



Covalent Organic Frameworks (COFs): A Review

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ABSTRACT: The search for supramolecular promising porous crystalline materials with diverse applications such as gas storage, catalysis, chemo-sensing, energy storage, and optoelectronic have led to the design and construction of Covalent Organic Frameworks (COFs). COFs are a class of porous crystalline polymers that allow the precise integration of organic building blocks and linkage motifs to create predesigned skeletons and nano-porous materials. In this review article, a historic overview of the chemistry of COFs, survey of the advances in topology design and synthetic reactions, basic design principles that govern the formation of COFs as porous crystalline polymers as well as common synthetic procedures and characterization techniques are discussed. Furthermore some challenges associate with the synthesis of COFs are highlighted. We hope that this review will help researchers, industrialists and academics in no mean feat.

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Covalent-Organic Frameworks (COFs) are made by the linking of well-defined organic building units with diverse functionalities through strong covalent bonding to give 1-D, 2-D or 3-D structures. Research in this area of chemistry was initially not very promising due to difficulties associated with the synthesis of crystalline COFs for X-ray characterization. (Furukawa & Yaghi, 2009) However, the shortcomings of COFs' crystallinity has been partly overcome by modifying synthetic methods and the emergence and application of reticular chemistry, which makes use of topologically designed building units for the construction of crystalline COFs via the use of boronic acids or boronate esters as precursors. (Jinang, 2012) Yaghi and co-workers used topological design principles to successfully prepare the first examples of COFs in 2005. (Ockwig *et al.*, 2005a) With this breakthrough, there has been rapid progress in COF chemistry in many parts of the globe as COFs display great potential for functional applications. COFs are constructed by using well defined organic building blocks, containing bonds such as C-C, C-O, C-N, C=N, C-Si, B-O and B-

N. (Ockwig *et al.*, 2005a; Saha *et al.*, 2013; Wan *et al.*, 2008) The reactions leading to the formation of COFs are usually reversible condensation reactions, such as the formation of B-O bonds as seen in boronate, boroxines and borosilicate, (El-Kaderi *et al.*, 2007; Hunt *et al.*, 2008) C-N bonds formed in triazine and imidazation, (Chem *et al.*, 2012; Fang, Zhuang, *et al.*, 2014; Kuhn, Antonietti, *et al.*, 2008; Sha Lin *et al.*, 2015; W. Zhang *et al.*, 2011) B-N bonds formed in boraxines, (Jackson *et al.*, 2012; Spitler & Dichtel, 2010) C=N bonds formed in imine, hydrazine and squaraine, (Jin *et al.*, 2017; Uribe-romo *et al.*, 2009, 2011; Y. Zhang *et al.*, 2013; Zhou *et al.*, 2014) as well as N-N bonds formed in azodioxides. (Beaudoin *et al.*, 2013) In comparison to other porous materials (zeolites and MOFs), COFs have the advantage of low density, high thermal and chemical stabilities, permanent porosity, tunable pore size and structure, columnar π -stacking structures as well as versatilities in covalent combination of building units. (Auras *et al.*, 2016; Gao *et al.*, 2018; Hisaki *et al.*, 2017; N. Huang, Zhai, *et al.*, 2016) The columnar stacking structure in some COFs provides a unique avenue to constructing

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ordered π -systems that are difficult if not impossible to achieve with conventional covalent or non-covalent approaches. These unique features of COFs have attracted considerable interests amongst scientists, engineers and industrialists thus making COFs novel materials for important applications such as gas adsorption, (Babarao & Jiang, 2008; Cui et al., 2017; Doonan et al., 2010; Furukawa & Yaghi, 2009; Jin-Tao Yu; Zhe Chen; Junliang Sun; Zhi-Tang Huang; Qi-Yu Zheng, 2012; Mendoza-Cortés et al., 2012; Yang et al., 2018; Bull *et al.* (2020)) optoelectronics and photovoltaics, (Calik et al., 2014; Dogru et al., 2013; N. Huang et al., 2015; Jiang, 2014; Xuan-he Liu et al., 2014; Wan et al., 2008, 2011) gas separation, (Lan et al., 2017; Ma, Heping; Ren, Hao; Meng, Shuang; Yan, Zhuojun; Zhao, Huanyu; Sun, Fuxing; Zhu, 2013; Oh et al., 2013) catalysis, (Article et al., 2014; S. Ding et al., 2011; Fang, Gu, et al., 2014; He et al., 2015; Song Lin et al., 2015; Pachfule et al., 2018) proton conductivity, (X. Ding et al., 2011; Guo et al., 2017; Kunjir and Banerjee, 2014; J. Li et al., 2018) chemical sensor, (Dalapati et al., 2013; Das, Gobinda; Biswal P, Bishnu; Kandambeth, Sharath; Venkatesh, V; Kaur, Gagandeep; addicoat, Matthew; Heine, Thomas; Verma, 2015; Nagai et al., 2013) drug delivery, (Guo et al., 2015) energy storage (Deblase et al., 2013; Xu et al., 2015) as well as in chromatographic separations. {Formatting Citation}. In recent times, great efforts have been directed towards the enhancement of COFs for CO₂ capture and rapid research and advancement has been reported. (Ge et al., 2016; Hug et al., 2015; Olajire, 2017; Zeng et al., 2016) However, there is still more to be done concerning COFs for CO₂ capture and purification as well as construction of COFs with large CO₂ adsorption and selectivity over other gases in the flue gas stream. (Olajire, 2017) In addition to the progress made in COF chemistry for CO₂ adsorption, the need for high thermal and chemical stabilities and the recyclability of COF materials without loss of performance in air are still major problems. Thus, new synthetic strategies, enhancement of crystallinity, stability and porosity, and CO₂ capture efficiency as well as improved selectivity with respect to other flue gas are all factors of COFs that need improvement.

COF Design

Dynamic Covalent Chemistry of COFs: Kinetic control of reactions leading to the synthesis of polymeric material is key to irreversible formation of COFs (containing mainly covalent bonds). (Diercks and Yaghi, 2017) It has always been a challenge to crystallize linked organic polymers into solids by means of irreversible reactions. (Qian et al., 2017; Uribe-romo et al., 2009) However, dynamic covalent chemistry which involves the breaking /formation

bonds leads to the reversible formation of covalent bonds. Dynamic covalent bond chemistry is thermodynamically driven, as a result, it offers reversible reactions process with “error checking” as well as “proof reading” features and thus leads to the formation of the most thermodynamically stable products. Thus, the application of dynamic covalent chemistry in COFs enables the polymer skeleton formation to occur alongside the crystallization process, while self-healing feedback reduces the incidence of structural defects and helps the formation of an ordered structure. (N. Huang, Wang, et al., 2016; N. Huang, Zhai, et al., 2016; Jinang, 2012; Smith et al., 2017) The end effect of the dynamic covalent chemistry is that the final COF product has an ordered crystalline structure having high thermodynamic stability. To design and synthesise a COF, two key factors must be considered in order to achieve thermodynamic control in reversible reactions. (Diercks and Yaghi, 2017; Jinang, 2012) These factors are: the functionality and structure of the building units, and the synthetic methodology (consideration of the reaction media and the reaction conditions are important).

Structure of Building Units: The structure of the building unit for COF construction must meet two requirements. Firstly, the reaction leading to the formation of the COF material should be a reversible reaction. This implies that the building units should be ones that undergo dynamic covalent bond formation. That is, there should be no irreversible reactions and the reaction system should contain only monomers, oligomers and polymers that are interchangeable under thermodynamic conditions. Secondly, the geometry of the secondary building units should be retained in the COF. This means that rigid building units as well as discrete directional bond formation are required. In a bid to satisfy the first requirement, the chemistry of boronic acids, triazines and imines has been explored for successful COFs syntheses. (Beuerle & Gole, 2018; Díaz & Corma, 2016; Jinang, 2012; San-Yuan Ding, 2013; Zeng et al., 2016)

Building Blocks for COFs

Boron-based COFs: A large number of known COFs depend on boron chemistry because boronic acids can undergo condensation reaction through either self-condensation or co-condensation with diols to give six-membered boroxine and five-membered boronate ester rings as shown Figure 1.

Boron-based COFs were among the first group of COFs designed and synthesised. (Ockwig et al., 2005a) COF-1 and COF-5 are boron-based 2-D COFs that were synthesised under solvothermal conditions using

a mixture of dioxane and mesitylene as solvents. COF-1 was obtained through the self-condensation of 1,4-benzenediboronic acid (BDDBA) with the removal of water to give a planar 6-membered B_3O_3 ring (boroxine). (Ockwig et al., 2005a) The co-condensation reaction of BDDBA and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) formed COF-5 alongside the release of water as by-product. COF-5 contains a 5-membered C_2O_2B ring (boronate group). (Ockwig et al., 2005b) The synthesis of COF-1 and COF-5 are shown below Scheme 1. In addition,

COF-18Å, (Tilford et al., 2006) a poly(boronate ester)-based COF, was synthesised via the condensation reaction of 1,3,5-benzenetriboronic acid and 1,2,4,5-tetrahydroxybenzene in 2% methanol/THF at reflux as shown in Scheme 2. COF-18Å, was reported to possess ester linkages that formed infinite 2-D hexagonally porous sheets. Furthermore, it was reported that COF-18Å, the ester-linked sheets atoms that are adjacent to the layers overlapped with each other to form a hexagonal array structure with 1.8 nm pores.

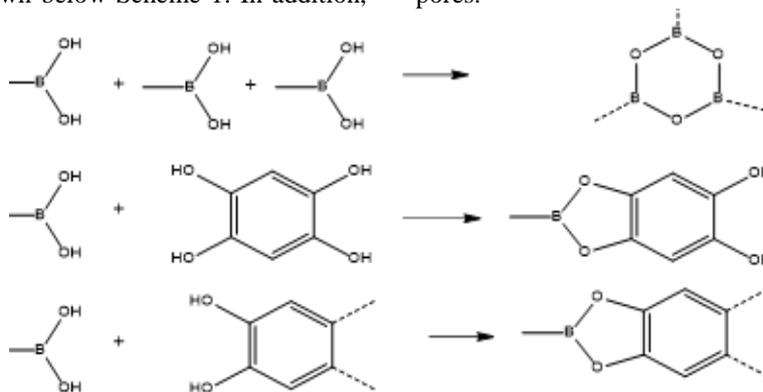
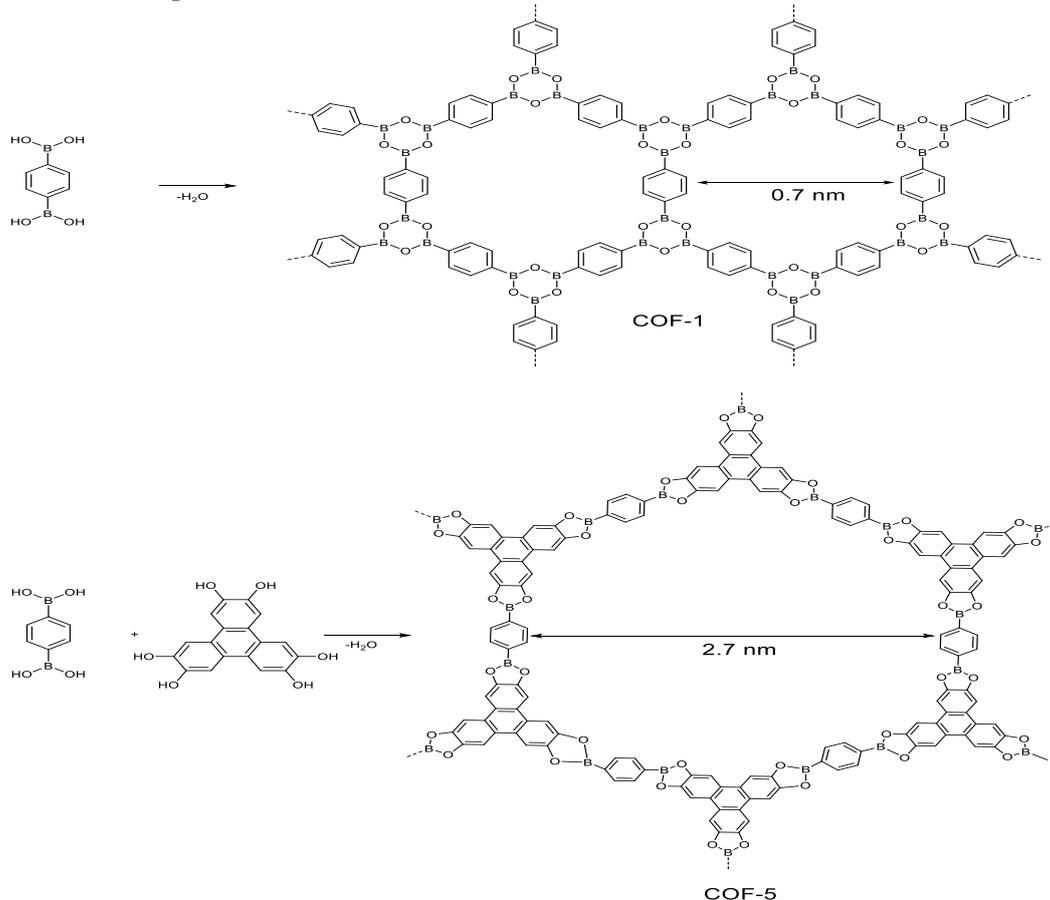


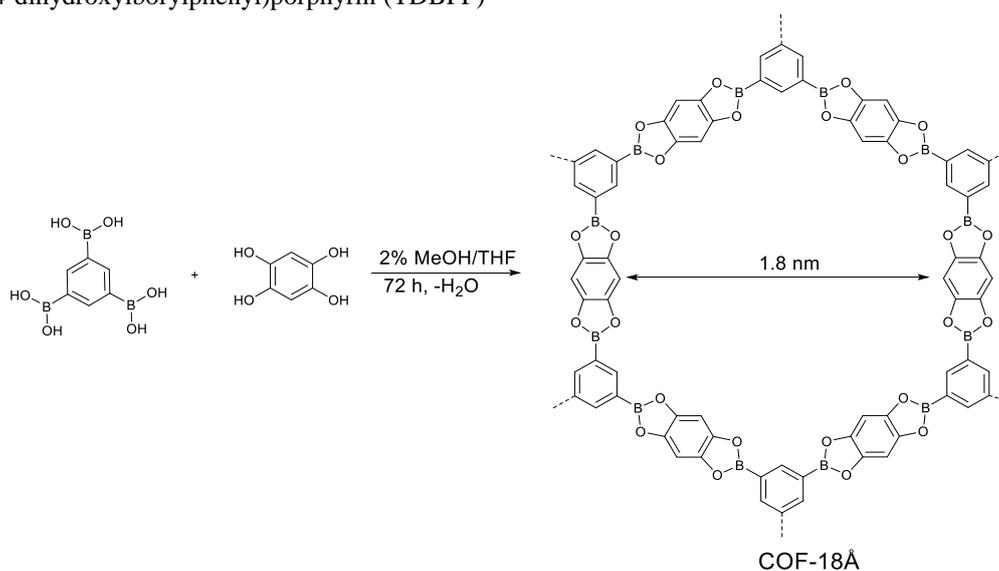
Fig 1: self- and co-condensation reaction of boronic acids to boroxine and boronate esters



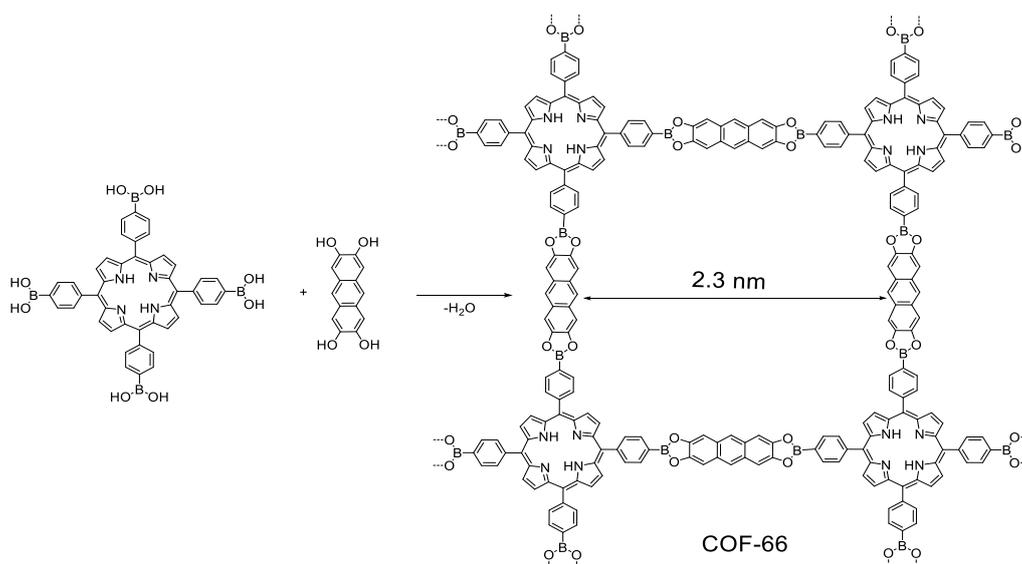
Scheme 1: Synthesis of COF-1 and COF-5. (Ockwig et al., 2005b)

In addition, COF-18Å was reported to exhibit thermal stability of up to 500 °C as well as a Brunauer-Emmett-Teller Surface Area (S_{BET}) and micropore volume of 1260 m²/g and 0.29 cm³/g respectively. These reactions prompted other researchers to apply the principle of dynamic covalent chemistry (DCC) reactions to prepare other 2-D COFs such as COF-6, COF-8, COF-10 and COF-66. COF-6, COF-8, COF-10 were formed via the co-condensation of (1,3,5-benzenetriboronic acid (BTBA), and HHTP, (1,3,5-tris [(4-dihydroxyboryl)phenyl]benzene (TDBPB), and HHTP, and (4,4'-biphenyldiboronic acid (BPDBA), and HHTP respectively.(Côté et al., 2007) COF-66 was made via the co-condensation of 5,10,15,20-tetrakis(4-dihydroxyborylphenyl)porphyrin (TDBPP)

and anthracene-2,3,6,7-tetraol (TPH) Scheme 3.(Wan et al., 2011). On the basis of pore size distribution, COF-1 and COF-6 are classified as Group 1 comprising 2-D structures with 1-D micropores, while COF-5, COF-8, COF-10 and COF-66 belong to Group 2 comprising of 2-D structures with 1-D mesopores.(Furukawa & Yaghi, 2009) COF-1, COF-6 have been reported to have pore sizes of 0.7 nm and 0.9 nm as determined by the Ar gas adsorption isotherm at 87 K. For COF-5, COF-8, COF-10 and COF-66 their pore sizes are 2.7, 1.6, 3.2 and 2.3 nm respectively.(Jinang, 2012; Olajire, 2017; Wan et al., 2011) The S_{BET} surface areas and CO₂ uptake of these 2-D COFs are summarised below in Table 1.



