

Porous, Fluorescent, Covalent Triazine-Based Frameworks Via Room-Temperature and Microwave-Assisted Synthesis

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Microporous organic polymers (MOPs) are exciting materials for gas adsorption, chemical separations, and heterogeneous catalysis.^[1] MOPs combine chemical stability with wide synthetic diversity.^[2] A range of MOPs have been developed including polymers of intrinsic microporosity (PIMs),^[3] hypercrosslinked polymers (HCPs),^[4] porous aromatic frameworks (PAFs),^[5] conjugated microporous polymers (CMPs),^[6] and covalent organic frameworks (COFs).^[7] In 2008, Kuhn et al. reported the ionothermal synthesis of covalent triazine-based frameworks (CTFs).^[8] Using molten ZnCl₂ as both molten solvent and catalyst, cheap aromatic nitriles were trimerized at high temperatures (400–700 °C) to give triazine-based network polymers with high surface areas (apparent BET surface area of more than 3000 m² g⁻¹ in some cases).^[9] CTFs have high thermal stability and CTF-1^[8] and CTF-2^[10] showed a limited degree of crystalline order. CTFs have been explored as sorbents for gas storage^[8] and organic dyes,^[5b,11] and their relatively low potential cost and avoidance of precious metal-catalyzed coupling chemistry make them appealing candidates for scale up. As an example of introducing functionality, 2,6-dicyanopyridine was trimerized to give an efficient, heterogeneous CTF solid catalyst for the selective, low-temperature oxidation of methane to methanol after coordination of platinum.^[12] Furthermore, CTFs have been used as solid supports for palladium nanoparticles in heterogeneous catalysis, significantly increasing the catalyst stability.^[13]

However, while the ionothermal method is efficient for triazine (C₃N₃) ring formation in these CTFs, the high temperature and long reaction times required might limit practical applications. For example, not all monomers will withstand such harsh reaction conditions, and even using the robust aromatic monomers described in the initial 2008 report,^[8] a degree of carbonization was observed in some cases. Zhang et al. shortened the reaction time (from the typical 40 h to less than

1 h) using microwave-assisted polymerization.^[14] However, in all cases the ZnCl₂ catalyst was difficult to remove, resulting in unavoidable contamination of up to 5 wt% inorganic (often mainly metallic) residue.

Strong Brønsted acids are also known to catalyze the trimerization of nitriles.^[15] Here, we present the synthesis of CTFs using trifluoromethanesulfonic acid (TFMS) as the catalyst under both room temperature and microwave-assisted conditions. Unlike the black-colored materials obtained via ionothermal synthesis,^[8] the polymers received after TFMS-catalyzed condensation are free-flowing, fluorescent powders, with absorption and photoluminescence spectra that depend on the choice of monomers. Intriguingly, in spite of the presence of a strong Brønsted acid, successful cyclotrimerization of aromatic nitriles such as 4,4'-oxydibenzonitrile was achieved, a monomer previously thought to be too unstable—both thermally and chemically—to form a CTF-type network.^[9a,10] The much lower temperature employed in TFMS-catalyzed condensation offers a significant advantage, avoiding many undesired decomposition and condensation reactions such as C-H bond cleavage and carbonization.^[16]

CTF-type polymers **P1-P6** and **P1M-P6M** were synthesized by the TFMS catalyzed reactions at room temperature and with microwave heating, respectively (**Scheme 1**). The chemical structures of **P1** and **P1M** are nominally identical to CTF-1.^[8] After extensive washing, the insoluble polymers were collected as fine powders with colors that ranged from pale-yellow to brown in yields greater 80% in case of the room temperature reaction, and as powders and glassy solids for the microwave-assisted synthesis. In both cases, the infrared spectra of these polymers (Figure S1, Electronic Supporting Information) show a significant decrease in the otherwise intense carbonitrile band around 2220 cm⁻¹ along with the emergence of strong triazine absorption bands around 1500, 1360, and 800 cm⁻¹, indicating, qualitatively, a high degree of polymerization. Elemental analysis of the polymers shows good overall agreement with the theoretical values for hypothetical fully-condensed networks, with some deviations common for microporous materials due to incomplete combustion and adsorbed water and gases in the pore structure.^[17] Compared with the polymers obtained from the ionothermal ZnCl₂ catalyzed synthesis,^[8,9b] **P1-P6** and **P1M-P6M** show a nitrogen content that is closer to the expected values, suggesting fewer overall defects (Table S1 and S2). To examine the thermal stability of these polymers, we heated the polymers at 400 °C for 40 h under a N₂ atmosphere for exactly the same temperature and time as reported by Kuhn et al.^[8,9b] After heating, elemental analysis of the polymers showed a negligible change in C to N ratios. Good thermal stability up to 600 °C

