Dr. Catherine Mollart | 17.10.2024

Inducing Crystallinity in Covalent Triazine Frameworks

SUMMARY: Covalent triazine frameworks (CTFs) exhibit different structures, degrees of crystallinity and resulting properties depending on the synthetic route alone.

Covalent triazine frameworks

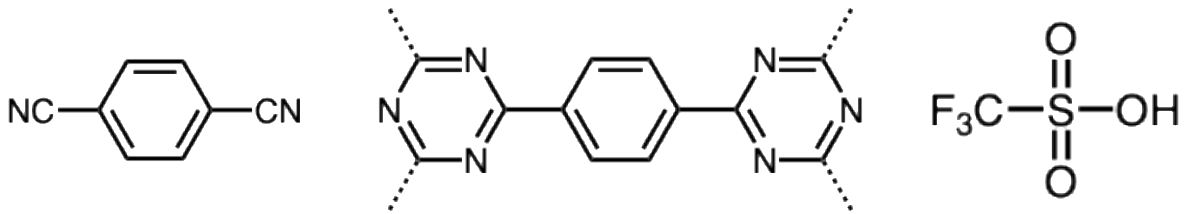
- A type of microporous organic polymer (MOPs) first reported in 2008.[1]
- Formed from commercially available, inexpensive starting materials.
- Chemically and thermally stable and covalent, with a π-conjugated skeleton.
- Applications in CO_2 capture, band gap engineering, drug delivery, *etc.*
- Depending on the synthetic route, can be considered either a sub-class of conjugated microporous polymer (CMP) or covalent organic framework (COF).

Synthesis

Three CTFs can be formed from the cyclotrimerisation of 1,4-dicyanobenzene:

- **CTF-1:** Original synthesis using an ionothermal reaction (400 °C, 40 h), using molten $ZnCl_2$ as catalyst and solvent.[1]
- **P1M:** Microwave-assisted synthesis using trifluoromethanesulfonic acid catalyst.[2]
- **P1:** Room temperature synthesis using trifluoromethanesulfonic acid catalyst.[2]

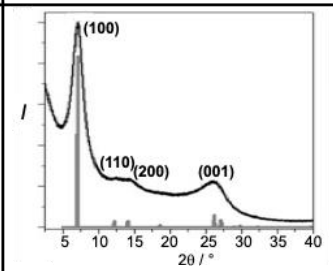
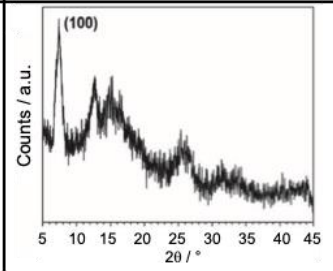
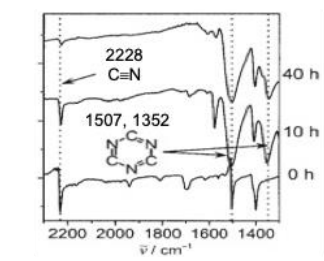
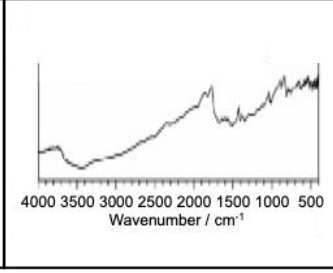
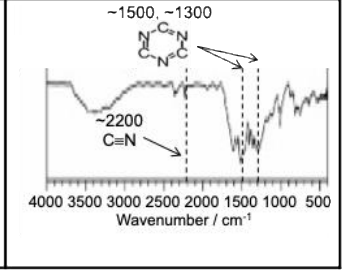
The synthetic routes to prepare **P1M** and **P1** were proposed as a milder synthesis that doesn't require the removal of $ZnCl_2$, however, trifluoromethanesulfonic acid is a 'superacid' (pKa ~ –14.7 ± 2.0 in water), so still not ideal conditions.



CTF-1/P1M/P1 a) monomer and b) repeat unit. c) Trifluoromethanesulfonic acid.

Properties

- **CTF-1** is porous (Brunauer–Emmett–Teller surface area [BET_{SA}] = 791 $m^2\ g^{-1}$) and crystalline with the same topology as COF-1.[1]
- **P1M** is non-porous and exhibits preferential ordering, shown in the powder x-ray diffraction (PXRD) pattern and attributed to the microwave synthesis.[2]
- **P1** is non-porous and amorphous, with no evidence of crystallinity.[2]
- The Fourier-transform infrared (FT-IR) spectrum of **P1** shows additional peaks compared to **CTF-1**, rationalised due to the additional structural diversity.[1–3]

Name	CTF-1	P1M	P1
PXRD pattern			▪ Not reported due to the amorphous nature of the material.
FT-IR spectrum			

Outlook

Ionothermal reactions can give increased crystallinity/porosity, yet there is more flexibility in the available monomers using the room-temperature or microwave reactions. There is a balance between crystallinity and monomer stability.

References: 1) *Angew. Chem. Int. Ed.* **2008**, *47*, 3450. 2) *Adv. Mater.* **2012**, *24*, 2357. 3) *PCCP* **2022**, *124*, 7318.