Scheme 2: Synthetic scheme and proposed structure for COF-18Å.(Tilford et al., 2006)



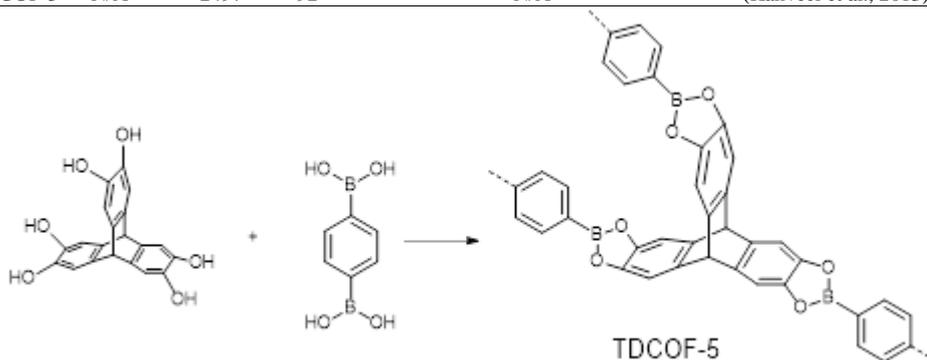
Scheme 3: Synthesis of COF-66.(Wan et al., 2011)

From the Table 1 above, it can be seen that the S_{BET} of the 2-D COFs decreases in the order: COF-10 > COF-5 > COF-8 > COF-6 = COF-1 > COF-66. But the CO_2 uptake capacities of these COFs at 273 K/1 bar decreases as follows: COF-6 > COF-1 > COF-8 > COF-5 > COF-10. Thus irrespective of the fact that COF-6 has a pore size of 0.9 nm as well a S_{BET} of 750 m^2/g , it has the highest CO_2 uptake capacity of 167 mg/g at 273 K/ 1bar compared to the other 2-D COF in the Table 1. This suggests that the CO_2 uptake of the COFs at low pressure depends more on the pore diameter than on the S_{BET} . However, at a higher pressure of 55 bar and 278 K, the order of the CO_2 uptake capacities of these COFs is: COF-10 (1010 mg/g) > COF-5 (870 mg/g) > COF-8 (630 mg/g) > COF-6 (310 mg/g) > COF-1 (230 mg/g). This implies

that at high pressures the CO_2 uptake capacities of these COFs is more related to their S_{BET} than on their pore sizes. In addition to the list of 2-D boron-based COFs, Kahveci *et al.* successfully synthesised a 2-D mesoporous triptycene-derived COF (TDCOF-5) using 1,4-benzenediboric acid and hexahydroxytriptycene solvothermally to give a boronate as shown in Scheme 2.3.(Kahveci et al., 2013) The S_{BET} and pore volume reported for TDCOF-5 were 2497 m^2/g and 1.3 cm^3/g at p/p_0 of 0.9. The S_{BET} for TDCOF-5 is higher than that of COF-5 (1670 m^2/g). (Díaz & Corma, 2016; Furukawa & Yaghi, 2009; Olajire, 2017) The reported CO_2 adsorption capacity of TDCOF-5 was 92 mg/g at 273 K/ 1 bar.(Kahveci et al., 2013)

Table 1: Summary of pore sizes, BET and CO_2 uptake 1 and 55 bars of some boron-based COFs

2-D COFs	Pore size (nm)	BET (m^2/g)	CO_2 Uptake capacity at 273 K/1 bar (mg/g)	CO_2 Uptake capacity at 55 bar 273 K (mg/g)	Ref
COF-1	0.7	750	100	230	(Furukawa & Yaghi, 2009)
COF-5	2.7	1670	60.9	870	(Furukawa & Yaghi, 2009)
COF-6	0.9	750	167	310	(Furukawa & Yaghi, 2009)
COF-8	1.6	1350	64.8	630	(Furukawa & Yaghi, 2009)
COF-10	3.2	1760	50	1010	(Furukawa & Yaghi, 2009)
COF-66	2.3	366	N/A	N/A	(Wan et al., 2011)
TDCOF-5	N/A	2497	92	N/A	(Kahveci et al., 2013)



Scheme 4: Synthesis OF COF TDCOF-5.(Kahveci et al., 2013)

The rigid conformation of the building units drives the topological design of the COFs. The rigid nature as well as discrete bonding direction of arene molecules makes aromatic π -systems good building units. The diversity of π -aromatic systems allows the combination of various building units which, results in the formation of COFs with very variable molecular design.(Jinang, 2012) Some building blocks used for the synthesis of boron-based COFs are summarised below Figure 2. These building blocks can be classified as either 2-D or 3-D on the basis of the directional symmetry of the coordinating groups. The geometry of the building units determines the final structure of the COF. There are fewer 3-D COFs than 2-D COFs due to the limited number of building

blocks available. Thus the self-condensation of tetrahedral nodes (3D-T4) or co-condensation of tetrahedral nodes with linear 2D-C₃ or triangular 2D-C₃ building units can lead to the construction of 3-D COFs with different crystalline space groups. However, a combination of 2-D (2D-C₂ + 2D-C₃, 2D-C₃ + 2D-C₃, or 2D-C₂ + 2D-C₄) will lead to formation of 2-D COFs.(Jinang, 2012). Cote *et al.* pioneered the construction of 3-D COFs (COF-102 and COF-103) from tetrakis (4-dihydroxyborylphenyl) methane (TDBPM) and tetrakis(4-dihydroxyborylphenyl)silane (TDBPS) as four connector nodes. Both COFs have *ctn* topology and are formed via dehydration of the boronic acid to give B_3O_3 rings as shown in Scheme 5.(El-Kaderi et al., 2007) .

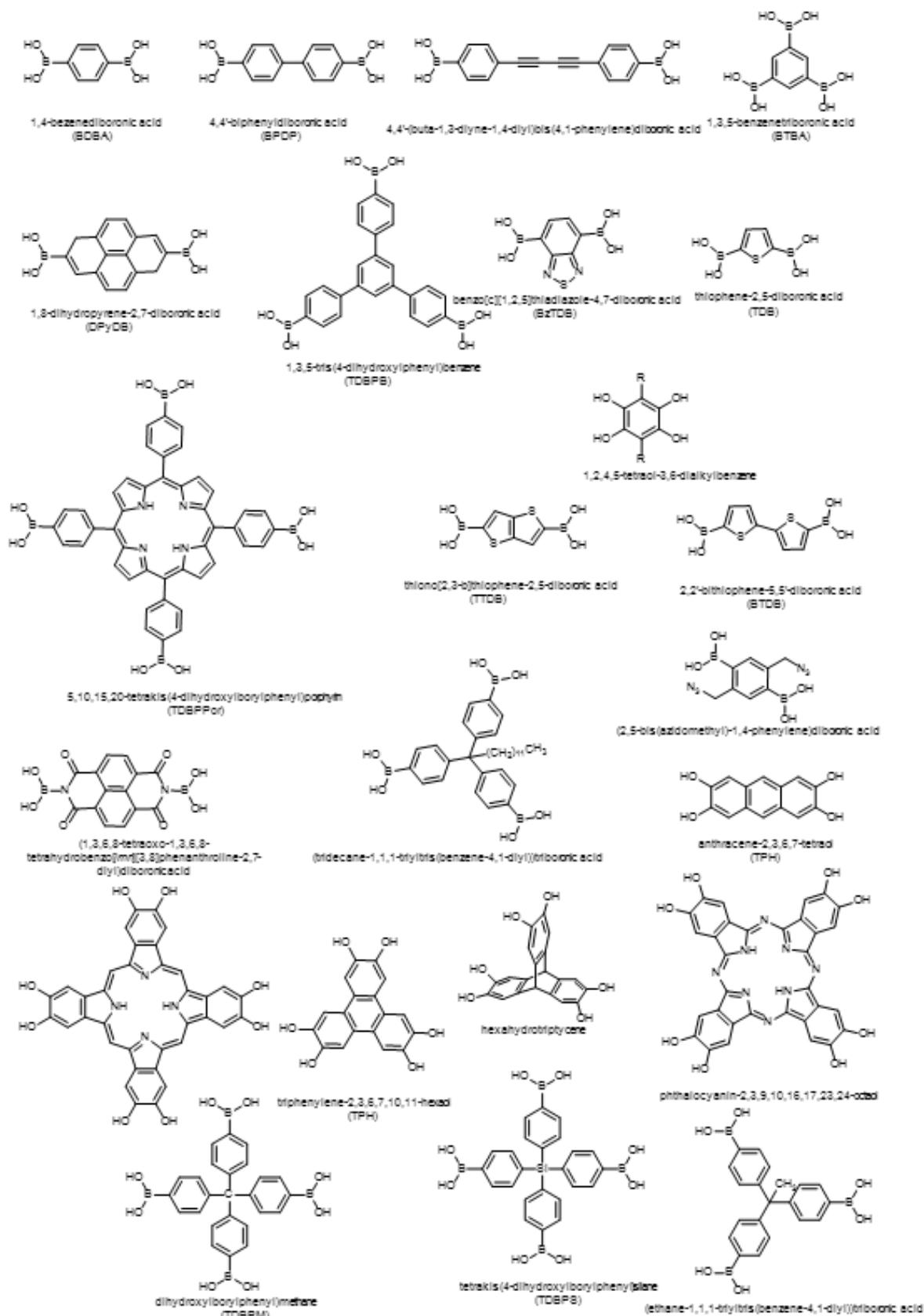
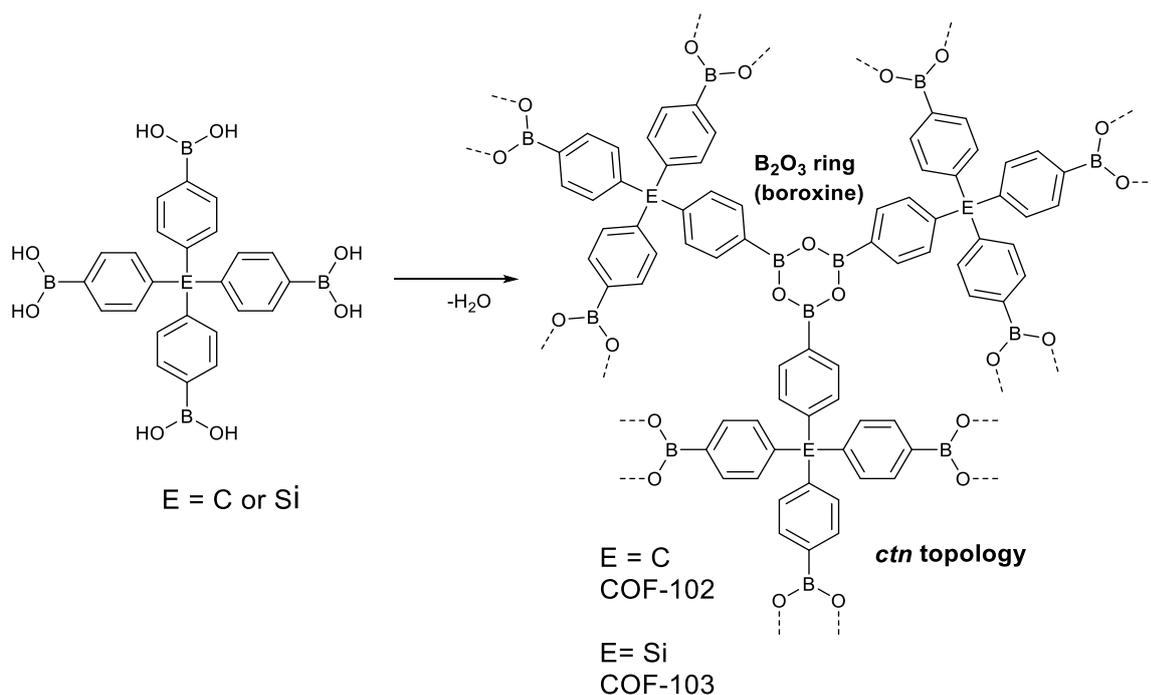
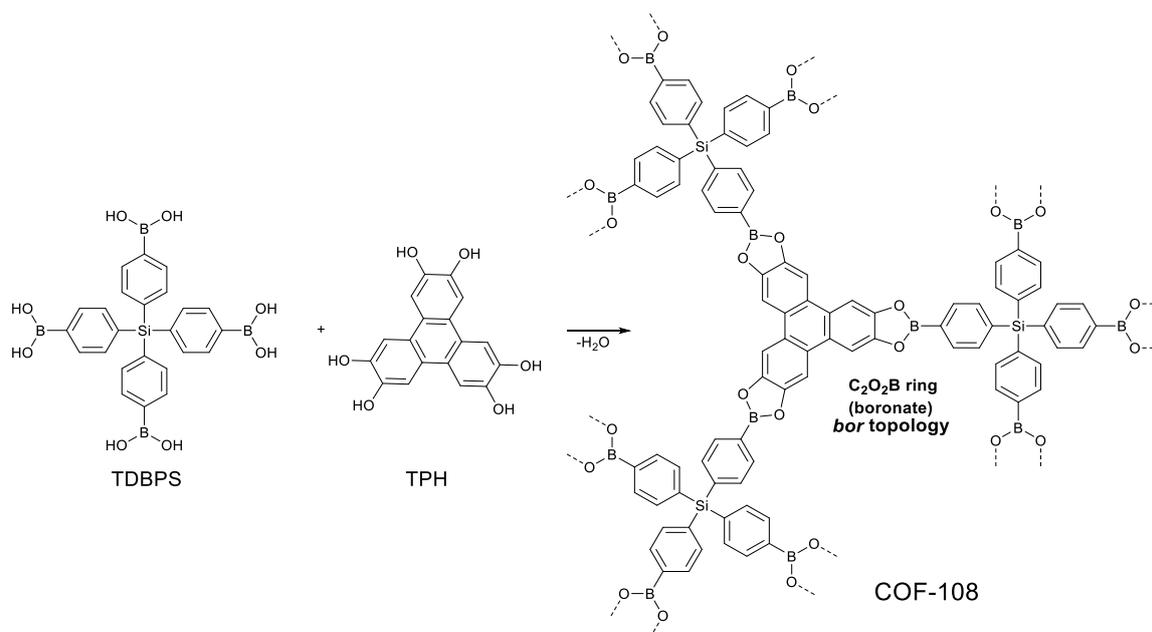


Fig 2: Monomers with different geometries for the design of boron-based COFs

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Scheme 5: Synthesis of 3-D COFs (COFs- 102 and 103) with *ctn* topology.(El-Kaderi et al., 2007)



Scheme 6: Synthesis of 3-D boron-based COF-108, with bor topology(El-Kaderi et al., 2007)

Table 2: S_{BET} , density and CO_2 uptake capacities of some 3-D boron-based COFs

Boron-based 3-D COFs	S_{BET} (m^2/g)	Density (g/cm^3)	CO_2 Uptake capacity at 55 bar, 273 K	Ref
COF-102	3427	0.41	1200	(El-Kaderi et al., 2007)
COF-103	4210	0.38	1190	(Furukawa & Yaghi, 2009)
COF-108	N/A	0.17	N/A	(Furukawa & Yaghi, 2009)

The S_{BET} , densities and CO_2 uptake capacities at low pressure of these 3-D COFs are summarised in **Table 2**. Another boron-based 3-D COF is COF-108 with a *bor* topology and a

pore size of 3.1 nm and low density of 0.17 g/cm^3 .(El-Kaderi et al., 2007; Jinang, 2012; Olajire, 2017) COF-108 was synthesised via the co-condensation of

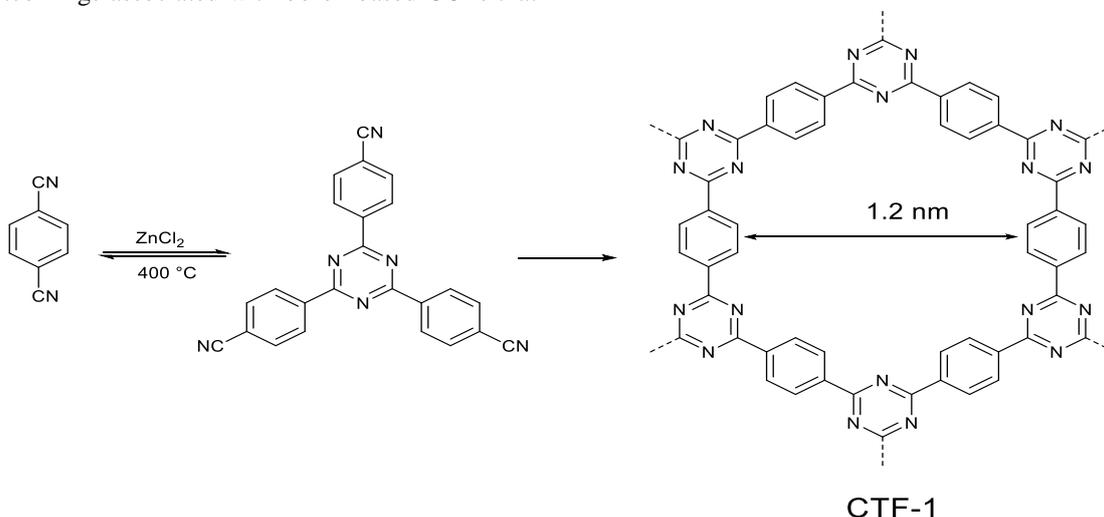
tetrakis(4-dihydroxyborylphenyl)silane (TDBPS) and triphenylene-2,3,6,7,10,11-hexaol (TPH) as shown below in Scheme 6.(El-Kaderi et al., 2007).

