1. Introduction

In an environment with an increasing need for fluid purification, such as CO₂ capture and desalination, adsorption and/or separation technologies are highly demanded. To tackle micro pollution, organic frameworks are vastly investigated as they are generally known to be very stable under various pressures, chemicals, and temperatures. Their properties, such as porosity and surface energy, are also highly tunable which makes them useful in specific applications. Metal organic frameworks (MOF) are micro/nanoparticles with a metal core surrounded by a cage of organic linkers, making them highly porous and crystalline. The downside to MOFs,
however, is the high material costs and their unknown effects in the open environment as an inorganic nano-material[1-7].

Covalent organic frameworks (COF) are an alternative as they are cost-efficient and more environmentally friendly due to their fully organic nature; a specific branch of COFs is the covalent triazine framework (CTF). CTFs are characterized by their triazine-ring monomers that are repeated to form a highly porous structural network. Trimerization - the process of constructing hexagonal triazine rings - is generally initiated via an ionothermal reaction, where a Lewis acid catalyst (e.g., ZnCl₂ and CF₃SO₃H) is added to the solution and heated. Not only are triazine rings mechanically strong channels that promote adsorption and permeability, but they also contain abundant nitrogen groups that encourage chemical selectivity. Inspired, scientists have proposed novel CTFs to test for adsorption and others have synthesized new CTF-modified membranes for separation processes. All in all, the following studies have discovered advantageous properties of CTFs and have advanced these frameworks as promising technology for large-scale purification systems[8-18].

This article reviews recent CTF studies on gas separation (namely CO₂ capture), desalination, and a few others. For each study, we discuss the synthesis of the CTF, the synthesis of the membrane (for some studies), characterizations, and finally adsorption/separation performances. The general fabrication of the CTF membrane and separation process are explained in Fig. 1 and study results are summarized in Table 1.

2. Covalent Triazine Framework Membranes

2.1 Gas Separation Membrane

Several CTFs were synthesized in a vacuum at 400°C for 48 h by an ionothermal reaction between aromatic nitriles and ZnCl₂ catalyst. Such nitriles included tetrakis(4-cyanophenyl)ethylene, terephthalonitrile, tetrafluoroterephthalonitrile, 4,4'-biphenyldicarbonitrile, and 1,3,5-benzenetricarbonitrile (the nitriles are referred to as M, M1, M2, M3, and M4, respectively)[19]. Mixed-nitrile CTFs were prepared similarly, but by combining M with M' during synthesis. Cross-polarization magic-angle-spinning nuclear magnetic resonance spectroscopy (CP-MAS-NMR) analyzed H/C and F/C in MM2 and suggested a copolymeric CTF. Brunauer-Emmett-Teller (BET) characterization obtained the surface area measurements, confirming the largest surface area for M-CTF and smallest for MM2-CTF. The CTFs were observed for CO₂ sorption and separation at 273 or 293 K and 1 bar. Five nitrile linkers (M and M1-4) were investigated for the synthesis of CTFs. Accordingly, five single-nitrile CTFs were created as the controls (M- and M'-CTF). This study by Dey et al. introduced a mixed-linker assembly strategy for nitrile-based CTFs and was the first to synthesize four novel mixed-linker CTFs that combines M with one other nitrile linker into a single separation CTF (MM'-CTF). Under BET analysis, all mixed-nitrile CTFs had significantly higher surface areas than their single-nitrile counterparts, with the exception of MM3-CTF; likewise, CO₂/N₂ selectivity for MM1-, MM2-, and MM4-CTF were higher. Interestingly, M-CTF had the largest surface area of 2,235 m² g⁻¹ - compared to 1,800, 1,360, 1,884, and 1,407 m² g⁻¹ for MM1-4, respectively. Although M-CTF had the largest surface area, results showed that MM1-, MM2-, and MM4-CTFs had the highest CO₂ uptake capacities (i.e., 3.68, 4.70, and 3.40 mmol g⁻¹, respectively), in which M-CTF was fourth highest with 3.26 mmol g⁻¹. Note that, despite having the smallest
Table 1. Summary of CTF and CTF membranes

