

Supporting Information

Conversion of amorphous polymer networks to covalent organic frameworks under ionothermal conditions: a facile synthesis route for covalent triazine frameworks

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S1. Experimental section – continued

S2. Infrared spectroscopy

S3. Thermogravimetric analysis

S4. Nitrogen sorption analysis

S5. X-ray diffraction analysis

S1. Experimental Section - continued

Alternative trimerization protocols to pre-CTFs.

HSOCl₃ catalyzed trimerization at RT (procedure according to literature.^{S1})

In a round bottom flask, chlorosulfonic acid (3.41 g, 29.3 mmol) was slowly added to 1,4-dicyanobenzene (0.50 g, 3.90 mmol) at 0 °C. The yellow reaction mixture was allowed to stand for 48 h under ambient conditions. After stopping the reaction with 300 ml ice water, the glassy yellow solid was isolated by vacuum filtration, ground, thoroughly washed with deionized water and EtOH and dried under vacuum for 12 h at 115 °C. The product (0.50 g, quantitative yield) was obtained as a dark yellow solid. FT-IR (ATR, cm⁻¹): 1506, 1354, 814. Anal. calcd for C₈H₄N₂: C, 74.99; N, 21.86; H, 3.15. Found: C, 64.49; N, 12.01; H, 4.05.

TFMSA catalyzed trimerization at RT

In a round bottom flask, trifluoromethanesulfonic acid (4.39 g, 29.3 mmol) was slowly added to 1,4-dicyanobenzene (0.50 g, 3.90 mmol) at 0 °C. The yellow reaction mixture was allowed to stand for 48 h under ambient conditions. After stopping the reaction with 300 ml ice water, the glassy yellow solid was isolated by vacuum filtration, ground, thoroughly washed with deionized water and EtOH and dried under vacuum for 12 h at 115 °C. The product (0.50 g, quantitative yield) was obtained as a dark yellow solid. FT-IR (ATR, cm⁻¹): 1506, 1354, 813. Anal. calcd for C₈H₄N₂: C, 74.99; N, 21.86; H, 3.15. Found: C, 61.34; N, 12.82; H, 3.52.

Synthesis of CTF-1_{open} materials

- For the time dependent synthesis, mixtures of pre-CTF (0.25 g) and ZnCl₂ (0.22 g) were prepared and heated for the desired time (X h). The respective yields are listed in table S1.

Table S1: Yields of CTF-1 materials in dependence of reaction time.

entry	reaction time	yield
1	5 h	53%
2	20 h	48%
3	40 h	52%

- To study the influence of the ZnCl_2 amount, mixtures of pre-CTF (1 eq) and ZnCl_2 (X eq) were prepared and heated for 40 h. The respective yields are listed in table S2.

Table S2: Yields of CTF-1 materials in dependence of ZnCl_2 amount.

entry	equivalents (ZnCl_2)	yield
4	0.1 eq	62%
5	0.6 eq	52%
6	0.7 eq	58%
7	0.9 eq	44%
8	1.0 eq	38%
9	1.5 eq	32%

- To test the sensitivity to air moisture, a mixture of pre-CTF (0.25 g) and ZnCl_2 (0.22 g) was prepared and exposed to air for 20 min before positioning the crucible in the argon oven and heating at 400 °C for 40 h. A black solid was obtained with 50% yield (see entry 10 in table S3).
- Furthermore, a mixture of pre-CTF (0.30 g) and ZnCl_2 (1.28 g) was prepared and heated for 20 h at 400 °C and another 20 h at 600 °C. A black solid was obtained with 30% yield (see entry 11 in table S3).

