The Islamic University Journal of Applied Sciences (JESC) Issue I, Volume IV, April 2022

Tetra(4-aminophenyl) porphyrin-based Covalent Organic Frameworks

Maher Fathalla*

***Department of Chemistry, Faculty of Science, Islamic University of Madinah, Madinah 42351, SA**

Email: maherfathalla@iu.edu.sa

Abstract: Covalent Organic Frameworks (COFs) are robust crystalline porous materials with unique properties and have promising applications in many fields such as gas adsorption, sensing and catalysis. COFs properties can be tailored by the judicious choice of their building units. Stemming from its unique properties, rigid structure and synthetic accessibility, tetra(4-aminophenyl)porphyrin (TAPP) has been employed as a building unit to construct various COF materials. This review highlights the different synthetic approaches that were exploited by researchers to assemble COF materials based on TAPP.

Keywords: Porphyrins; Covalent Organic Frameworks; Porous Organic Polymers; Imide; Imine.

الهياكل العضوية التساهمية القائمة على البورفيرين Tetra(4-aminophenyl)

الملخص: الأطر العضوية التساهمية (COFs) هي مواد بلورية قوية مسامية ذات خصائص فريدة ولها تطبيقات واعدة في العديد من المجالات مثل امتصاص الغاز والاستشعار والحفز. يمكن تصميم خصائص COFs من خلال الاختيار الحكيم لوحدات البناء الخاصة بهم. تم استخدام البورفيرين رباعي (4-أمينوفينيل) بورفيرين (TAPP) كوحدة بناء لبناء مواد COF المختلفة ، نظرًا لخصائصه الفريدة وهيكله الصلب وإمكانية الوصول إليه الاصطناعية. تسلط هذه المراجعة الضوء على الأساليب التركيبية المختلفة التي استغلها الباحثون لتجميع مواد COF بناءً علىTAPP .

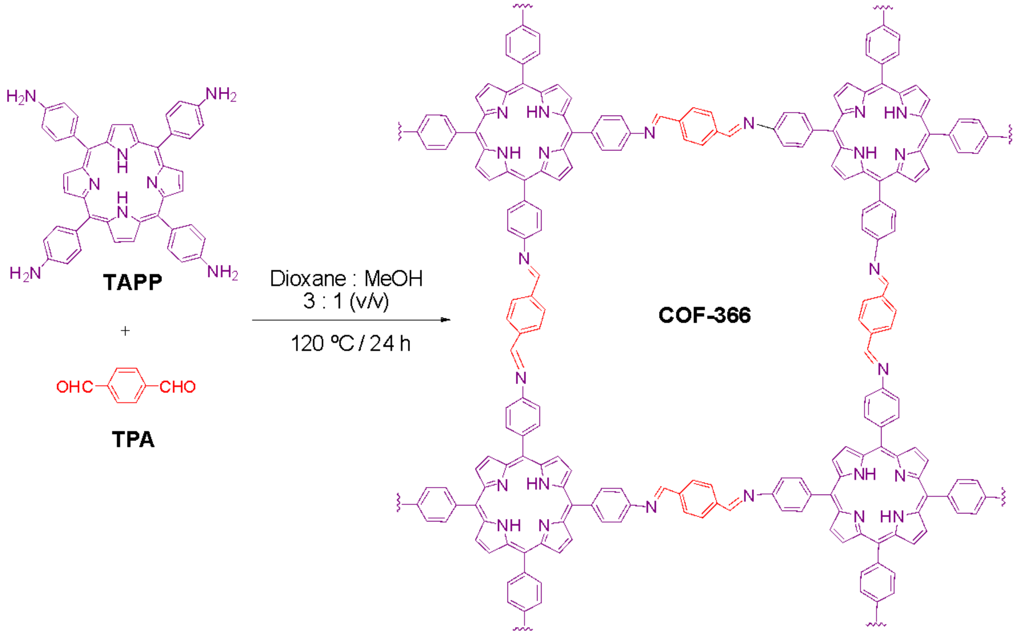
1. Introduction.