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Catalyst</th>
<th>CTF membrane</th>
<th>Adsorption (Ads) or Permeability (Per)</th>
<th>Selectivity (Se) or Rejection (Re)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>ZnCl₂</td>
<td>MM2-CTF</td>
<td>Ads: (4.70 mmol g⁻¹; CO₂)</td>
<td>Se: (23; N₂), (5; CH₄)</td>
<td>[19]</td>
</tr>
<tr>
<td>PSF</td>
<td>ZnCl₂</td>
<td>CTF-1</td>
<td>Per: (12.7 barrer; CO₂)</td>
<td>Se: (5; O₂), (26; N₂), (22; CH₄)</td>
<td>[20]</td>
</tr>
<tr>
<td>-</td>
<td>ZnCl₂</td>
<td>CTF-DI</td>
<td>Ads: (89.2 cm³ g⁻¹; CO₂)</td>
<td>Se: (53; N₂), (15; CH₄)</td>
<td>[21]</td>
</tr>
<tr>
<td>PIM-1</td>
<td>ZnCl₂</td>
<td>FCTF-1</td>
<td>Per: (7300 barrer; CO₂)</td>
<td>Se: (16.6; CH₄)</td>
<td>[22]</td>
</tr>
<tr>
<td>-</td>
<td>ZnCl₂</td>
<td>Hexene-CTF</td>
<td>Ads: (3.85; C₂H₆), (2.75; C₆H₆) mmol g⁻¹</td>
<td>Se: (19.9; C₂H₆), (10; CH₄)</td>
<td>[23]</td>
</tr>
<tr>
<td>-</td>
<td>ZnCl₂</td>
<td>CTF-PO71</td>
<td>Ads: (104 cm³ g⁻¹; C₂H₆)</td>
<td>Se: (2; C₂H₆)</td>
<td>[24]</td>
</tr>
<tr>
<td>PEBA*-</td>
<td>C₆H₆N₃</td>
<td>CTPP</td>
<td>Per: (73 barrer; CO₂)</td>
<td>Se: (79; N₂), (25; CH₄)</td>
<td>[25]</td>
</tr>
<tr>
<td>-</td>
<td>Sim</td>
<td>CTF-0</td>
<td>Per*: (&gt;10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹; He, H₂)</td>
<td>Se: (4x10⁸ ~ 6x10³⁸; Ne, CO₂, CO, N₂, Ar, CH₄)</td>
<td>[26]</td>
</tr>
<tr>
<td>ICA</td>
<td>ZnCl₂</td>
<td>CTF-1</td>
<td>Per*: (1.7x10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹; H₂)</td>
<td>Se: (17.4; CO₂)</td>
<td>[27]</td>
</tr>
<tr>
<td>-</td>
<td>CF₃SO₂H</td>
<td>TFM-1</td>
<td>Per: (518 mmol g⁻¹; CO₂)</td>
<td>Se: (29; N₂)</td>
<td>[28]</td>
</tr>
<tr>
<td>-</td>
<td>Sim</td>
<td>CTF-1</td>
<td>Per*: (64.2 L cm⁻² day⁻¹ MPa⁻¹; H₂O)</td>
<td>Re: (&gt;91%; salt ions)</td>
<td>[29]</td>
</tr>
<tr>
<td>PES</td>
<td>C₆H₆N₃</td>
<td>NENP-1</td>
<td>Per: (75.4 L m⁻² h⁻¹; H₂O)</td>
<td>Re: (93.3%; MgCl₂)</td>
<td>[30]</td>
</tr>
<tr>
<td>-</td>
<td>CF₃SO₂H</td>
<td>CTFNS/CNNS</td>
<td>Photocatalysis degradation efficiency: 95.8%</td>
<td></td>
<td>[31]</td>
</tr>
<tr>
<td>AAO</td>
<td>CF₃SO₂H</td>
<td>CTF-1</td>
<td>Per*: (141.5 L m⁻² h⁻¹; H₂O)</td>
<td>Re: (&gt;95%; NaCl, MgCl₂, AlCl₃, MgSO₄)</td>
<td>[32]</td>
</tr>
<tr>
<td>AAO</td>
<td>CF₃SO₂H</td>
<td>CTF-1</td>
<td>Per*: (179 L m⁻² h⁻¹; H₂O)</td>
<td>Re: (&gt;94%; CBB, MB, CR)</td>
<td>[33]</td>
</tr>
<tr>
<td>PSF</td>
<td>COF</td>
<td>TpBdMe/PSF</td>
<td>Per: (62.2 L m⁻² h⁻¹ bar⁻¹; H₂O)</td>
<td>Re: (&gt;99%; CR)</td>
<td>[34]</td>
</tr>
<tr>
<td>-</td>
<td>Triazine-based MOF1</td>
<td>Ads: (50 mg g⁻¹; Cu²⁺)</td>
<td>Se: (&gt;99%; Ni²⁺, Co²⁺, Mn²⁺, and Zn²⁺)</td>
<td></td>
<td>[35]</td>
</tr>
</tbody>
</table>

CTF: MM2-CTF, tetranitrile tetrakis(4cyanophenyl)ethylene (M) + tetrafluoroterephthalonitrile (M₂); CTF-DI, diimidazole (DI); PIM-1@FCTF-1, perfluorinated CTF; CTF-PO71, pigmented orange 71; CTPP/PEBA*, covalent triazine piperazine polymer; GO-assisted CTF-1, graphene oxide-assisted; TFM-1, triazine-framework-based porous membranes; NENP-1-PSA/PES, nitrogen-enriched nanoporous polytrizine + polysulfonamide/PES; CTFNS/CNNS, covalent triazine-based framework/graphitic carbon nitride nanosheets; CdS/CTF-1, cadmium sulfide; TpBdMe/PSF, 1,3,5-triformylphloroglucinol (Tp) + benzidine (Bd) + melamine (Me)

Other: Simulation (Sim); Polysulfone (PSF); Polymer of intrinsic microporosity (PIM); Poly(ether-block-amide) (PEBA® 1657); Isopore cellulose acetate (ICA); Polyethersulfone (PES); Anodic aluminum oxide (AAO); Congo red (CR); Coomassie brilliant blue (CBB), Methylene blue (MB); Permeance or flux (*); 1 Barrer = 3.35 x10⁻¹⁶ mol m⁻² s⁻¹ Pa⁻¹

Surface area among mixed-nitrile CTFs in this study, MM2-CTF showed the second highest CO₂ uptake capacity among reported CTFs synthesized at 400°C. The reason for these enhancements was most likely due to the higher micropore volume for CO₂ accessibility created by defluorination carbonization during synthesis. It was concluded that, in CO₂ storage at low pressures, surface area may not be a significant factor compared to CO₂-accessible micropore volume.