From the Table 2, it can be seen that COF-103 has higher S_{BET} than COF-102. However, the density of COF-102 as well as its CO_2 uptake capacity is higher than that of COF-103. The boron-based 2-D COFs (COF-1, COF-5, COF-6, COF-8, COF-10, COF-66, TDCOF-5) and 3-D COFs (COF-102, COF-103, and COF-108) have good crystallinity, low densities, large S_{BET} , high thermal and chemical stabilities as well as diversity in structure. Other boron-based COFs reported in the literature include ZnPcPy COFs,(Spitler et al., 2012) thiophene-containing COFs (TCOFs),(Bertrand et al., 2013) ZnP-COF,(Feng et al., 2011) 100%N₃-COF-5, 50%ACTrz-COF-5 and 100%Trz-COF-5.(Nagai et al., 2011) However, some shortcomings associated with boron-based COFs that

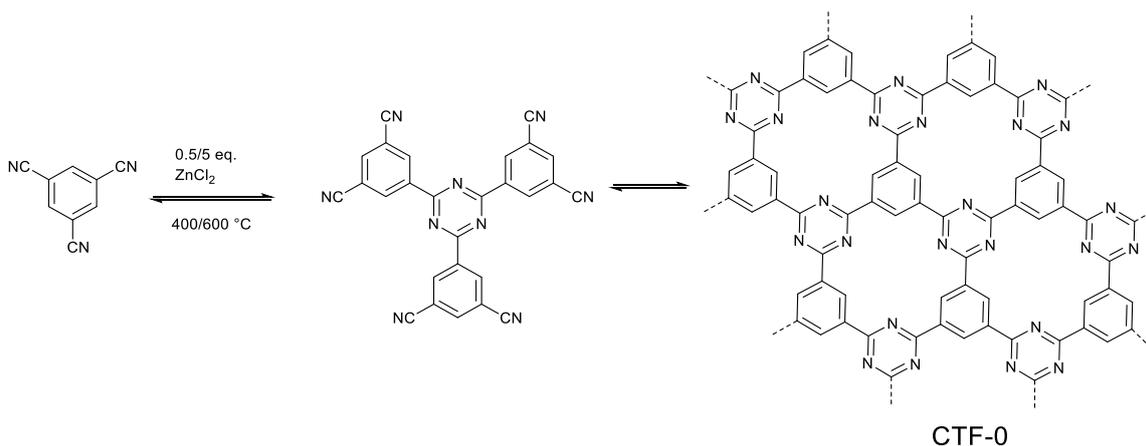
limit their applications as CO_2 capture porous materials are: their low CO_2 uptake at low pressures and their instability in moist air or aqueous environments.(Smith et al., 2016) Thus further research on COFs using other building blocks such as triazines has been carried out.

Triazine-based COFs (CTF)

The pioneers of the use of cyano-aromatic compounds for the synthesis of triazine-based crystalline COF (COF-CTF-1) were Thomas and co-workers (2008).(Kuhn, Antonietti, et al., 2008) The synthesis of CTF-1 was done by the reversible cyclotrimerization reaction of aromatic nitrile building unit (1,4-dicyanobenzene) in the presence of $ZnCl_2$ which served as a catalyst as well as a solvent at 400 °C as shown in Scheme 7 (Kuhn, Antonietti, et al., 2008)



Scheme 7: Synthesis of 2D triazine-based COF (CTF-1).(Kuhn, Antonietti, et al., 2008)



Scheme 8: Trimerization of 1,3,5-tricyanobenzene to CTF-0.(Katekomol et al., 2013)

CTF-1 has a 2-D hexagonal COF structure with pore size of 1.2 nm, 1-D pore channels and S_{BET} of ca. 1000

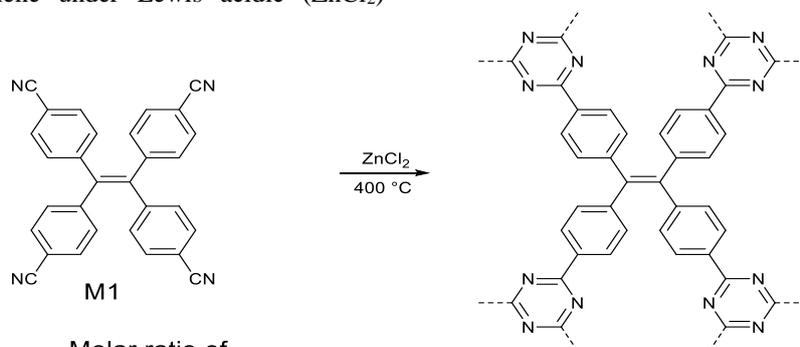
m^2/g . In addition, Thomas and co-workers(Katekomol et al., 2013) also synthesised CTF-0 via the

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trimerization of 1,3,5-tricyanobenzene in molten ZnCl_2 as shown in Scheme 8. It was reported that the crystalline framework (CTF-0) possessed a S_{BET} of $500 \text{ m}^2/\text{g}$ and CO_2 uptake capacity of 186 mg/g at 273 K , while CTF-0 derivatives obtained at higher temperatures had an increased S_{BET} of $2000 \text{ m}^2/\text{g}$.

The transformation of tetrakis(4-cyanophenyl)ethylene under Lewis acidic (ZnCl_2)

conditions at $400 \text{ }^\circ\text{C}$ was studied for different ratios of tetrakis(4-cyanophenyl)ethylene and ZnCl_2 to give two porous covalent triazine-based frameworks (PCTF-1 & PCTF-2, which have the same overall structure but a different porosity dependent on the reaction conditions) with S_{BET} of 2235 and $784 \text{ m}^2/\text{g}$ respectively (Bhunia, Vasylyeva, et al., 2013) Scheme 9.

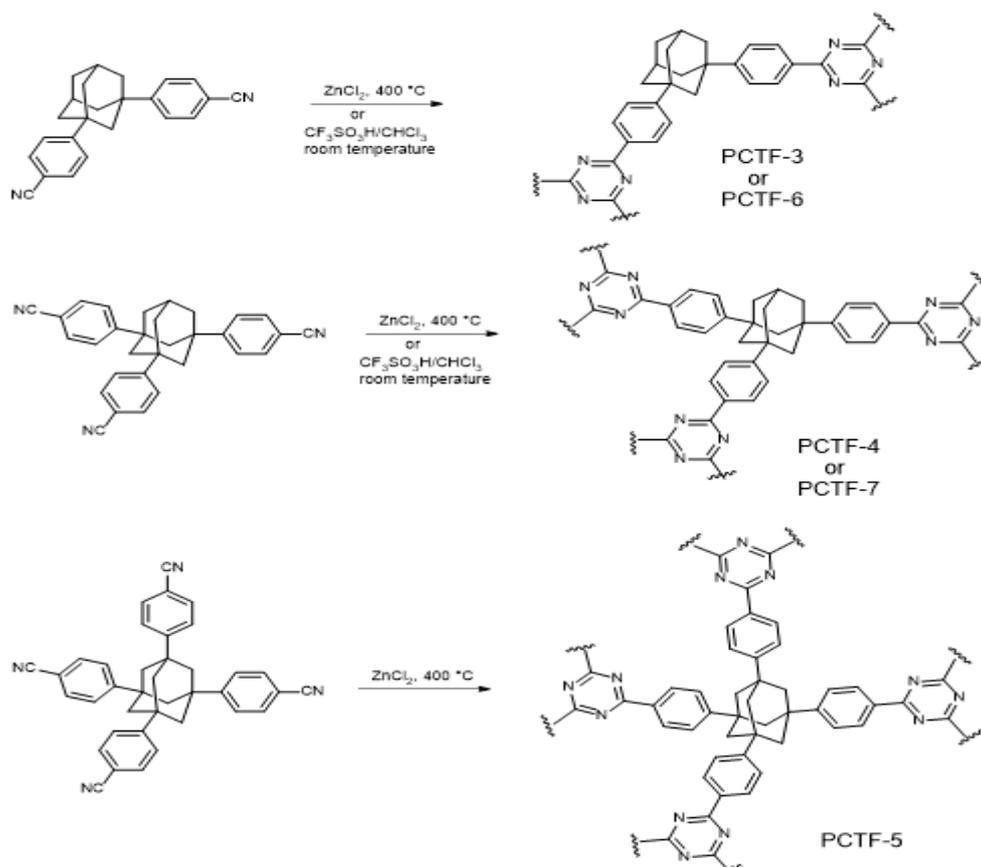


Molar ratio of
M1 : ZnCl_2

1 : 10 = PCTF-1

1 : 5 = PCTF-2

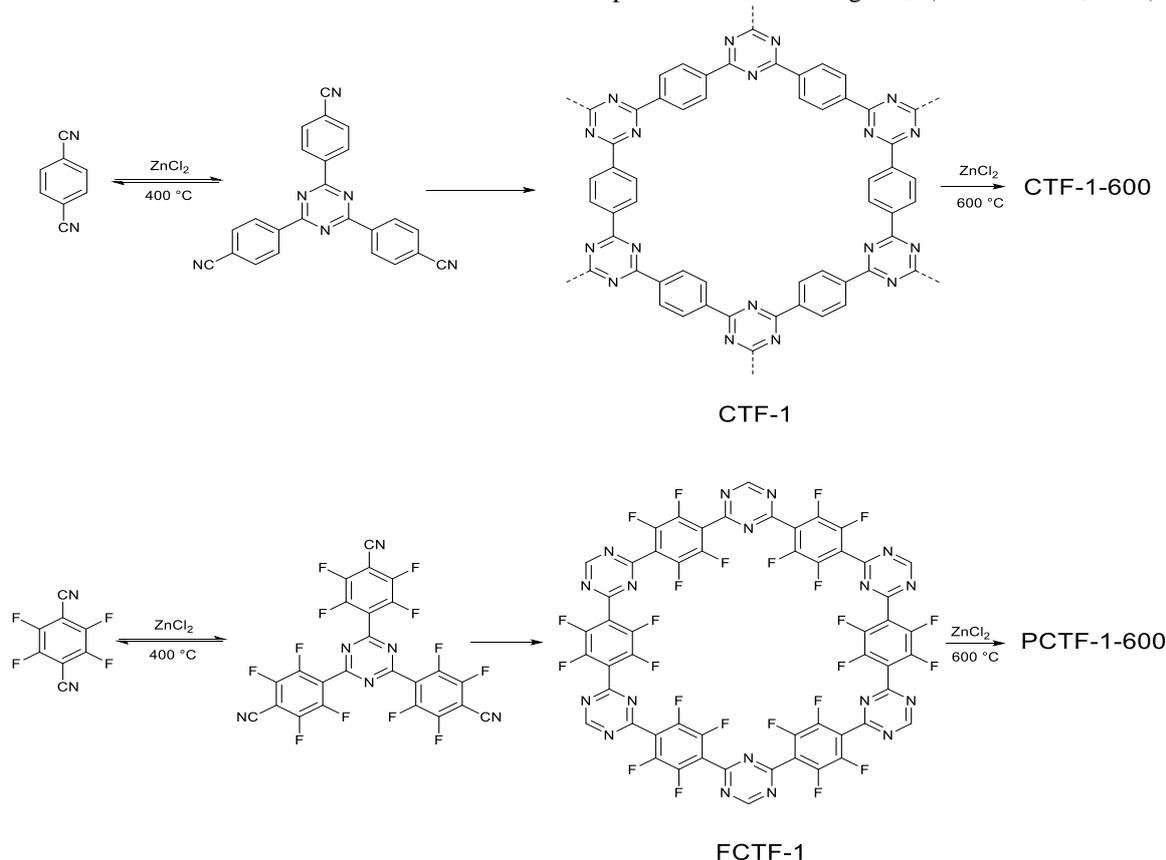
Scheme 9: Synthesis of (PCTF-1 & PCTF-2). (Bhunia, Vasylyeva, et al., 2013)



Scheme 10: Synthesis of porous covalent triazine-based frameworks (PCTF-3 - PCTF-7). (Bhunia, Boldog, et al., 2013)

The S_{BET} of these four triazine-based COFs was reported to decrease as the length of the branched arm elongates. Thus PCTF-1 Scheme 11 (containing biphenyl as the branched arm, PCTF-2 with terphenyl branched arm and PCTF-3 with four-phenyl branched arm) have S_{BET} 853, 811 and 395 m^2/g , respectively. It was reported that PCTFs containing monomers with longer branches packed more efficiently, which resulted in higher density and lower surface areas. However, comparing PCTF-4 containing benzothiadiazole in the place of the central benzene in PCTF-2, the N_2 adsorption isotherms showed its S_{BET} to be 1404 m^2/g , which ranked highest among the PCTFs, almost twice that of PCTF-2. The three nitrogen atoms in the C_3N_3 triazine rings in them, which are reported to be responsible for the high affinity of these frameworks toward the adsorption of CO_2 . The CO_2 uptake capacity reported for PCTF-4 was 205 mg/g at 273 K/ 1 bar, one of the highest reported for this class of CTF materials. The high CO_2 adsorption capacity of PCTF-4 is attributed to the presence of the benzothiadiazole in the framework. The benzothiadiazole served as a polar group that enhanced the affinity of the framework toward CO_2 .

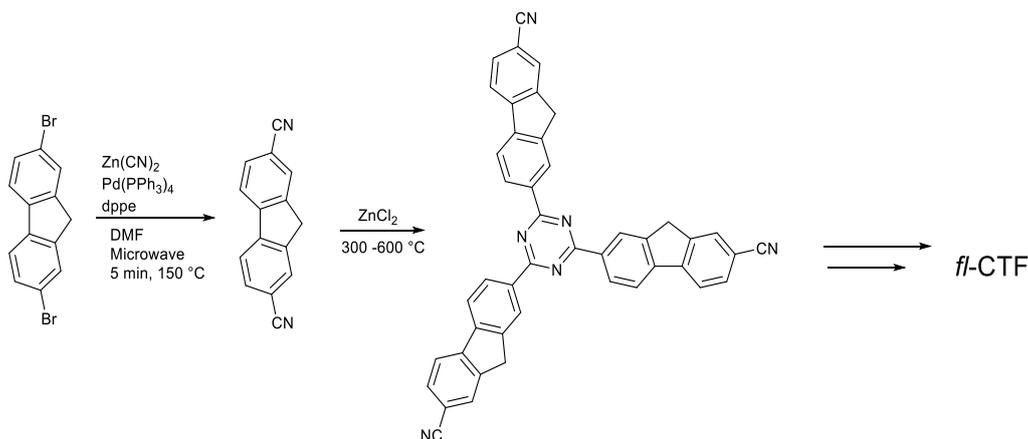
This observation suggests that the incorporation of strong polar groups such as benzothiadiazole into the framework of a microporous polymer could improve the binding affinity of CO_2 molecules towards the polymer. PCTF-4, was also reported to have CO_2/N_2 and CO_2/CH_4 selectivity ratios ranging from 14–56 and 11–20 respectively, at 273 K. (Gu et al., 2015). Hydrocarbons containing fluorine atoms are more hydrophobic and lipophilic than corresponding hydrocarbons lacking fluorine and show stronger affinity toward CO_2 than hydrocarbons without fluorine substituents. Similar observations of the positive effects concerning fluorine atoms in framework materials were reported by Smaldone and co-workers (Alahakoon et al., 2017) who reported that increasing the ratio of non-fluorinated to fluorinated monomers led to significant improvement in both crystallinity and porosity of TFX-COFs (Alahakoon et al., 2017). With this in mind, Han and co-workers (Y. Zhao et al., 2013) designed and constructed two triazine-based covalent frameworks (CTF-1 & FCTF-1) as shown in Scheme 12 (Zhao et al., 2013). The target for synthesis of FCTF-1 was to prepare a material with high water tolerance and a strong preference for binding CO_2 . (Y. Zhao et al., 2013)



Scheme 12: Synthesis of CTF-1 and perfluorinated covalent triazine-based framework (FCTF-1) (Y. Zhao et al., 2013)

The addition of fluorine in FCTF-1 was reported to create an F-rich framework which enhanced the CO₂ adsorption capacity of FCTF-1 in comparison to CTF-1 without fluorine atoms. The fluorine atoms in the framework are highly electronegative and thus produce strong polar covalent C-F bonds which increase CO₂ electrostatic interactions. In addition, it was reported that the presence of F atoms in the PCTF-1 compared to CTF-1 reduced the pore size considerably to <0.5 nm, thus increasing the high CO₂ uptake capacity as well as the kinetic selectivity for CO₂/N₂ separation. In the mixed-gas breakthrough experiments, FCTF-1 was reported to display a remarkable CO₂/N₂ selectivity ratio of 77 under kinetic flow conditions. The ratio 77 is much higher than predicted selectivity ratio of 31 from single-gas equilibrium uptake data. Most framework materials tend to perform poorly in their adsorption of CO₂ in the presence of moisture. However, the performance of FCTF-1 in terms of CO₂ adsorption was also reported to remain excellent even in the presence of moisture in the flue gas stream. This was attributed to the hydrophobic nature of the C-F groups. (Olajire, 2017; Y. Zhao et al., 2013). Although, both CTF-1 and FCTF-1 were reported to have poor crystallinity, they were heated at 600 °C to give CTF-1-600 and PCTF-

