



Porous Covalent Triazine-Based Frameworks: Synthesis and Applications in Adsorption and Catalysis

Somayeh Nasrian¹, Massoumeh Bagheri^{2*}

^{1,2} Chemistry Department, Faculty of Science, Azarbaijan Shahid Madani University, Tabriz, Iran

E-mail: massomehbagheri@yahoo.com

Received: 2024-02-28, Accepted: 2024-05-03

Abstract

In recent years, porous organic polymers (POPs) have received much attention due to their porous nature and high surface area, and have found wide applications in many fields. An important class of POPs are porous covalent triazine frameworks (CTFs). CTFs have several advantages including high thermal and chemical stability, rich nitrogen contents and tunable porosities. Their structure consists of light elements (C, N, H) and they consist of strong aromatic C=N linkage. These unique properties endow CTFs with great prospects in various applications such as separation and storage of gases, energy storage, adsorption of pollutants, photocatalysis and heterogeneous catalysis. A series of synthetic strategies have been developed, i.e., ionothermal synthesis, superacid-catalyzed method, phosphorus pentoxide-catalyzed method, amidine-aldehyde condensation method, Friedel–Crafts and Schiff-Base reaction methods. Our aim in this review is to take a short look at different synthetic methods of CTFs, and some of their applications.

Keywords: Porous organic polymers, Covalent triazine frameworks, Trimerization, Catalysis, Adsorption

Introduction

Porous organic polymers (POPs) are new types of porous materials that have been discovered in recent years [1]. POPs have been used in many applications, including drug delivery, adsorption, separation, and catalysis [2-9]. Porous materials are divided into three classes based on the size of their pores by IUPAC. Microspores have a diameter of less than 2 nm, mesoporous between 2 and 50 nm, and pore sizes above 50 nm are classified as macropores.

POPs can be divided into several representative groups, for example conjugated microporous polymers (CMPs), covalent organic frameworks (COFs), porous aromatic frameworks (PAFs), hyper-cross-linked polymers (HCPs), and polymer of intrinsic micro polymers porosity (PIMs).

Among these compounds, COFs are a group of crystalline porous materials that are made of molecular organic structural units composed of light elements and connected by covalent bonds. These porous solids were first synthesized by Yaghi et.al in 2005 [10]. Covalent organic frameworks are of various class based on the type of bond, including: boronate ester-linked COFs [11], covalent triazine-based frameworks (CTFs) [12], and imine and hydrazone-linked COFs [13].

Covalent triazine frameworks (CTFs) are an emerging type of porous organic polymers that have recently attracted much attention due to their unique properties. In general, CTFs are extensive porous frameworks containing triazine units connected by covalent bonds (C=N), which have higher

stability compared to many COFs that include weak bonds such as imines, boronate esters, borazines, hydrazones, etc. [14].

In 2008, Cohen and co-workers reported for the first time the synthesis of CTF-1 with a surface area of about $1000 \text{ m}^2 \text{ g}^{-1}$ and a hexagonal structure via trimerization of 1,4-dicyanobenzene at $400 \text{ }^\circ\text{C}$ [15]. This synthesis method is performed at a high temperature, usually above $400 \text{ }^\circ\text{C}$ and in a sealed ampoule tube. These very harsh conditions do not allow large-scale synthesis. And since then, attempts to synthesize CTFs with new methods have been made by researchers.

The recyclability and reusability of CTFs make them potential candidates for industrial applications such as batteries [16-18], supercapacitor [19, 20], catalyst and photocatalysts [21-23], gas separation [24, 25], removal of pollutants [26], sensors and many other applications.

In this review, we discuss recent developments in the synthetic methods of CTFs and their applications in different fields.

Advantages of nitrogen-rich polymer

CTFs have been investigated due to their conjugated structure, high chemical and thermal stability, as well as high nitrogen content, along with the ability to adjust the structure in various fields of application.

It has been found that nitrogen-rich polymers can be suitable for increasing CO_2 gas adsorption and selectivity towards nitrogen and methane. Their selective adsorption of CO_2 can be due to intermolecular

interactions, guest and polymer, through hydrogen bonding or dipole-quadrupole interactions, and the introduction of heteroatoms, especially nitrogen, into the polymer structure that provides more polar surfaces and increases the selectivity towards CO₂ [27, 28]. In general, the CTFs are a promising prospect for sustainable and green development for various applications, including gas storage and separation, pollutant removal, and catalysis due to their high stability.

CTFs synthesis methods

The triazine ring is the main part of CTFs that contributes to the properties and diverse applications of CTFs. On the other hand, the CTF synthesis methods are classified into two categories based on how the triazine unit is introduced:

The first method is through the synthesis of triazine units by the trimerization reaction and the second method, the synthesis of CTFs, directly introducing the triazine unit through the monomer. The structure of CTFs is highly dependent on the synthesis process,

the type of monomer and the type of bond between monomers. Therefore, it is very important to use the appropriate monomer as well as carefully examine the conditions of CTFs synthesis in adjusting the structure of CTFs.

Herein, we aim to explain some synthetic methods for synthesizing CTFs. Various methods have been developed for the synthesis of CTFs, which include ionothermal methods, polycondensation methods, and methods based on superacids.

Synthesis of CTFs by trimerization reaction

Ionothermal synthesis

It was in 2008 that Kuhn et.al [15] synthesized the first CTFs using ionothermal synthesis. In this work CTF-1 using 1-4, dicyanobenzene was synthesized in the presence of zinc chloride as a solvent and catalyst in a sealed glass at 400 °C (Figure 1).

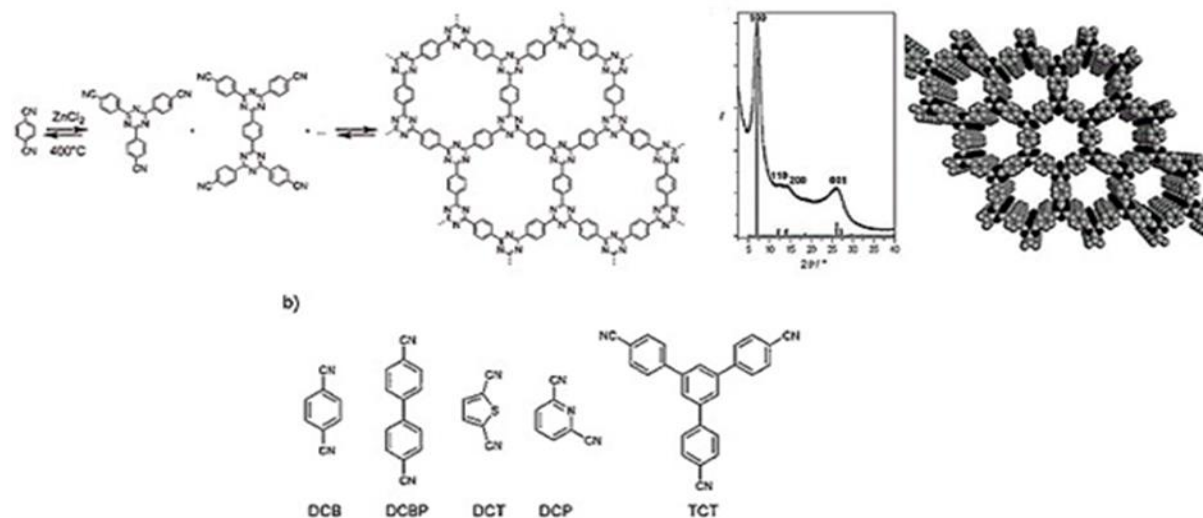


Figure 1. Ionothermal synthesis of polytriazine networks b) Nitrile monomers used in the ionothermal synthesis of triazine frameworks [15].

These synthesized triazine frameworks have high specific surface area, high porosity, and also showed excellent chemical and thermal stability. Temperature had a significant effect on the process of this reaction, because high temperatures cause destruction and carbonization of the structure of the resulting polymers.

The reaction was reversible at a temperature of 400 °C, but a reaction temperature higher than 400 °C would cause irreversible side reactions, because the thermal decomposition of simple aromatic compounds is carried out through the carbonization process and C-C bonds are formed by activating the C-H bond with the successive evolution of H₂.

Also, zinc chloride used in this reaction is molten at temperatures between 300 and 700 °C and boils at 730 °C. The maximum temperature evaluated in order to keep the salt in the liquid state was 700 °C. ZnCl₂ at a temperature of 400 °C can be useful for the preparation of crystalline and porous

polytriazines. First, because ZnCl₂ melts at high temperature and the aromatic nitrile monomers are completely dissolved in this ionic melt with strong Lewis's acid-base interactions and form a clear solution in this molten salt.