S2. Infrared spectroscopy

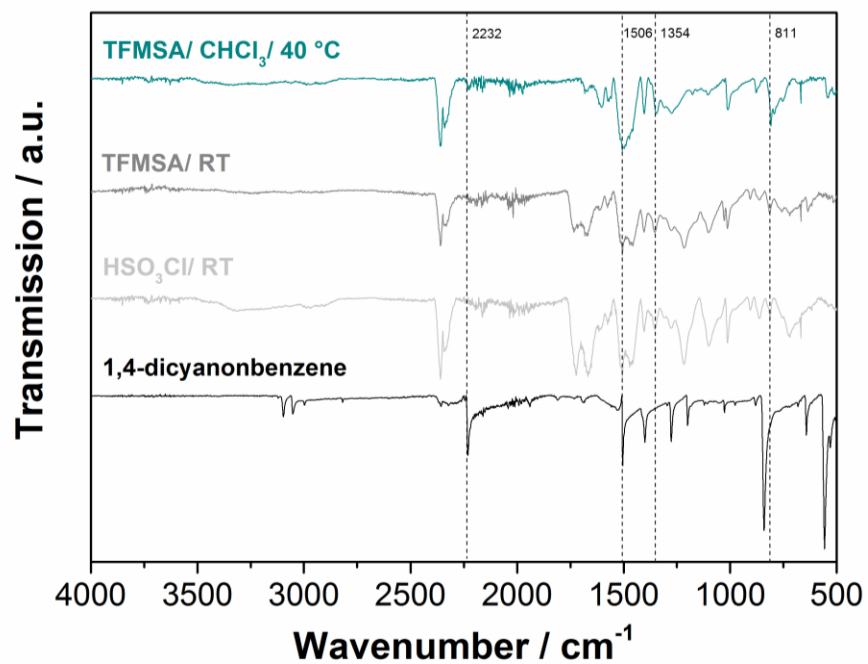


Figure S1: Infrared spectra of three different pre-CTFs (HSO₃Cl/ RT: light grey, TFMSA/ RT: grey, TFMSA/ CHCl₃/ 40 °C: cyan) and DCB (black).

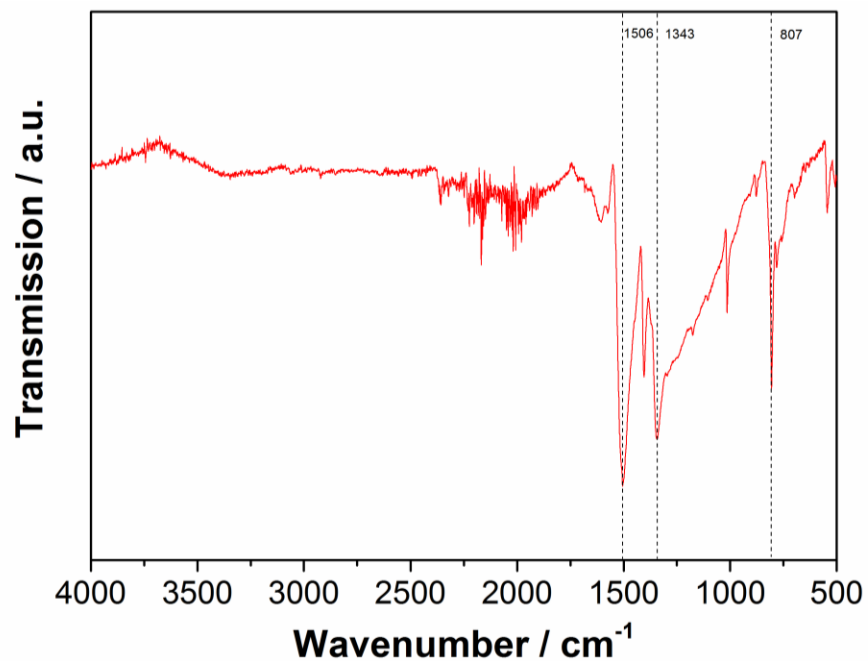


Figure S2: Infrared spectra of CTF_{open_40h} (entry 3).