CTF-1 was synthesized by mixing terephthalonitrile and ZnCl₂ via the ionothermal process at 400°C for 48 h in a vacuum. Polysulfone (PSF) was dissolved and
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Mixed with different loadings of CTF-1 (i.e., 8, 16, or 24 wt%) to fabricate the novel mixed-matrix membrane (MMM) [20]. Scanning electron microscopy (SEM) characterization on the surface of the MMMs showed uniform dispersion of CTF-1 in the MMMs (Fig. 2). Accelerated Surface Area and Porosimetry (ASAP) analyzed the membrane surface, showing strong interfacial contact between the CTF-1 particles and PSF. The fabricated CTF-1@PSF MMMs and pure PSF membrane (0 wt%) was tested for gas separation at 25 °C and 3 bar. According to Dey et al., CTF membranes were synthesized to study the separation of CO₂ from O₂, N₂, and CH₄ gases. For good gas storage and separation CTF membranes, the parameters used were high surface area, low density, thermal and chemical stability, and plentiful nitrogen functionalities. Hence, CTF-1 and PSF were selected to form mixed-matrix membranes. Although O₂, N₂, and CH₄ permeabilities showed no significant increase with the incorporation of CTF-1, CO₂ permeability showed noticeable improvement. For instance, the 24 wt% MMM exhibited 5.4 barrer higher than the pure PSF membrane. In addition, CO₂/N₂ selectivity showed improvement with increasing loadings of CTF-1, the 24 wt% MMM exhibiting 26 compared to 23 from the pure PSF. Theoretical approaches, such as Maxwell models, have been successfully applied, which predicted that MMMs have the potential to yield about six times the permeability of pure PSF for CO₂ and CH₄ gases. Further analysis suggested that filler porosity has significant influence on the permeability of the membrane.

The novel 2,6-bis(4-cyanophenyl)-1,5-dihydro-benzo[1,2-d:4,5-d']diimidazole (BCDI) was synthesized by combining benzene-1,2,4,5-tetraamine tetrahydrochloride, 4-cyanobenzaldehyde, and NaHSO₃ at 140°C for 24 h [21]. The prepared BCDI was mixed with ZnCl₂ in N₂ atmosphere to undergo an ionothermal trimerization reaction at 550°C to form the novel CTF-DI. Thermogravimetric analysis (TGA) confirmed CTF-DI to have good thermal stability. BET characterization obtained surface areas that greatly varied across nine CTF-DIs that were synthesized under different conditions. CO₂ capture and separations were tested at 273 K and 1 bar. Previous investigations on porous benzodiiimidazole (BDI) based CTFs for gas separation found this CTF to be very inefficient because of strict conditions and unsatisfying permeability. BDI, however, was found to enhance the binding affinity between the CTF and CO₂; therefore, an alternative CTF-DI synthesis methodology was proposed by Du et al. For the first time, BCDI was created and used to synthesize the novel CTF-DI. The prepared CTF-DIs were characterized to have high surface areas up to 1,877 m² g⁻¹ and were tested for gas separation. Results indicated a high CO₂ uptake of 89.2 cm³ g⁻¹ and high adsorption heats of 52 kJ mol⁻¹. Furthermore, selectivities were significant according to the ideal adsorbed solution theory (IAST): CO₂/CH₄ was up to 15, and CO₂/N₂ was a record showing up to 53. These selectivities were due to the abundant presences of active nitrogen species. Pore tunability of the CTF-DIs was also notable as adjusting catalyst ratios and synthesis temperatures was shown to greatly impact pore characteristics and surface area.

A fluorine-based CTF, FCTF-1, was prepared via an ionothermal reaction between 2,3,5,6-tetrafluorotere-
phthalonitrile (TFTPN) and ZnCl₂ in a vacuum at
400°C for 40 h (Fig. 3). To synthesize a polymer of
intrinsic microporosity (PIM), TFTPN, 5,5',6,6'-tetrahy-
droxy-3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI),
and K₂CO₃ were dissolved at 70°C for 40 h to create
PIM-1[22]. The PIM-1 and FCTF-1 were then combined
through solvent evaporation to fabricate the novel
PIM-1@FCT-1 MMM. TGA investigated the thermal
stability of FCTF-1, which indicated a relatively high
thermal stability, most likely due to high bond energy
of the triazine rings (Fig. 4). SEM characterization of
the membranes analyzed cross-sectional images, which
showed that adding FCTF-1 increased roughness and
were dispersed uniformly within the matrix due to its
organic nature. Indeed, some aggregates began forming
at higher loadings, such as at 5 and 10 wt%, but no
cracks or defects were detected. The MMMs were test-
ed for CO₂ separation at 35°C and 1 atm. PIMs are
known to have excellent permeability with the draw-
back of only moderate selectivity in gas separations.
This study by Jiang et al. aimed to improve gas se-
lectivity, specifically CO₂/CH₄, by fabricating a novel
FCTF-1 MMM. The FCTF-1 was combined with and
PIM-1 matrix, which showed strong interfacial compat-
ibility between the two phases because of the organic
nature of the CTF. Moreover, fluorine’s naturally at-
traction to polar CO₂ over nonpolar CH₄ - in addition
to the CTF’s microporous triazine-ring structure (Fig. 5)
- increased CO₂ sorption through the membrane while
increasing CH₄ rejection. The PIM-1@FCTF-1 MMM
synthesized with 2 wt% filler loading exhibited the
best overall performance, exhibiting 7300 barrer for
CO₂ permeability and 16.6 selectivity (Fig. 6). In addi-
tion, all fabricated MMMs (1-10 wt%) showed better
permeability and selectivity than the pure PIM-1 mem-
brane, which was 5800 barrer and 11.5, respectively.
Even though the addition of FCTF-1 blocked many gas

Fig. 3. Synthesis Procedure of FCTF-1 (Reproduced with
permission from Jiang et al., 22, Copyright 2020, American
Chemical society).

Fig. 4. (a) FT-IR spectrum of FCTF-1; (b) XRD pattern of
FCTF-1, indicating the amorphous structure of FCTF-1;
(c) TEM image of FCTF-1; (d) TGA curve of FCTF-1,
showing the high thermal stability (Reproduced with per-
mission from Jiang et al., 22, Copyright 2020, American
Chemical society).

