Hydrogen Bonding: The Foundation for Future 2D-Covalent Organic Framework Development

Sampath B. Alahakoon [a,*] and Yifan Zhu [b]

[a] Institute for Combinatorial Advanced Research and Education, General Sir John Kotelawala Defence University, Kandawala Road, Rathmalana, Sri Lanka, 10390

[b] Department of Materials Science and NanoEngineering, Rice University, 6100 Main Street, Houston, Texas, United States, 77005

* Corresponding author email address: alahakoonamcsb@kdu.ac.lk

Abstract

Two dimensional covalent organic frameworks (2D-COFs) are a class of crystalline porous polymers whose structures are dictated by dynamic covalent bond formation and non-covalent interactions. 2D-COFs are made out of two-dimensional sheets formed by dynamic covalent reactions stacked together *via* supramolecular interactions. Since the first report, the main focus was given to develop new dynamic covalent reactions for 2D-COFs and much attention was not given for the development of new strategies to effective utilization of non-covalent interactions for better quality materials. Out of the common supramolecular interactions found in 2D-COFs, relatively few reports are found describing the efforts made to establish intra- and interlayer hydrogen bonds. This review will focus on the design parameters used in developing hydrogen bonded 2D-COFs with superior materials' properties. The importance of hydrogen bonding in 2D-COFs to address the current and future materials need will also be discussed.

Keywords: 2D-COFs, Covalent organic frameworks, Interlayer hydrogen bonding, Intralayer hydrogen bonding

Introduction

Covalent Organic Frameworks (COFs) are a class of crystalline porous polymers whose structures are controlled by dynamic covalent chemistry and supramolecular interactions[1]. Since the inception of work done by Omar M. Yaghi in 2005[2], this class of materials became popular among porous materials chemists. COFs are one of the promising materials which are used in a plethora of applications including gas storage[3], electrical and capacitive energy storage[4], drug delivery[5], water remediation[6], sensory applications[7], catalysis[8] and *etc*. These framework structures are composed of lightweight elements (*i.e.,* C, N, O, H, S, *etc.*) and can be classified as purely organic porous materials with no toxic metal involvement. COFs have become an essential part of the micro- and meso-porous materials chemistry due to their unique properties such as low density, high surface area, tunability of pores, crystallinity, the capability of pore-wall engineering, relatively easy synthesis, and availability of materials. Depending on the geometry of starting monomers and the direction of polymerization COFs can be divided into two basic categories as 2D and 3D-COFs. 2D-COFs- in which the monomers are more or less planar in geometry and the polymerization occurs in a 2D fashion. Then the formed sheets stack in the z crystallographic axis through supramolecular interactions to make the 3D framework (Fig. 1A). In the case of 3D-COFs, the monomers have to be three-dimensional (3D) in geometry and the polymerization occurs

in a 3D fashion. Here the effect of supramolecular interactions is less prominent and the rigidity of 3D monomers accounts for the structure and stability of the 3D framework. Usual polymer synthesis is dominated by kinetically controlled reactions which make irreversible covalent bonds. It is very hard to obtain crystalline polymer materials using kinetically driven reactions. However, dynamic covalent reactions lead to reversible formation of bonds which yield thermodynamically controlled crystalline polymer products *via* "error checking" and "proof reading" mechanisms[1]. Therefore, when studying the chemistry of COFs, the concept of dynamic covalent chemistry (DCC) is critically important[9]. Physical and chemical properties of COFs are different from common linear and non-linear polymers. Therefore, COFs cannot be characterized through general polymer characterization techniques *i.e.*, GPC (Gel Permeation Chromatography) as these crosslinked polymers are insoluble in normal laboratory solvents. COFs are characterized through diverse techniques including powder X-ray diffraction, gas sorption, infrared spectrometry/ solid-state ^{13}C NMR, thermogravimetric analysis, and microscopy (SEM-scanning electron microscopy, TEM-transmission electron microscopy) to determine the quality of the polymers for crystallinity, surface area, structural integrity, thermal stability, and morphology respectively[10]. Due to the greater interest among scientists' numerous kinds of COFs have been reported to date depending on the type of DCC utilized in COF synthesis. Boroxine[2], boron ester[11], imine[12], azine[13], hydrazone[14], imide[15],
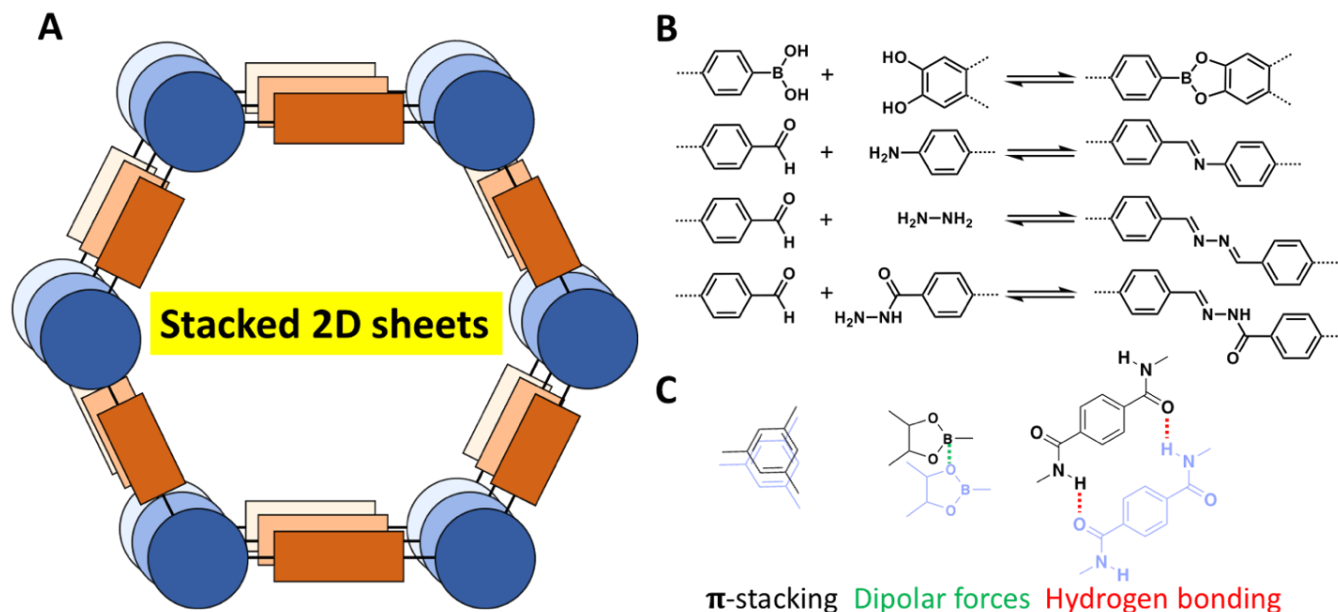
Fig. 1. A). 2D-sheets arranged in the crystallographic z direction by supramolecular forces to make the framework. B). Popular dynamic covalent reactions used in COFs synthesis. C). Different types of supramolecular interactions found in 2D-COFs.