Second, ZnCl₂ is a Lewis acid, and it can play a catalytic role in the conversion of nitriles to triazines, and facilitate the trimerization reaction, as well as act as a porous catalyst.

These triazine networks were found to be useful for H₂ adsorption. For example, the 4,4'-biphenylcarbonitrile (DCBP) network (1.55 wt% H₂ at 1.00 bar and 77 K) is comparable to metal organic frameworks (MOFs), mesoporous carbon materials, and zeolites, and can provide high thermal, chemical, and mechanical stability and formability of a thermoset polymer material.

Then, in 2010, the same research group synthesized a second member of the family of covalent triazine frameworks, CTF-2, by ionothermal condensation of 2, 6-naphthalenedinitrile at 400 °C for 40 h (Figure 2). CTF-2 showed a relatively smaller surface area than CTF-1.

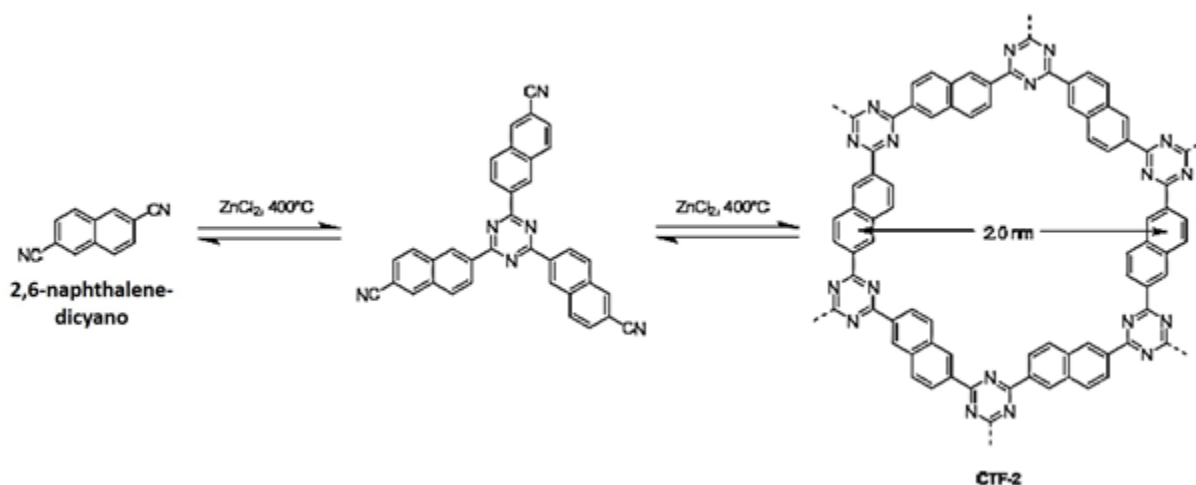


Figure 2. 2,6-Dicyanonaphthalene trimerization reaction to prepare CTF-2 [29].

Adsorption and desorption isotherms of CTF-2 showed the surface area of about $90 \text{ m}^2 \text{ g}^{-1}$ and a pore size of micropores. Indicating that the bulk of micropore content cannot be addressed due to an eclipsed conformation of sheets [29].

Subsequently, in 2013, Thomas' and co-workers synthesized CTF-0 using 1, 3, 5-tricyanobenzene (TCB) monomer by ionothermal method (Figure 3). They found that the reversible trimerization of this monomer leads to a framework that has a smaller pore size than CTF-1 and CTF-2, that's why they named the new framework CTF-0 [30].

This framework showed a high percentage of nitrogen atoms (19.3% by weight) in its structure and showed exceptional CO_2 adsorption due to its high nitrogen content and high surface area. Additionally, CTF-0 has been a suitable metal-free catalyst for the formation of cyclic carbonates from the reaction between CO_2 and epoxides (Figure 4). Investigation of the thermal stability of CTF-0 showed that it is even more stable than CTF-1 and is stable in oxygen atmosphere up to $600 \text{ }^\circ\text{C}$.

CTFs-0 were prepared under different conditions including temperature, time and molar ratio of ZnCl_2 to monomer, and their names were used in the same order. For example, CTF-0-400-40-1.5 was a framework that was prepared at a temperature of $400 \text{ }^\circ\text{C}$ and within 40 hours and a molar ratio of 1.5, ZnCl_2 to monomers. The catalytic efficiency of CTFs-0 (prepared under different conditions) and CTF-1 in the preparation of cyclic carbonates using epoxides and carbon dioxide was

investigated. All CTFs-0 catalyzed the formation of cyclic carbonates under mild and solvent-free conditions and increased the reaction efficiency compared to non-catalyzed conditions (2.3% efficiency). So that CTF-0-400/600-20/20-5 increased the efficiency to 100% but CTF-0-400-40-1, CTF-0-400-40-1.5 showed less activity, which the authors stated that here the pore size is the controlling factor.

Small micropores accommodate CO_2 , but epichlorohydrin cannot fit inside the pores because it is larger, and for this reason, the catalytic activity of CTF-0-400/600-20/20-5 increases with the increase of the surface area and the size of pores increases and reaches 100% [30].

Also, various other monomers have been used to make triazine frameworks with the aim of introducing functional groups into the frameworks (e. g. heterocycle monomers) and also increasing the nitrogen content in the frameworks (e. g. pyridine and pyrimidine monomers) [31-35].

In general, ionothermal synthesis has some limitations along with its advantages. First, because of the high reaction temperature, the monomer must be stable up to at least $400 \text{ }^\circ\text{C}$ in molten ZnCl_2 . However, aromatic nitriles are mostly stable at high temperatures and decompose above of $400 \text{ }^\circ\text{C}$. Second, increasing the reaction temperature or increasing the ratio of ZnCl_2 to monomer leads to the synthesis of amorphous triazine polymers, because the high reaction temperature causes carbonization. However, the effect of temperature and carbonization has been investigated by several groups [36].

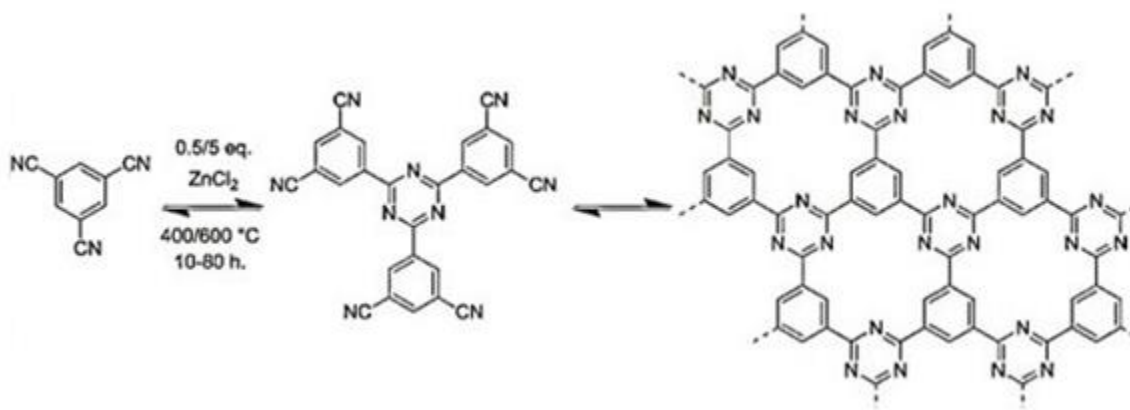


Figure 3. Ionothermal trimerization of 1,3,5-tricyanobenzene [30].

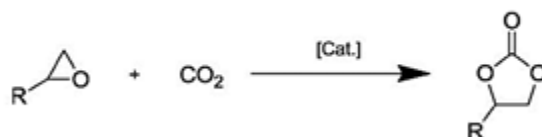


Figure 4. Synthesis of cyclic carbonates in the presence of triazine organic frameworks as catalysts [30]

Superacid- catalyzed synthesis

Despite the success of the ionothermal method for the synthesis of CTFs, due to the long reaction time and high reaction temperature, this method has limitations for some applications. For example, many monomers are not stable under these temperature conditions. The formation of amorphous CTFs as well as the carbonization of materials, the enlargement of pores and the occurrence of some side reactions can occur at high temperatures and long reaction times.