S3. Thermogravimetric analysis

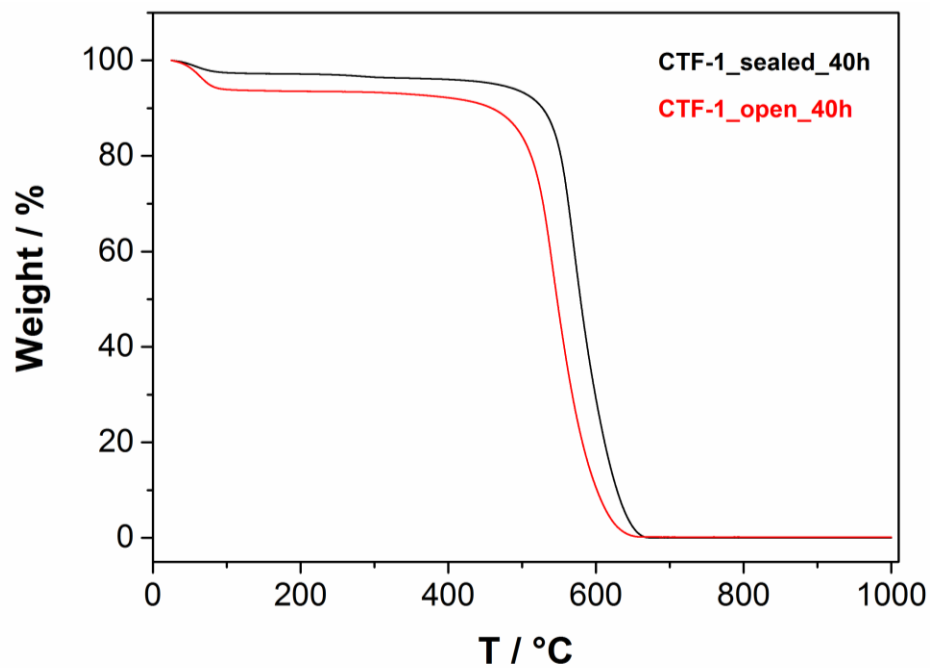


Figure S3: Thermogravimetric analysis of CTF-1_open_40h (red) and CTF-1_sealed_40h (black) under oxygen (heating rate of 10 °C min^{-1}). Residual mass at 1000 °C is 0.0% for CTF_sealed and 0.2% for CTF_open.

S4. Nitrogen sorption analysis

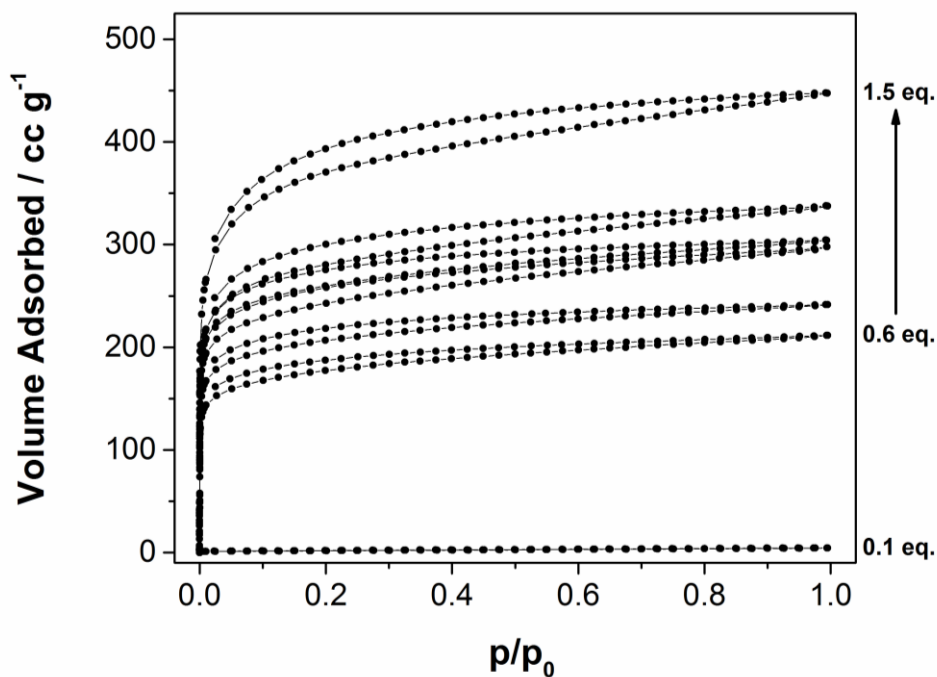


Figure S4: Nitrogen sorption isotherms for CTFs prepared with a series of $\text{ZnCl}_2/\text{pre-CTF}$ values.