and triazine[16] are just a few on the list (Fig. 1B). When the formation and stability of the 2D-COF structures are considered, DCC and supramolecular interactions are equally important. π-stacking, dipolar forces, and hydrogen bonding are the major types of supramolecular forces found in 2D-COFs (Fig. 1C). Even though π-stacking and dipolar forces are extensively reported in the literature, 2D-COFs arranged through hydrogen bonding are less common as special monomers and functionalities are needed to establish hydrogen bonding between monomers.

Hydrogen bonding (HB) is a ubiquitous supramolecular force found in nature. Starting from DNA, water to proteins, hydrogen bonding plays a key role in the assembly of matter. HB is usually seen as an electrostatic interaction (D-H•••A) between an electronegative atom (A) and a hydrogen atom attached to a second electronegative atom (D-H) where D is the hydrogen bond donor and A is the hydrogen bond acceptor[17]. However, the HB definition with electrostatic interactions alone cannot account for all theoretical and experimental observations such as the NMR downfield chemical shift and change in H-D stretching frequency. Thus, a complete understanding of HB would be possible when all energy components electrostatic interactions, orbital interactions, pi-resonance assistance, cooperative effects, steric repulsion, dispersion interactions and secondary electrostatic interactions are considered[18]. Even though there are many arguments on the definition of HB, the strength of a HB is commonly recognized using the concept of electronegativity. When O-H•••N and N-H•••N HB are considered as an example, O-H•••N is identified as much stronger as O (3.5) is more electronegative than N (3.0), a H atom attached to O will be more positively charged creating an intense dipole-dipole interaction.

Apart from nature, HB is frequently utilized to gain substantial strength in synthetic polymers such as Nylon 6,6 and Kevlar (polyamides)[19]. Even though 1D polymers with interchain hydrogen bonding has extensively studied for decades, 2D-polymers assembled with the aid of intra/interlayer hydrogen bonding are relatively new. Over the past decades 2D-polymer researchers have extensively focused on introducing new dynamic covalent reactions, new monomer topologies to control pore-size and shape, and pore-wall functionalization targeting applications. The majority of 2D-COFs have been developed through manipulation of aromatic interactions and dipolar forces. Recently, researchers have looked into the possible strategies to utilize much stronger supramolecular interactions *i.e.* hydrogen bonding when designing 2D-COFs that could cater the future materials need with superior electrical conductivity, pore-size control, hydrolytic stability, polymer strength, processability and scalability. Therefore, this review will focus on how the chemistry of monomers and polymers has been tuned to facilitate hydrogen bonding to address current limitations and future material needs. This effort will provide an insight on how hydrogen bonding will create the foundation for future 2D-COFs development.

2D-COFs facilitated by intralayer hydrogen bonding

Even though, majority of 2D-COFs reported in the literature are rely on aromatic stacking or dipolar forces between layers, COFs with intra- or interlayer hydrogen bonding are not common[20]. In this part of the review, how the monomer designs are made to facilitate intralayer hydrogen bonding will be discussed. In 2013[21], Banerjee and co-workers reported a COF (COF-DhaTph) stabilized by intramolecular hydrogen bonding. This imine COF was synthesized by the reaction between 2,5-dihydroxyterephthalaldehyde (Dha) and the 5,10,15,20-