Covalent Organic Frameworks (COFs) are emerging class of crystalline porous organic materials that have attracted the interest of researchers worldwide owing to their potential applications in a large variety of domains, such as gas adsorption and separation, chemosensors, heterogeneous catalysis, energy storage and optoelectronics [1-3]. Based on reticular chemistry, COFs are constructed by the integration of organic building blocks by strong covalent bonds to make highly porous materials with predictable structures. The pore dimensions as well as the skeletons of COFs can be tailored by the judicious predesign of the knots and linkers whose symmetries determine the COFs shape and whose dimensions dictate COFs pore sizes. Owing to their excellent thermal and chemical stabilities as well as synthetic accessibility, COFs are considered an attractive alternative to MOFs (Metal Organic Frameworks) [4]. Various organic molecules have been applied as building units to construct wide range of COFs. Among these molecules, porphyrin macrocycles are considered attractive building units for making COFs owing to their rigid structures, synthetic accessibility, as well as broad-ranging optoelectronic and catalytic properties that could be tuned by substituent effects and incorporation of various metals in porphyrin macrocycle. Consequently, various porphyrin derivatives have been applied as building block to make a wide-range of porphyrin-based COFs [5] among which tetra(4-aminophenyl)porphyrin (TAPP) has been one of the most used building unit to construct COFs since the pioneering work by Yaghi's group [6]. This review summarizes the common approaches the were employed by researchers to construct COFs by using tetra(4-aminophenyl)porphyrin (TAPP) as a building unit. As shown in scheme 1, the four amino groups of TAPP have been harnessed to construct various COFs through two main synthetic strategies, namely, formation of imine- or imide-bonds.

2. Synthesis of TAPP-based COFs.

2.1. Imine-linked porphyrin COFs.

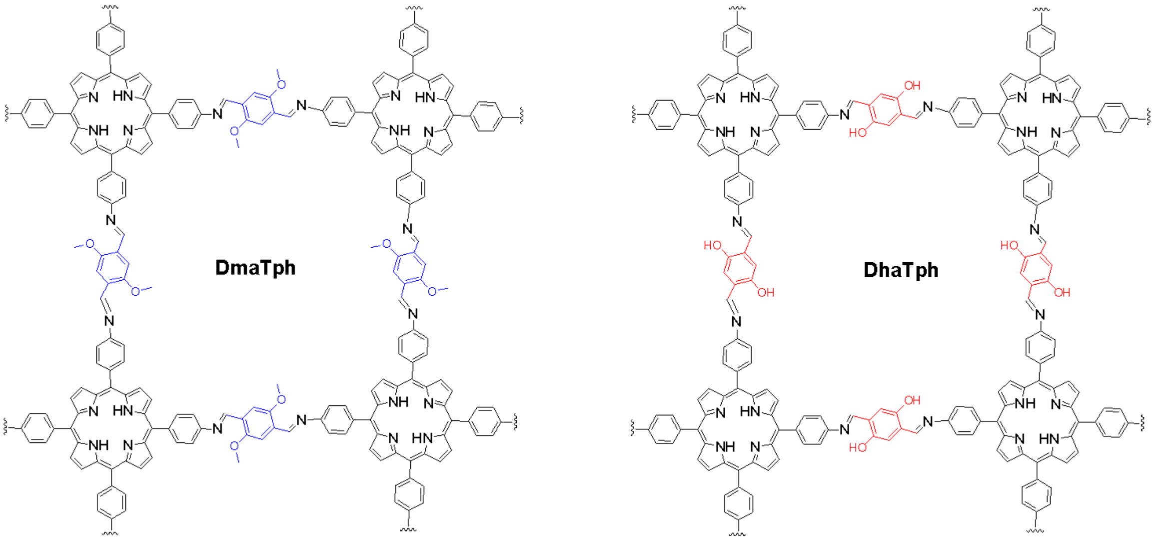
The reversible condensation between amines and aldehydes is one of the oldest reactions in organic chemistry. The dynamic nature of this reaction allows "error checking" and "proof-reading" of the resulting materials. Yaghi's group harnessed the condensation between TAPP and terephthaldehyde to construct imine-linked porphyrin COFs known as COF-366 by solvothermal reactions. As shown in scheme 1, COF-366 has square channels with porphyrin moieties located at the nodes of the square skeletons and are linked by the imine-bonds [7].



Scheme 1. The synthesis of COF-366.