1-600 respectively. However, no fluorine atoms were detected in FCTF-1-600, which suggested that F species had been removed from the polymer framework by thermal decomposition at high temperatures. At 600 °C both FCTF-1 and FCTF-1-600 were reported to display type-I isotherms. The CO₂ adsorption isotherms for CTF-1, PCTF-1, CTF-1-600, and PCTF-1-600 were determined, their uptake capacities at 273 K/1bar was stated to be in the order: FCTF-1-600 (243.6 mg/g) > FCTF-1 (206 mg/g) > CTF-1-600 (169 mg/g) > CTF-1 (108 mg/g). FCTF-1 showed the highest initial isosteric heat of adsorption (Q_{st}) value of 35.0 kJ/mol at low coverage, demonstrating the moderate affinity to CO₂. The CO₂/N₂ (10:90 v/v) selectivity established on single-gas adsorption isotherms at 298 K/1 bar, for these triazine-based COFs using ideal adsorption solution theory (IAST)(O'Brien & Myers, 1988) was also stated to decline as follows: 31 (FCTF-1) > 20 (CTF-1) > 19 (FCTF-1-600) > 13 (CTF-1-600). (Olajire, 2017). Other covalent triazine-based frameworks (CTFs) containing fluorene building blocks (*fl*-CTF300, *fl*-CTF350, *fl*-CTF400, *fl*-CTF500, *fl*-CTF600) have been synthesised by Lotsch and co-workers as shown in Scheme 13 (Hug et al., 2014)



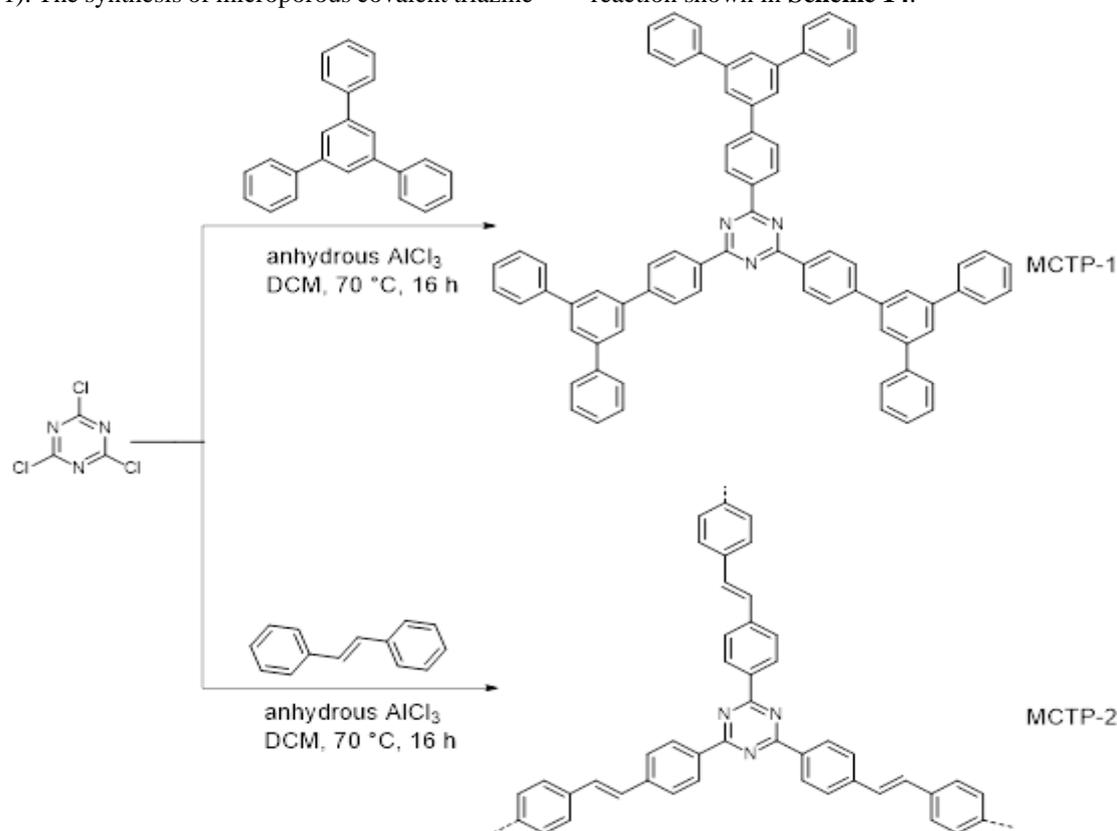
Scheme 13: Synthesis pathway for *fl*-CTFs. (Hug et al., 2014)

However, the CTfs obtained at lower temperatures were reported mainly to possess ultramicropores and moderate surface areas of 297 m²/g at 300 °C. But the porosities of *fl*-CTFs materials obtained at higher temperatures were reported to increase significantly, giving rise to surface areas in excess of 2800 m²/g. (Hug et al., 2014) The COF *fl*-CTF-350 was reported to have a high CO₂/N₂ selectivity ratio of 37 as well as possess the highest fraction of micropores and moderate S_{BET} of 1235 m²/g. However, the adsorption value for *fl*-CTF-350 (188 mg/g) is lower than the reported value for FCTF-1 (205–243 mg/g) (Olajire, 2017) but higher than values reported

for other CTF materials such as CTF-0 (186 mg/g) (Katekomol et al., 2013), CTF-1 (109–168 mg/g) (Y. Zhao et al., 2013), CTF-P2–P6 (82.7–149 mg/g) (S. Ren et al., 2012) CTF-P1M–P6 M (41.44–184.8 mg/g) (S. Ren et al., 2012), MCTF300–500 (99–139 mg/g) (Xiaoming Liu et al., 2013), PCTF-1–7 (81–142 mg/g) (Bhunja, Boldog, et al., 2013; Bhunja, Vasylyeva, et al., 2013) and TPI-1–7 (29.9–107.8 mg/g) (Liebl & Senker, 2013) In addition, the CO₂ adsorption capacity of *fl*-CTF-350 is higher than the uptake capacities of various Microporous Organic Polymers (MOPs) such as covalent organic frameworks (COFs; 53.2–169.8 mg/g), (Dawson et al.,

2011; Furukawa & Yaghi, 2009) microporous polyimides (MPIs; 99–167.6 mg/g)(G. Li & Wang, 2013) and hyper-cross-linked organic polymers (HCPs; 84–172.5 mg/g).(Luo et al., 2013; Martín et al., 2011). The synthesis of microporous covalent triazine-

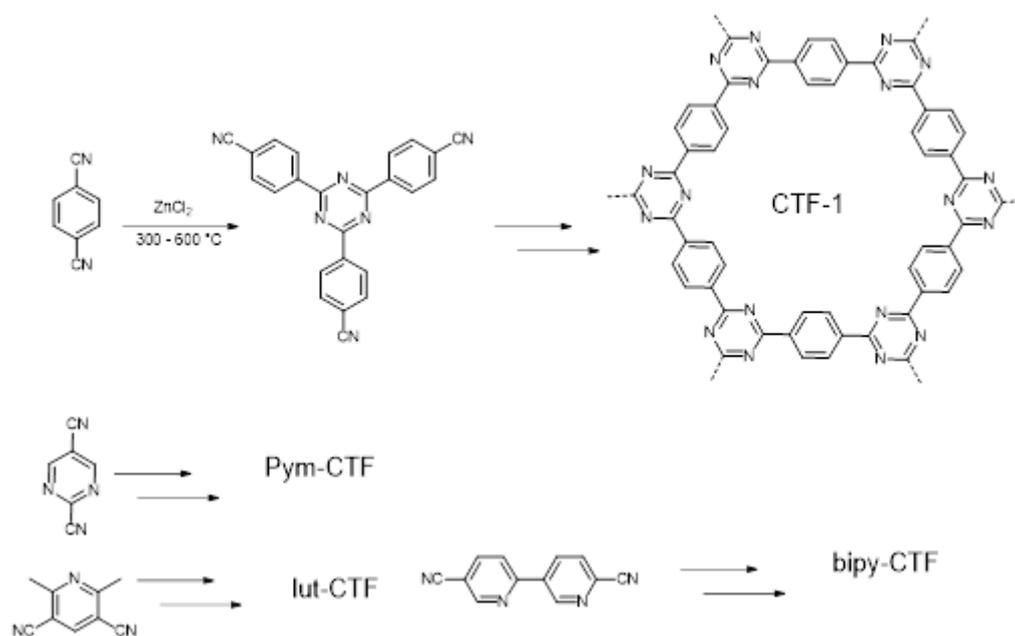
based organic polymers MCTP-1 and MCTP-2 was conducted by Ahn and coworkers(Puthiaraj et al., 2015) using cyanuric chloride with 1,3,5-triphenylbenzene/trans-stilbene via Friedel-Craft reaction shown in **Scheme 14**.



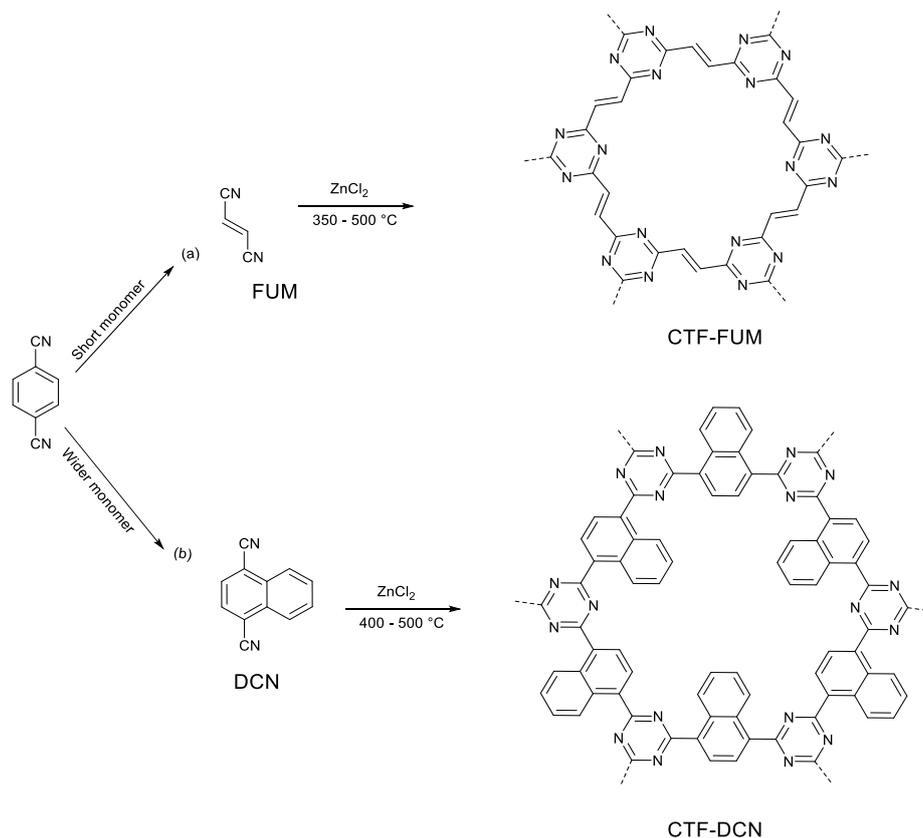
Scheme 14: synthetic pathway for the MCTP networks.(Puthiaraj et al., 2015)

These materials (MCTP-1 and MCTP-2) were reported to possess high S_{BETs} of 1452 and 859 m^2/g respectively. The reported CO_2 adsorption capacity for MCTP-1 is 204.3 mg/g at 273 K/1 bar as well as a moderate CO_2/N_2 selectivity ratio of 54.4. However, MCTP-2 was reported to show a moderate CO_2 uptake of 160 mg/g at 273 K/1 bar with a moderately high CO_2/N_2 selectivity ratio of 68.6 compared to 54.4 for MCTP-1. In a bid to obtain new functionalized COF materials for gas capture, Hug *et al.*(Hug et al., 2015) synthesized nitrogen rich covalent triazine frameworks (CTFs) based on lutidine, pyrimidine, bipyridine and phenyl units in order to study their CO_2 adsorption capacities. These materials were synthesized via ionothermal synthesis at different temperatures as shown in Scheme 15. These porous organic polymers (POPs) were reported to display high gas uptakes and exceptionally high CO_2/N_2 selectivity ratios. The CO_2 adsorption capacity of bipy-CTF-600 (BP-CTF-600) was reported to be the highest in the family of CTFs synthesized, with CO_2 uptake capacity of 245.5 mg/g at 278 K and CO_2/N_2 selectivity ratio of 20.1; while

pyrimidine-based CTF-500 (Py-CTF-500) which contained the highest nitrogen content was reported to possess the highest CO_2/N_2 selectivity ratio of 50.2 based on IAST but with a lower CO_2 capture capacity of 185 mg/g. In addition, Hug, *et al.* (2015) also reported that the trends in the gas adsorption behaviour within the CTF family and nitrogen-containing POPs, revealed the dominant role of the micropore volume for maximum CO_2 uptake performance, while the N-content is a secondary factor for improving the CO_2 adsorption capacity. However, the nitrogen content in the frameworks was stated to be a key contributor to the high CO_2/N_2 selectivity ratios of the produced CTFs.(Hug et al., 2015). Zhong and coworkers(Keke Wang et al., 2016) also designed and synthesized two covalent triazine-based frameworks with both ultramicropores and high nitrogen content for the purpose of CO_2 capture. They successfully synthesized two covalent triazine-based frameworks (CTF-FUM and CTF-DCN) with ultramicropores of width less than 7 Å using fumaronitrile (FUM) and 1,4-dicyanophthalene (DCN) as shown in Scheme 16.



Scheme 15: Synthesis of the CTFs CTF1 (top), pym-CTF(middle), lut-CTF (bottom left), and bipy-CTF (bottom right).(Hug et al., 2015)



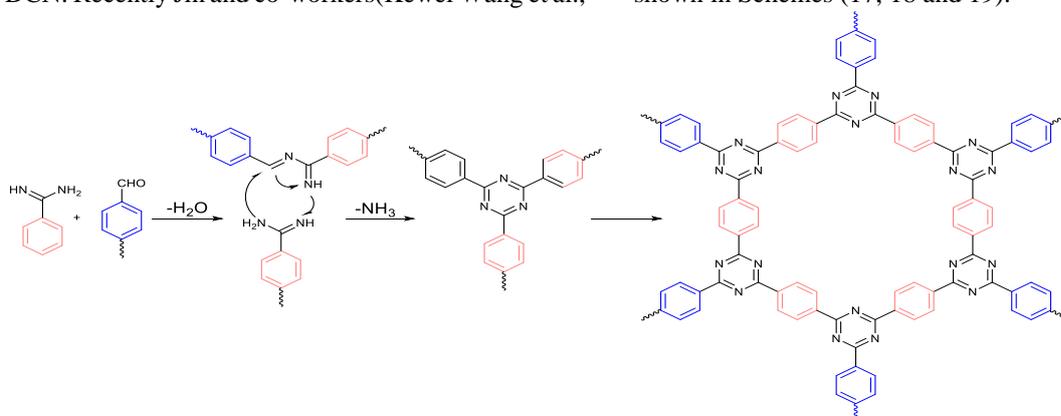
Scheme 16: Synthesis of CTF-FUM and CTF-DCN.(Keke Wang et al., 2016)

Both CTF-FUM and CTF-DCN were reported to have excellent chemical and thermal stability with ultra-micro-pores of 5.2 and 5.4 Å width respectively. These CTFs were also reported to have excellent abilities to

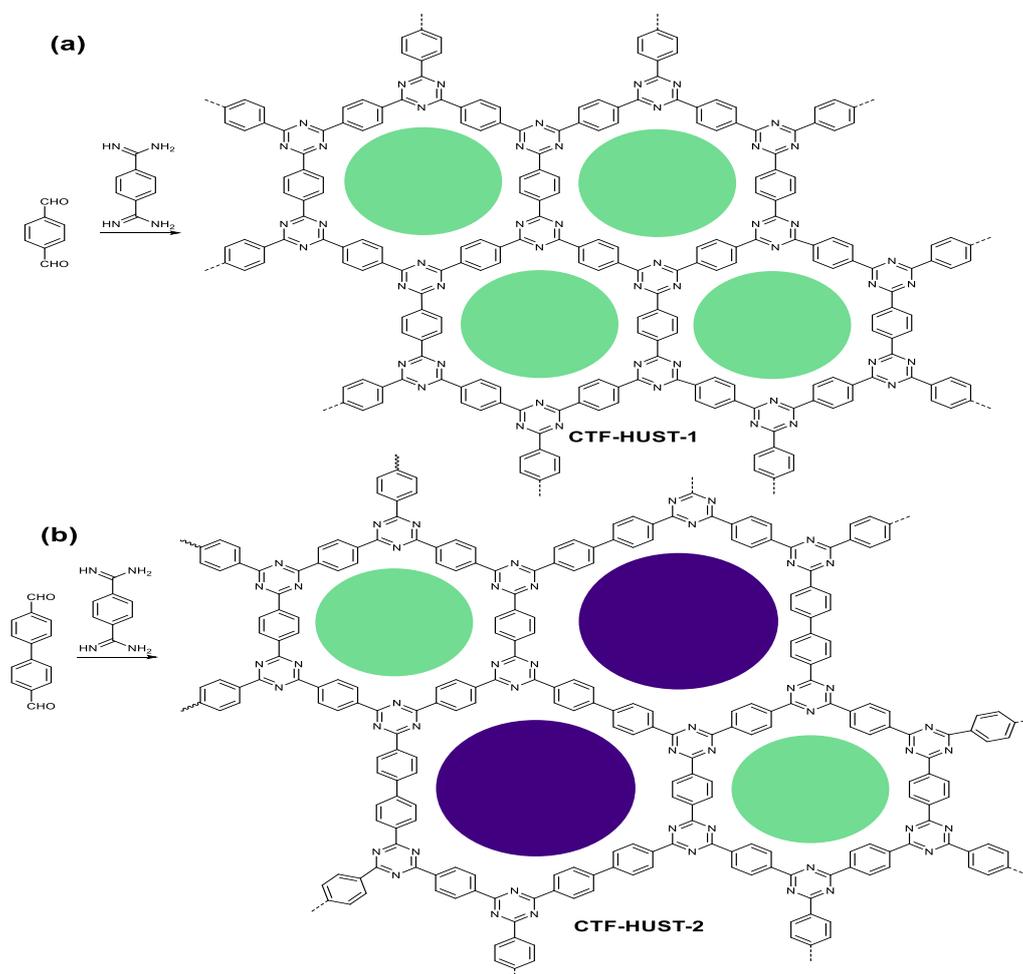
selectively adsorb CO₂ because of the ultra-micro-porous nature of the materials as well as their rich nitrogen content.(Keke Wang et al., 2016) CTF-FUM-350 which contained the highest nitrogen content of