Superacids are a group of highly reactive media with greater potential than pure sulfuric acid. Trifluoromethanesulfuric acid (TFMS) and fluorosulfonic acid are examples of superacids. The catalytic role of superacids in the formation of triazine polymers has already been established. In 2012, Cooper et al. [37] used superacids as catalysts in the synthesis of CTFs, and the successful trimmization of aromatic nitriles was achieved with this method both in room temperature and under microwave conditions (Figure 5).

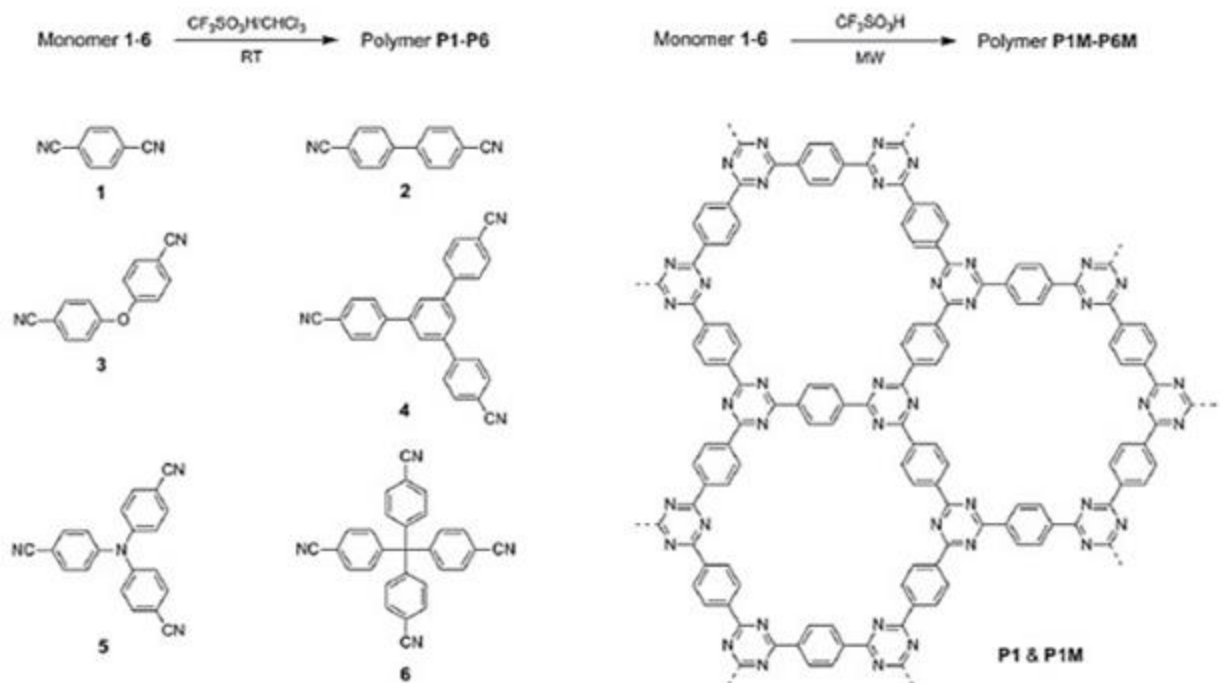


Figure 5. Synthesis of CTF polymers with super acid catalyst at room temperature and under microwave conditions [37].

They emphasized that the much lower temperature used in this method provides a significant advantage and prevents many condensations and side decomposition reactions. Using both of these methods, the infrared spectrum of these polymers showed a significant decrease in the intense nitrile carbon band, along with the appearance of strong triazine bands around 1500, 1360, 800 cm^{-1} indicating a high degree of polymerization. The obtained frameworks were amorphous at room temperature, while in the microwave assisted method some products showed limited regular structure.

Compared to the ionothermal ZnCl_2 catalyzed synthesis, the polymers synthesized via TFMS-catalyzed method show nitrogen contents that are closer to the expected values, suggesting fewer overall defects. The color of CTFs prepared by

superacid catalyzed synthesis ranges from pale yellow to brown, and unlike ZnCl_2 , the CTFs prepared are not black.

In general, this method is a milder method, without carbonization, with easy washing of the products and the obtained frameworks are free of any ZnCl_2 residues. The resulting frameworks were evaluated for carbon dioxide adsorption at a pressure of 1 bar at 273 K and the highest adsorption value (4.17 mmol g^{-1}) was obtained,

In the same year, Dai's research team applied this approach to produce triazine-framework-based porous membranes (TFMs) due to milder synthesis conditions [38]. which was one of the highest values obtained in the organic polymer network under these conditions. The resulting membranes also

showed permanent pores, which enabled efficient CO₂/N₂ separation (Figure 6).

Using the Brønsted acid method, only a few semi-crystalline CTFs were produced, only under microwave-assisted conditions, in general, this method was unable to produce large crystalline structures. The polymers obtained from this method were porous, but lacked the long-range order required by crystalline frameworks. Also, the prepared CTFs did not have a layered structure, and acid-sensitive building blocks cannot be used in this method.

In the next step, in order to prepare crystalline CTFs, Dai's research team used a two-step method in which trifluoromethane sulfonic acid played a catalytic role [39]. In order to investigate the synthesis of crystalline CTFs, the temperature of 250 °C was chosen for the first stage of the reaction, which was above the melting temperature of terephthalonitrile but lower than the carbonization temperature of triazine frameworks.

Terephthalonitrile and sulfuric acid were reacted after being placed inside the ampoule and degassing in a sealed system for 12 hours, and after purifying the precipitates, orange-colored products were obtained. Unlike the ionothermal method, the products were black powder.

In the second step, in order to completely remove the residual trifluoromethane sulfonic acid that was physically absorbed in the frame skeleton, the orange powder obtained in this step was subjected to heat treatment in an inert atmosphere at 350 °C, CTF-1-AB obtained in the first stage had a

small surface area (22 m²g⁻¹), while after heat treatment, obtained CTF-1-AA showed a significant increase in surface area (646 m²g⁻¹).

In the Paxred pattern, after heat treatment, two additional peaks were observed at 12.61° and 14.38°. This pattern was consistent with the AA-stacking model and indicated that after the he stacking mode had changed from staggered AB to eclipsed AA stacking. In the treatment and complete removal of CF₃SO₃H, the stacking mode has changed from staggered AB to eclipsed AA stacking.

After 2 hours it turned green. The change in texture characteristics after step 2 was complete (Figure 7). Investigations showed that after heat treatment, the stacking mode changed from stepped AB mode to radial AA stacking.

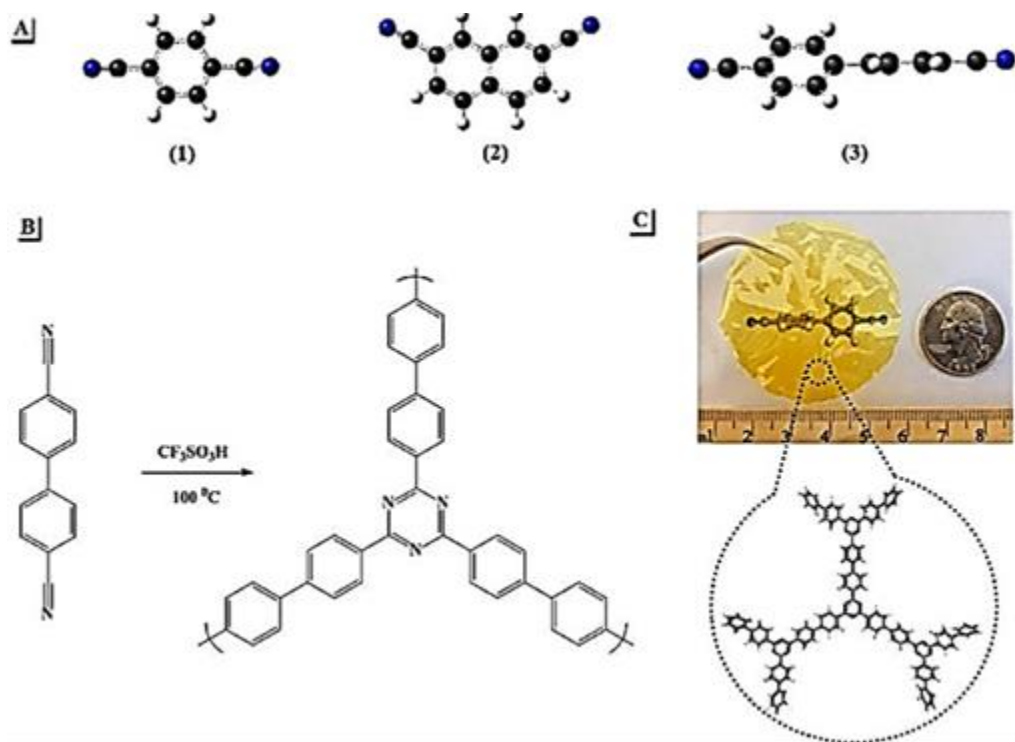


Figure 6. (A) Density functional theory (DFT)-optimized structures of the nitrile monomers used for the membrane synthesis. (B) Trimerization reaction of 4,4'-biphenyldicarbonitrile in $\text{CF}_3\text{SO}_3\text{H}$ at $100\text{ }^\circ\text{C}$. (C) Photograph of a directly synthesized sample of the transparent and flexible triazine-framework-based membrane TFMS [38].