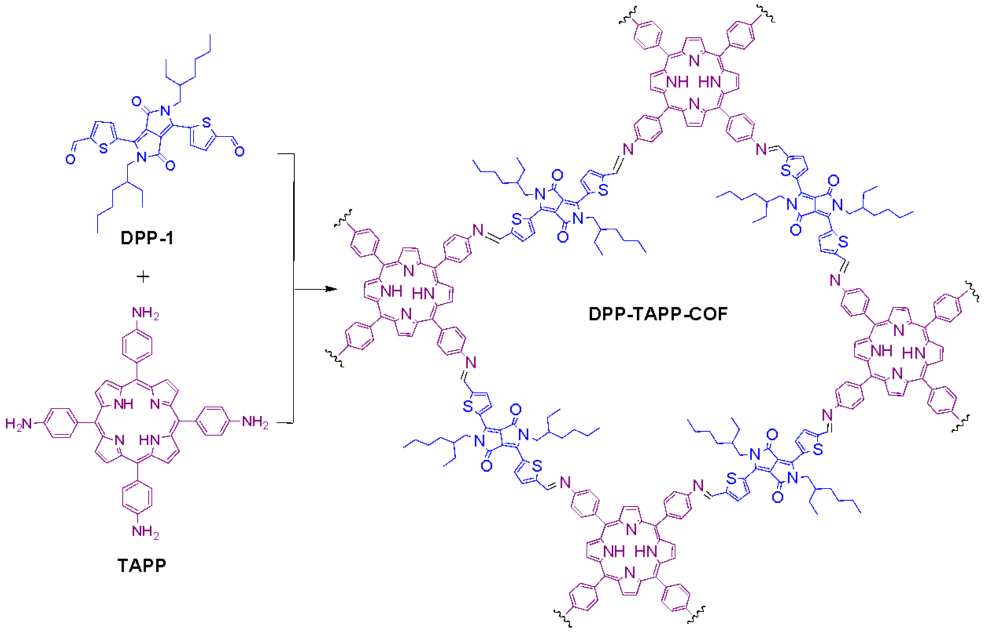
Later on, the effect of incorporating hydrogen bonding on the stability of the resulting imine-linked COFs was investigated through the synthesis of DmaTph and DhaTph via the condensation of TAPP with either 2,5-dimethoxyterephthaldehyde or 2,5-dihydroxyterephthaldehyde, respectively [8].

It was concluded that, DhaTph exhibits higher thermal, water, and acid stability than DmaTph owing to the OH....N=C intramolecular hydrogen bonding within the DhaTph structure (scheme 2).



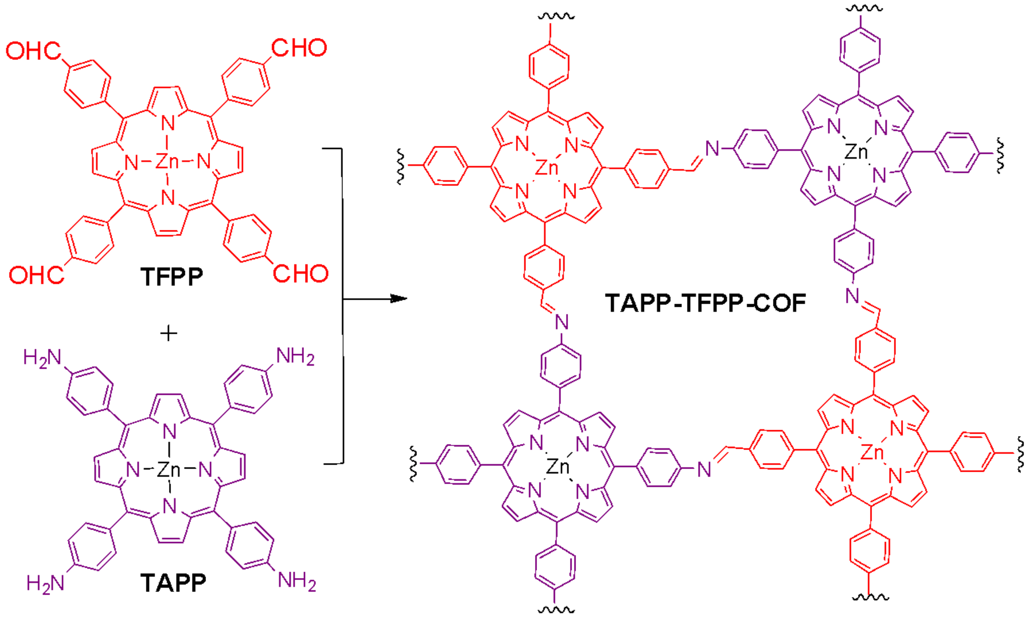
Scheme 2. Structures of imine-linked DmaTph and DhaTph porphyrin COFs.

