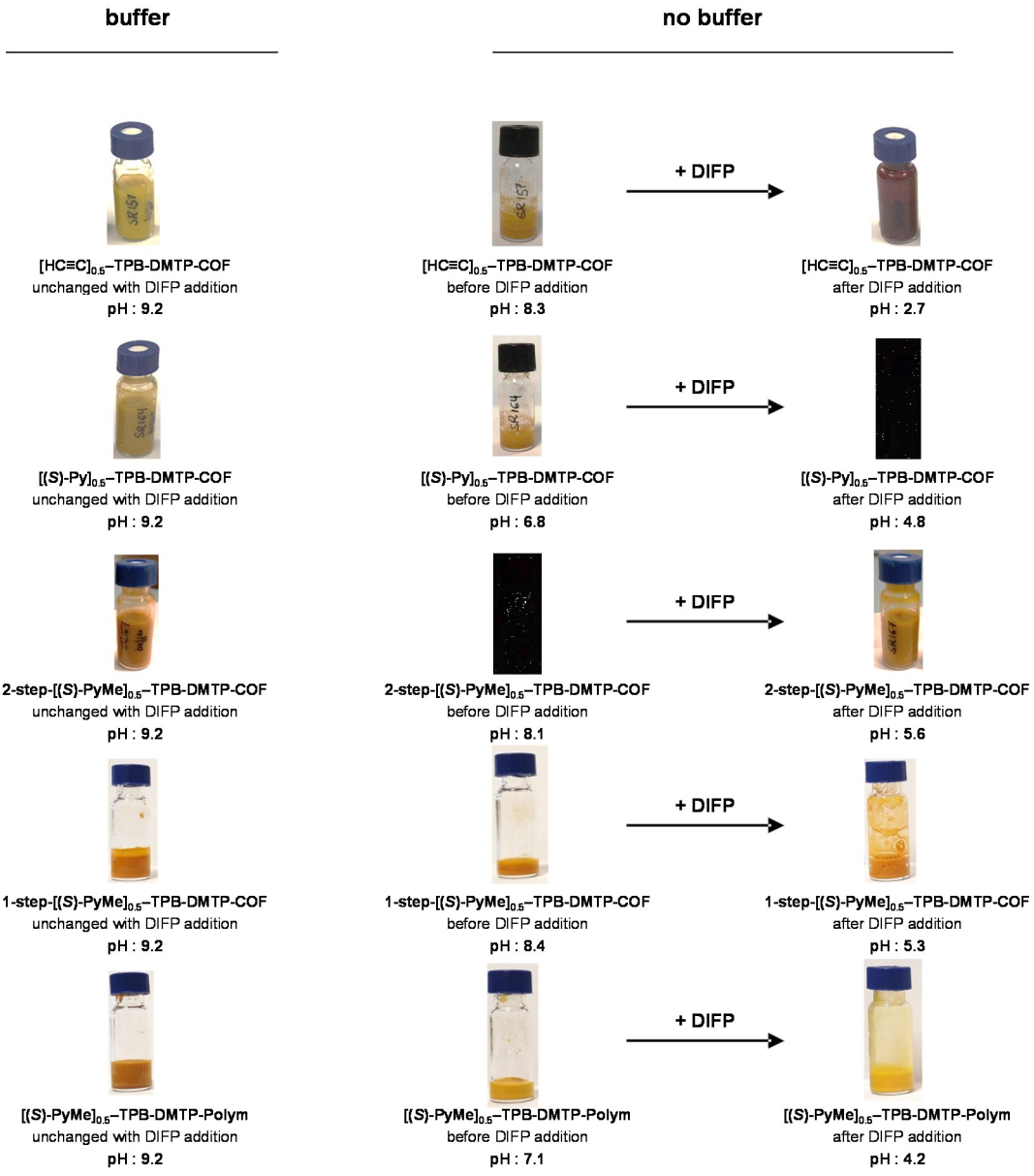

Figure S22. Effect of DIFP of addition to the essayed COF materials suspension on the pH and color in both buffer and unbuffered conditions.

- **Catalysis in buffered media**

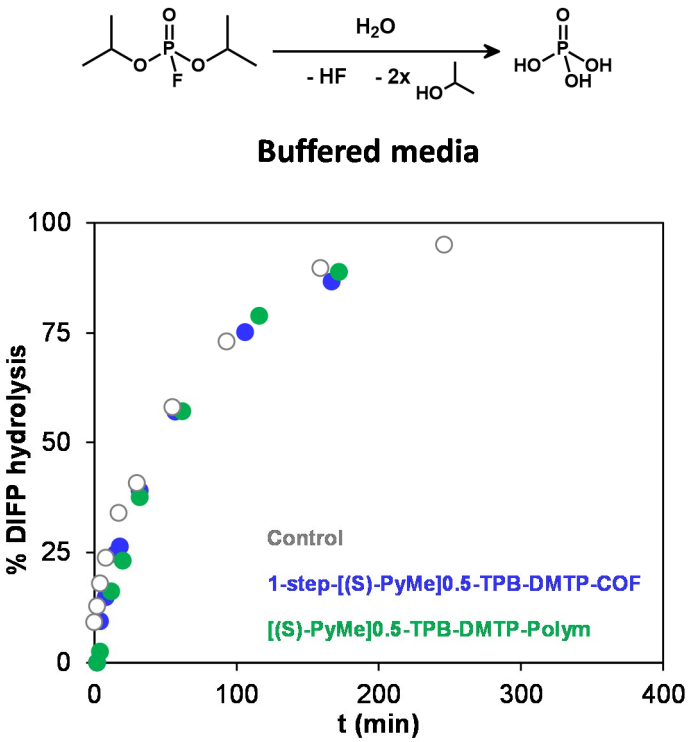

Figure S23. DIFP degradation studies in basic *N*-ethylmorpholine buffered media (pH=9.2). Reaction profiles for **1-step-[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-COF** (blue) and **[(*S*)-PyMe]$_{0.5}$-TPB-DMTP-Polym** (green).