Fig. 5. (a) Nitrogen adsorption and desorption isotherms
of FCTF-1; (b) NLDFT pore size distribution of FCTF-1
(Reproduced with permission from Jiang et al., 22, Copyright
2020, American Chemical society).
transport paths, the good CO₂ solubility of the fillers encouraged permeance through the membrane. Further experiments on propene/propane gas separation proved successful with the novel MMMs, indicating potential in other small molecule separations.

The hexene-CTFs were synthesized by the ionothermal process of trans-3-hexenedinitrile and ZnCl₂ at 400 or 500°C for 48 h on a vacuum. Higher temperatures reorganized the nitrile groups into larger frameworks of triazine rings[23]. Powder X-ray diffraction (PXRD) characterization observed the crystallinity of the CTFs, which showed increased amorphous nature and surface area with more ZnCl₂. This was supported by SEM and transmission electron microscopy (TEM), which visualized the crystalline clusters that were more prominent in CTFs that were synthesized with less ZnCl₂ and lower temperature. The CTFs were tested for acetylene (C₂H₂), ethylene (C₂H₄), and CO₂ separation from CH₄ at 0 or 25°C under pressures up to 1 bar. Conventional hydrocarbon separation methods are energy-intensive, which hinders efficiency in large industries. As a low-energy alternative, Krishnaraj et al. introduced the hexene-CTF, being the first to have utilized a family of aliphatic olefin in the synthesis of a separation CTF. Various synthesis temperatures and conditions have shown to alter texture and porosity, indicating tunable properties (e.g., surface areas are higher at 500°C than 400°C due to defects causing mesopores). Additionally, microscopic images showed significant structural variations, showing the largest crystalline clusters for the hexene-CTF_400_1 (notation: CTF_synthesis temperature_ZnCl₂ ratio) while showing spaghetti-like lattice planes for hexene- CTF_500_10. The structural significance was supported by test results of C₂H₂, C₂H₄, and CO₂ adsorptions, which suggested that pore structure had greater influence in performance compared to surface area. In general, at low pressures, a higher-ordered CTF showed better adsorption of C₂H₂ and C₂H₄ despite having a smaller surface area, most likely due to the increased availability of existing functional groups. The highest adsorption was of C₂H₂ uptake with 3.85 mmol g⁻¹ at 0°C and 1 bar, and both selectivities for C₂H₂ and C₂H₄ from methane (CH₄) were also good due to the CTFs’ better interactions with molecules with double bonds compared to single bonds. CO₂ adsorption and selectivity, however, were only average among reported CTFs, explained by hexene-CTF’s fewer interactive nitrogen groups compared to others.

In the synthesis of CTF-PO71, Pigment Orange-71 (PO71) and ZnCl₂ were combined at 400°C for 40 h under N₂ atmosphere. The ionothermal trimerization process formed triazine rings to finalize the framework[24]. Fourier transform infrared (FTIR) characterization indicated complete polymerization and structural integrity of PO71 monomer during trimerization. Thermal analysis of the CTF-PO71 showed excellent chemical and thermal stability in air and N₂, a highly demanded property in temperature-intensive industries. The novel CTF was tested for C₂H₂/C₂H₄ separation at 273 or 298 K and 100 kPa (1 bar). Pure C₂H₄ is in high demand as it is a key ingredient in the most commonly manufactured plastic: polyethylene (PE). A novel CTF, the CTF-PO71 created by Lu et al., was a simpler and cost-effective alternative to traditional industrial methods when it comes to removing difficult traces of C₂H₂ from C₂H₄. As it was prepared from an organic pigment molecule, the CTF-PO71 possessed functional sites and electrostatic potentials at the pore.

![Fig. 6. CO₂ Permeability and CO₂/CH₄ selectivity of MMMs incorporating different content of FCTF-1 (Reproduced with permission from Jiang et al., 22, Copyright 2020, American Chemical society).](image-url)
surface that were more compatible with C₂H₂ than C₂H₄. This enabled a strong interaction between the CTF and C₂H₂ and therefore effectively captured remnants of C₂H₂ while rejecting C₂H₄ molecules. For example, CTF-PO71 demonstrated one of the highest C₂H₂ adsorptions reported: 104 and 74 cm³ g⁻¹ at 273 and 298 K, respectively. Ethylene separation from other gases were also tested at 1 bar: CO₂ adsorptions were only 78.1 and 48.5 cm³ g⁻¹ for 273 and 298 K, respectively (similarly, CH₄ did not show any promising results). The reduction in performance for smaller gas molecules suggest that the properties of the pore surface were significant factors in addition to the pore shape and size. Being the first to report a successful C₂H₂/C₂H₄ separation method using porous organic polymer, this study is useful when considering large-scale gas separation processes.