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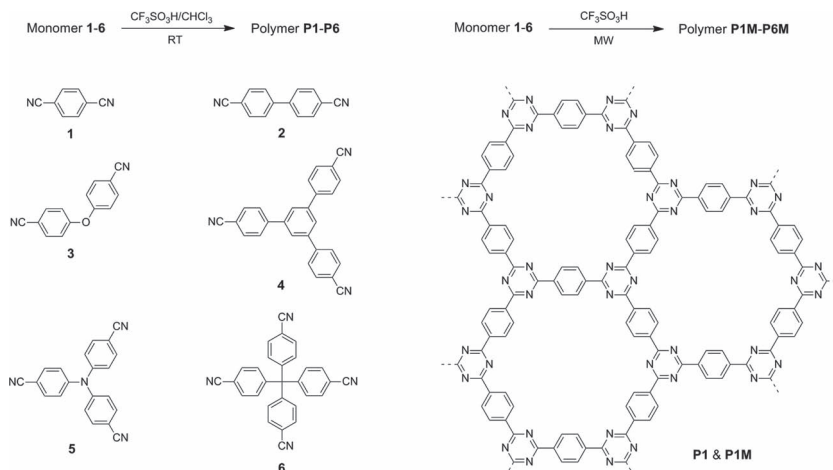
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was confirmed by thermogravimetric analysis (TGA) performed under air (Figure S2). As an example, **P6** was characterized at the molecular level by ^1H - ^{13}C CP/MAS NMR and $^{13}\text{C}\{^1\text{H}\}$ MAS NMR (Figure S10). Peaks at 171.5 ppm ($-\text{C}=\text{N}-$) and 149.6 ppm ($-\text{C}=\text{C}=\text{N}-$) are consistent with the triazine ring motif.^[18] The low intensity peaks at 119.3 and 111.6 ppm are ascribed to ($-\text{C}\equiv\text{N}$) and ($-\text{C}=\text{C}=\text{N}$) functionalities from residual cyano end groups.

The porosity in the CTF-type polymers was investigated by nitrogen adsorption/desorption experiments at 77 K (Table 1). Surprisingly, both **P1** and **P1M** synthesized from 1,4-dicyanobenzene showed no porosity, while **CTF-1**,^[8,9b] and the nominally isostructural **COF-1**,^[7a] show permanent microporosity. We hypothesize that the high porosity of **CTF-1** might stem from the template effect of ZnCl_2 or, potentially, from other defects introduced during the high temperature synthesis. The CTFs **P2-P6** and **P2M-P6M** had apparent BET surface areas ranging from $464\text{ m}^2\text{ g}^{-1}$ (**P2M**) to $1152\text{ m}^2\text{ g}^{-1}$ (**P6**). As a general trend, polymers made from more highly branched monomers showed higher surface areas. All polymers gave rise to typical Type I sorption isotherms,^[19] indicating a predominantly microporous structure. While still mainly Type I, networks **P3** and **P3M** show evidence of a H3 hysteresis loop, indicative of the existence of mesopores and/or small macropores. Pore size distributions were calculated using nonlocal density functional theory (NL-DFT) (Figure S3). **P6**, which has the highest surface area, shows the smallest pore size centering at 1.0 nm. An apparent peak at about 5 nm for **P3** shows that there is some mesopore content in the polymer, in agreement with the shape of the N_2 isotherms (Figure 1).

The level of microporosity in the materials was assessed by the ratio of micropore volume to the total pore volume ($V_{0.1}/V_{\text{tot}}$).^[6a] All of the polymers except **P3** and **P3M** show $V_{0.1}/V_{\text{tot}}$ values greater than 0.67, demonstrating micropores are dominant in the networks, while for **P3** and **P3M**, a $V_{0.1}/V_{\text{tot}}$ value of 0.49 and 0.58, respectively, indicates the existence of mesopores.

The carbon dioxide uptake of the networks was measured up to 1 bar at 273 K. The highest uptake (4.17 mmol g^{-1}) was observed for **P6M**, which is one of the highest values reported for any organic polymer network under these conditions. Non-systematic variances were observed for the CO_2 uptakes of CTFs prepared by the two different methods (room temperature and microwave-assisted). For example, **P4** showed a higher CO_2 uptake than **P4M**, but **P6** showed a lower uptake than **P6M**. In addition to the absolute CO_2 uptake, gas selectivity is also important.^[20] For post-combustion carbon capture, CO_2 should be preferentially adsorbed over N_2 . CO_2/N_2 selectivities were calculated at 273 K using the Ideal Adsorbed Solution Theory (IAST) method. Selectivities in the range of 16 to 31 were calculated for these CTFs. **P1M** showed the highest selectivity (31.2) of all the networks, despite having the lowest absolute CO_2 uptake. Network **P6** and **P6M** showed the lowest selectivities (14.1 and



Scheme 1. Synthesis of the CTF-type polymers **P1-P6** and **P1M-P6M** and representative structure of **P1** and **P1M**. Note that the structural representation is schematic and that these network materials possess, at best, only a limited degree of long range order.