27.4% was reported to display the highest CO₂ adsorption capacity of 112.4 mg/g at 298 K and CO₂/N₂ and CO₂/CH₄ selectivity ratios of 102.4 and 20.5 respectively at 298 K for CTF-FUM and CTF-DCN. Recently Jin and co-workers (Kewei Wang et al.,

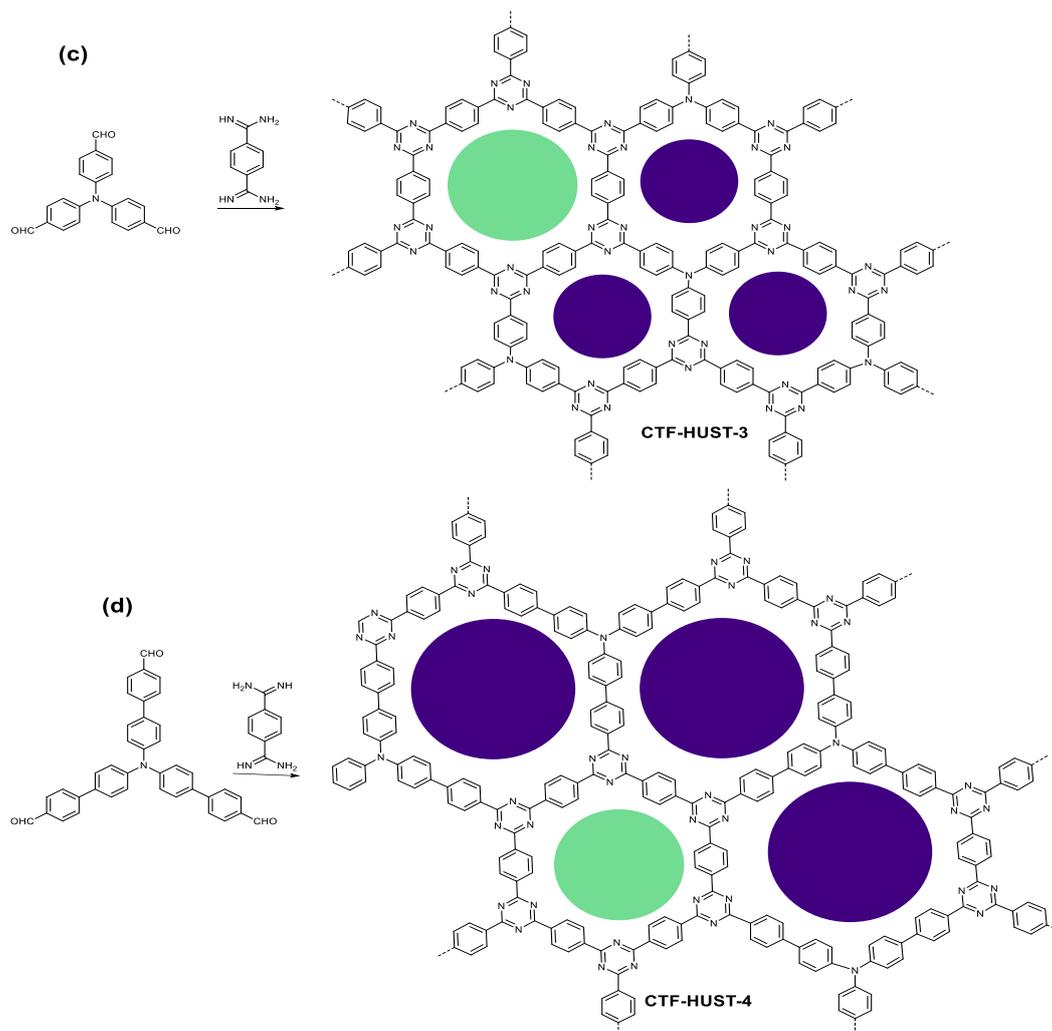
2017) reported the synthesis of triazine COFs (CTF-HUST) via polycondensation reactions that allowed the synthesis of CTFs under mild conditions (low-temperature) using a variety of building blocks as shown in Schemes (17, 18 and 19).



Scheme 17: Triazine formation in the synthesis of CTF-HUST. "HUST" = "Huanzhong University of Science and Technology". (Kewei Wang et al., 2017)



Scheme 18: Synthesis of CTF-HUSTs (a) CTF-HUST-1 (b) CTF-HUST-2; the different coloured circles represent two types of pores. (Kewei Wang et al., 2017)



Scheme 19: Synthesis of CTF-HUSTs (c) CTF-HUST-3 (d) CTF-HUST-4; the different coloured circles represent two types of pores. (Kewei Wang et al., 2017)

The CTF-HUST materials were reported to display good performance in the fields of photocatalyst, gas separations as well as in sodium ion batteries. (Kewei Wang et al., 2017) Building units such as dicyano- and / or multicyno-, pyridine and thiazole compounds (Bojdys et al., 2010; Grill et al., 2007; Kuhn et al., 2009; Kuhn, Forget, et al., 2008) are the main monomers used for the construction of various 2-D CTFs. Some of these building units are shown in **Figure 3**. Triazine-based COFs show better thermal and chemical stability when compared to boron-based COFs, although they show poor crystallinity and porosity, as well as poor structural integrity. Irrespective of these shortcomings, CTFs show high CO₂ uptake capacities and selectivity as well as being reported to show good reusability after several regenerations without loss of their CO₂ adsorption abilities even in the presence of water vapour. (Olajire, 2017).

Imine-based COFs

Imine-based COFs were first investigated by Yaghi and coworkers (Uribe-romo et al., 2011) and are crystalline porous polymeric material containing C=N bonds. The Yaghi group applied the principles of dynamic covalent chemistry for the construction of imine based COFs. These COFs were of a ‘‘Schiff base’’ type formed by the co-condensation of aldehydes and amines or a ‘‘hydrazine’’ type that was made by the co-condensation of aldehydes and hydrazides. An imine-linked porous porphyrin polymer CuPor-BPDC was also synthesized by Neti *et al.* (Neti et al., 2013) using a Schiff base condensation reaction between 5, 10, 15, 20-terakis (*p*-aminophenyl) porphyrin Cu(II) and 4,4'-biphenyl dicarboxaldehyde as shown in Scheme 20.

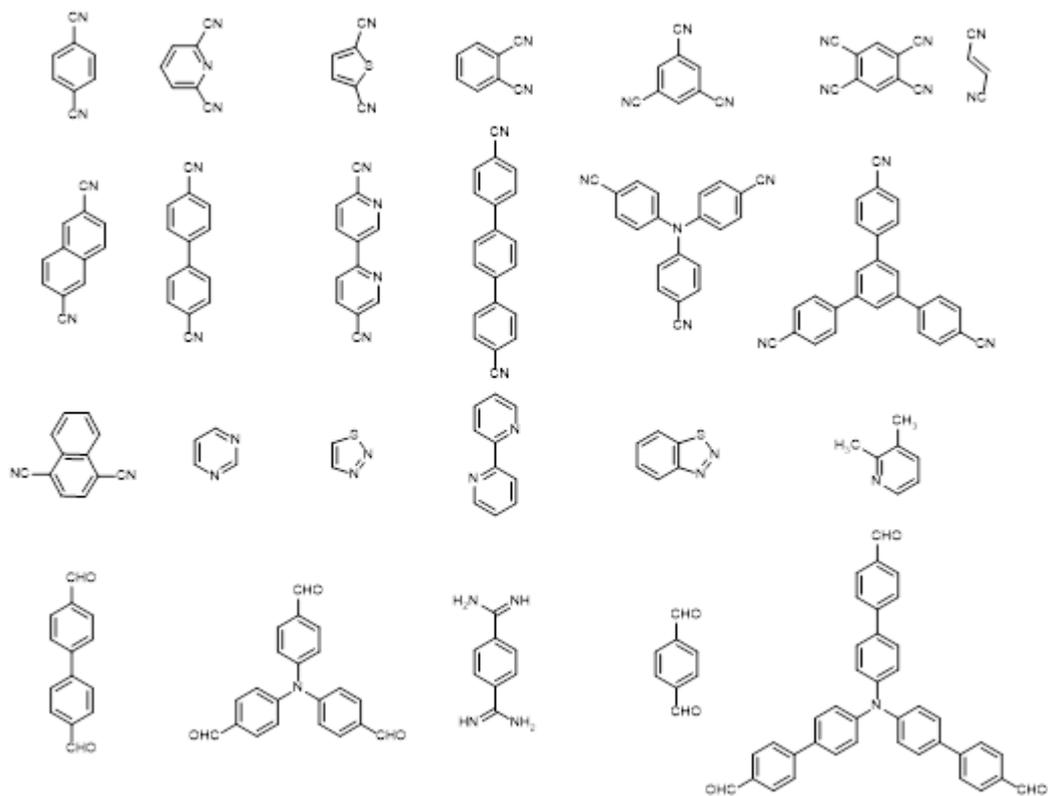
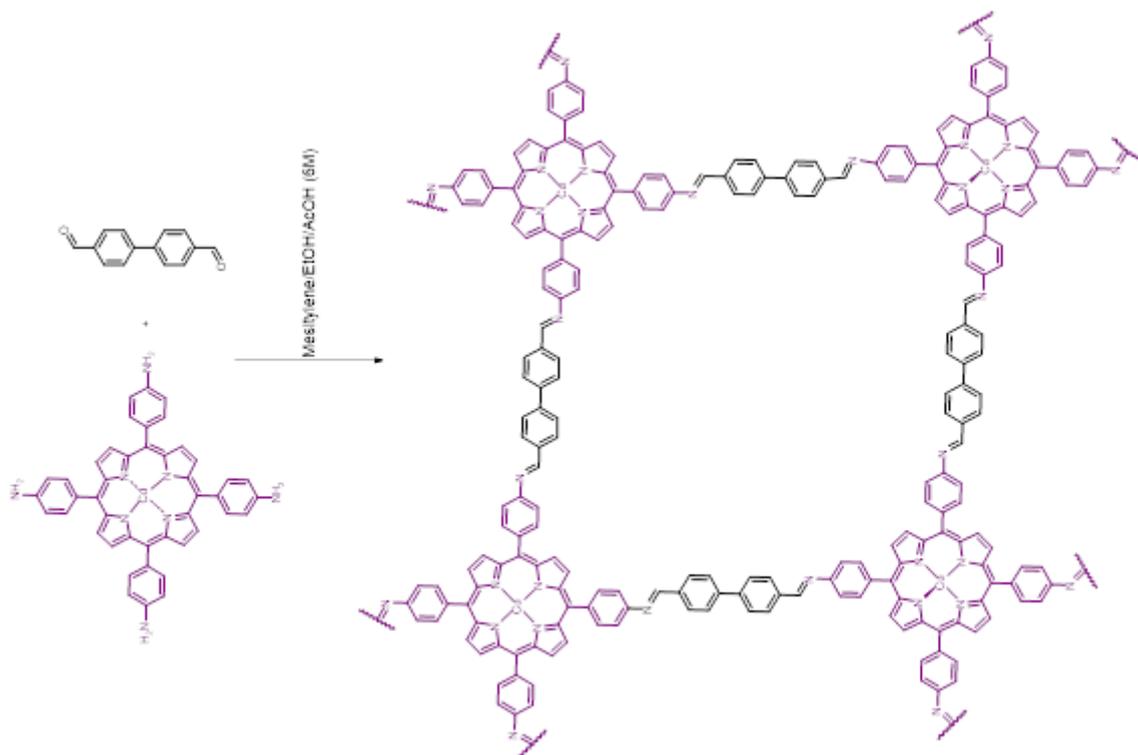


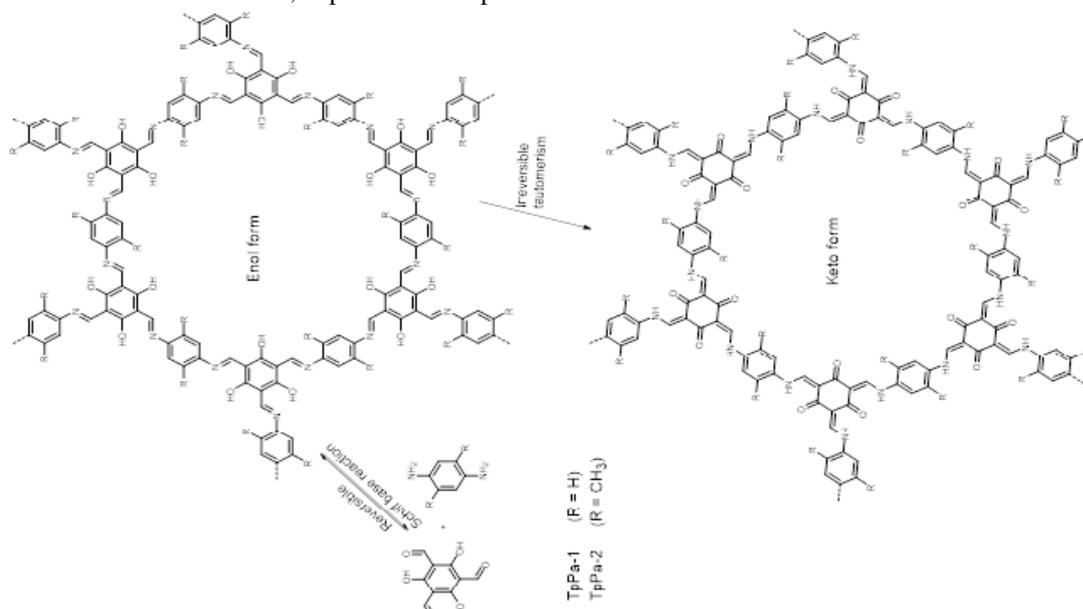
Figure 3: Monomers used for the construction of CTFs of different dimensions



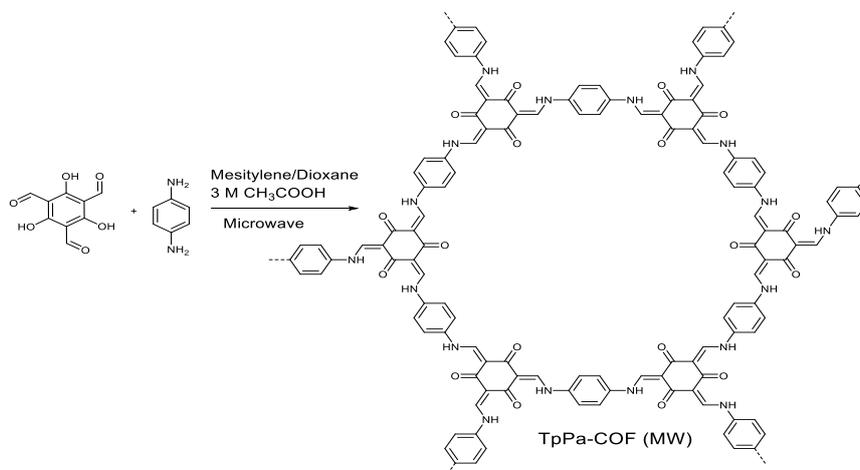
Scheme 20: Synthesis of CUPor-BPDC COF.(Neti et al., 2013)

CuPor-BPDC was reported to display a S_{BET} of 442 m^2/g and high thermal stability of up to 400 $^{\circ}\text{C}$. In addition, CuPor-BPDC also showed CO_2 uptake capacity of 55 mg/g at 273 K/1 bar as well as a CO_2/CH_4 selectivity ratio of 5.6 at 273 K/1 bar. Two other 2-D imine-based COFs, TpPa-1 and TpPa-

2,(Kandambeth et al., 2012) were synthesised by the combination of reversible and irreversible reaction of 1,3,5-triformylphloroglucinol (TP) with *p*-phenylenediamine (PaP-1) and 2,5-dimethyl-*p*-phenylenediamine (PaP-2) respectively as shown on **Scheme 21**.