tetrakis(4-aminophenyl)-21H,23H-porphine (Tph) (Fig. 2). Here they have introduced hydroxyl (-OH) functionalities adjacent to the imine centers of the COF to promote intramolecular hydrogen bonding between the imine nitrogen and the hydroxyl groups (O-H•••N=C). This protects the imine bond from nucleophilic attacks providing greater stability to the COF. The greater chemical stability of the COF has been proved by the retention of its crystallinity after soaking in boiling water or 3M HCl (aq) over 7 days. The methoxy-substituted COF showed a lack of chemical stability and crystallinity under the same conditions further proving the importance of intramolecular hydrogen bonding.
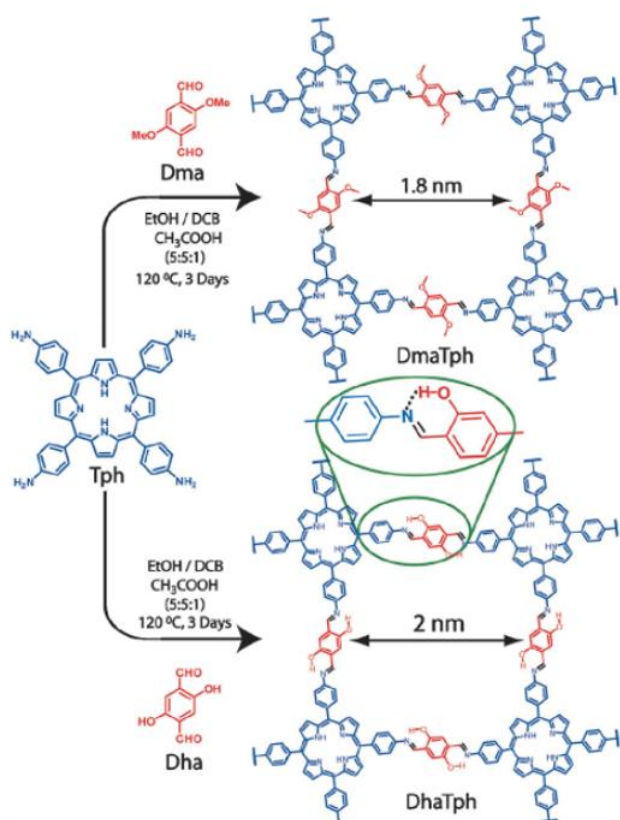

Fig. 2. Syntheses of DmaTph and DhaTph by the condensation of square planar Tph building unit (blue) and linear Dma/Dha building unit (red). COF DhaTph show intralayer hydrogen bonding but COF DmaTph. Reproduced from ref. [21] Wiley-VCH Verlag GmbH & Co., copyright 2013.
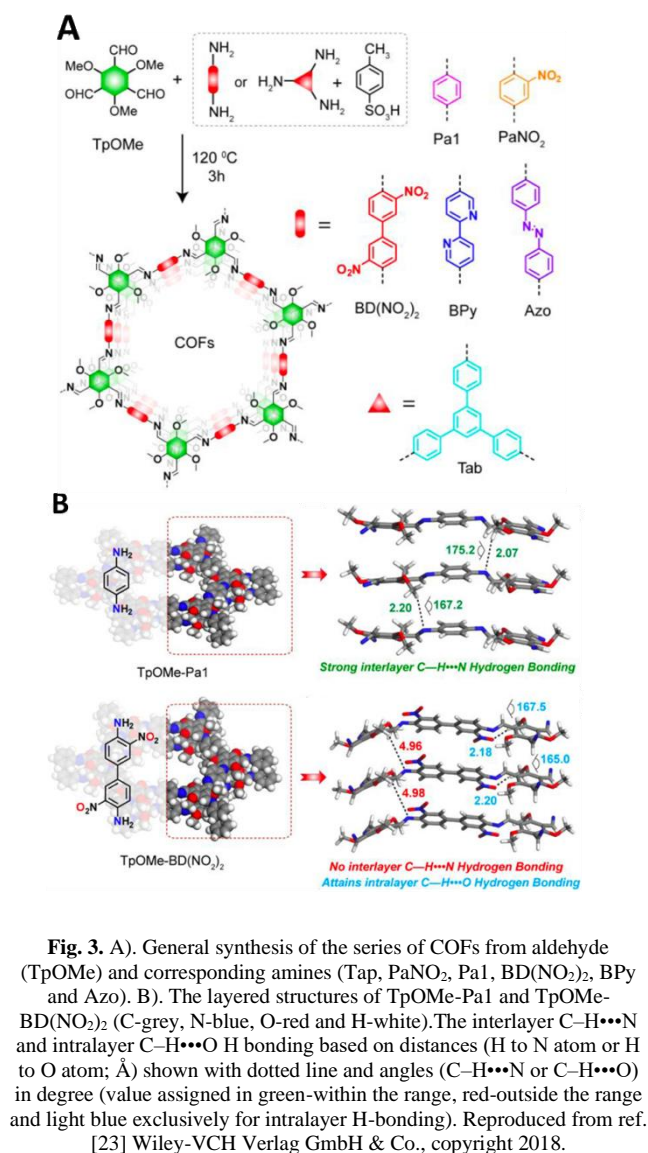
Later in 2015 the same group reported a hollow spherical imine COF (COF-DhaTab) which was synthesized by the reaction between 2,5-dihydroxyterephthalaldehyde (Dha) and the 1,3,5-tris(4-aminophenyl) benzene (Tab)[22]. Similarly, strong intramolecular hydrogen bonding protects the imine nitrogen from the nucleophilic attack which leads to greater chemical stability. Further, the hydrogen bonding locks the phenyl rings in one plane which facilitates long range ordering and high surface area. Retention of COF crystallinity under 3N HCl for 7 days and in phosphate buffer of pH 7.4 provides the experimental proof of its chemical stability. However, the stability of the COF in NaOH was less due to the deprotonation of the phenolic

hydrogen (OH) which break the hydrogen bonding. Further, association of Na^+ ions near the phenolate anion disturb the ordered stacking which cause the disintegration of the hollow spheres of the COF-DhaTab.