Covalent triazine piperazine polymer (CTPP) was synthesized by mixing piperazine, o-dichlorobenzene, N-diisopropylethylamine, and cyanuric chloride (C₃Cl₃N₃) at 180°C for 3 days in normal atmosphere. To synthesize a pure poly(ether-block-amide) (PEBAX® 1657) matrix, a solution made from PEBAX powder was casted and dried[25]. The CTPP/PEBAX MMMs were prepared similarly with the addition of CTPP loadings in the PEBAX powder solution. TGA measurements of the MMM showed thermal stability up to 400°C. FTIR characterization confirmed the presence of triazine rings, although indications were not clear due to overlap with the PEBAX. The analysis, however, also showed increase in hydrogen bonding within the matrix when CTPP was added to the PEBAX. All membranes were tested for CO₂ separation at 293K and 3 bar. As PEBAX is a matrix that exhibits high CO₂ permeability but moderate N₂ and CH₄ selectivities, this study by Thankamony et al. incorporated CTPP into the matrix to create a new enhanced MMM for advanced CO₂ separation processes. CTPP’s organic structure paired well with the PEBAX polymer due to strong hydrogen bonding, so the novel CTPP/PEBAX MMM was mechanically stable. In addition, the prepared CTPP was characterized and shown to be stable both chemically and thermally, which are favorable characteristics for any separation membrane. Further characterization showed increased chain rigidity and shrinkage in CO₂ transport channels in the PEBAX when CTPP was added. Interestingly, this drawback was completely compensated for with the natural CO₂-philic properties of the CTPP. In the separation of CO₂/N₂ and CO₂/CH₄, the CTPP/PEBAX MMM with only 0.025 wt% filler loading significantly improved membrane performance compared to the pure PEBAX membrane. More specifically, CO₂ permeability increased from 53 to 73 barrer, and selectivities increased by 28 and 8 for N₂ and CH₄, respectively. The enhancement was explained by CTPP’s high porosity, surface area, and nitrogen content; overall permeability was greatly enhanced because the nitrogen attracts CO₂ over N₂ and CH₄, which increased pure CO₂ adsorption.

In the computational synthesis of CTF-0, the trimerization reaction of carbonitriles was applied to create C₃N₃H₃ triazine rings. These triazine building units were formed into two-dimensional (2D) sheets, which were then exfoliated into ultrathin nanosheets to be stacked into a porous monolayer membrane[26]. Density functional theory (DFT) calculations of the membrane described gas adsorption and permeation, indicating chemical stability with various gases; this is advantageous over other 2D membranes that are highly reactive, such as graphene. The Arrhenius equation was applied to estimate the membrane selectivities for He and H₂, which showed a decrease in selectivity with increasing temperatures. COFs have intrinsic tunable pore properties that are beneficial for gas separation applications. By layering ultrathin 2D COF nanosheets, micropores can be uniformly distributed in a separation membrane. Inspired by the potential in 2D frameworks, Wang et al. simulated a novel CTF-0 monolayer membrane for He and H₂ gas separation (Fig. 7). Diffusion energy barrier calculations on the CTF-0 membrane for eight different gases showed a direct correlation between membrane diffusion and electron density overlap, i.e., a higher density overlap corresponds to higher diffusion energy barrier. Existing as the two lightest el-
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Fig. 7. Top view of the fully optimized 2 × 2 supercell of the monolayer CTF-0 (C, gray; N, blue; H, white) (Reproduced with permission from Wang et al., 26, Copyright 2016, American Chemical society).

Fig. 8. Energy profiles for (a) He and (b) H$_2$ diffusion through the pore of monolayer CTF-0. (Insets) Corresponding configurations of IS, TS, and FS. For TS, both top and side views are given (Reproduced with permission from Wang et al., 26, Copyright 2016, American Chemical society).

He and H$_2$ had the lowest diffusion barrier, exhibiting excellent permeance through the CTF-0 membrane at middling temperatures (Fig. 8). For instance, He and H$_2$ exceeded the industrially acceptable permeance standard (10$^{-10}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$) at 300 and 355 K, respectively, improving with increasing temperatures. Contrastingly, permeance was significantly lower for Ne, CO, CO$_2$, N$_2$, CH$_4$, Ar and gases - never reaching industrial standards up to 500 K - confirming the membrane’s exceptional selectivity for He and H$_2$ over other gases (Fig. 9).

CTF-1 was synthesized by the ionothermal reaction between 1,4-dicyanobenzene (DCB) and ZnCl$_2$ at 673 K in a vacuum. The resulting bulk powder was exfoliated into ultrathin nanosheets, which were mixed with graphene oxide (GO) nanosheets. Isopore cellulose acetate was used as the support membrane[27]. The GO-assisted CTF-1 membrane was fabricated by mixing and layering the two kinds of nanosheets thinly onto the substrate. It is difficult to restack exfoliated 2D-COF without defects. FTIR characterization confirmed both the presence of triazine rings and undisrupted structures of CTF-1 nanosheets during membrane synthesis. Energy dispersive spectroscopy (EDS) illustrated the even dispersion of nitrogen atoms of the CTF in the membrane, which proved the continuous layering of the membrane. The prepared membranes were tested for hydrogen adsorption and separation at 298 K and 3.0 bar. 2D framework layering techniques to create gas separation membranes have shown to exhibit a high selectivity due to uniform pore structures. For example, GO and CTFs can be formed into 2D

Fig. 9. Electron density isosurfaces for (a) He, (b) Ne, (c) H$_2$, (d) CO$_2$, (e) Ar, (f) N$_2$, (g) CO, and (h) CH$_4$ passing through the pore of a monolayer CTF-0 membrane at the transition states. The isovalue is 0.12 e/Å$^3$ (Reproduced with permission from Wang et al., 26, Copyright 2016, American Chemical society).

Fig. 10. Selectivities of the monolayer CTF-0 membrane for (a) He and (b) H$_2$ over other gases as a function of temperature (Reproduced with permission from Wang et al., 26, Copyright 2016, American Chemical society).
nanosheets, which, when stacked into membranes, are proven to be effective for separation processes. By stacking CTF-1 and GO nanosheets, Ying et al. fabricated a unique GO-assisted CTF-1 membrane. Because the GO contained abundant functional groups, it acted as a magnet between the CTF-1 layers, strongly adhering the nanosheets onto the cellulose support. (Note that insufficient amounts of GO were shown to produce defects due to poor adhesion). The membrane properties were tunable, meaning, different thicknesses (different amounts of nanosheets) adjusted narrowness of inter-layer passages, which in turn affected selectivity and permeability. H$_2$/CO$_2$ separation using the 100 nm membrane indicated the highest recorded H$_2$ permeance of 1.7 x10$^{-6}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$, and the 290 nm membrane indicated good selectivity of 17.4. Indeed, with increasing thickness, permeance decreased and selectivity increased. Nonetheless, the performance surpassed the Robeson’s 2008 upper bound standard for gas separation, deeming the GO-assisted CTF-1 membrane useful for practical H$_2$ purification applications.