Scheme 21: Synthesis of TpPa-1 and TpPa-2 by combined reversible and irreversible reactions.(Kandambeth et al., 2012)



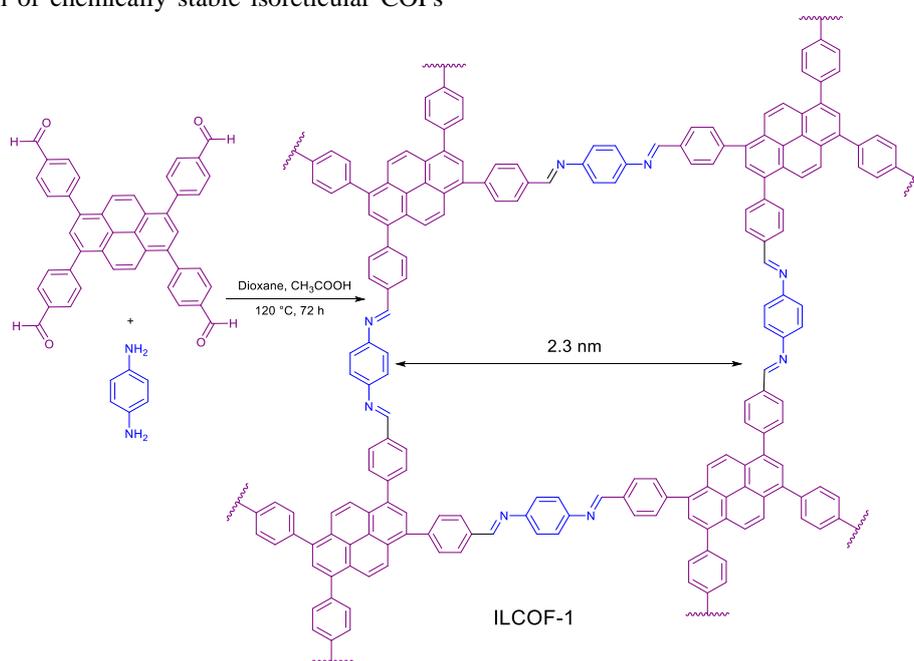
Scheme 22: Synthesis of TpPa-COF (MW).(Wei et al., 2015)

It was reported that TpPa-1 and TpPa-2 showed strong resistance to acid (9 N HCl) as well as boiling water as a result of the irreversible tautomerism from the enol-imine (OH) form to the keto-enamine form. In addition, TpPa-2 was reported to show excellent stability in base (9 N NaOH). The pore size and S_{BET} reported for TpPa-1 are 1.25 nm and 535 m^2/g respectively; whereas TpPa-2 possessed 1.32 nm pore size and S_{BET} of 339 m^2/g as determined from N_2 adsorption isotherms at 237 K. The CO_2 adsorption capacities of TpPa-1 and TpPa-2 were reported to be

15 and 126 mg/g at 273 K/1 bar respectively. Another synthetic method (mechanochemical grinding) was employed in the synthesis of other TP COFs (TpPa-1) (MC), (TpPa-2) (MC) and TpBD using Tp and other amines as building units. These COFs were synthesised via room temperature solvent free mechanochemical grinding using a Schiff base aldehyde-amine condensation reaction. In addition TpBD was also synthesised solvothermally and the CO_2 uptake of TpBD obtained via solvothermal method was reported to be 84.5 mg/g at 273 K/ 1 bar

which is comparable with TpPa-1 (153 mg/g) and TpPa-2 (128 mg/g) obtained by Banerjee and co-workers.(Kandambeth et al., 2012) By way of expanding Tp COFs, Chandra *et al.*(Chandra et al., 2013) used the same Tp organic linkers with other amines to synthesise more COFs and measured their CO₂ uptake capacities at 273 K/ 1 bar. They reported the trend to decrease in the order: TpPa-1 > TpPa-NO₂ (143.4 mg/g) > TpPa-2 (126 mg/g) > TpBD-(NO₂)₂ (102 mg/g) > TpBD (85.5 mg/g) > TpBDMe₂ (72.7 mg/g) > TpPa-F₄ (68.8 mg/g) > TpBD-(OMe) (53 mg/g). To expand further the methods for the making of Tp COFs, Yang and co-workers(Wei et al., 2015) synthesised the same TpPa by using a rapid microwave-assisted solvothermal synthesis method to obtain TpPa-COF (MW) as shown in **Scheme 22**. TpPa-COF (MW) was reported to possess a higher S_{BET} of 725 m²/g as well as better crystallinity than TpPa-COF (CE) synthesised by the simple solvothermal method. TpPa-COF (MW) is rich in N-H sites on its pore wall; these N-H sites were reported to interact more strongly with polarizable CO₂ molecules via hydrogen bonding interactions. These interactions were proposed to be responsible for the CO₂/N₂ adsorption selectivity ratio of 32 recorded for TpPa-COF (MW). In addition, the CO₂ uptake capacity for TpPa-COF (MW) was reported to be 218 mg/g at 273 K/1 bar.(Wei et al., 2015). Other researchers, such as Biswal *et al.*(Biswal et al., 2016) targeted the incorporation of chemically stable isorecticular COFs

(TpPa-1 and TpPa-2) as the active phase at 50% loading within the substituted polybenzimidazole (PBI-Bul) matrix to produce self-supported TpPa-1(50)@PBI-Bul and TBD(50)@PBI-Bul crossbreed membranes. It was reported that the permeability of TpBD(50)@PBI-Bul hydrid ($PCO_2 = 14.8$) performed better than some commonly used gas separation membrane materials such as Matrimid, Polysulfones (PSF) and Polycarbonate (PC).(Biswal et al., 2016) Furthermore, it was reported that the CO₂/CH₄ selectivity ratio of TpBD(50)@PBI-Bul-based membranes materials (48.7) was higher than that of Matrimid (36), PSF (22) and PC (19).(Robeson, 2008; Yong et al., 2012) In addition, the TpBD(50)@PBI-Bul-based membrane material was also reported to demonstrate a better CO₂ and CH₄ permeability ($PCO_2 = 14.8$ and $PCH_4 = 0.3$) with marginally higher CO₂/CH₄ selectivity ratio of 48.7 than Z₃₀@PBI-Bul ($PCO_2 = 5.23$ and $PCH_4 = 0.12$) and CO₂/CH₄ selectivity ratio of 43.6. However, the CO₂/N₂ selectivity ratio for TpBD(50)@PBI-Bul-based membrane was reported to be 23.(Bhaskar et al., 2014). As a follow up, Elkaderi and co-workers(Rabbani et al., 2013) synthesised the mesoporous imine-linked COF (ILCOF-1) by the condensation reaction of 1,3,6,8-tetraakis (4'-formyl-phenyl)-pyrene and p-phenylenediamine in 1,4-dioxane containing aqueous acetic acid as shown in **Scheme 23**.



Scheme 23: Synthesis of ILCOF-1.(Rabbani et al., 2013)

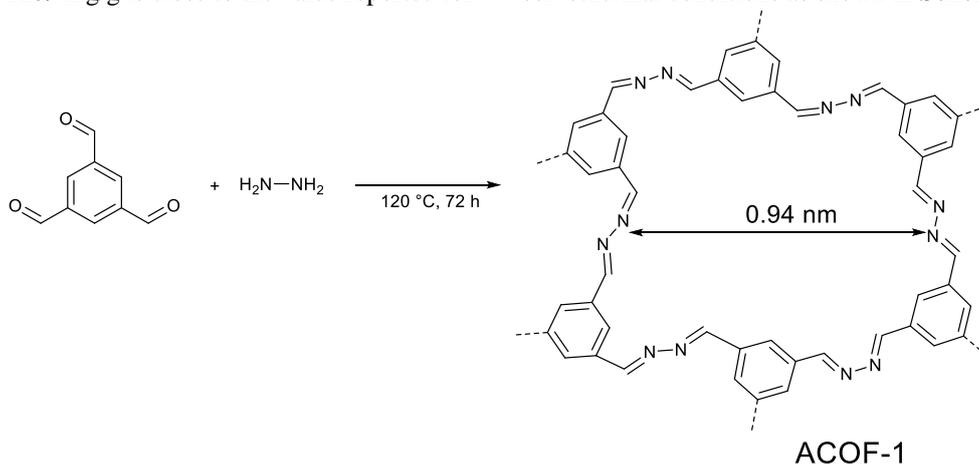
ILCOF-1 was reported to have a high S_{BET} of 2723 m²/g. In addition, ILCOF-1 was also reported to be stable up to 400 °C under air as well as possessing a

pore size distribution centred at around 2.3 nm. The CO₂ uptake capacity reported for ILCOF-1 was 60.9 mg/g at 273 K/1 bar.(Olajire, 2017; Rabbani et al.,

BULL, OS; BULL, I; AMADI, GK; ODU, CO

2013) However, the CO₂ uptake capacity at 298 K and 40 bar reported in the literature was 1289 mg/g. (Rabbani et al., 2013) A comparison of this value to other values in the literature shows that it surpasses most of the reported CO₂ adsorption capacities of many 2-D and 3-D COFs including some hyper-branched conjugated polymers such as HCPs (467.5 – 589 mg/g) at 298 K/ 35 bar. (Martín et al., 2011) However, 1289 mg/g is close to the value reported for

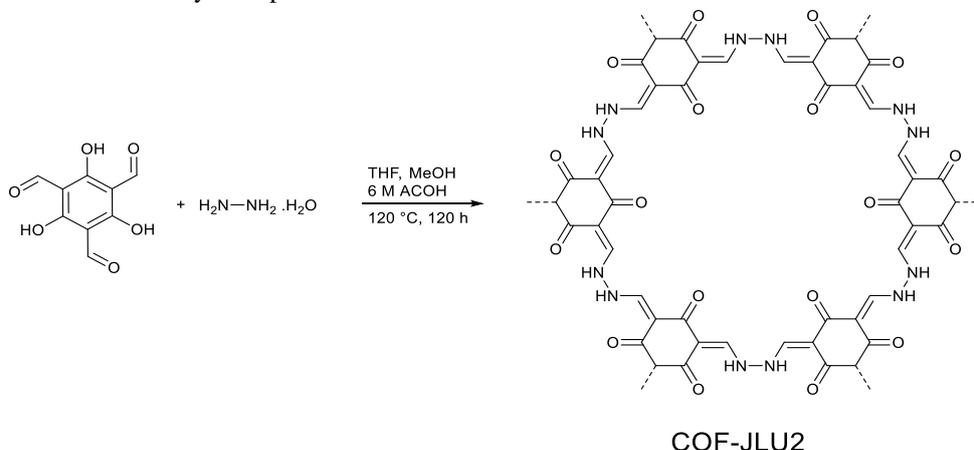
PAF-1 (1300 mg/g) at 298 K/40 bar. (Ben et al., 2009) The CO₂ uptake performance of ILCOF-1 was attributed to the presence of nitrogen-functionalized pore walls, which enhance CO₂ adsorption via N...CO₂ interaction. An azine-linked 2-D COF (ACOF-1) was designed and synthesised by Lui and co-workers (Z. Li et al., 2014) using the condensation reaction of hydrazine hydrate and 1,3,5-triformylbenzene under solvothermal conditions as shown in **Scheme 24**.



Scheme 24: The synthesis of ACOF-1. (Z. Li et al., 2014)

ACOF-1 was reported to possess an S_{BET} and pore size of 1176 m²/g and 0.94 nm respectively. In addition, it was reported that the CO₂ uptake capacity of ACOF-1 was 177 mg/g at 273 K/1 bar as well as a CO₂/N₂ selectivity of 40 at 273 K in the very low pressure

range of 0 – 0.1 bar. Another 2-D azine-linked COF is COF-JLU2, reported by Li *et al.* (2015) also used a condensation reaction of hydrazine hydrate and 1,3,5-triformylphloroglucinol under solvothermal conditions as shown in **Scheme 25**.



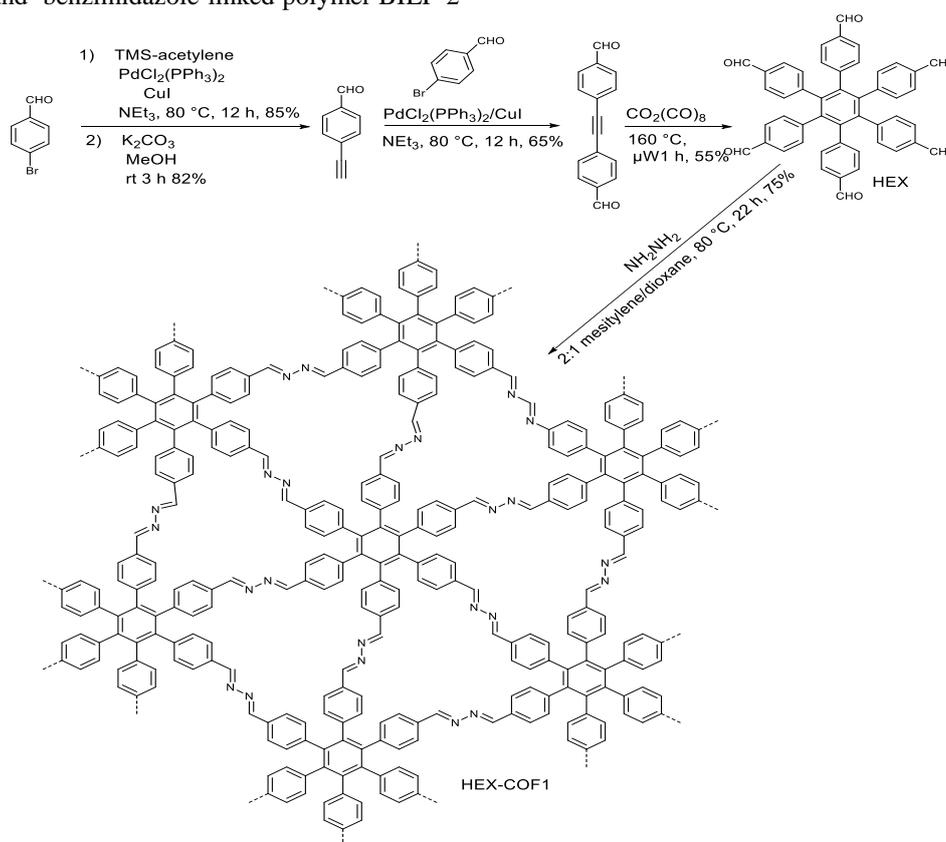
Scheme 25: The synthesis of COFJLU2. Li *et al.*, (2015)

COF-JLU2 contains many heteroatom sites in its skeleton, which are believed to enhance its functionality. COF-JLU2 was reported to be highly crystalline and to possess a moderate S_{BET} and pore size of 410 m²/g at 77 K and 0.96 nm respectively as well as display good chemical (towards acid and base) and thermal stability. In addition, the CO₂ adsorption capacity reported for COF-JLU2 was 216 mg/g at 273

K/1 bar. This CO₂ uptake capacity value is higher than adsorption capacity values for some other COFs in the literature such as COF-103 (76.6 mg/g), (Furukawa & Yaghi, 2009) TDCOF-5 (92 mg/g) (Kahveci et al., 2013) and ACOF-1 (177 mg/g). (Z. Li et al., 2014) Nevertheless, the uptake capacity of COF-JLU2 (216 mg/g at 273 K/1 bar) is comparable to uptake capacities of some amorphous COFs such as porous

organic polymer CPOP-1 (212 mg/g)(Q. Chen et al., 2012), azo-linked polymer ALP-1 (267 mg/g)(Arab et al., 2014) and imine-linked porous polymer PPF-1 (269 mg/g).(Zhu et al., 2013) The reported CO₂ uptake capacity of COF-JLU2, was ascribed to the in-built micro-porosity of the network and the pore walls which are nitrogen- and oxygen-rich. The reported CO₂/N₂ selectivity ratio for COF-JLU2 was 77 which is higher than the CO₂/N₂ selectivity ratio for ACOF-1 (40)(Z. Li et al., 2014) and PPFs (21).(Zhu et al., 2013) However, this same value (77) is less than CO₂/N₂ selectivity ratio for some microporous organic polymers (MOPs) such as tetraphenyladamantane-based polycyanurate network PCN-AD (112)(Shen et al., 2014) and benzimidazole-linked polymer BILP-2

(113).(Rabbani & El-Kaderi, 2012) In addition, the reported CO₂/CH₄ selectivity ratio for COF-JLU2 at temperatures of 273 K and 298 K were 4.1 and 3.2 respectively.(Z. Li et al., 2015) These two selectivity values are comparable to values reported in the literature for other microporous organic polymers (MOPs).(Arab et al., 2014; Q. Chen et al., 2012; Zhu et al., 2013). Another group of researchers, Smaldone and co-workers Alahakoon *et al.* (2016) also reported the synthesis of an azine-linked COF containing a six-fold symmetric hexaphenylbenzene (HEX) monomer functionalized with aldehyde groups which was thereafter treated with hydrazine to give HEX-COF1 as shown in **Scheme 26**.