14.2, respectively) of the networks whilst having the highest CO_2 uptakes (Figure S4 to S9, and Table 1). The inverse proportionality between uptake and selectivity is in line with previous reports.^[21]

All of the networks obtained at room temperature were totally amorphous, but some CTFs prepared by microwave-assisted methods (**P1M**, **P2M** and **P4M**) show preferred orientation and some limited evidence of crystallinity, as evaluated by powder X-ray diffraction (PXRD, Figure 2).

Monomers **1**, **2** and **4** are either inherently planar or can conceivably be connected via triazine-linkers into 2D extended sheets with cavity sizes and periodic repeats determined by the

Table 1. Porosity data for polymers **P1-P6** and **P1M-P6M** from N_2 isotherms collected at 77 K.

Polymer	S_{ABET} [$\text{m}^2\text{ g}^{-1}$] ^{a)}	$V_{0.1}$ [$\text{cm}^3\text{ g}^{-1}$] ^{b)}	V_{tot} [$\text{cm}^3\text{ g}^{-1}$] ^{c)}	$V_{0.1}/V_{\text{tot}}$	CO_2 uptake [$\text{cm}^3\text{ g}^{-1}$] ^{d)}	CO_2/N_2 selectivity ^{e)}
P1	2	–	–	–	–	–
P2	776	0.30	0.45	0.67	41.78	20.3
P3	571	0.22	0.45	0.49	50.37	22.5
P4	867	0.35	0.44	0.80	69.36	16.6
P5	960	0.38	0.55	0.69	66.79	24.1
P6	1152	0.45	0.58	0.78	75.39	16.1
P1M	4	–	–	–	20.95	31.2
P2M	464	0.21	0.28	0.75	42.46	21.0
P3M	523	0.24	0.41	0.58	50.17	15.8
P4M	542	0.19	0.28	0.68	41.48	22.4
P5M	542	0.25	0.32	0.78	46.15	20.1
P6M	947	0.38	0.48	0.80	93.46	14.2

^{a)}BET surface area calculated over the pressure range 0.01–0.05 P/P_0 at 77 K; ^{b)} $V_{0.1}$, pore volume at $P/P_0 = 0.1$ at 77 K; ^{c)} V_{tot} , total pore volume calculated at $P/P_0 = 0.99$; ^{d)} CO_2 uptake measured at 273 K and 1 bar; ^{e)} CO_2 and N_2 uptakes measured at 273 K.

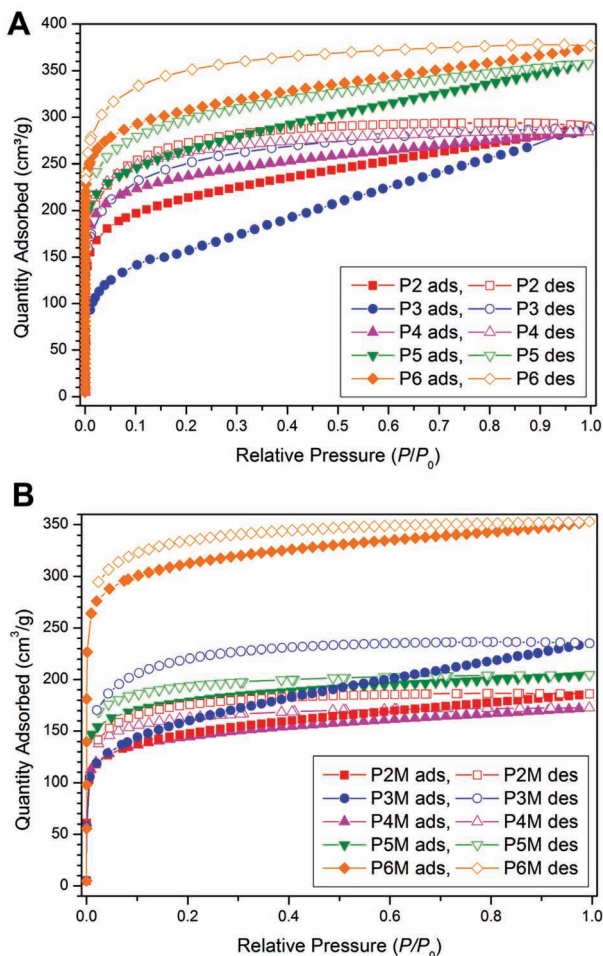


Figure 1. Nitrogen adsorption and desorption isotherms measured at 77 K of the polymers **P1-P6** (A) and **P1M-P6M** (B). The adsorption and desorption branches are labelled with filled and empty symbols, respectively.