To synthesize the triazine-framework membrane (TFM-1), 4,4′-biphenyldicarbonitrile was combined with trifluoromethanesulfonic acid (CF$_3$SO$_3$H) by trimerization and solvent evaporation at 100°C for just over 1.5 h under N$_2$ atmosphere[28]. Two more membranes were fabricated using similar procedures, but with 1,4-dicyanobenzene and 2,7-naphthalenedicarbonitrile (TFM-2 and -3, respectively) (Fig. 11). TGA measurements of the membrane showed high thermal stability that parred with conventionally-prepared CTF membranes (Fig. 12). Energy dispersive X-ray spectroscopy (EDX) indicated negligible acid defects, which was contrasted to conventional CTF membranes that are commonly synthesized with acidic ion remnants. The prepared TFMs were then tested for CO$_2$ adsorption and separation at 273 K and 1 bar. CTFs are commonly synthesized via the ionothermal trimerization reaction catalyzed by a Lewis acid, such as ZnCl$_2$. Although results are usually impressive, the preparation conditions of using such acids are extreme - high pressures and temperatures of at least 400°C - making

![Fig. 11.](image-url)  
Fig. 11. (A) Density functional theory (DFT)-optimized structures of the nitrile monomers used for the membrane synthesis. (B) Trimerization reaction of 4,4′-biphenyldicarbonitrile in CF$_3$SO$_3$H at 100°C. (C) Photograph of a directly synthesized sample of the transparent and flexible triazine-framework-based membrane TFM-1. Inside the circle is shown an “optimized” fragment of the hypothesized framework obtained using Materials Studio (Reproduced with permission from Zhu et al., 28, Copyright 2016, American Chemical society).

![Fig. 12.](image-url)  
Fig. 12. (A) Comparison of the stabilities of (a) the 4,4′-biphenyldicarbonitrile precursor (blue) and (b) the new synthesized membrane TFM-1 (red) under N$_2$. (B) FTIR spectrum of TFM-1 prepared at 100°C. (C) $^{13}$C CP-MAS NMR spectrum of TFM-1. (D) Deconvolution of the N 1s peak in the XPS spectrum of TFM-1 (Reproduced with permission from Zhu et al., 28, Copyright 2012, American Chemical society).
CTFs both difficult and dangerous to create. An alternative preparation methodology was proposed by Zhu et al., where the Lewis acid is replaced by the fluorescent superacid, CF$_3$SO$_3$H. This strong protic catalyst was found to achieve trimerization of three nitrile groups at low temperatures of around 100°C. In terms of experimental results, the TFM-1 exhibited an ideal CO$_2$/N$_2$ selectivity (29±2) and CO$_2$ permeability (518±25 barrer). When compared to COF-102, which had a 5-times greater surface area, the TFM-1 exhibited a better CO$_2$ uptake of 1.3 mmol g$^{-1}$. The high CO$_2$/N$_2$ selectivity was explained by the nitrogen content in the triazine rings that attracted polarizable CO$_2$ more than N$_2$. Furthermore, the yellow TFM-1 membrane may be applicable in optoelectronics as the membrane possessed strong electron capture, emitting blue fluorescent under UV light (Fig. 13).

2.2 Desalination membrane

Theoretical 2D CTF models were designed using classical molecular dynamics (MD) simulations. The membrane was created under Lennard-Jones parameters, water molecules followed the SPC/E model, and salt ions followed parameters proposed by Joung et al.[29]. The REPEAT algorithm based off of DFT calculations derived charges of membrane atoms. By using an approach by Cohen-Tanugi et al., the mechanical integrity of the membranes under reverse osmosis (RO) pressure was tested, measuring stress as a function of PA pore radius. Desalination membranes are widely studied as precious water sources are increasingly polluted and require utmost attention. Pure polymeric substrates, such as polyamide (PA), are known to exhibit high salt rejection but poor water permeability. To improve permeability, many studies have implemented porous nano frameworks into the substrate, such as carbon nanotubes, zeolites, and MOFs. As there is a lack of COF studies for liquid separations, this computational study by Lin et al. was the first to consider 2D CTF membranes for RO desalination. Simulations applying MD were employed under previously proposed water- and salt-molecule parameters, resulting in the formation of four ultrathin CTF membrane models. Theoretical desalination results for the CTF membranes showed complete salt rejection and 2-3 times the water permeability of PA-based membranes; these enhancements were greatly influenced by pore properties, especially pore size. Factors that were not considered in the experiments include membrane flexibility, thermal fluctuations, and deformation caused by pressure. However, easy tunability and structural integrity of the 2D CTF materials is very promising in the field of water purification.