2D-COFs facilitated by Interlayer hydrogen bonding

It is evident that the intralayer hydrogen bonding in 2D-COFs has positively effect on the quality of the materials by improving the chemical stability, crystallinity and surface area. Apart from that, many research groups have looked into different approaches to establish hydrogen bonding between layers to further improve the quality of COFs targeting applications. The major challenge for designing interlayer hydrogen bond stabilized COFs is the incorporation of functional groups in appropriate sites of the monomers and arranging them in an out-of-planar conformation to the aromatic monomer to facilitate interlayer over intralayer hydrogen bonding. Different structural monomer designs and modifications to promote hydrogen bonding between layers and how those designs effect on the overall quality of the 2D-COFs will be discussed in this part of the review. To date there are a couple of theoretical and experimental reports available in the literature which discuss the use of classical and non-classical interlayer HB in COFs.
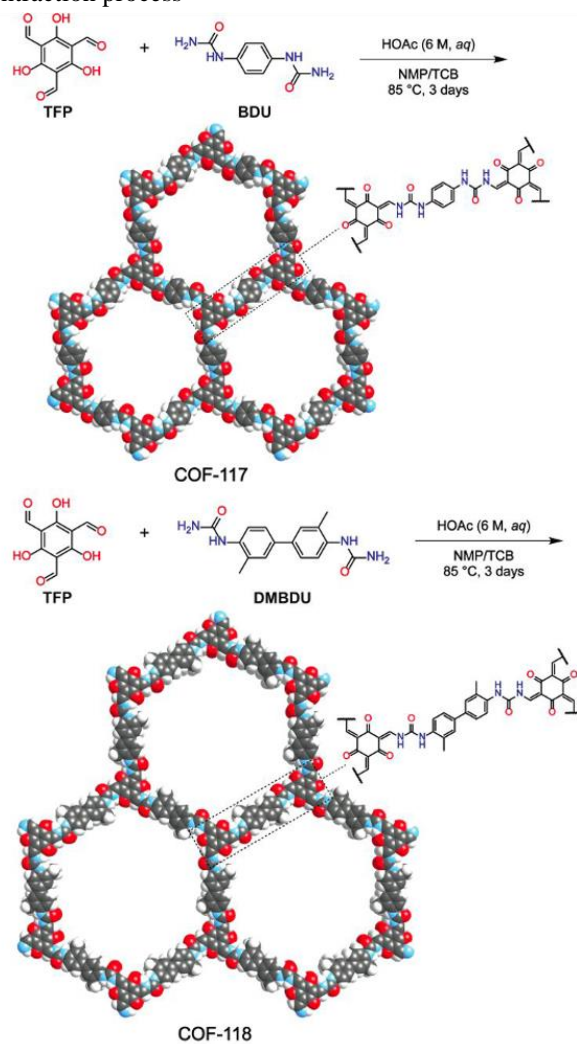
In 2018[23], Banerjee and co-workers reported the synthesis of a series of imine COFs (TpOMe-Tab, TpOMe-PaNO$_2$, TpOMe-Pa1, TpOMe-BD(NO$_2$)$_2$, TpOMe-BPy, and TpOMe-Azo) made through solid-state mixing approach using 2,4,6-trimethoxy-1,3,5-benzenetricarbaldehyde (TpOMe) as a prime aldehyde building unit (Fig. 3A). The bulky methoxy (-OCH$_3$) groups substituted *ortho* to aldehyde groups in the monomer (TpOMe) create significant steric hindrance so that the C-H of methoxy groups orient in such a way to facilitate interlayer hydrogen bonding with the imine nitrogen of the next layer. The formation of significant numbers of interlayer C–H•••N hydrogen bonding has been further proved by the density functional theory. This type of hydrogen bonding is referred to as non-classical hydrogen bonding. These COF materials have shown exceptionally high chemical stability in conc. H$_2$SO$_4$ (18 M), conc. HCl (12 M), NaOH (9 M), boiling water and common organic solvents, for several days. The exceptional stability of the imine COFs has been attributed to the presence of interlayer C–H•••N HB which provides significant steric and hydrophobic environment around the imine bonds (Fig. 3B). This further protects the imine bonds from being hydrolyzed in harsher conditions. Further, Banerjee and the team were able to convert the powdered material of COF TpOMe-Azo to a self-standing, crack-free, continuous COF membrane and studies for potential wastewater treatment. The study revealed that the COF membranes are stable for high solvent flux (280 L m^{-2} h^{-1} bar^{-1} for acetonitrile and 260 L m^{-2} h^{-1} bar^{-1} for acetone). Furthermore, they found that the COF membranes are suitable for recovery of H$_2$SO$_4$ acid and removal of toxic substances from drinking water.

Fig. 3. A). General synthesis of the series of COFs from aldehyde (TpOMe) and corresponding amines (Tap, PaNO$_2$, Pa1, BD(NO$_2$)$_2$, BPy and Azo). B). The layered structures of TpOMe-Pa1 and TpOMe-BD(NO$_2$)$_2$ (C-grey, N-blue, O-red and H-white).The interlayer C–H•••N and intralayer C–H•••O H bonding based on distances (H to N atom or H to O atom; Å) shown with dotted line and angles (C–H•••N or C–H•••O) in degree (value assigned in green-within the range, red-outside the range and light blue exclusively for intralayer H-bonding). Reproduced from ref. [23] Wiley-VCH Verlag GmbH & Co., copyright 2018.