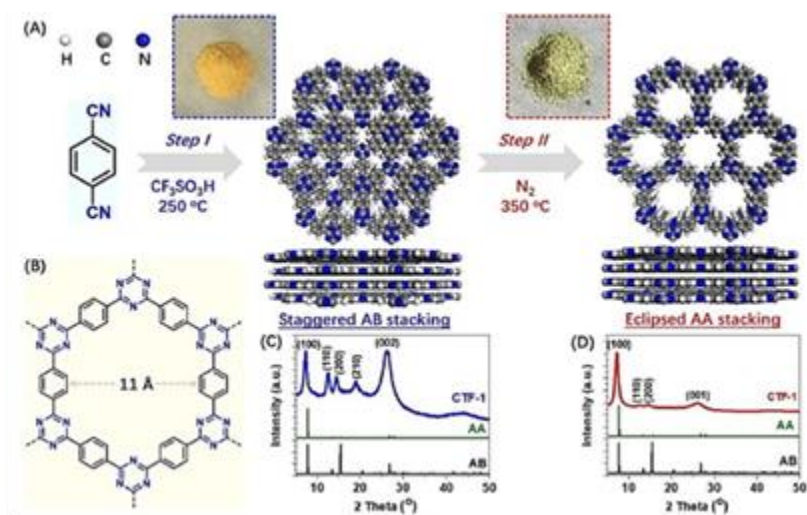


Figure 7. (A) Two-step synthesis of CTF-1 (B) Structure of one triazine unit cell in CTF-1 [39].

Phosphorus pentoxide-catalyzed synthesis

Phosphorus pentoxide (P_2O_5) is one of the known catalysts for dehydrating amides and converting them to nitriles, and it is also a catalyst that is used for the trimerization of nitriles.

In 2018, Beck et al. presented another synthetic strategy using phosphorus pentoxide and aromatic amides. P_2O_5 was used as a catalyst to first convert primary aromatic amides into nitriles and then by applying heat, nitriles were converted into s-triazines rings (Figure 8) [40].

This method is more environmentally friendly compared to CTF synthesis using metal catalysts or acid method. The CTF prepared by this method has high specific surface area, good stability and high crystallinity. The CTFs synthesized by Beck's group showed good crystallinity and relatively high porosity. As a result, due to both the high surface area ($2034.1 \text{ m}^2\text{g}^{-1}$) and suitable micropores, it showed a high efficiency as a gas absorber.

Amidine–aldehyde condensation

In 2017, Kapur and Tan [41] developed a strategy to prepare ordered crystalline CTFs via in situ oxidation of alcohols followed by polyamidine-aldehyde, which pointed out that the low nucleation concentration and slow nucleation process cause crystallinity (Figure 9).

Compared with ionothermal polymerization or superacid catalyst, this method enables the use of a wide range of monomers for the synthesis of CTFs, and eliminate the contamination of $ZnCl_2$ present in ionothermal polymerization. However, the decomposition of frameworks cannot be avoided due to the high temperature.

In this method, to reduce the rate of nucleation, first the alcohols are slowly oxidized to aldehydes in situ, then the subsequent polymerization starts when the temperature reaches $180 \text{ }^\circ\text{C}$.

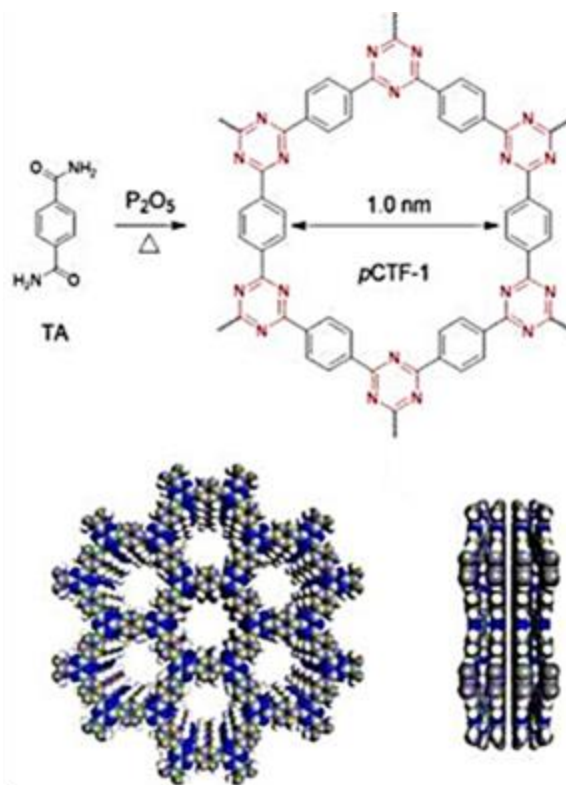


Figure 8. Synthesis of pCTF-1 in the presence of P_2O_5 [40].

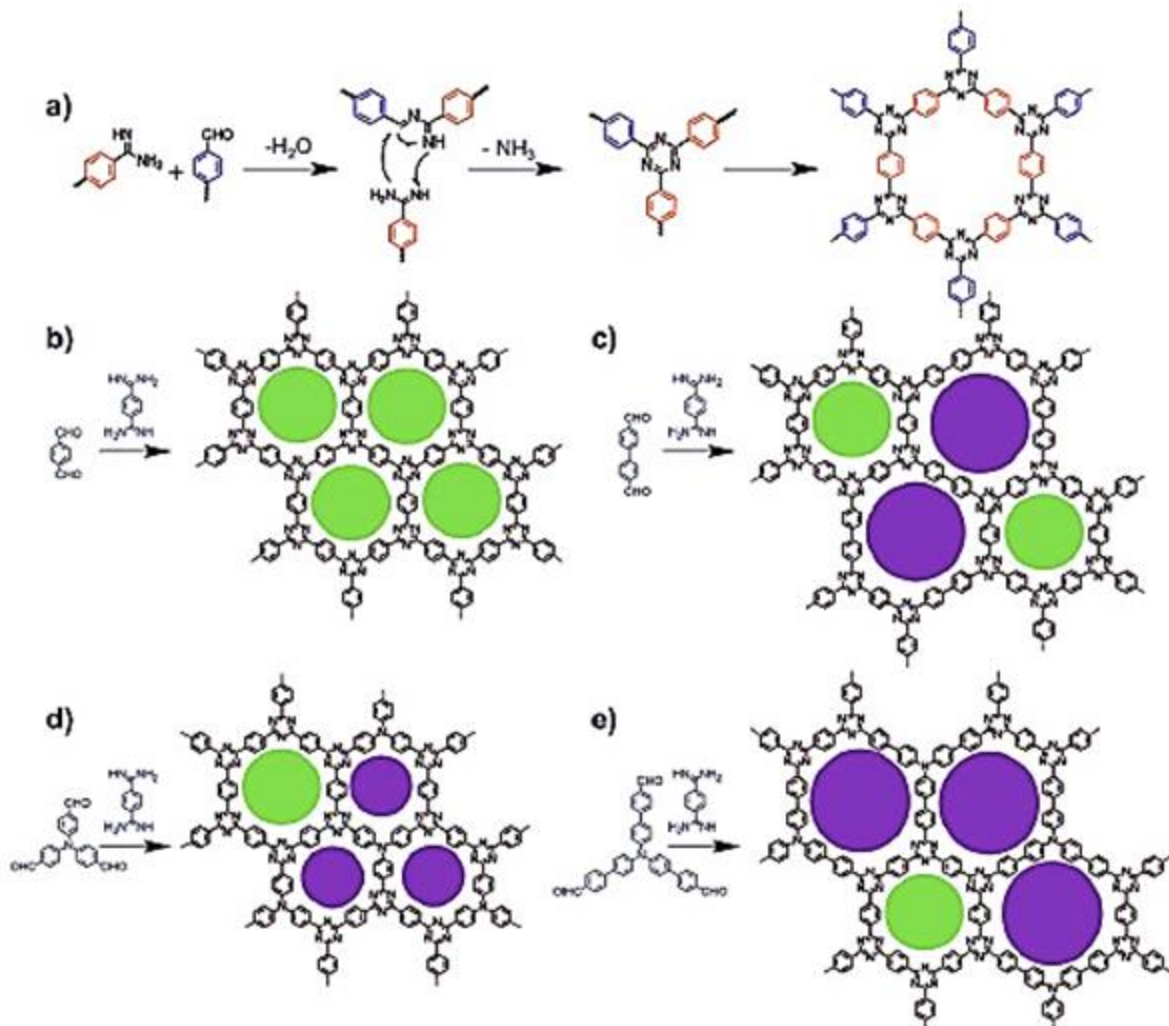


Figure 9. Synthesis of CTF-HUST, based on amidine-aldehyde condensation P2O5 [41].