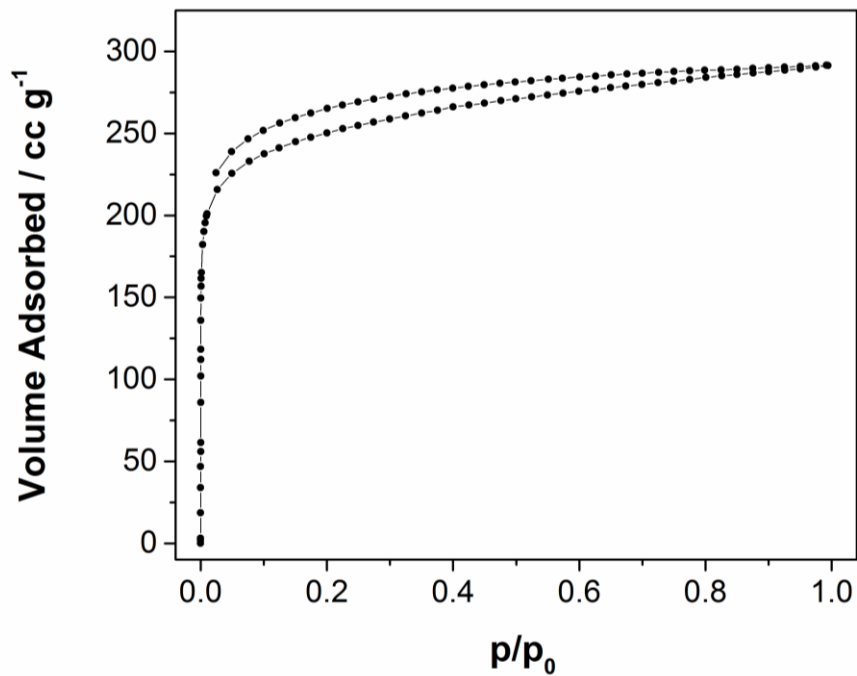


Figure S5: Nitrogen sorption isotherms of CTF-1 prepared from pre-CTF in an open crucible after exposure to air moisture (entry 10).

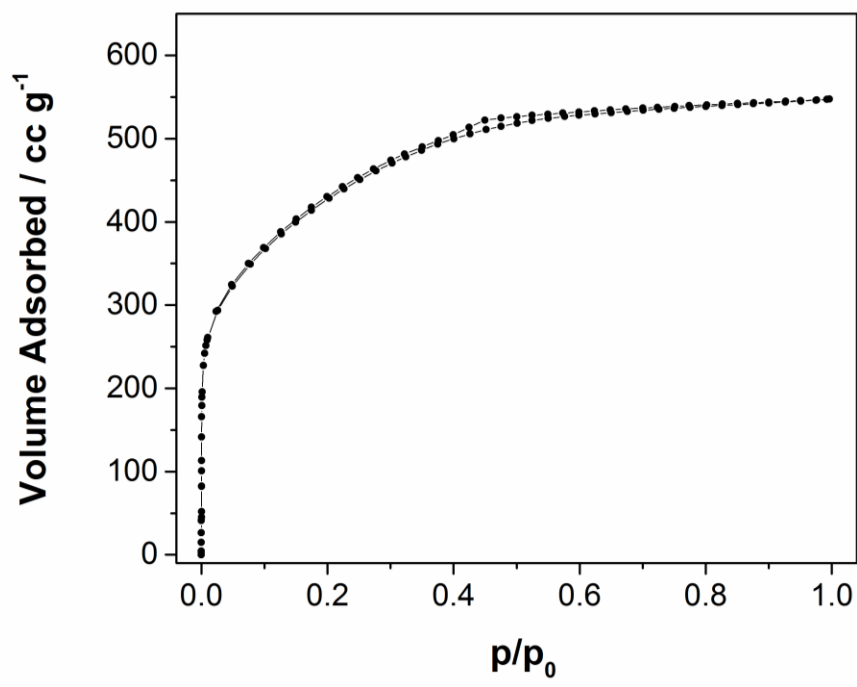


Figure S6: Nitrogen sorption isotherms of CTF prepared from pre-CTF in an open crucible at 600 °C (entry 11).