In another report, Beuerle et al. exploited the condensation between TAPP and a diketopyrrolopyrrole (DPP) to assemble a novel imine-linked porphyrin COFs (DPP-TAPP-COF) with an enhanced absorption capability up to 800 nm [9]. Furthermore, the resulting COF self-assembles into a hollow microtubular with outer and inner tube diameters of around 300 and 90 nm, respectively (scheme 3).



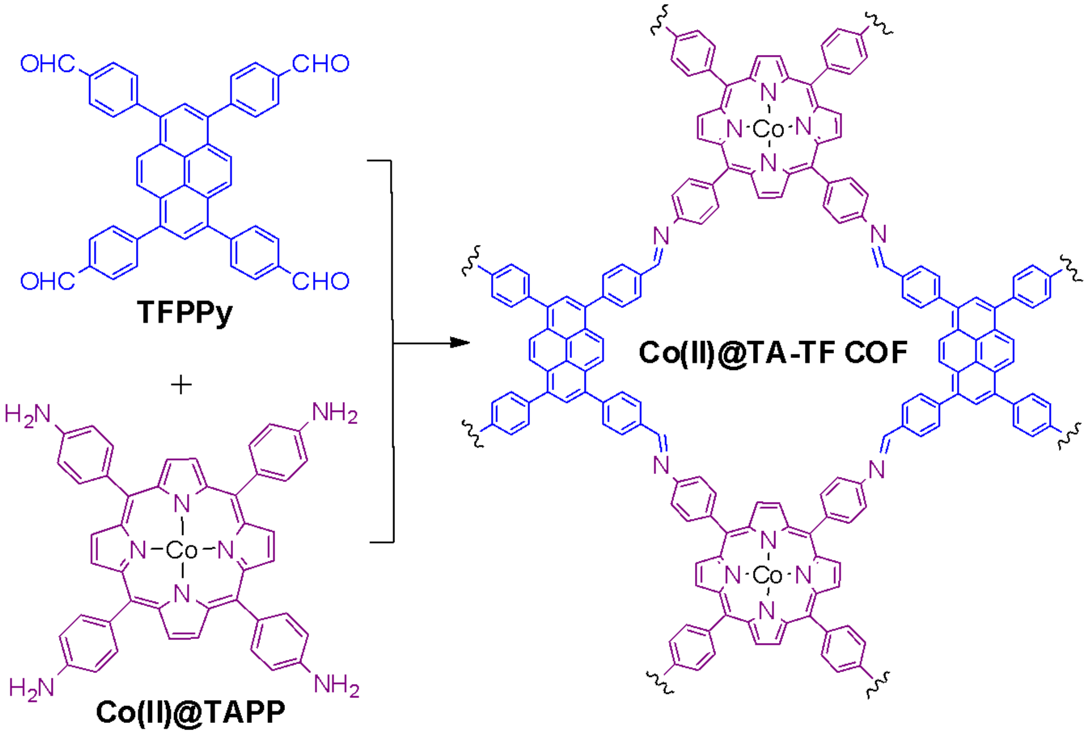
Scheme 3. Synthesis of DPP-TAPP-COF.

Huang et al. reported the synthesis of another imine-linked porphyrin COF (TAPP-TFPP-COF) through the condensation between TAPP and tetra(4-formylphenyl)porphyrin TFPP under typical solvothermal conditions (scheme 4) [10]. The resulting COF has a tetragonal micropores at a size of 1.8 nm and exhibited high crystallinity, excellent stability, and good porosity. In addition, the conductivity of TAPP-TFPP-COF can be greatly enhanced after doping with iodine.



Scheme 4. Synthesis of TAPP-TFPP-COF.