Polymerization at high temperature increases crystallization. Indeed, the slow production of aldehyde slows down the overall reaction rate and controls the rate of nucleation, enabling the formation of crystalline CTF.

The CTFs prepared by this method had a layered structure and a high surface area (663 to 807 m² g⁻¹). One of the advantages of this method is the mild synthesis process (temperature of 120 °C, and no acid) and CTFs can be prepared up to several grams using this method. These CTFs were

promising for use in the field of energy storage and photocatalyst. So that the adsorption of CO₂ for these CTFs was higher than other nitrogen-rich porous organic frameworks.

The formation of CTFs in this method is the condensation between aldehyde and dihydrochloride of amidine, which was initially formed by Schiff base and then increased by Michael. And sodium carbonate was used as base, DMSO as solvent, and 120 °C as the optimal condition.

They stated that this method is scalable due to one-pot polymerization, low temperature, reaction conditions carried out at ambient pressure and an open system.

Synthesis of CTFs by direct triazine ring insertion

In this method, monomers that have triazine units are used for the synthesis of triazine polymers. In this section, Friedel-Crafts and Schiff-Base reactions are discussed.

Friedel-Crafts reaction

Another method for the synthesis of CTFs is the Friedel-Crafts reaction. In the Friedel-Crafts reaction, alkyl groups are attached to the aromatic ring.

Cyanuric chloride is reacted with aromatic compounds to synthesis triazine frameworks

using Frederic-Crafts method. There are two synthetic routes for this reaction.

Cyanuric chloride is the starting material for the synthesis of triazine compounds. Any of the chlorine groups can be substituted by reacting cyanuric chloride with nucleophiles such as amines, alcohols and thiols. Also, due to electron deficiency, carbons can combine with aromatic compounds under the electrophilic substitution reaction and accordingly, cyanuric chloride is used as an electron-deficient monomer in the Friedel-Crafts reaction.

Different monomers have been used for this reaction (Figure10), which can be performed with two different methods: Methane sulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$) or anhydrous aluminum chloride (AlCl_3) is used as a catalyst in this reaction.

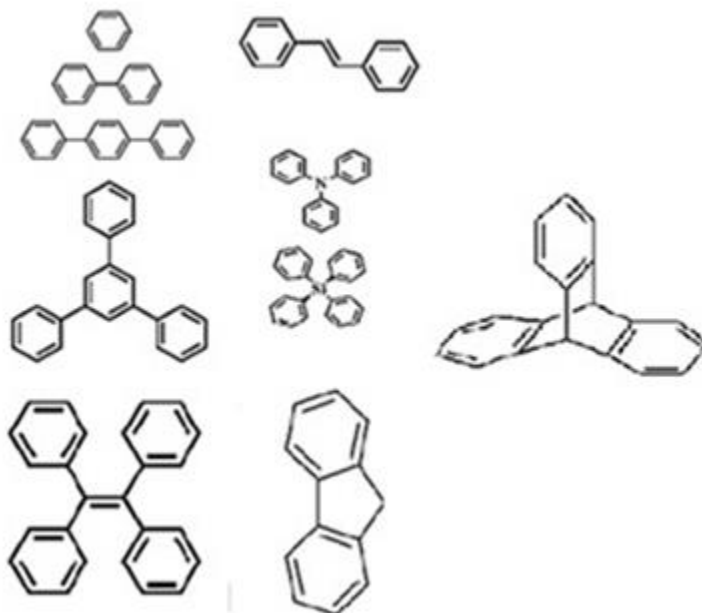


Figure 10. Some monomers used for the synthesis of CTFs in the Friedel-Crafts method.

In the first method, dry aluminum chloride without water is used as a catalyst: In the method, dry aluminum chloride was used as a catalyst, and three triazine compounds were synthesized from the reaction of 2,4,6-trichloro-1,3,5-triazine with benzene, biphenyl, and terphenyl in dichloromethane in the presence of aluminum chloride under reflux for 24 hours [42], respectively (Figure 11).

They reported that the Brunauer-Emmett-Teller (BET) surface area of the resulting polymers depended on the length of the aromatic linker and ranged from 558 to 1266 m² g⁻¹, although the BET surface area for the

benzene-derived polymer from the N₂ adsorption isotherm at 77 K was almost zero, which could be because the polymer has very small pores in which N₂ cannot diffuse.

However, when CO₂ was used at 195 K, a BET surface area of 558 m² g⁻¹ was obtained, which is probably due to the smaller kinetic diameter of CO₂ (3.30 Å) than that of N₂ (3.64 Å).

The use of these polymers in adsorption of gases was investigated and the results showed that the polymers have a high capacity to absorb CO₂ at ambient pressure and temperature.

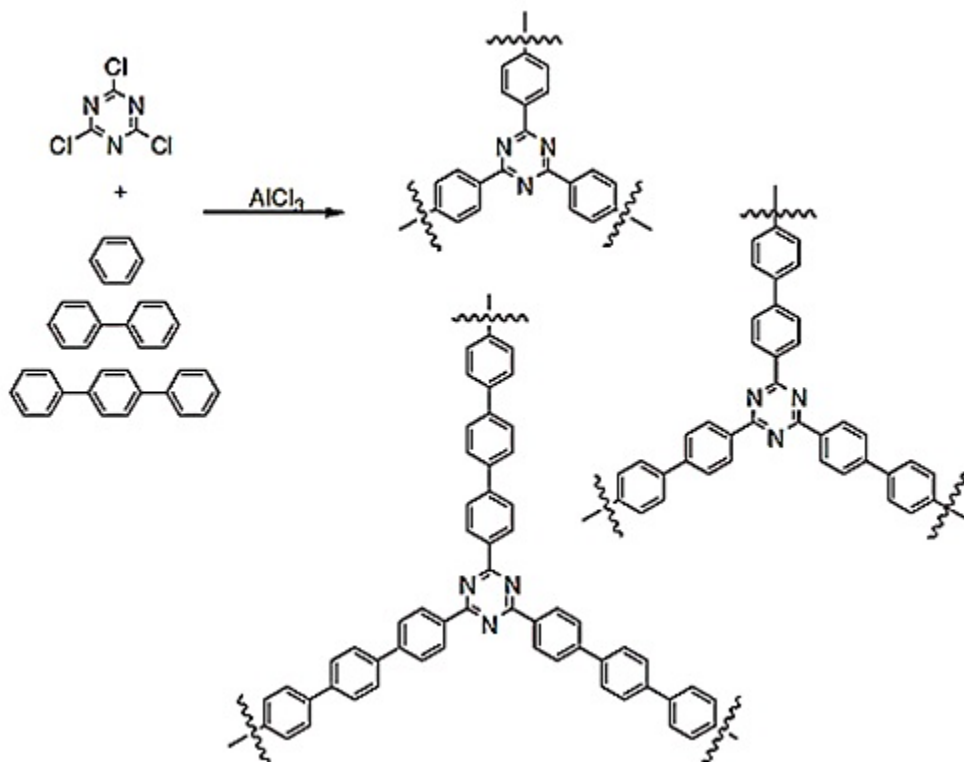


Figure 11. Synthesis of triazine frameworks by Friedel-Crafts method with AlCl_3 catalyst [42].

In the second way, methane sulfonic acid is used as a catalyst.