The same group has reported a redox-active TpOMe-DAQ COF using the reaction between the same aldehyde monomer (TpOMe) and 2,6-diaminoanthraquinone (DAQ) for supercapacitor applications[24]. This COF also demonstrated an ultrahigh stability in conc. H$_2$SO$_4$ (18 M), conc. HCl (12 M) and NaOH (9 M) due to the chemical stability gained through interlayer hydrogen bonding as described earlier. The anthraquinone moieties act as the redox active sites and those are responsible for the supercapacitance of the COF. The researchers were able to fabricate the COF into continuous, uniform, free-standing sheets and use as a supercapacitor electrode in 3M H$_2$SO$_4$ as an electrolyte. Due to the superior chemical stability and the robustness of the COF yielded an outstanding capacitance 1600 mF cm^{-2} with excellent cyclic stability (>100,000 cycles).

In 2018[25], Yaghi group introduced urea-linked COFs which is an introduction of a new linkage to the COF chemistry. These COFs are capable of interlayer hydrogen bonding due to the hydrogen bond doner-acceptor capability of urea linkages. This type can be categorized as a classical type hydrogen bonding. General practice in COF synthesis is to utilize rigid aromatic monomers as it benefits the crystallinity through minimal possible orientations. However, here they have been able to overcome the challenge by making two crystalline COFs (COF-117 and COF-118) by condensation of 1,3,5-triformylphloroglucinol (TFP) with two flexible urea linkages, 1,4-phenylenediurea (BDU) or 1,1'-(3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diyl)diurea (DMBDU), respectively (Fig. 4). Both COF-117 and COF-118 were crystalline and exhibited a BET surface area of 114 m^2/g and 1524 m^2/g, respectively. The observed difference in the surface area has been attributed to the significant structural deformation caused by hydrogen bonding observed in COF-117 due to the higher weight percent of urea groups compared to COF-118. Further they observed the crystalline COF-117 became amorphous upon activation while COF-118 remained crystalline under the same activation procedure. This was attributed to the capability of the biphenylene linker to with stand to contraction process

Fig. 4. Syntheses of ureal-inked COF 117 and COF-118. (Color code for space-filling diagrams: H, white; C, gray; N, blue; and O, red.) Reproduced from ref. [25] with permission from ACS Publications, copyright 2018.

in COF-118 while this phenomenon is not observed in COF-117. Furthermore, COF-118 displayed excellent stability in HCl (12 M), boiling water and saturated NaHCO₃ for 24 h. These two frameworks exhibited reversible structural dynamics upon guest inclusion and removal as the first evidence of such phenomenon in 2D-COFs.

In 2019[26], Yang and coworkers reported a triazine-based 2D-COF (PDC-MA-COF) with interlayer hydrogen bonding for supercapacitor applications. This COF was synthesized by the imine condensation reaction between the redox active triazine containing melamine (MA) and 1,4-piperazinedicarboxaldehyde (PDC). According to the powder X-ray diffraction studies the PDC-MA-COF doesn't look very crystalline but showed a higher BET surface area (748.2 m^2/g), narrow pore width (1.9 nm) with larger pore volume (1.21 cm^3/g). Further, the team reported an excellent electrochemical performance in this COF with the highest specific capacitance of 335 F/g in a three-electrode system and 94 F/g in a two-electrode system at a 1.0 A/g current density. This was attributed to the availability of interlayer hydrogen bonding (C–H•••N) which could avoid slipping the 2D layers by "locking" adjacent layers. Hence fast charge transfer between electrode interface and triazine units due to ordered pore structures. PDC-MA-COF//AC the asymmetric supercapacitor assembled with the COF and activated carbon (AC) showed a high energy density (29.2 W h kg⁻¹) with a power density of 750 W kg⁻¹ with excellent cyclic stability after 20,000 GCD cycles.

In 2018[27], Wetzel and the team at U.S. Army Research Laboratory have reported an excellent theoretical work on "Graphamid" which is the 2D version of the linear polymer poly(p-phenylene terephthalamide) or commercially known as Kevlar. Graphamid closely resembles the chemical structure of Kevlar with a great advancement of mechanical properties being a 2D-polymer. According to the theoretical calculations, they show that the graphamid comprised of 2D covalent sheets bridged
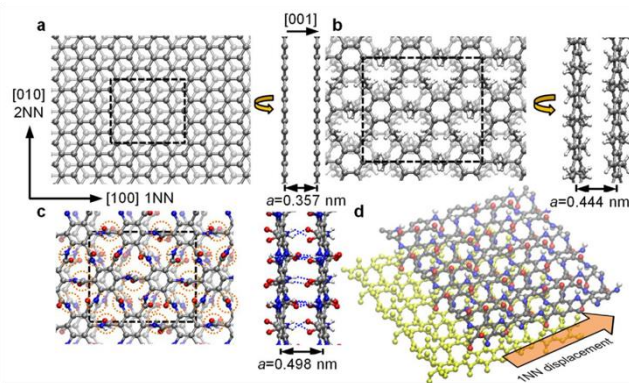

Fig. 5. The Comparison of bilayer structures of A) graphene, B) graphylene, C) graphamid, and D) Graphamid lateral displacement. Reproduced from ref. [27] with permission from the Royal Society of Chemistry, copyright 2016.

through a high density of strong interlayer hydrogen bonding (Fig. 5). This type of hydrogen boding (N-H•••O) is classified as classical hydrogen bonding which occur between adjacent graphamid layers due to the out-of-plane orientation of the amide groups. Further, the calculations predict that graphamid possess high strength (6-8 GPa) compared to graphene (0.1-0.5 GPa) in which the 2D layers are arranged by weak intermolecular interactions. This is the first report of the theoretical demonstration of a 2D-polymer linked through amide bonds in which the sheets are bridged by strong amide hydrogen bonding. This work generates new ideas of designing and synthesizing 2D-polymers like graphamide which would be light weight, scalable, processable to high performance polymers with superior mechanical properties for future material needs.