Table S3: BET surface areas of CTFs prepared in this study.

entry	molar ratio ZnCl ₂ /pre-CTF	time	SA _{BET} in m ² g ⁻¹
1	0.8 eq	5 h	545
2	0.8 eq	20 h	828
3	0.8 eq	40 h	910
4	0.1 eq	40 h	n.p.
5	0.6 eq	40 h	667
6	0.7 eq	40 h	781
7	0.9 eq	40 h	988
8	1.0 eq	40 h	1060
9	1.5 eq	40 h	1377
10 ^a	0.8 eq	40 h	950
11 ^b	4 eq	40 h	1551

^aafter exposure to air moisture, ^bprepared at 600°C

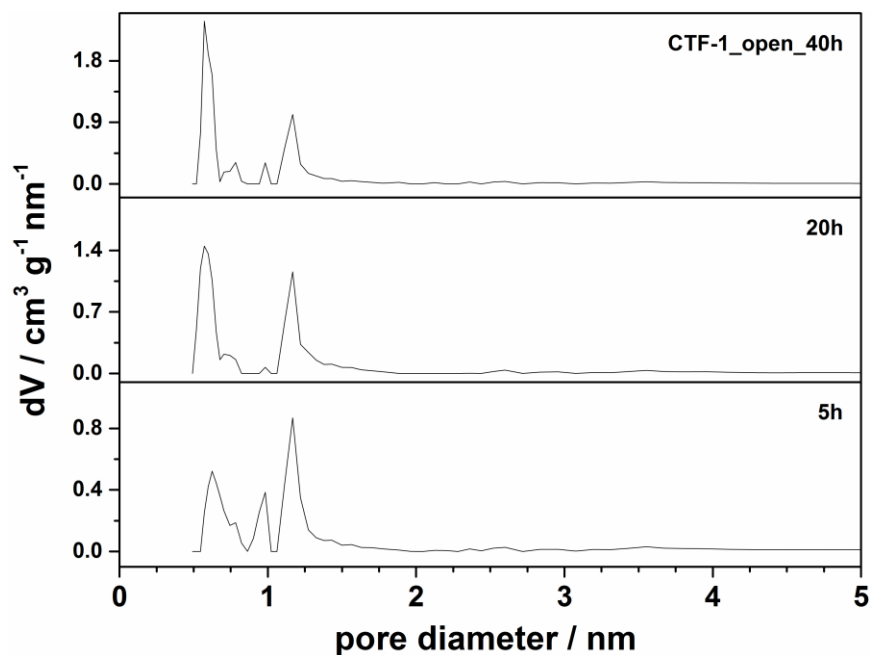


Figure S7: Pore size distribution of CTFs prepared at different reaction times.

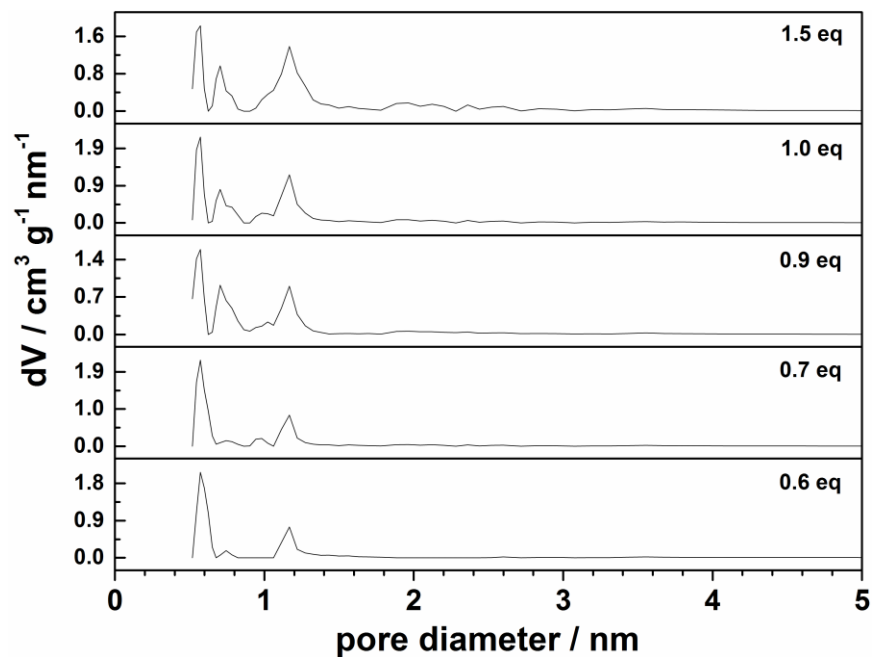


Figure S8: Pore size distribution of CTFs prepared with a series of $\text{ZnCl}_2/\text{pre-CTF}$ values.