Another group of triazine polymers were synthesized through the Friedel-Crafts reaction and using $\text{CH}_3\text{SO}_3\text{H}$ as a catalyst (Figure 12), cyanuric chloride (as the triazine part), triphenylamine (NOP1-NOP3) and triphenylsilane (NOP4-NOP6). They also investigated the effect of raw material concentration on surface area and pore size. To study the effect of concentration on porosity and surface area, NOPs (NOP-1~3,

NOP-4~6) were prepared with different concentrations of CC (molL^{-1}) (0.025, 0.050 and 0.100 molL^{-1}).

The results showed that high reaction concentration is suitable to increase the pore parameters to some extent, because the properties of pores depend on the degree of polymerization. The degree of polymerization also depends on the concentration of the system (Table 1). Also, the resulting polymers showed a high adsorption capacity for CO_2 .

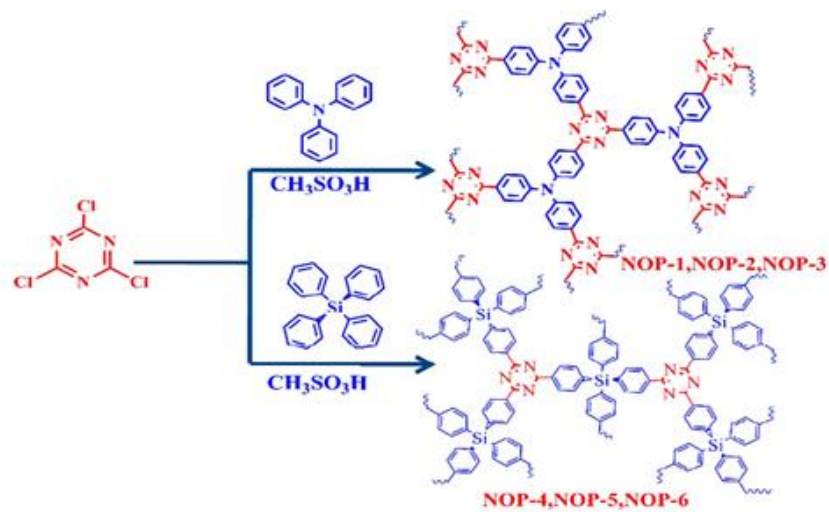


Figure 12. Synthesis of triazine frameworks by Friedel-Crafts method with $\text{CH}_3\text{SO}_3\text{H}$ catalyst [43].

Table 1. Pore parameters of NOPs [43]

Polymer	C_{CC}	SA_{BET}	SA_{LAN}	V_{Total}	V_{Micro}
	mol/l	m ² /g	m ² /g	cm ³ /g	cm ³ /g
NOP-1	0.025	749	978	0.41	0.23
NOP-2	0.050	803	1055	0.44	0.25
NOP-3	0.100	894	1198	0.54	0.25
NOP-4	0.025	428	635	0.67	0.08
NOP-5	0.050	613	913	0.71	0.12
NOP-6	0.100	720	1130	1.44	0.03

NOPs were useful in the field of adsorption and storage, so that NOP-3 hydrogen storage (1.14% by weight) was observed at 77 K (1 bar) and carbon dioxide adsorption 11.03 wt% at 273 K and 6.20 wt% at 298 K (1 bar) which was comparable to many reported organic materials [43].

Schiff-Base reaction

The Schiff-base reaction was discovered in 1864 by Hugo Schiff and has been one of the most important reactions in organic chemistry ever since. The Schiff-base mechanism involves several reversible steps. The reversibility and dynamic nature of imine bonds can be used to create complex crystal structures. As a result, the Schiff-base reaction can be used for the synthesis of triazine-based polymers. In 2009, Mullen et al. [44] using the Schiff-base reaction, succeeded in synthesizing triazine-based polymer networks (Figure 13).

By heating the monomers at a temperature of 180 °C in an inert environment, Schiff-base networks (SNW) were obtained with

relatively good efficiency. The resulting networks were stable under humidity and in acidic/alkaline environments, and the thermogravimetric analysis of these materials showed the high thermal stability of these materials (above 400 °C).

In this method, melamine is used as an amine component, which, in addition to being a cheap industrial material, leads to the production of materials that contain up to 40% by weight nitrogen content, which has not been achieved before for a microporous material [44].

In a similar research work done in 2013 by Bu and co-workers, a series of new nitrogen-rich aminal-linked porous organic polymers (APOPs) were synthesized from the condensation reaction between diaminotriazines and various benzaldehydes (Figure 14). They showed a surface area in the range of 1402-724 m²/g. The APOPs exhibit good thermal stability with onset of decomposition above 400 °C as proven by thermogravimetric analysis [45].

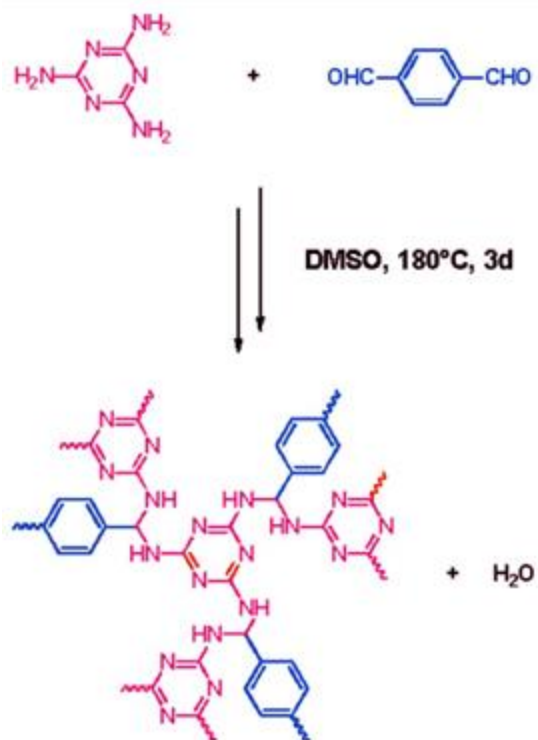


Figure 13. Synthesis route of triazine networks by Schiff-Bass reaction [44].

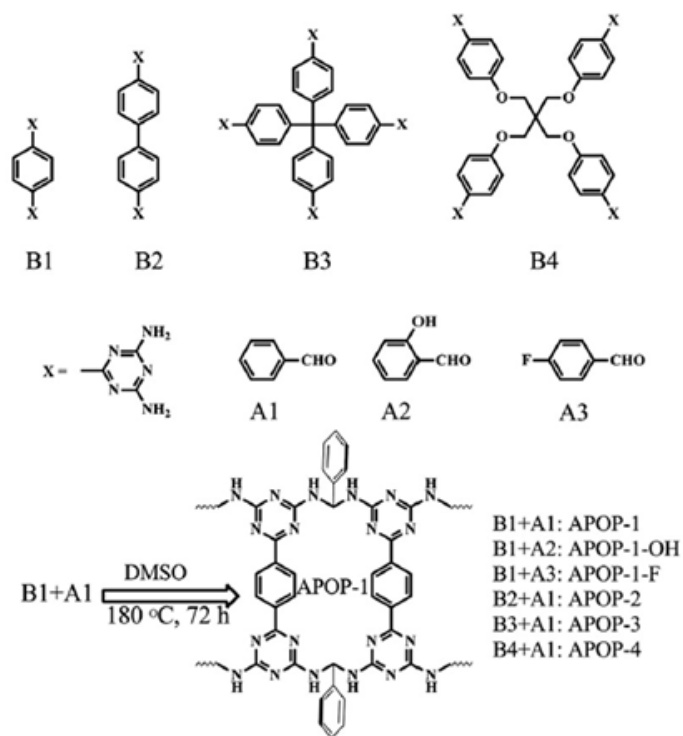


Figure 14. Synthesis of the APOPs [45].

Subsequently, a ferrocene-based nanoporous organic polymer (FNOPs-1) aimed at clean energy applications was synthesized by Zhou et al. by coupling 1,1'-ferrocene-carboxaldehyde with melamine (Figure 15). FNOPs-1 had a surface area of $752.4\text{m}^2\text{g}^{-1}$ and showed good physico-chemical stability. Also, due to the withdrawing electron nature of ferrocene, it had a high capacity for gas adsorption [46].

Applications of CTFs

Adsorption and separation of pollutants

Due to their porous and microporous nature, high surface area, as well as the possibility of introducing different functional groups into their structures, CTFs have a promising prospect for the adsorption and separation of various pollutants, including metal ions [32, 47], dyes [48, 49], organic pollutants [50] and especially in the field of CO_2 gas adsorption and separation. With the increase of industrial life, followed by the increase in the production of greenhouse gases, the problem of global warming has become one of the most important challenges, and many researchers are looking for a solution to this problem.