The synthesis of materials like graphamid is not easy in practice due to the lack of reversibility of amide formation reaction under normal reaction conditions as well as
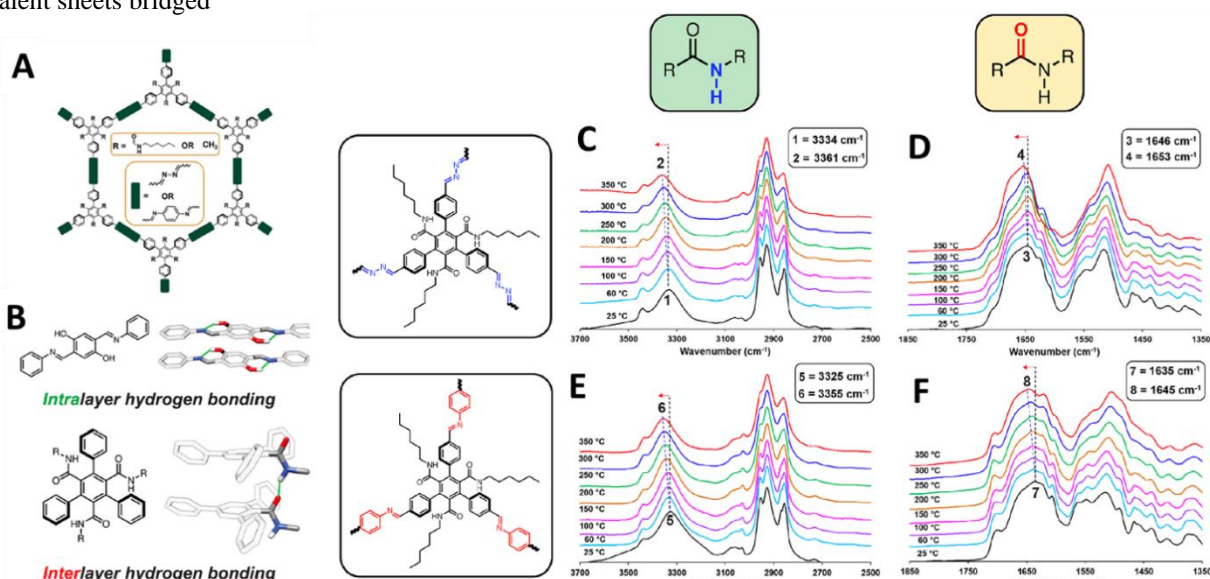

Fig. 6. A). Structure of the amide and control COFs linked through azine and imine bonds. B) Intralayer hydrogen bonding (O−H⋯N) promoted by coplanar functional groups, whereas interlayer hydrogen bonding (N−H⋯O) promoted by out of planar amid functionalities. VT-IR spectra of Amide COFs: COFamide-1 C). Expanded amide N−H stretching region and D) amide carbonyl stretching region. COFamide-2: E) Expanded amide N−H stretching region and F) amide carbonyl stretching region. Reproduced from ref. [28] with permission from ACS Publications, copyright 2020.

synthesizing monomers with the desired orientation to facilitate interlayer hydrogen bonding. To make the hypothetical "graphamid" polymers to real, the monomer design with amide functionalities oriented in a proper direction to facilitate the desired interlayer hydrogen bonding and selecting a suitable dynamic covalent reaction are challenging.

In 2020[28], Smaldone and co-workers have reported a series of COFs named as COFamides accepting all the challenges (Fig. 6A). Here they have synthesized two imine COFs, COFamide-1 and COFamide-2 in which the 2D sheets are arranged through classical interlayer hydrogen bonding (N-H•••O) with the aid of amide side chains. The properties of the COFamides have been compared with Me-COF-1 and Me-COF-2 which are not capable of making hydrogen bonding. For COFamides, they have designed a new monomer containing secondary amides at the 1,3,5-positions of the central phenyl ring of the monomer. Due to the steric crowding created by the phenyl rings at the 2,4,6-positions, the amide functionalities adopt an out of plane conformation to facilitate interlayer hydrogen bonding during polymer synthesis. Here the amide hydrogen (N-H) of one layer oriented with the carbonyl oxygen of the adjacent layer to create strong amide hydrogen bonds between layers (Fig. 6B). The amide containing monomer was reacted with hydrazine or p-phenylenediamine to yield COFamide-1 and COF-amide-2, respectively. BET surface areas of amide COFs were 1390 m^2/g (COFamide-1) and 1202 m^2/g (COFamide-2) with significant bulk crystallinity and narrow pore size distribution compared to the control COFs (Me-COF-1 and Me-COF-2). Further, they have experimentally proved the presence of interlayer hydrogen bonding using variable temperature infrared spectroscopy (VT-IR). There, they observed a blue shift in the vibrational frequencies of the amide carbonyl and the amide N-H upon the temperature of the sample increases from room temperature to 350 °C, which provides clear evidence of the presence of interlayer hydrogen bonding (Fig.6 C-F). Computational modeling and DFT calculations were further supports the presence of strong interlayer hydrogen bonding. This is the very first report of establishing strong amide hydrogen bonding between layers of 2D-COFs. This is clearly a milestone in the design principles of 2D-COFs for future materials need.