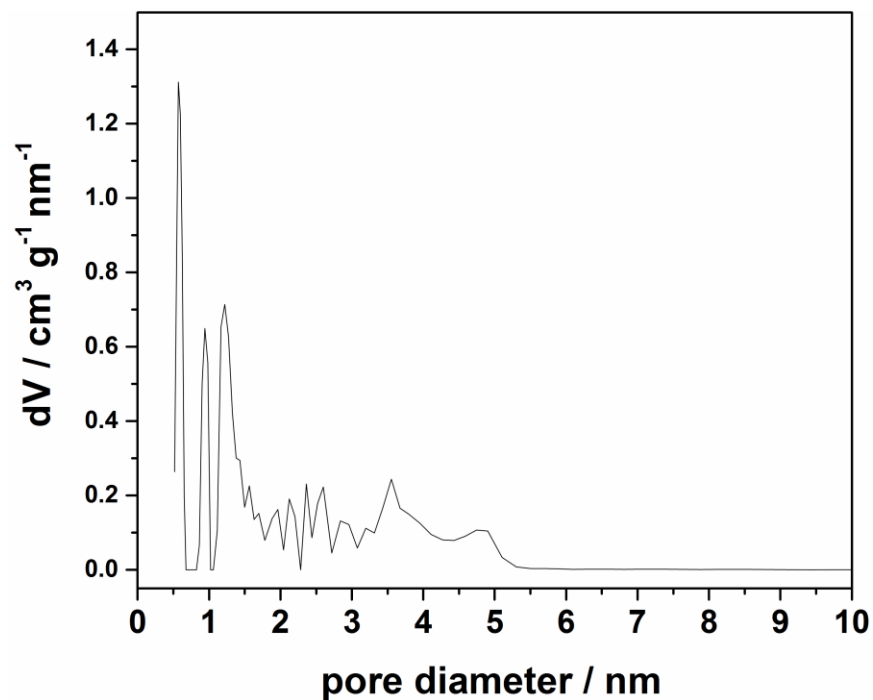


Figure S9: Pore size distribution of CTF prepared from pre-CTF in an open crucible at 600 °C (entry 11).

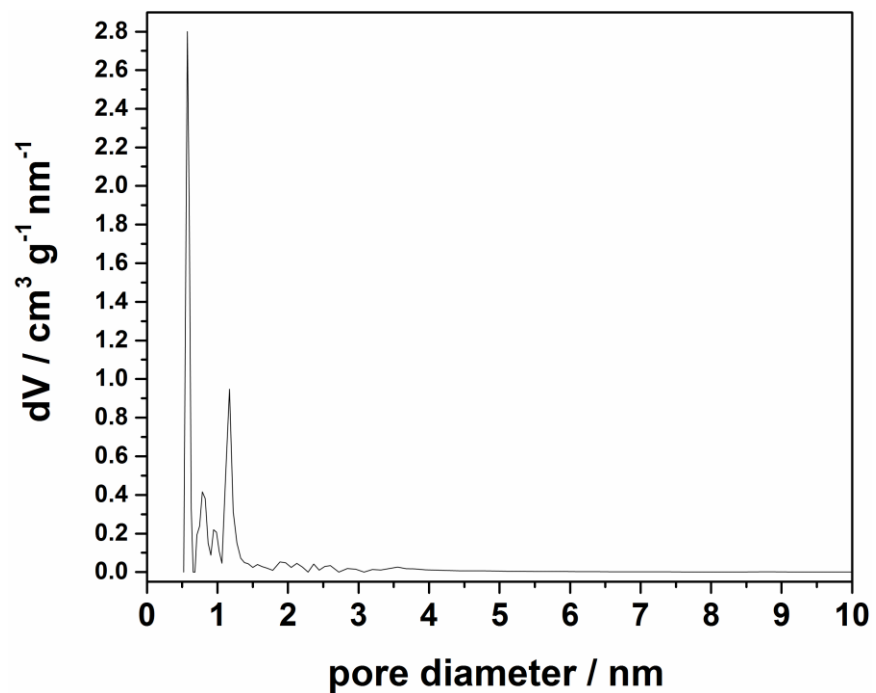


Figure S10: Pore size distribution of CTF-1 prepared from pre-CTF in an open crucible after exposure to air moisture (entry 10).