The synthesized FNOPs-1 was insoluble in any common organic solvent such as DMSO, N, N'-dimethylformamide (DMF), and tetrahydrofuran (THF), as well as in diluted HCl solution ($\sim 10\text{ wt}\%$).

CO_2 gas is one of these gases that plays a role in the problem of pollution and global warming. On the other hand, it has been proven that CTFs are useful in adsorption and separation of CO_2 gas due to their rich nitrogen content and micro and ultra-microporous pores.

In 2012, Cooper's group synthesized a series of CTFs using Brønsted acid as a catalyst [37], and used it to separation of CO_2 gas. These CTFs showed high CO_2 adsorption capacity (up to 4.17 mmol g^{-1}). Subsequently, Dai et al. used this approach to produce triazine framework-based porous membranes (TFMs) for CO_2/N_2 separation [38]. The obtained membrane showed a good CO_2 adsorption equal to 1.73 mmol g^{-1} at 273 K and 1 bar pressure, and the membrane showed more selectivity for separation of CO_2 from N_2 .

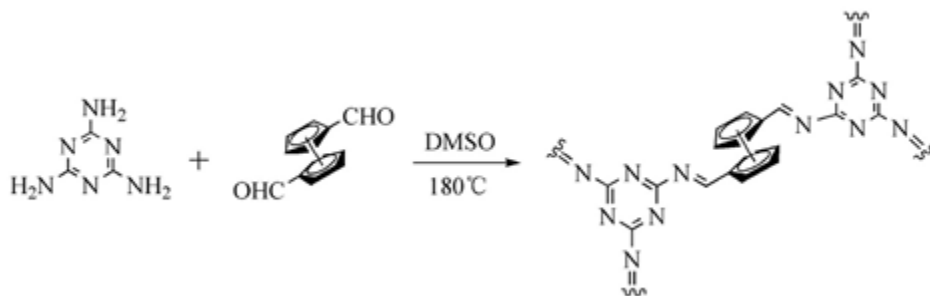


Figure 15. Synthesis of the FNOPs-1 [46].

In 2013, Janiak et al. synthesized a series of adamantane-based CTFs (PCTFs) for CO₂ adsorption, both under Brønsted acid conditions and ionothermal conditions, and proved that the CTFs prepared In 2013, Janiak et al. synthesized a series of adamantane-based CTFs (PCTFs) for CO₂ adsorption, both under Brønsted acid conditions and ionothermal conditions, and proved that the CTFs prepared by the later method showed better adsorption due to their high surface area, porosity, and micropore volume [51]. Also, the results showed that CO₂ adsorption increases with the increase in the number of cyano groups.

On the other hand, introducing CO₂-philic in the structure of CTFs such as oxygen, nitrogen and fluorine increases CO₂ adsorption due to the increase of electrostatic interactions. Accordingly, using the properties of perfluorocarbon compounds, Han's group synthesized a perfluorinated CTF (FCTF) with micro-pores for selective CO₂ adsorption. The replacement of H atoms with F atoms improved the surface area and reduced the pore size, which was favorable for the separation of CO₂ from N₂ [52].

Also, recent research showed that the introduction of polar and ionic groups as well as the introduction of heteroatoms in the structure of CTFs improved the CO₂ adsorption in CTFs [53-56].

Catalytic applications

CTFs can be used as catalysts in many organic reactions according to the structure and functional groups in the framework. Also, the ability to adjust the structure (using the synthetic method) and chemical (by

choosing the appropriate monomers) allows for a more detailed investigation of the catalytic properties of CTFs. On the other hand, CTFs are suitable catalysts for the synthesis of cyclic carbonates due to their high nitrogen content and good stability in the synthetic conditions of these compounds using epoxides and carbon dioxide.

In 2012, CTF-1 was first used as catalyst for the conversion of carbon dioxide and epoxides to cyclic carbonates, and they catalyzed the conversion of carbon dioxide to cyclic carbonates with very good efficiency and selectivity under solvent-free conditions [57]. In 2013, Thomas' group used CTF-0 as a catalyst in this reaction, and the results showed that CTF-0 showed higher catalytic activity than CTF-1 [30]. Also, other CTF with different functional groups in the framework structure were synthesized and used for this purpose, including imidazolium-based CTFs [58, 59], carbazole-decorated-CTF [60] and pyridine-rich cationic CTFs [61].

Of course, the catalytic role of CTFs is not only limited to cycloaddition reactions, and it can play a good catalytic role in various reactions such as Novenagle reaction [62], oxidation of alcohols [63], also as a photocatalyst [64] in many other reactions [65].

Conclusions

CTFs can be synthesized by various methods, either through trimerization reactions or direct use of monomers containing triazine rings. Many advances have been made in the field of CTFs synthesis. But the synthesis of CTFs under milder conditions and high

scales, as well as the synthesis of CTFs with high crystallinity, is still the goal of many research works.

CTFs can be used in a broad spectrum of applications including highly efficient and selective adsorption of pollutant, adsorption and storage of gases, metal-free catalysts and photocatalyst, etc. due to structural design capability, high porosity, high nitrogen content, high physicochemical stability and the ability to introduce functional groups into the structure of these compounds.

References

[1] Das, S.; Heasman, P.; Ben, T.; Qiu, S. *Chem. Rev.* 2017, 1515.

[2] Morris, R. E.; Wheatley, P. S. *Angew. Chem. Int. Ed.* 2008, 47, 4966.

[3] Bügel, S.; Hähnel, M.; Kunde, T.; de Sousa Amadeu, N.; Sun, Y.; Spieß, A.; Janiak, C. *J. Mater.* 2022, 15, 2807.

[4] Erdosy, D. P.; Wenny, M. B.; Cho, J.; DelRe, C.; Walter, M. V.; Jiménez-Ángeles, F.; Mason, J. A. *Nature.* 2022, 608, 712-718.

[5] Bügel, S.; Hähnel, M.; Kunde, T.; de Sousa Amadeu, N.; Sun, Y.; Spieß, A.; Janiak, C. *Mater.* 2022, 15, 2807.

[6] Yang, J.; Qiu, H.; Huang, L.; Meng, S.; Yang, Y. *Chem Plus Chem.* 2023, 88, e202300292.

[7] Sayari, A.; Hamoudi, S.; Yang, Y. *Chem. Mater.* 2005, 17, 212.

[8] Zhang, J.; Chen, J.; Peng, S.; Peng, S.; Zhang, Z.; Tong, Y.; Yan, X. *P. Chem. Soc. Rev.* 2019, 48, 2566.

[9] Zhao, X. *S. J. Mater. Chem.* 2006, 16, 623.

[10] Cote, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. *Sci.* 2005, 310, 1166-1170.

[11] Wan, S.; Gándara, F.; Asano, A.; Furukawa, H.; Saeki, A.; Dey, S. K.; Yaghi, O. M. *Chem. Mater.* 2011, 23, 4094-4097.

[12] Bojdys, M. J.; Jeromenok, J.; Thomas, A.; Antonietti, M. *Adv Mater.* 2010, 22, 2202-2205.

[13] Uribe-Romo, F. J.; Hunt, J. R.; Furukawa, H.; Klock, C.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* 2009 131, 4570-4571.

[14] Liu, M.; Guo, L.; Jin, S.; Tan, B. *J. Mater. Chem. A* 2019, 7, 5153– 5172.

[15] Kuhn, P.; Antonietti, M.; Thomas, A. *Porous Angew. Chem., Int. Ed. Engl.*, 2008, 47, 3450-3453.

[16] Xu, F.; Yang, S.; Jiang, G.; Ye, Q.; Wei, B.; Wang, H. *ACS Appl. Mater. Interfaces.* 2017, 9, 37731-37738.

[17] Gao, G.; Jia, Y.; Gao, H.; Shi, W.; Yu, J.; Yang, Z.; Zhao, Y. *ACS Appl Mater Interfaces.* 2021, 13, 50258-50269.

[18] Mahato, M.; Nam, S.; Lee, M. J.; Koratkar, N.; Oh, I. K. *Small.* 2023, 2301847.

[19] Bhanja, P.; Bhunia, K.; Das, S. K.; Pradhan, D.; Kimura, R.; Hijikata, Y.; Bhaumik, A. *ChemSusChem.* 2017, 10, 921-929.