The synthesis of NENP-1 CTF involved mixing melamine, dimethyl sulfoxide (DMSO), and C$_2$Cl$_3$N$_3$ at 150°C for 4 days in a vacuum. Poly(ether sulfone) (PES) was used as the support membrane[30]. The novel NENP-1-PSA/PES membrane was fabricated via the interfacial polymerization of poly(allylamine hydrochloride) (PAH) aqueous phase - combined with NENP-1 CTF nanosheets - and 1,3-benzenedisulfonyl dichloride (BDSC) organic phase to form a CTF-doped polysulfonamide (PSA) layer on the PES substrate (Fig. 14). Cross-polarization magic-angle-spinning (CP-MAS) analysis verified the presence of triazine rings, indicating the successful trimerization of NENP-1. FTIR characterized NENP-1 surface area and pore size, showing pathways larger than water molecules for smoother
permeation (Fig. 15). The CTF membranes were tested for desalination at room temperature and 0.5 MPa. Few studies have ventured into COF technologies in liquid separations, and even fewer have explored COF use in purifying metal-contaminated waters. Hence, Wang et al. recently synthesized a 2D CTF, NENP-1, and fabricated a novel NENP-1-PSA/PES membrane for the nanofiltration of acidic wastewaters. The NENP-1 nanosheets were chosen for their hydrophilic properties, positive charge surfaces, and appropriate pore size to simultaneously improve water permeability and inorganic salt rejection (Fig. 16). PSA was chosen as the matrix as it proved to have good interfacial interactions and stability with NENP-1. The 0.1 w/v% CTF-infused membrane exhibited 75.4 L m$^{-2}$ h$^{-1}$ for pure water permeability and 93.3% MgCl$_2$ rejection (Fig. 17). When compared to an un-doped PSA membrane, the NENP-1-PSA/PES membrane was shown to increase permeability by 149% and rejection by 4.6%. Furthermore, various tests confirmed the intrinsic structural stability of the novel membrane, which was complemented by excellent long-term acid stability and performance in pressurized water separation processes.
Although research for COF/CTF membranes in desalination procedures is just beginning, there is great potential for such technological advancements in the near future.

2.3 Others

Basic CTFs were synthesized by the ionothermal reaction of 4,4'-biphenyldicarbonitrile and CF$_3$SO$_3$H in an ice bath for 1.5 h, then 100°C for 20 min under N$_2$ atmosphere. These CTFs were then exfoliated with sulfuric acid into CTF nanosheets (CTFNS). Bulk graphitic carbon nitride (GCN) was amine-functionalized before also being exfoliated into nanosheets (CNNS)[31]. To synthesize the CTFNS/CNNS composite, a fixed amount of CNNS was mixed with different loadings of CTFNS (1, 5, 10, and 20%) and gone through the electrostatic self-assembly method (i.e., annealed at 200°C for 2 h (2°C min$^{-1}$) in normal atmosphere). TEM characterization visualized and confirmed the porous 2D structures of both CTFNS and CNNS in the composite. X-ray photoelectron spectrum (XPS) analysis indicated a stronger intensity of N and O in the composite compared to pure CTFNS and CNNS, respectively, suggesting the presence of both nanomaterials in the composite. Photocatalysis with the CTFNS/CNNS composite was tested under the irradiation of simulated solar light. The increase in the use of sulfonamide antibiotics have significantly contributed to environmental pollution, which calls for methods to remove it, especially in wastewaters. Photocatalysis is a cost-effective and green method for degrading sulfonamide antibiotics, and Cao et al. proposed the novel CTFNS/CNNS composite, which is a metal-free 2D/2D heterojunction photocatalyst. Individually, GCNs and CTFs are semiconductors that exhibit weak photocatalytic activity, which can be moderately improved by changing their morphologies to 2D nanosheet. When combined, the binary Langmuir-Hinshelwood model explained that these 2D carbon-based materials had significant electrostatic interfacial contact, which enhanced the transfer and separation of excited-state electrons. In terms of results, the 5 wt% CTFNS/CNNS showed the highest photocatalytic activity, decomposing 10 ppm of sulfamethazine (SMT) in 180 min (95.8% degradation efficiency). Further experiments suggested that the composite’s photocatalytic performance can improve in the presence of chlorine ions as they encourage the production of reactive species (e.g., O$_2^\cdot$ and OH$^\cdot$). In addition, an experiment with high performance liquid chromatography-mass spectrometer identified several intermediate products during the degradation of SMT, such as sulfanilamide and sulfanilic acid, which helped propose possible pathways of SMT degradation. The novel CTFNS/CNNS composite showed great potential for 2D/2D heterojunction carbon materials as photocatalysts in water purification processes.

The 2D-CTF-1 nanosheets were synthesized by ionothermal cyclotrimerization of CF$_3$SO$_3$H with DCB and dichloromethane (CH$_2$Cl$_2$) solution on micro-interfaces at 100°C for and dried in a vacuum. Anodic aluminum oxide (AAO) was used as the substrate[32]. The nanosheets were evenly dispersed in dimethylformamide (DMF) before being coated (with different thicknesses) onto AAO substrate via gas-driven pressure filtration. The CTF and membrane morphology was characterized by SEM, where a uniform carbon matrix is visualized on the surface, and the cross-sectional layering of each nanosheet in the membrane can be seen. XRD analyzed the crystallinity of the membranes, indicating an interlayer spacing between the 2D-CTF-1 to be 3.3 Å, which was similar to graphene. The prepared membranes were tested for desalination from molecules or ions at room temperature (25°C) and increasing pressures. Separation membranes using 2D building blocks is highly researched as they exhibit exceptional tunability. In this study, Li et al. synthesized the novel 2D-CTF-1 nanosheet and tested its desalination abilities when fabricated into a membrane. (GO-doped membranes are also fabricated for comparison). The 2D-CTF-1 nanosheets were shown to possess high crystallinity and were successfully, and thinly, dispersed onto the substrate. In addition to the 2D properties, the 2D-CTF-1 nanosheets were very porous due to their triazine structures, or “skeleton pores”, which en-
hanced permeability for water while maintaining high selectivity for larger molecules and ions. For instance, the novel membrane exhibited excellent water permeance of 141.5 L m⁻² h⁻¹ under 1 bar of pressure and rejection above 95%. Even under increasing pressures up to 5 bar, rejections remained consistently higher than 95%, and permeance linearly increased as the highly crystalline 2D-CTF-1 nanosheets encouraged membrane rigidity and stability. Furthermore, the exact nano size of the hexagonal skeleton pores (i.e., 1.39 nm) was extremely beneficial for molecule/ion sieving. In addition to its advanced separation performance, the 2D-CTF-1 membrane was shown to be stable in aqueous environments and higher pressures, deeming it largely advantageous in the separation field.