In 2022[29], the Smaldone group again reported the use of the same tritopic aldehyde monomer containing amide side chains to synthesize a large pore COF (PyCOFamide) with a pore diameter over 6 nm (Fig.7A). Synthesis of larger pore COFs are challenging because the propensity of lager pore COFs to collapse upon solvent removal. Further, if there is no strong means for efficient stacking, that lead to the interpenetration of lengthy monomers rather than the formation of crystalline COFs. Here they have utilized strong interlayer amide hydrogen bonding to stack monomers efficiently to synthesize a larger pore PyCOFamide. This is among the largest pore COFs reported for 2D-COFs. The PyCOFamide was highly crystalline and had a BET surface area of 1682 m^2/g. The theoretical pore diameter (6.5 nm) matched well the experimentally obtained pore diameter (6.1 and 6.7 nm) with gas sorption studies. Taking the benefit of having a stable larger pore 2D-COF, they have studied the inclusion of two β-barrel fluorescent proteins: superfolder green fluorescent protein (sfGFP) (Fig. 7D) and mNeonGreen (mNG) (Fig. 7E) since the inclusion of biomolecules to the individual pores is less common in COFs. The successful encapsulation of proteins by PyCOFamide was demonstrated by the fluorescent microscopic images in comparison with COF-42 (Fig. 7F-I). This work revealed the potential of 2D-COFs to be used in the future enzyme hosts or as biosensors for proteins or as delivery vehicles for biomolecule-based therapeutics.
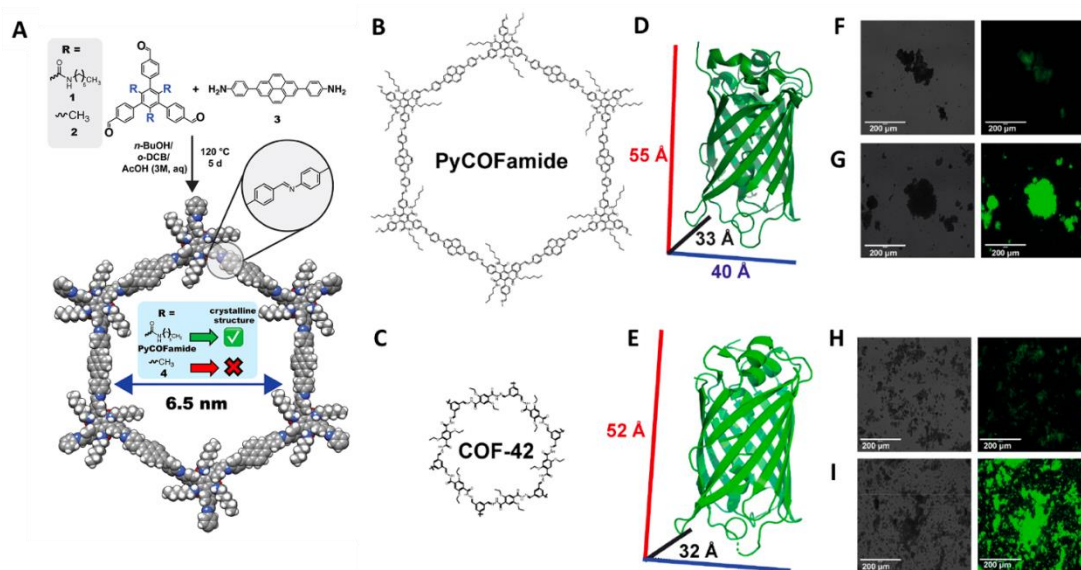

Fig. 7. A). Structure of PyCOFamide linked through imine bonds. B)-C) Comparison of the pore apertures of large pore PyCOFamide with literature reported hydrazone COF-42. D). sfGFP (PDB ID: 2B3P) and E) mNG (PDB ID: 5LTR. Fluorescence microscopy images of F) sfGFP loaded COF-42 pellet, G) sfGFP loaded PyCOFamide pellet, H) mNG loaded COF-42 pellet, and I) mNG loaded PyCOFamide pellet. Reproduced from ref. 29 with permission from ACS Publications, copyright 2022.

Future Directions

2D-Covalent organic frameworks are an amazing class of porous materials whose structures resemble graphene. However, COFs are much more tunable and versatile compared to graphene due to their inherent properties. Diverse monomer topologies, pore size control, high surface area, crystallinity, and low density provide more promise on their applications over conventional 2D-polymers like graphene. Over the past decade, a significant number of dynamic covalent reactions have been introduced in COF synthesis focusing applications. However, the attention given to develop strategies to effectively utilize supramolecular interactions is relatively less compared to the studies on dynamic covalent reactions in COFs. Weak non-covalent interactions in vast majority of 2D-COFs limit their practical applications. Therefore, by taking examples from nature, further developments are needed to improve the materials quality by strong non-covalent forces like hydrogen bonding.