[20] Lin, K. Y.; EL-Mahdy, A. F. *Mater. Chem. Phys.* 2022, 281, 125850

- [21] Chan-Thaw, C. E.; Villa, A.; Veith, G. M.; Kailasam, K.; Adamczyk, L. A., Unocic, R. R.; Thomas. *Chem. Asian J.* 2012, 7, 387-393.
- [22] Iemhoff, A.; Vennewald, M.; Palkovits, R. *Angew. Chem., Int. Ed. Engl.* 2023 62, e202212015.
- [23] Qian, Z.; Wang, Z. J.; Zhang, K. A. *Chem. Mater.* 2021, 33, 1909-1926.
- [24] Carta, M.; Malpass-Evans, R.; Croad, M.; Rogan, Y.; Jansen, J. C.; Bernardo, P.; McKeown, N. B. *Sci.* 2013, 339, 303-307.
- [25] Lan, Z. A.; Wu, M., Fang, Z.; Zhang, Y.; Chen, X.; Zhang, G.; Wang, X. *Angew. Chem., Int. Ed. Engl.* 2022, 61, e202201482.
- [26] Liu, J.; Zong, E.; Fu, H.; Zheng, S.; Xu, Z.; Zhu, D. J. *Colloid Interface Sci.* 2012, 372, 99-107.
- [27] Rabbani, M. G.; El-Kaderi, H. M. *Chem. Mater.* 2011, 23, 1650-1653.
- [28] Zheng, B., Bai, J.; Duan, J.; Wojtas, L.; Zaworotko, M. J. *J. Am. Chem. Soc.* 2011, 133, 748-751.
- [29] Bojdys, M. J.; Jeromenok, J.; Thomas, A.; Antonietti, M. *Adv Mater.* 2010, 22, 2202-2205.
- [30] Katekomol, P.; Roeser, J.; Bojdys, M., Weber, J.; Thomas, A. *Chem. Mater.* 2013, 25, 1542-1548.
- [31] Bavykina, A. V.; Olivos-Suarez, A. I., Osadchii, D.; Valecha, R., Franz, R.; Makkee, M.; Gascon, J. *ACS Appl. Mater. Interfaces.* 2017, 31, 26060-26065.
- [32] Farrokhi, H., Bagheri, M. J. *Polym. Res.* 2023, 30, 45.
- [33] Mukherjee, S.; Das, M.; Manna, A., Krishna, R.; Das, S. J. *Mater. Chem. A.* 2019, 7, 1055-1068.
- [34] Jena, H. S.; Krishnaraj, C.; Schmidt, J.; Leus, K.; Van Hecke, K.; Van Der Voort, P. *Chem. Eur. J.* 2020, 26, 1548-1557.
- [35] Park, K.; Lee, K.; Kim, H.; Ganesan, V.; Cho, K.; Jeong, S. K.; Yoon, S. J. *Mater. Chem. A.* 2017, 5, 8576-8582.
- [36] a) Kuhn, P.; Forget, A.; Su, D.; Thomas, A., & Antonietti, M. *J. Am. Chem. Soc.* 2008, 130, 13333-13337. b) Osadchii, D. Y.; Olivos-Suarez, A. I.; Bavykina, A. V.; Gascon, J. *Langmuir* 2017, 33, 14278-14285.
- [37] Ren, S.; Bojdys, M. J.; Dawson, R., Laybourn, A.; Khimiyak, Y. Z.; Adams, D. J.; Cooper, A. I. *Adv Mater.* 2012, 24, 2357-2361.
- [38] Zhu, X.; Tian, C.; Mahurin, S. M.; Chai, S. H., Wang, C., Brown, S.; & Dai, S. J. *Am. Chem. Soc.* 2012, 134, 25, 10478-10484.
- [39] Yang, Z.; Chen, H.; Wang, S.; Guo, W.; Wang, T.; Suo, X.; & Dai, S. J. *Am. Chem. Soc.* 2020 .142, 6856-6860.
- [40] Yu, S. Y.; Mahmood, J.; Noh, H. J.; Seo, J. M.; Jung, S. M.; Shin, S. H.; Baek, J. B. 2018. *Angew. Chem., Int. Ed. Engl.* 2018, 57, 8438-8442.
- [41] Wang, K.; Yang, L. M.; Wang, X.; Guo, L.; Cheng, G.; Zhang, C.; Cooper, A. *Angew. Chem., Int. Ed. Engl.* 2017, 56, 14149-14153.

- [42] Lim, H.; Cha, M. C.; Chang, J. Y. *Macromol Chem Phys.* 2012, 213, 1385-1390.
- [43] Xiong, S.; Fu, X.; Xiang, L.; Yu, G.; Guan, J.; Wang, Z.; Pan, C. *Polym. Chem.* 2014, 5, 3424-3431.
- [44] Schwab, M. G.; Fassbender, B.; Spiess, H. W.; Thomas, A.; Feng, X.; Mullen, K. J. *Am. Chem. Soc.* 2009, 131, 7216-7217.
- [45] Song, W. C.; Xu, X. K.; Chen, Q.; Zhuang, Z. Z.; Bu, X. H. *Polym. Chem.* 2013, 4, 4690-4696.
- [46] Liu, Q.; Tang, Z.; Wu, M.; Liao, B., Zhou, H.; Ou, B.; Li, X. *RSC Adv.* 2015, 5, 8933-8937.
- [47] Chakraborty, A.; Sarkar, S.; Kyarikwal, R.; Nag, P.; Vennapusa, S. R.; Mukhopadhyay, S. *ACS Appl. Polym. Mater.* 2022, 4, 8118-8126.
- [48] Kumar, S.; Kumari, K.; Singh, S. K.; Dholakiya, B. Z.; Jangir, R. *New J Chem.* 2023, 47, 13676-13686.
- [49] Ghanbari, J.; Mobinikhaledi, A. *Sci. Rep.* 2023, 13, 12962.
- [50] Aslam, A. A.; Irshad, A.; Nazir, M. S.; & Atif, M. J. *Clean. Prod.* 2023, 400, 136737.
- [51] Bhunia, A.; Boldog, I.; Möller, A.; Janiak, C. J. *Mater. Chem.* 2013, 1, 14990-14999
- [52] Zhao, Y.; Yao, K. X.; Teng, B.; Zhang, T.; Han, Y. *Energy Environ Sci.* 2013, 3684-3692.
- [53] Xu, G.; Zhang, S.; Xie, W.; Wang, L.; Xue, X.; Qiao, Y.; Su, Z. *J. Polym. Res.* 2022, 29, 153.
- [54] Rangaraj, V. M.; Reddy, K. S. K.; Karanikolos, G. N. *J. Chem. Eng.* 2022, 429, 132160.
- [55] Lin, K. Y.; EL-Mahdy, A. F. *Mater. Chem. Phys.* 2022, 281, 125850.
- [56] Park, K.; Lee, K.; Kim, H.; Ganesan, V.; Cho, K.; Jeong, S. K.; Yoon, S. *Mater. Chem.* 2017, 5, 8576-8582.
- [57] Roeser, J.; Kailasam, K.; Thomas, A. *ChemSusChem.* 2012, 5, 1793-1799.
- [58] Liu, T. T.; Xu, R.; Yi, J. D.; Liang, J.; Wang, X. S.; Shi, P. C.; Cao, R. *ChemCatChem.* 2018, 10, 2036-2040.
- [59] Liu, F.; Duan, X.; Liu, M.; Du, J.; Ma, J.; & Liu, F. *Ind. amp; Eng. Chem. Res.* 2021, 60, 15027-15036.
- [60] Yu, W.; Gu, S.; Fu, Y.; Xiong, S.; Pan, C.; Liu, Y.; & Yu, G. *J. Catal.* 2018, 362, 1-9.
- [61] Zhao, Y.; Huang, H.; Zhu, H.; & Zhong, C. *Microporous Mesoporous Mater.* 2022, 329, 111526.
- [62] M. B. Ansari, M. N. Parvin and S.-E. Park, *Res. Chem. Intermed.* 2013, 40, 67-75.
- [63] Huang, W.; Ma, B. C.; Lu, H.; Li, R.; Wang, L.; Landfester, K.; & Zhang, K. A. *ACS Catal.* 2017, 7, 5438-5442.
- [64] Sun, R.; Tan, B. *Chem. Res. Chin.* 2022, 38, 310-324.

[65] Iemhoff, A.; Vennewald, M.; Palkovits, R. *Angew. Chem., Int. Ed. Engl.* 2023. 62, e202212015.