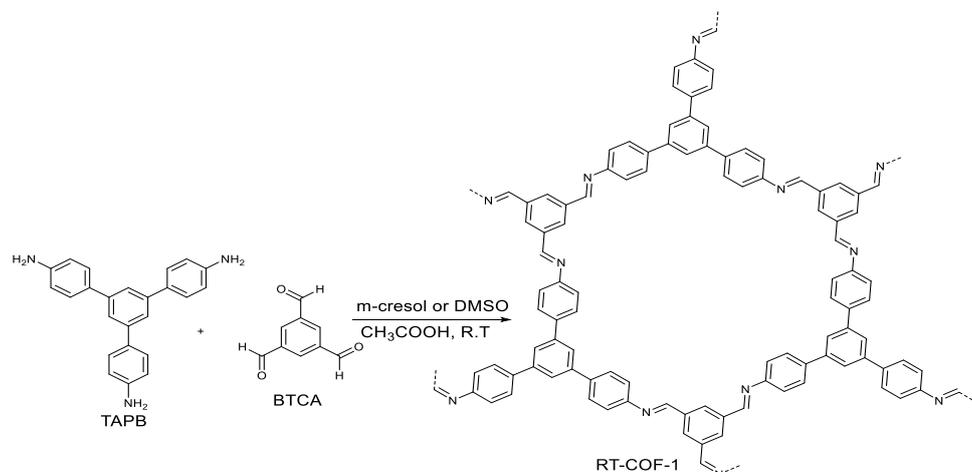
Scheme 26: synthesis of HEX and HEX-COF1. Alahakoon *et al.* (2016)

HEX-COF-1 was reported to have a mean pore size of 1 nm and a surface area in excess of 1200 m²/g as well as to demonstrate outstanding CO₂ uptake capacity of 200 mg/g at 273 K and 1 atmosphere pressure. In addition, the design and construction of a laminar COF (RT-COF-1) from the reaction of 1,3,5-tris(4-aminophenyl)benzene (TAPB) and 1,3,5-benzenetricarbaldehyde (BTCA) through a Schiff base reaction at room temperature in air was conducted by Zamora and co-workers Delapeñaruigómez *et al.* (2015) as shown in **Scheme 27**. The S_{BET} and pore volume reported for RT-COF-1 at N₂ isotherm of 77 K

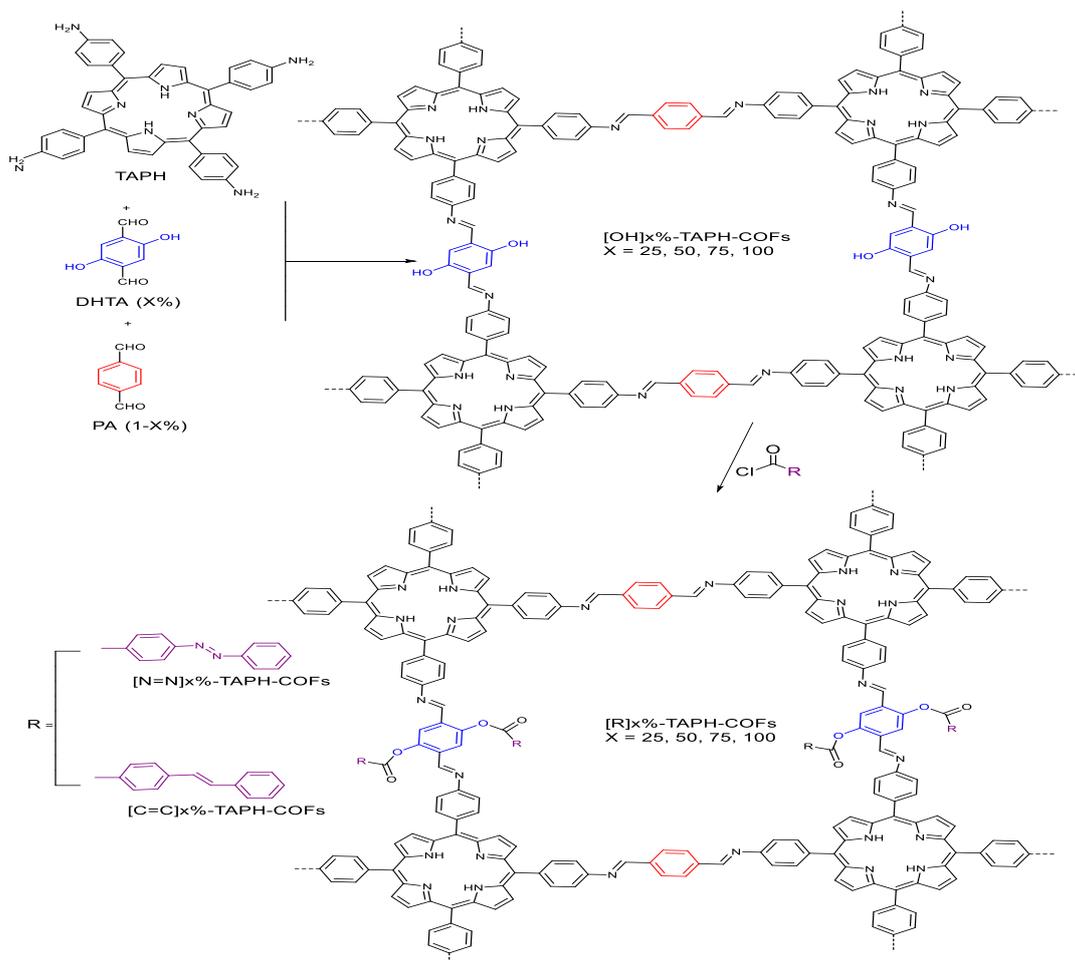
were 329 m²/g and 0.224 cm³/g respectively.(Delapeñaruigómez *et al.*, 2015) Furthermore, it was reported that activated RT-COF-1 adsorbed ca. 86 mg/g of CO₂ at 273 K/1 bar.(Delapeñaruigómez *et al.*, 2015). Furthermore, Gao and co-workers(Ge *et al.*, 2016) synthesized an azo-based COF, COF-Tpazo via a Schiff base condensation reaction of 4,4'-azodianiline (Azo) and 1,3,5-triformylphloro-glucinol (Tp). COF-Tpazo was reported to have an S_{BET} of 1552 m²/g and a pore volume of 0.97 cm³/g as well as a CO₂ uptake capacity of 112 and 68 mg/g at 273 and 298 K/1 bar

respectively. In addition, COF-Tpazo was also found to exhibit a high CO_2/N_2 selectivity ratio of 127 at 273 K; while the CO_2/N_2 selectivity ratio recorded at 298 K was 45. However, the CO_2/CH_4 selectivity ratios at

273 and 298 K, were reported to be 39 and 43 respectively. The CO_2 -philic and N_2 -phobic ends of COF-Tpazo were proposed to be responsible for the reported properties of the material. (Ge et al., 2016)

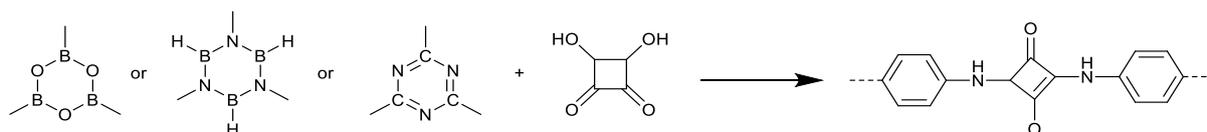


Scheme 27: The room-temperature polyimine condensation to form RT-COF-1. Delaño et al. (2015)



Scheme 28: Synthesis of [N=N]x% -TAPH-COFs with azobenzene group and [C=C]x% -TAPH COFs with stilbene group via nucleophilic substitution reaction from [OH]x% -TAPH-COFs (X = 25, 50, 75, 100). Zhao et al. (2016)

Furthermore, Gao and Co-workers also synthesised a range of tailored COFs, i.e. $[N=N]_x\%$ -TAPH-COFs and $[C=C]_x\%$ -TAPH-COFs by post-modification of $[OH]_x\%$ -TAPH-COFs with 4-phenylazobenzoyl chloride and stilbenecarbonyl chloride (PhStil), (S. Zhao et al., 2016) respectively as shown in **Scheme 28**. These COFs were reported to possess moderate surface areas, narrow pore sizes as well as good physicochemical stability. The $[N=N]_x\%$ -TAPH-COFs were reported to show higher CO_2 adsorption capacity of up to 207 mg/g at 273 K/1 bar and CO_2/N_2 selectivity ratio of 78 at 273 K than the corresponding $[C=C]_x\%$ -TAPH-COFs (16-27). (S. Zhao et al., 2016)



Scheme 29: Synthesis pathway for three 2-D squaraine-bridge COFs. Huang and Cao (2016)

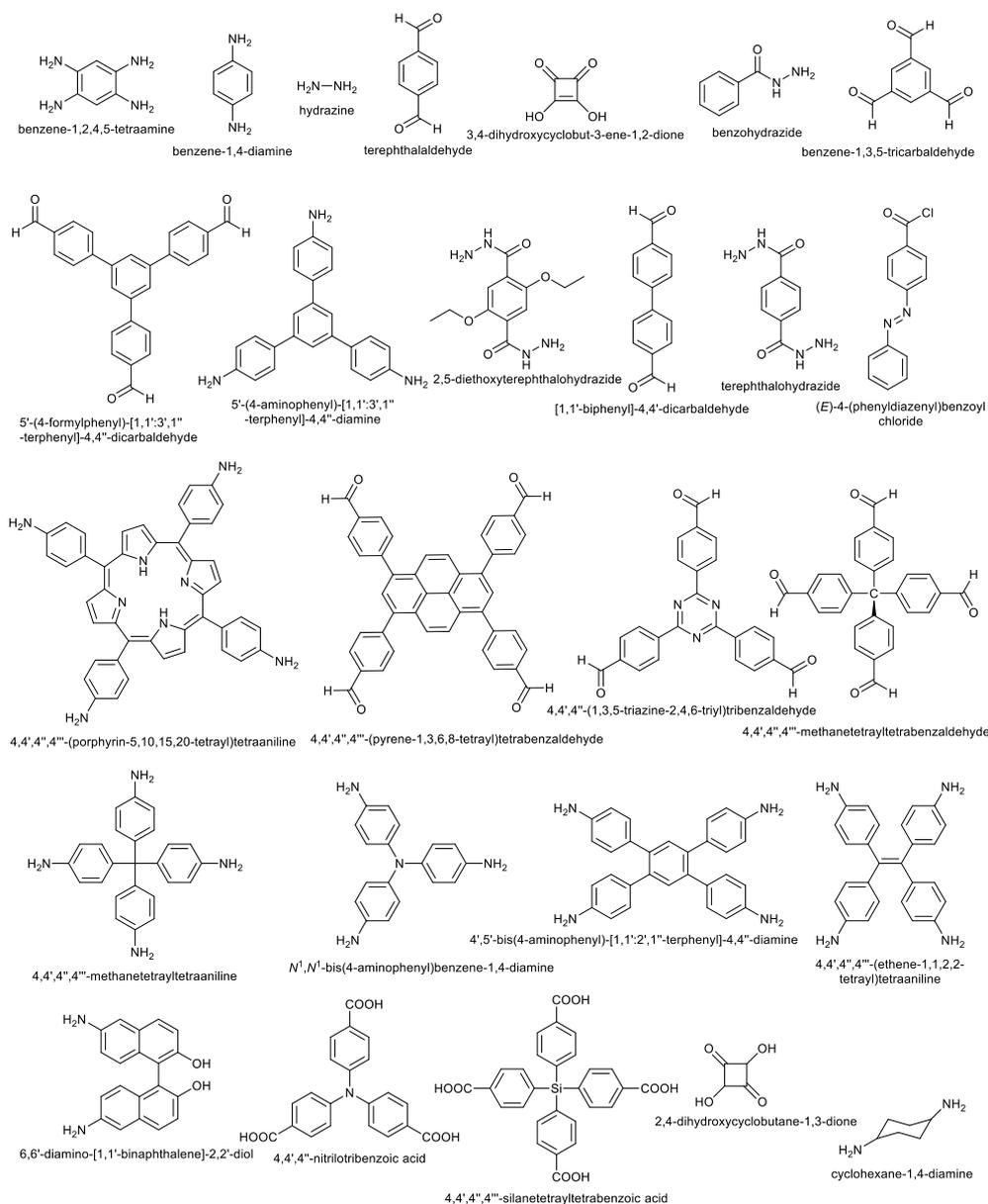
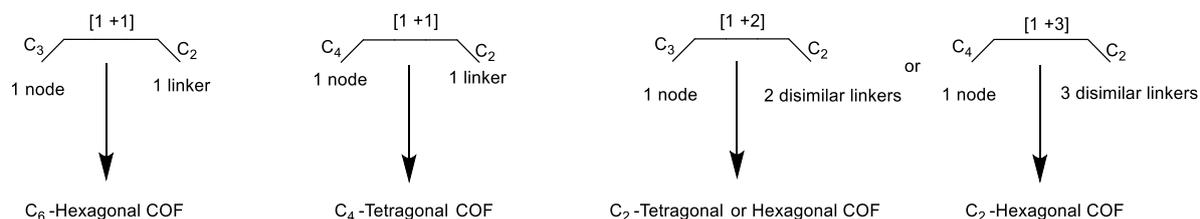
These 2-D squaraine COFs (SQ-COP-1, SQ-COP-2 and SQ-COP-3) were calculated to exhibit exceptional high S_{BET} of 8686, 8938 and 8585 m^2/g respectively. The high S_{BET} s associated with these 2-D squaraine COFs were attributed to the presence of the extended squaraine linkage in the framework materials. These exceptionally high S_{BET} s are however, smaller than those of some microporous coordination polymers MCPs (10436 – 10577 m^2/g) (Schnobrich et al., 2010) but higher than those of MOF-210 (6240 m^2/g), (Furukawa et al., 2010) PAF-1 (5460 m^2/g) (Ben et al., 2009) and Nu-110SP (7800 m^2/g) (Farha et al., 2012). The CO_2 uptake capacities of SQ-COP-1, SQ-COP-2 and SQ-COP-3 were also estimated to be 990, 737 and 833 mg/g at 298 K/50 bar respectively. Nevertheless, it was reported that at 298 K/30 bar, the CO_2 uptake capacities for SQ-COP-1, SQ-COP-2 and SQ-COP-3 were 804, 575 and 633 mg/g respectively which is significantly higher than the value 326 mg/g reported for a benchmark zeolite 13X. (Yuan et al., 2012) In addition, SQ-COPs COFs were reported to display a good selective adsorption of CO_2 over N_2 , CH_4 , and H_2 . For example, the calculated CO_2/N_2 of SQ-COP-1 is comparable to that of PAF-302 (3-4) (Z. Yang et al., 2013) and AIBDC MOF (4.3). (Sun et al., 2015) Other imine-based COFs have also reported in the literature. (Ascherl et al., 2016; Furukawa et al., 2016; Zou et al., 2017). The results described above show that imine-based COFs possess better crystallinity as well as structural regularity which can be tuned to achieve desired pore size more easily than triazine-based COFs (CTFs). In addition, imine-based COFs have better stability in water as well as in most organic solvents when compared with boron-based and triazine-based COFs. A summary of the main

The differences in properties between these two groups of COFs were attributed to the dipole interaction between the azo group and the CO_2 as well as the N_2 -phobic behaviour of the azo group. Three hypothetical 2-D squaraine-bridge covalent organic polymers (SQ-COP-1, SQ-COP-2 and SQ-COP-3) were proposed by Huang and Cao (L. Huang & Cao, 2016) by the use of linear squaraine unit and heterocyclic molecules such as $(CH_3)_3B_3O_3$, $H_3B_3N_3$ and $(CH_3)_3C_3N_3$ as shown in Scheme 29 as well as the use of grand canonical Monte Carlo (GCMC) simulations.

building units used for the construction of imine-based COFs is depicted below in **Figure 4**. The boron-, triazine- and imine-linked COFs discussed above make use of a conventional two-component [1 + 1] condensation design scheme. The design and synthesis of these COFs as well as new ones largely depends on the exploration of new nodes and linkers which can be difficult, time consuming and often do not give the desired results. In contrast to conventional two [1 + 1] design systems, multiple-component (MC) COF design makes use of three [1 + 2] i.e. one node and two linker units or four [1 + 3] i.e. one node and three linker units for their synthesis. Huang, Zhai, *et al.* (2016).

Multiple-component COFs

Multiple-component COFs (MC-COFs) feature asymmetric tiling of organic building units into anisotropic skeletons with uncommon shaped pores. Thus the application of the MC method has enabled the expansion of structural complexity of framework materials and their pores as well as the enhancement of their structural diversity. In addition, the multiple-component strategy has also provided new platforms for considerable expansion and design of functionalized structures of porous organic materials. The design and synthesis of both hexagonal and trigonal COF topologies using two-component [1 + 1] copolymerisation of a C_3 - or C_4 -symmetric node and a C_2 -symmetric linker (Ascherl et al., 2016; Furukawa et al., 2016; Nagai et al., 2011; Ockwig et al., 2005c; San-Yuan Ding, 2013; Spitler et al., 2012) as shown in **Figure 5 a**, and three- or four-component systems **Figure 5 b** using one node and two or three dissimilar linkers. Chen *et al.*, 2015; Huang, Zhai, *et al.*, 2016; Zeng *et al.* (2015)


Figure 4: Some monomers used for constructing imine-based COFs.


(a) Conventional [1 + 1] two-component strategy

(b) Three- [1 + 2] or Four- [1 + 3] component strategy

Fig 5 a and b: Conventional two-component [1+1] and multiple-component [1+2] or [1+3] strategies for the design and synthesis of COFs. Adapted from refs. Chen et al., 2015; Huang, Zhai, et al.;2016; Zeng et al. (2015)

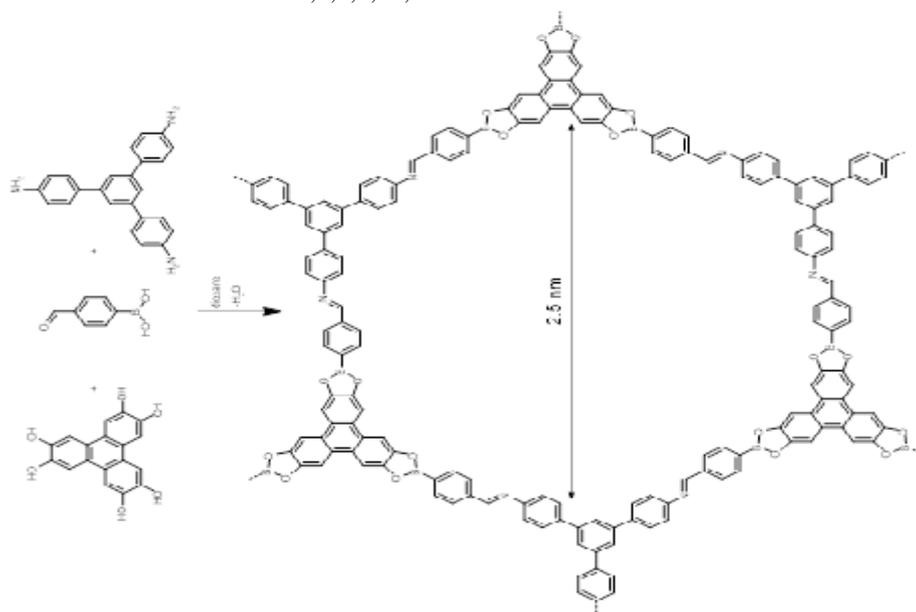
In a bid to enhance and expand the research of COF materials using multiple-component orthogonal reaction strategies, Zhao and co-workers used 4-

formylphenyl boronic acid (a bifunctional linker) for the synthesis of MC-COF (NTU-COF-2). NTU-COF-2 was reported to consist of two dissimilar boronate

BULL, OS; BULL, I; AMADI, GK; ODU, CO

and imine linkages in its skeleton that are not accessible for conventional [1 + 1] based COFs. (Zeng et al., 2015) By way of using different starting materials, Zhao and co-workers also designed a new three [1 + 2] multiple-component COF (NTU-COF-2) with the use of 2,3,6,7,10,11-

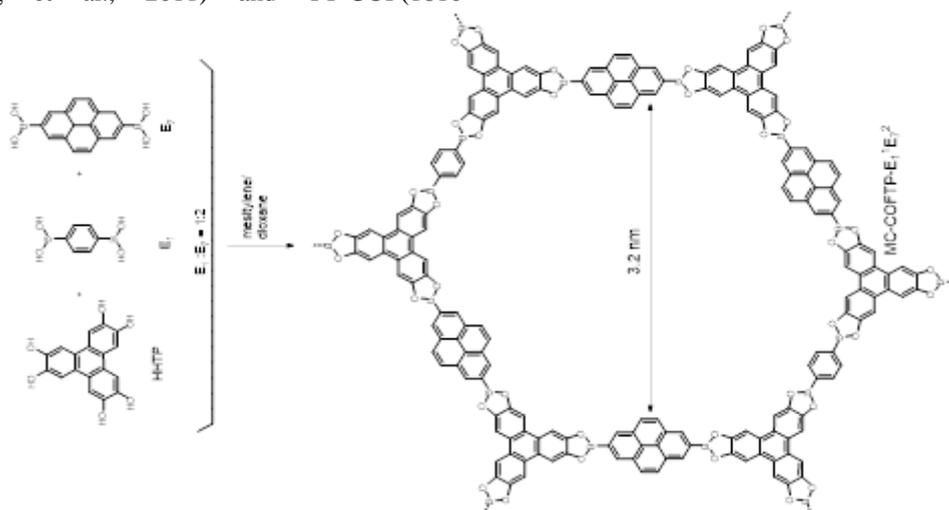
hexahydroxytriphenylene (HHTP) which served as node while 4-formylphenylboronic acid (FPBA) and 1,3,5-tris(4-amino-phenyl)-benzene (TAPB) acted as the linkers to give an imine group and a C_2O_2B boronate ring as shown in **Scheme 30**.