The micro-interface method was deployed to synthesize 2D-CTF-1 nanosheets, i.e., trimerization of DCB and CH₂Cl₂ solution with CF₃SO₃H at 100°C for 1 h. CdS/CTF-1 nanocomposite sheets were synthesized by heating a solution of CTF-1, cadmium acetate, and DMSO at 180°C for 3 h[33]. Using AAO as the substrate, membranes were synthesized by mixing the three prepared samples with DMF before evenly coating onto the substrate via gas-driven filtration method. Atomic force microscopy (AFM) characterization confirmed the successful fabrication of CTF-1 nanosheets, showing two layers with the combined thickness of about 5 nm. Electron-spin paramagnetic resonance (EPR) spectrometer was used to detect free radicals, which found characteristic peaks for *O₂⁻ and *OH after irradiation. The prepared membranes were tested for dye separation at 2.0 bar. Due to their advanced crystalline imide structures, COFs are highly desirable ingredients in separation membranes. A unique blend of monomers (i.e., Me, Bd, and Tp) was presented in this study by Wang et al. for the purpose of synthesizing a COF composite membrane. Two composite membranes, TpBd/PSF and TpBdMe/PSF, were shown to be very hydrophilic due to an increase in surface roughness compared to pure PSF. For instance, TpBd/PSF had high water permeability of 33.6 L m⁻² h⁻² bar⁻¹ and TpBdMe/PSF was two times greater with 62.2 L m⁻² h⁻² bar⁻¹ of permeability. The superior permeability of TpBdMe/PSF compared to TpBd/PSF was due to the introduction of benzene rings and amino groups from Me, which greatly enhanced hydrophilicity of the membrane. Moreover, the introduction of Me significantly modified the molecular structure, which...
consequently increased crystallinity and pore aperture. Dye rejection was also superior for both membranes, showing more than 99% rejection for Congo red. The membranes were highly sustainable as they showed good stability (chemically and thermally) and anti-fouling properties. This research explored imine-linked COF membranes and showed the promising tunability of membrane properties by introducing amine monomers.

The triazine-based MOF1 was synthesized by the solvothermal reaction between a mixture of 5,5',5''-((1,3,5-triazine-2,4,6-triyl)tris(azanediyl))-tris(2-methylbenzoic acid)/cadmium nitrate hexahydrate and a solution of dimethylacetamide/methanol at 120°C for 72 h[35]. PXRD characterization measured the crystallinity of MOF1, which was in accordance with simulated patterns, indicating successful synthesis without defects. TGA measured the thermal stability of MOF1 and determined a maximum of 360°C before it began decomposing. The ion adsorption performance and Cu\(^{2+}\) selectivity was observed via ICP-MS experimental analysis after filtration through a DMF solution of various metal nitrates. Excessive copper pollution is a potential hazard to life forms in the form of disabilities or birth defects. According to a study by Yousaf et al., adsorption of Cu\(^{2+}\) ions is an effective method to remove copper from the environment, and the novel MOF1 - which is triazine-based - is a great candidate. MOFs are inherently porous and stable, and with the incorporation of nitrogen-abundant sites, can improve selectivity for Cu\(^{2+}\) over other ions. In detail, after dispersing MOF1 in a solution of various metal ions, the MOF1 crystal was extracted and analyzed. Results indicated a high Cu\(^{2+}\) adsorption capacity of 50 mg g\(^{-1}\), which is the same performance as in a pure solution of only copper. In other words, there was no decrease in adsorption capacity for Cu\(^{2+}\). Column chromatography using these bright metal-ion solutions was also deployed to test MOF1’s separation properties. All mixtures of Cu\(^{2+}\) with one other metal ion, such as Co\(^{2+}\), were completely separated; that is, the copper-adsorbed MOF1 remained at the top of the column whereas the rest were easily drained (using DMF as the eluting agent). Similar adsorption tests were done with organic dyes, where Methylamine blue (MB\(^{+}\)) was adsorbed much quicker than Acridine orange (AO), suggesting a greater influence of ionic selectivity for cationic dyes rather than size. Finally, the triazine-based MOF1 was tested for encapsulating luminescent species, which, when combined with green terbium (Tb\(^{3+}\)) and red Europium (Eu\(^{3+}\)), the blue MOF1 could be tuned to emit quality white light. Not only did MOF1 show excellent copper ion selectivity, but it also showed its potential as a luminescent material.

3. Conclusions

Microporous frameworks are advanced technologies that are crucial for efficient purification of gas and liquid systems by separation. CTFs are a branch of COFs that have recently caught attention for their facile and cost-efficient synthesis procedures as well as their excellent separation performances. Various microscopies that characterize morphologies, such as SEM and AFM, have shown the successful fabrication of defect-free triazine networks. Other characterization procedures have measured specific properties of the CTFs: generally, BET measured specific surface areas, TGA indicated thermal stability, and XRD confirmed crystallinity. In terms of performance, CTFs have shown consistently remarkable performance, improving upon substrates in the form of composite membranes and even improving upon itself by manipulation of nano-properties (e.g., exfoliation into 2D nanosheets). Additionally, some studies have investigated CTF's potential in the field of photocatalysis, which resulted in discovering green methods to efficiently recycle fouled membranes via sun irradiation. In conclusion, covalent triazine frameworks are easily tunable organic materials with abundant nitrogen sites, which, in addition to their high porosity, have great potential in future advanced purification industries.
Reference