size and shape of the respective molecular building blocks, analogous to boron-linked COFs.^[7] The PXRD peaks are too broad and weak to deduce any atomistic structural information, or to comment on the potential stacking order of triazine-linked sheets. However, the diagnostic, low-angle peak marked as (100) can be interpreted as the principle in-plane reflection of three hexagonal unit cells based on the respective aromatic units bridged by triazine-linkers (Figure 2). Ideal 2D hexagonal lattice parameters are $u = v = 14.574 \text{ \AA}$ for **P1M**, $u = v = 22.016 \text{ \AA}$ for **P2M**, and $u = v = 14.574 \text{ \AA}$ for **P4M** corresponding to the respective

primary (100) reflections. This is in broad agreement with unit cell parameters calculated and observed for the corresponding triazine bridged network, **CTF-1** (with $a = b = 14.547 \text{ \AA}$)^[8] or for the isoelectronic boroxine (B_3O_3) bridged network, **COF-1** (with $a = b = 15.420 \text{ \AA}$)^[7a] further supporting the formation of partially ordered CTFs via this route. Possible stacking distances of individual layers are in the range of 3.45–3.56 Å as seen from the diagnostic region around 25–27° 2 θ , which is in good agreement with layered aromatic systems such as graphite (3.35 Å).

The residual crystallinity or preferential ordering achieved in these frameworks is a direct consequence of the solvothermal microwave route, since no order was apparent in the room temperature analogues. It is widely believed that the key to the synthesis of the well-ordered organic frameworks lies in the reversibility of the reaction that links together the building blocks.^[7a,10] Cyanamide can cyclotrimerize to the related tri-s-triazine molecule without the aid of a catalyst at temperatures of around 137 °C,^[22] which in turn remains intact at temperatures exceeding 300 °C.^[23] It is conceivable that the combination of increased pressure (<4 bar) during the microwave-assisted reaction, and the Brønsted acidic environment, can facilitate the making-and-breaking of the triazine unit at lower temperatures, hence promoting the thermodynamic formation of ordered domains in an overall amorphous network. We note that the microwave-assisted method generates materials with lower BET surface areas than the room temperature method. The observation that more ordered materials can result in lower porosity is in line with our recent observations for some porous organic cages^[24] as well as the original report on CTFs.^[8]

Unlike CTFs prepared by the ZnCl_2 catalyzed synthesis, the CTFs prepared here are not black, but range in color from pale yellow to brown as noted above. Solid-state UV-vis spectra of **P1-P6** and **P1M-P6M** all showed relatively broad absorptions, consistent with other porous polymers (Figure S11A and B).^[6b] **P1-P6** and **P1M-P6M** exhibited bright fluorescence under UV light. Photoluminescence (PL) spectra are shown in Figure S11C and D. The photophysical properties of the CTFs