Development of new monomers with hydrogen bondable functional groups and design strategies to control the geometries of these functionalities that facilitates useful hydrogen bonds between layers with high density of interactions are prime important to cater the future materials need. Current commercial 1D-polymers (e.g. Nylon and Kevlar) which take the advantage of hydrogen bonding for their strength are associated with some limitations. Lack of processability, tunability and high product weight detrimentally affects their practical applications. Therefore, 2D-COFs with high density of strong interlayer hydrogen bonding interactions, channel wall functionalization, variable topologies, higher long-range order, high surface area and porosity, and light weight could overcome the limitations associated with the current 1D-polymers. However, further developments are needed in synthesis, scalability, cost and processability aspects to explore amazing properties of 2D-polymers that are seen in their 1D counter parts. As per theoretical and experimental developments and directions to date, it can be predicted that the hydrogen bonding interactions would be the platform for next generation of 2D-COFs/polymer materials which could overcome the current limitations.

Conflicts of Interest

The authors declare no conflicts of interest.

References

[1] Feng X, Ding X, and Jiang D 2012 Chem. Soc. Rev.18 6010–6022

[2] Côté A. P, Benin A. I, Ockwig N. W, O'Keeffe M, Matzger A. J, and Yaghi O. M 2005 Science 310 1166–1170

[3] Zhu L and Zhang Y. B 2017 Molecules 22 1149

[4] Alahakoon S. B, Thompson C. M, Occhialini G, and Smaldone R. A 2017 ChemSusChem 10 2116

[5] Wu M. Y and Yang, Y. W 2017 Chinese Chem. Lett. 28 1135–1143

[6] Zhou W, Wei M, Zhang X, Xu F, and Wang Y 2019 ACS Appl. Mater. Interfaces 11 16847-16854.

[7] Guo L, Yang L, Li M, Kuang L, Song Y, and Wang L 2021 Coord. Chem. Rev. 440 213957

[8] Gonçalves R. S. B, Oliveira A. B. V, Sindra, H. C, Archanjo B. S, Mendoza M. E, Carneiro L. S. A, Buarque C. D and Esteves P.M 2016 ChemCatChem 8 743–750

[9] Hu J, Gupta S. K, Ozdemir J, and Beyzavi H 2020 ACS Appl. Nano Mater. 3 6239–6269

[10] Jiang D 2020 Chem 6 2461–2483

[11] Thompson C. M, Occhialini G, McCandless G. T, Alahakoon S. B, Cameron V, Nielsen S. O, and Smaldone R. A 2017 J. Am. Chem. Soc. 139 10506-10513

[12] Romo F. J. U, Hunt J. R, Furukawa H, Klöck C, O'Keeffe M, and Yaghi O. M 2009 J. Am. Chem. Soc. 131 4570–4571

[13] Dalapati S, Jin S, Gao J, Xu Y,Nagai A, and Jiang, D 2013 J. Am. Chem. Soc. 135 17310–17313

[14] Romo F. J. U, Doonan C. J, Furukawa H, Oisaki K, and Yaghi O. M 2011 J. Am. Chem. Soc. 133 11478–11481

[15] Fang Q, Zhuang Z, Gu S, Kaspar R. B, Zheng J, Wang J Qiu S and Yan Y 2014 Nat. Commun. 5 4503

[16] Zhao Y, Yao K. X, Teng B, Zhang T, and Han Y 2013 Energy Environ. Sci. 6 3684–3692

[17] Karas L. J, Wu C. H, Das R and Wu J. I C 2020 WIREs Comput. Mol. Sci. 10 477

[18] van der Lubbe S. C. C, and Guerra C. F 2019 Chem. – An Asian J. 14 2760–2769

[19] Schroeder L. R, and Cooper S. L 1976 J. Appl. Phys. 47 4310–4317

[20] Alahakoon S. B, Diwakara S. D, Thompson C. M, and Smaldone R. A 2020 Chem. Soc. Rev. 49 1344-1356

[21] Kandambeth S, Shinde D. B, Panda M. K, Lukose B, Heine T, and Banerjee R 2013 Angew. Chemie Int. Ed. 52 13052–13056

[22] Kandambeth S, Venkatesh V, Shunde D. B, Kumari S, Halder A, Verma S and Banerjee R 2015 Nat. Commun. 6 6786

[23] Halder A, Karak S, Addicoat M, Bera S, Chakraborty A, Kunjattu S. H, Pachfule P, Heine T, and Banerjee R 2018 Angew. Chemie Int. Ed. 57 5797–5802

[24] Halder A, Ghosh M, Abdul K. M, Bera S, Addicoat M, Sasmal H. S, Karak S, Kurungot S, and Banerjee R 2018 J. Am. Chem. Soc.vol. 140 10941–10945

[25] Zhao C, Diercks C. S, Zhu C, Hanikel N, Pei X, and Yaghi O. M 2018 J. Am. Chem. Soc. 140 16438–16441

[26] Li L, Feng L, Xue R, Ma B, Li Q, Wu N, Liu H, Yao W, Guo H, and Yang H 2019 ACS Appl. Mater. Interfaces 11 26355–26363

[27] Sandoz-Rosado E, Beaudet T. D, Andzelm J. W, and Wetzel E. D 2018 Sci. Rep. 8 1–11

[28] Alahakoon S. B,Tan K, Pandey H, Diwakara S. D, McCandless G. T, Grinffiel D. I, Durand-Silva A, Thonhauser T, and Smaldone R. A 2020 J. Am. Chem. Soc.142 12987-12994

[29] Diwakara S. D, Ong W. S. Y, Wijesundara Y. H, Gearhart R. L, Herbert F. C, Fisher S. G, McCandless G. T, Alahakoon S. B, Gassensmith J. J, Dodani S. C, and Smaldone R. A 2022 J. Am. Chem. Soc. 144 2468–2473