S5. X-ray diffraction analysis

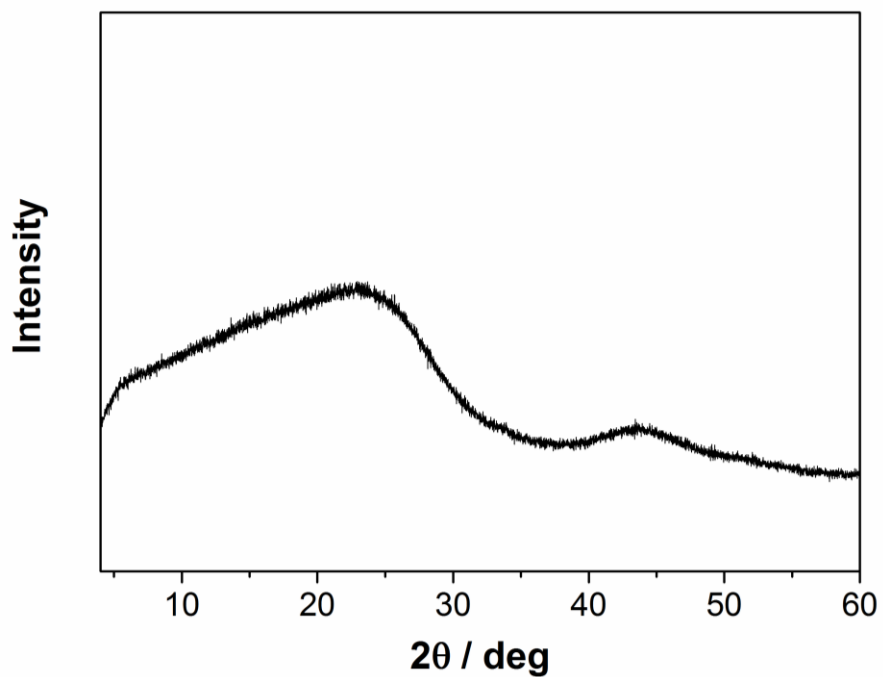


Figure S11: Powder XRD pattern of CTF prepared from pre-CTF in an open crucible at 600 °C (entry 11).

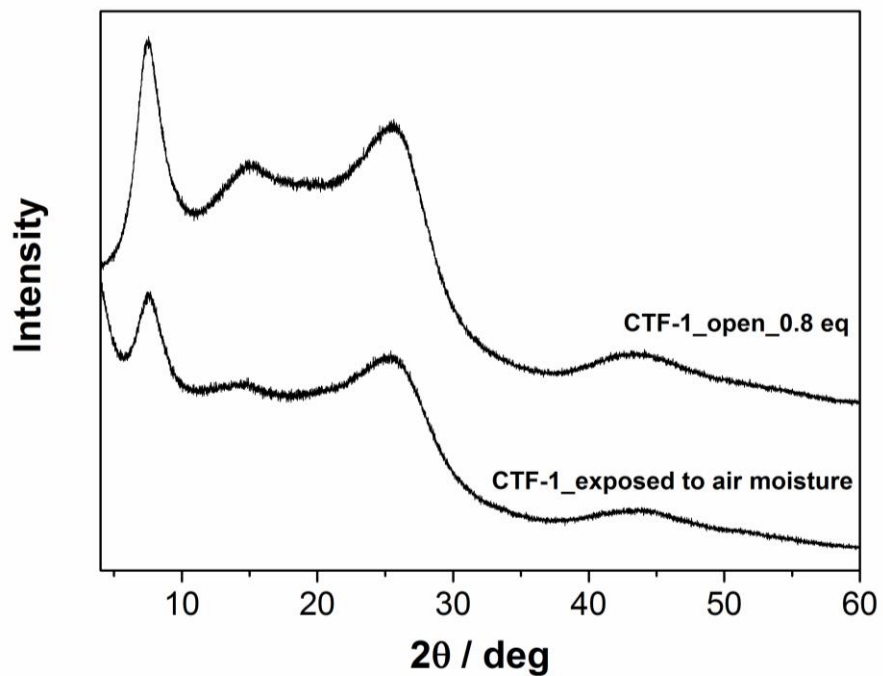


Figure 12: Powder XRD pattern of CTF-1 prepared from pre-CTF in an open crucible after exposure to air moisture (entry 10).

References

- (S1) Anderson, D. R.; Holovka, J. M.; Corporation, X. *J. Polym. Sci. Part A Polym. Chem.* **1966**, *4*, 1689.