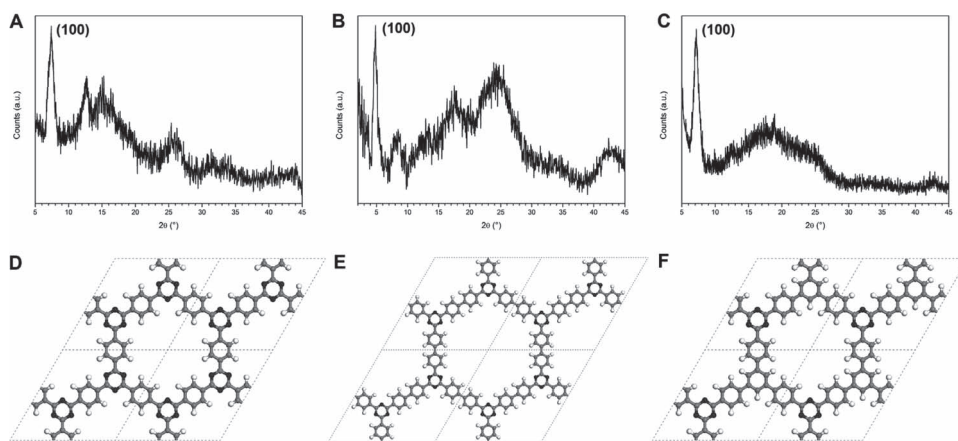


Figure 2. PXRD patterns for **P1M** (A), **P2M** (B) and **P4M** (C), respectively. Below: Structural representations of idealized, defect free lattices for **P1M** (D), **P2M** (E) and **P4M** (F) with carbon, nitrogen and hydrogen shown as grey, black and white spheres. Assumed 2D hexagonal lattice parameters (unit cells shown in dashed lines) are $u = v = 14.574 \text{ \AA}$ for **P1M**, $u = v = 22.016 \text{ \AA}$ for **P2M**, and $u = v = 14.574 \text{ \AA}$ for **P4M** corresponding to the respective primary (100) reflexes. Based on these models, stacking distances of individual layers would be in the range 3.45–3.56 Å.

prepared by the TFMS-catalyzed method can be adjusted by judicious choice of monomers and synthetic conditions, suggesting potential applications in optoelectronic devices, bandgap engineering and, potentially, supercapacitors.^[25]

In summary, TFMS can be used as a room-temperature catalyst for the cyclotrimerization of common, readily-available aromatic carbonitriles into porous, fluorescent microporous CTF networks. The relatively mild synthetic conditions allow incorporation of functional groups that are intolerant to previous approaches. This, along with the relatively low cost and good scalability of this route, will be important for applications that seek to combine extended conjugation with microporosity.

Experimental Section

Chemicals: Compound **1**, **2** and trifluoromethanesulfonic acid were purchased from Sigma-Aldrich, compound **3** was purchased from TCI. Compounds **4-6** were synthesized using the procedure reported previously.^[26]

Detailed synthetic procedures for P1-P5 and P1M-P5M can be found in the ESI. The synthesis of the highest surface area polymers, **P6** and **P6M**, are given below as representative examples.

Synthesis of P6: Trifluoromethanesulfonic acid (0.75 g, 5 mmol) in 5 mL of CHCl₃ was charged into a pre-dried 2-neck round bottom flask under N₂ atmosphere. The mixture was cooled to 0 °C and 4,4',4'',4'''-Methanetetrayltetrabenzonitrile (**6**, 390 mg, 0.93 mmol) in 35 mL of CHCl₃ was added into the solution dropwise over 30 min.^[27] The mixture was stirred at 0 °C for another 2 h before left overnight at room temperature. The solution turned red and a solid precipitate was formed. Then, the mixture was poured into 200 mL of water containing 10 mL of ammonia solution and stirred for 2 h. The precipitates were filtered and washed with water, ethanol, acetone and chloroform successively. **P6** (386 mg, 99% yield) was obtained as a yellow solid. FT-IR (KBr, cm⁻¹): 2229, 1500, 1362, 1015, 813. Anal. Calcd for C₂₉H₁₆N₄: C, 82.84; H, 3.84; N, 13.32. Found: C, 69.84; H, 3.93; N, 15.27.

Synthesis of P6M: Trifluoromethanesulfonic acid (2 mL, 3.4 g, 22.4 mmol) and 4,4',4'',4'''-methanetetrayltetrabenzonitrile (**6**, 0.2 g, 0.48 mmol) were charged into a 10 mL glass reaction vessel (CEM, Discover and Explorer SP Vessels). A PTFE encapsulated rare earth stirring magnet was added and the vessel was sealed with a pressure control cap (CEM, ActiVent Pressure Control Technology). The reaction mixture was prepared immediately before the microwave-treatment in order to prevent condensation to the predominantly kinetic product at room temperature. The reaction was stirred and heated dynamically at max. 300 W in a CEM Discover SP microwave to 110 °C and kept at that temperature for 30 min (internal pressure < 4 bar). The solution changed color to red-brown and became too viscous for stirring less than 10 min into the reaction, as monitored by the integrated camera (CEM, Discover and Explorer SP Accessories). Solid precipitate formed as particles. The product was grounded carefully and washed with 0.1 M ammonia solution in the filter until neutral. Subsequently, the powder was washed with water, ethanol, acetone and THF and finally dried under dynamic vacuum (< 1 × 10⁻³ mbar) at 180 °C to remove residual solvent and traces of TFMS. **P6M** (186 mg, 93% yield) was obtained as a light yellow powder. FT-IR (KBr, cm⁻¹): 3059, 2231, 1504, 1360, 1013, 811. Anal. Calcd for C₂₉H₁₆N₄: C, 82.84; H, 3.84; N, 13.32. Found: C, 80.21; H, 3.97; N, 12.86.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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