Scheme 30: Synthesis of NTU-COF-2 involving the formation of two kinds of covalent bonds from orthogonal reactions. Zeng et al. (2015)

NTU-COF-2 was reported to have pore volume of $0.86 \text{ cm}^3/\text{g}$ and CO_2 uptake capacity of 102 mg/g at $273 \text{ K}/1 \text{ bar}$. In addition, an S_{BET} of $1619 \text{ m}^2/\text{g}$ was reported for NTU-COF-2; this S_{BET} value is larger than those reported for other COFs such as COF-5 ($1590 \text{ m}^2/\text{g}$), (Ockwig et al., 2005c) DZnPcANDI-COF ($1410 \text{ m}^2/\text{g}$), and TCOF-1 ($927 \text{ m}^2/\text{g}$) (Bertrand et al., 2013) and smaller than the S_{BET} s reported for COF-10 ($1760 \text{ m}^2/\text{g}$), (Furukawa & Yaghi, 2009) ZnP-COF ($1742 \text{ m}^2/\text{g}$) (Feng et al., 2011) and TT-COF (1810

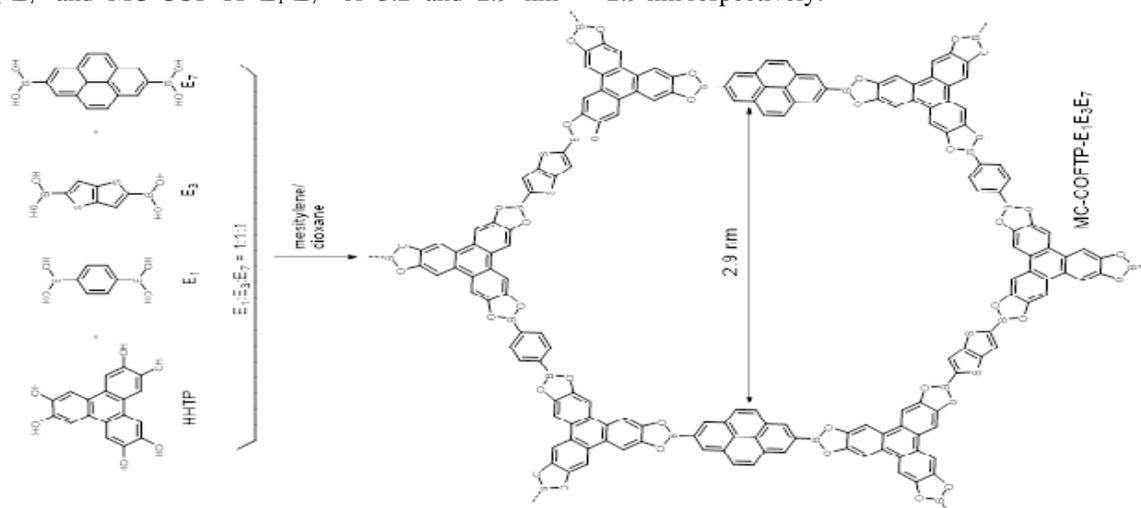
m^2/g). (Dogru et al., 2013) In a manner similar to Zhao and co-workers, (Zeng et al., 2015) Jiang and co-workers (N. Huang, Zhai, et al., 2016) also applied a multiple-component strategy with two or three dissimilar linkers to obtain hexagonal MC-COFs (MC-COF-TP- $E_1^1E_7^2$ and MC-COF-TP- $E_1^2E_7^1$) as shown in **Scheme 31**. $E_1^1E_7^2$ and $E_1^2E_7^1$ are defined as the 1:2 and 2:1 molar ratio reported respectively, for the E_1 and E_7 in the units in the COF.



Scheme 31: Synthesis and structures of typical [1 + 2] hexagonal MC-COFs. Huang, Zhai, et al. (2016)

The syntheses of MC-COF-TP-E₁¹E₇² and MC-COF-TP-E₁²E₇¹ were carried out by the application of three [1 +2] component solvothermal copolymerisation of HHTP as node with a short linker (E₁) and longer linker (E₇) (molar ratio of 1:2 or 2:1) in a mixture of mesitylene and dioxane. These two MC-COFs (MC-COF-TP-E₁¹E₇² and MC-COF-TP-E₁²E₇¹) were reported to possess S_{BET} of 1892 and 1534 m²/g respectively. In addition, these MC-COFs were reported to be highly porous with a type-IV sorption isotherm profile as well possessing only one type of mesopore overall with pore sizes for MC-COF-TP-E₁¹E₇² and MC-COF-TP-E₁²E₇¹ of 3.2 and 2.9 nm

respectively. These pore sizes are similar to those of other similar [1+1] COFs such as COF-5 (2.7 nm)(Ockwig et al., 2005c) and TPCOF (3.2 nm).Wan *et al.* (2008). Furthermore, the same researchers used the MC synthetic strategy for the design and synthesis of four [1+3] component hexagonal MC-COFs (MC-COF-TP-E₁E₃E₇). (N. Huang, Zhai, et al., 2016) MC-COF-TP-E₁E₃E₇ was constructed with one node (HHTP) and three linkers (E₁, E₃ and E₇) using the same molar ratio of node and linkers of 2:1:1:1 as shown in **Scheme 32**. The S_{BET} and mesopore size reported for MC-COF-TP-E₁E₃E₇ were 1887 m²/g and 2.9 nm respectively.



Scheme 32: Synthesis and ordered structure of MC-COF-TP-E₁E₃E₇

The same research(N. Huang, Zhai, et al., 2016) group used the MC/COF strategy with a [1+2] component reaction for the construction of tetragonal MC-COF (NiPc-E₁E₇) by the use of nickel phthalocyanine (NiPc) as the knot and two linkers (E₁ and E₇) as depicted in Scheme 33. It was reported that NiPc-E₁E₇ contained only one type of mesopore with pore size of 2.6 nm and S_{BET} of 672 m²/g.

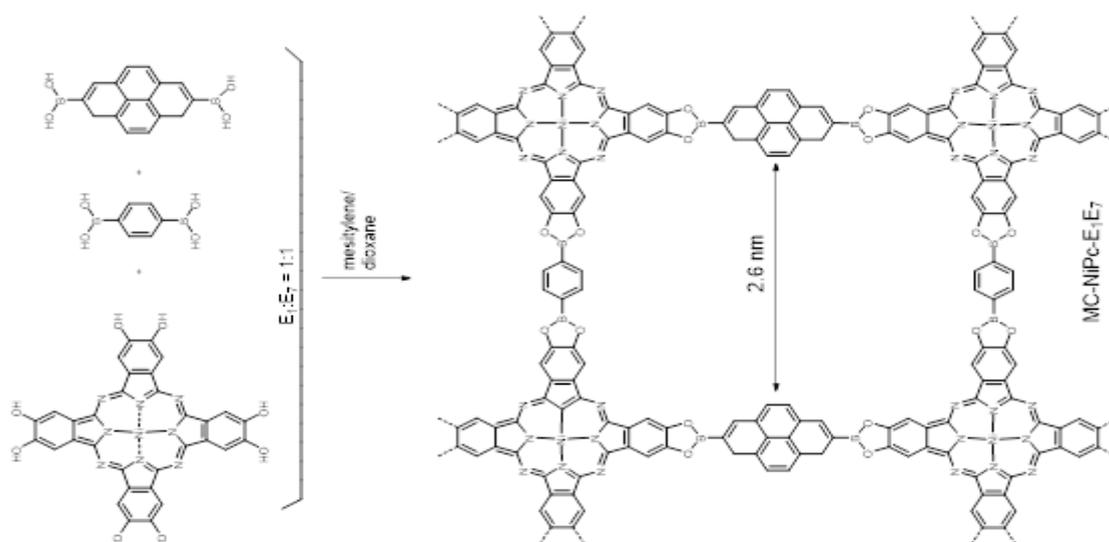
The MC strategy of constructing COFs make use of a selective combination of three or more blocks (usually the building units used for the making of boron-, triazine- and imine-based COFs) consisting of one node and two or three linkers leading to the formation of hexagonal and tetragonal COFs. The MC strategy has opened new insight for the expansion and construction of structurally complex frameworks via asymmetric tiling of building units with provision for platforms for further construction of anisotropic π -columnar arrays and unconventional shaped pores.

Synthetic Methods Used in the preparation of COFs:

In addition to the building units for the construction of COFs the synthesis conditions are also important to regulate the thermodynamic equilibrium involved in

the formation of covalent bonds. Thus, the reaction media and conditions (temperature, pressure as well as presence or absence of template) are crucial factors for the formation of thermodynamically stable crystalline polymeric products. Since the pioneering work of Yaghi and co-workers,(Ockwig et al., 2005a) many other researchers globally have exploited and expanded the synthetic possibilities by developing mixed solvent systems and molten metal salts that have provided platforms such as solvothermal, ionothermal, microwaves and room temperature methods for COF synthesis.

Solvothermal Synthesis of COFs: Most of the reported COFs were obtained through solvothermal synthetic methods. A typical solvothermal method for synthesising COFs involves the mixing of monomers with a suitable solvent or a mixture of solvents and then putting the monomer mixture in a Pyrex or Parr-autoclave followed by degassing with several freeze-pump-thaw cycles. Following the degassing process, the tube or the autoclave is sealed and heated to a given temperature (usually 80 °C and above) for some reaction time (usually 1- 9 days).



Scheme 33: Synthesis of tetragonal [1+2] MC-NiPc-E₁E₇. Huang, Zhai, *et al.* (2016)

This treatment of monomers usually leads to the formation of precipitates. The precipitates are collected and washed with suitable solvent followed by drying under vacuum to give the COF material (usually a powder product). Factors such as solvent combination and ratios as well as temperature and duration of reaction processes are crucial when designing a solvothermal reaction process for COFs synthesis, due to issues such as solubility, reaction rate, crystal nucleation and crystal growth as well as ‘self-healing’ of structures during the formation of COFs. Solvent combination and ratios are important points to consider for the purpose of forming crystalline framework materials. For example, the influence of solvents on the crystallinity of a COF material was demonstrated by Jiang and co-workers (Feng *et al.*, 2011) who found that co-condensation of zinc(II) 5,10,15,20-tetrakis(4-(dihydroxyboryl)phenyl)porphyrin and 1,2,4,5-tetrahydroxybenzene in a mixture of mesitylene and dioxane (1/1, v/v) produced amorphous solids. On the other hand, when the v/v ratio of mesitylene/dioxane was changed to 19/1 or 9/1, COF materials with high crystallinity were obtained. Furthermore, in the formation of boronate ester and boroxine-linked COFs, mesitylene/dioxane (Colson & Dichtel, 2013; Ockwig *et al.*, 2005a) DMAC-*o*-dichlorobenzene (Ding *et al.*, 2011) and THF/methanol (Tilford *et al.*, 2006) have been used as solvent combinations. In the formation of borosilicate COFs, dioxane/toluene solvent mixtures have been used (Hunt *et al.*, 2008). Dioxane/aqueous acetic acid was used as solvent mixture in some imine-based COFs (Uribe-romo *et al.*, 2009). Mesitylene/dioxane/acetic acid solvent mixture (Kandambeth *et al.*, 2015) was used as solvent mixture in the synthesis of some hydrazone-linked COFs (Uribe-romo *et al.*,

2011). Recently Zhao and co-workers used a mixture of mesitylene/dimethylacetamide/AcOH (6M, aqueous) (5:5:1 by volume) which was heated in a sealed glass ampoule at 120 °C for 3 days to produce COF-BTA-DAB and COF-BTA-BZ (Tian *et al.*, 2017). A suitable temperature appropriate to the solvent used is also important to ensure the reversibility of the reaction. In general, most reported COFs in the literature were prepared in the temperature range 80 - 120 °C depending on the chemical reactivity of the building units. A closed reaction system enhances the retention of any water molecules that could trigger a reverse reaction in the system. The final products of solvothermal methods are often powdered COF materials which may limit their practical applications under certain circumstances, e.g. interfaced incorporation into devices. To this end, Dichtel and co-workers (Colson *et al.*, 2011) developed a solvothermal method for producing 2-D COF materials as thin films on single-layer graphene. It was reported that the obtained COF materials exhibited improved crystallinity in comparison with the powder samples (Colson *et al.*, 2011).

Ionothermal Synthesis of COFs: Ionothermal synthesis involves the growing of single crystals from an ionic liquid in an autoclave at high temperature (300-600 °C) and pressure. Thomas and co-workers were the first to apply ionothermal method to produce crystalline porous COFs (Kuhn, Antonietti, *et al.*, 2008). As mentioned in **Section 2.3.2**, they used reversible cyclotrimerisation of nitrile building units (1,4-dicyanobenzene) in molten ZnCl₂ to generate covalent triazine-based frameworks (CTFs) with high crystallinity alongside outstanding chemical and thermal stabilities. The molten ZnCl₂ functioned both as a solvent and as a catalyst for the reversible

cyclotrimerisation reaction that lead to the formation CTFs. A comparison of COF materials obtained through solvothermal methods, and CTF polymers obtained from ionothermal method can be made; CTF polymers have the drawback of lack of crystallinity control because the reversible cyclotrimerisation reaction takes place under harsh reaction conditions that often lead to the formation of amorphous materials that lack long-range molecular order. (Jinang, 2012) In addition, the constraint of high reaction temperature limits the choice of suitable building units. (H. Ren et al., 2010) Based on these limitations, ionothermal methods at present have limited application. (San-Yuan Ding, 2013).

Microwave-assisted Synthesis of COFs: Microwave heating has many applications in accelerating chemical reactions. (Wei et al., 2015) Cooper and co-workers developed a rapid microwave-assisted protocol for the synthesis of boronate ester linked COFs. (Campbell et al., 2009) For example, 2-D (COF-5) and 3-D (COF-102) COFs could be synthesised using microwave heating in 20 minutes. (Wei et al., 2015) The syntheses of these COFs were achieved by conventional solvothermal methods in 72 h. (Ockwig et al., 2005a; Ritchie et al., 2010) Thus the microwave-assisted synthesis is 200 times faster than the solvothermal method. In addition, the S_{BET} obtained for the product under microwave was reported to be 2019 m^2/g ; whereas the S_{BET} of the same material but obtained via solvothermal means was reported to be 1590 m^2/g . (Campbell et al., 2009) Thus by way of comparison, it can be seen that (1) Microwave-assisted synthesis can produce COFs more rapidly than solvothermal methods. (2) In microwave-assisted syntheses, the methods for the removal of solvent and residual impurities trapped in the frameworks are more efficient than in solvothermal methods, and thus microwave-assisted syntheses enhance the formation of materials with better porosity. (Jinang, 2012).

Challenges in the synthesis of COFs: Boron-, triazine- and imine-based COFs that are obtained via condensation, Schiff-base reaction, Friedel-Crafts reactions, cyclotrimerization and post-synthesis exfoliation have all opened many opportunities for exploring novel functional materials using existing building units. (Beuerle & Gole, 2018; Diaz & Corma, 2016; Furukawa & Yaghi, 2009; San-Yuan Ding, 2013; Tong et al., 2014; Zeng et al., 2016; W. Zhao et al., 2018) However, some major challenges that are yet to be fully addressed are: further improvement on how to achieve the combined properties of stability and crystallinity as well as porosity in COF materials; the growing of extended and high quality crystalline

molecular materials; and the design of COF materials with flexible monomers. Despite these challenges large S_{BET} s and pore volumes as well as better structural integrity with low CO_2 adsorption capacities at low pressures have been reported for boron-, boron/imine-, triazine and imine-based COFs. (Beuerle & Gole, 2018; Gao et al., 2018; Olajire, 2017) However, in terms of chemical/water stability as well as diversity for different applications, further work is still needed. Ways forward to solving these challenges in COF synthesis are: (1) The development of new synthetic methodologies to improve the stability of COF materials, (2) The construction of COFs with more flexible monomers as well as diverse 3-D architectures for high-pressure CO_2 uptake. (3) Development of room temperature methods for the synthesis of COFs.

Conclusion: We have successfully reviewed the subject matter of COFs. The design methodologies and some applications of COFs and challenges associated with the making of COFs. Our anticipation is that this review article will help researchers to follow the global trend in order to achieve better molecular porous materials with ease.

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