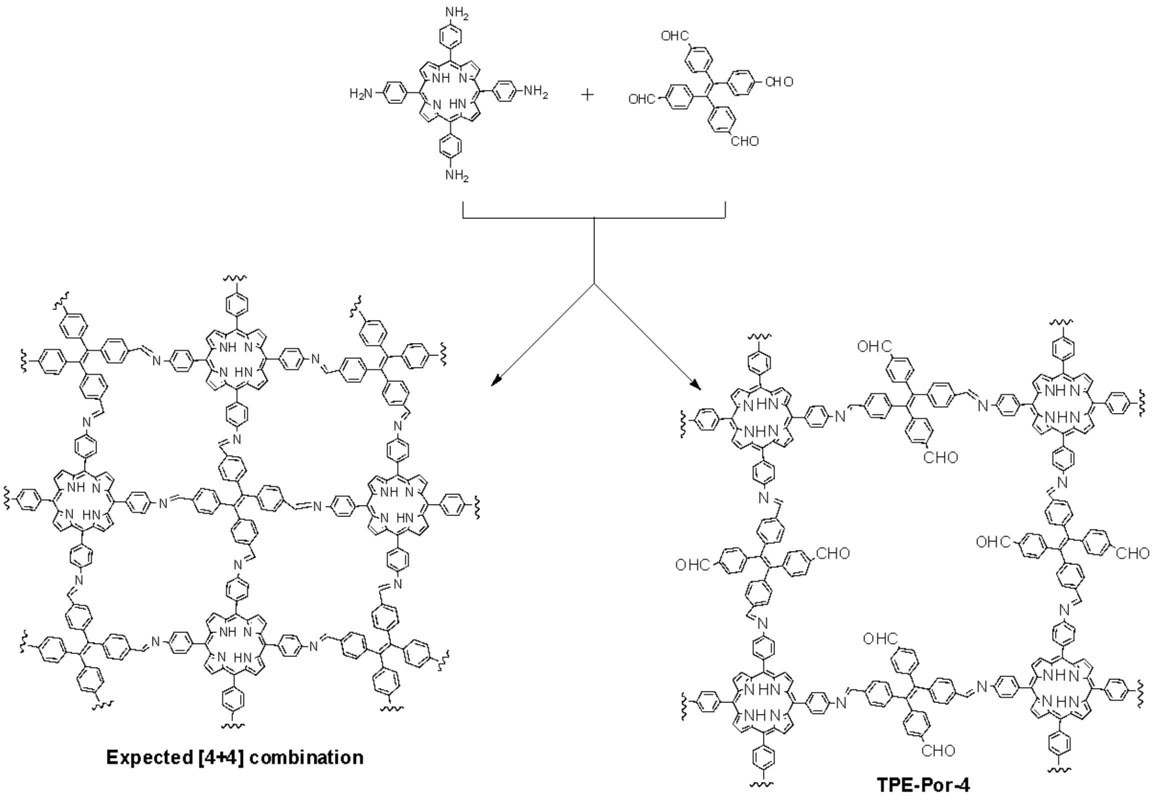
Recently, Gao et al. reported the synthesis of another imine-linked porphyrin COF, termed Co(II)@TA-TF COF by the solvothermal reaction of cobalt(II) TAPP and 1,3,6,8-tetrakis(4-formylphenyl)pyrene (TFPPy) (scheme 5) [11]. The resulting Co(II)@TA-TF COF possesses micropores suitable for CO_2 adsorption owing to the alternate stacking of the building units, and was equipped with cobalt(II) porphyrin units as catalytic sites into the vertices of the layered tetragonal networks that enable the conversion of CO_2 into cyclic carbonates under mild conditions.



Scheme 5. Synthesis of Co(II)@TA-TF COF.

Chen et al. reported a recent imine-linked porphyrin COF, termed TPE-Por-4, by the condensation of TAPP and 4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)tetrabenzaldehyde (D_{2h}-symmetric) [12]. The expected route for the [4+4] condensation was not observed based on a series of structure characterization of TPE-Por-4 (scheme 6). The resulting COF suspension shows unique fluorescent properties originated from its building units and displays an apparent response to pH fluctuation ranging from 2 to 4, rendering it suitable for spectroscopic monitoring of medium pH value.

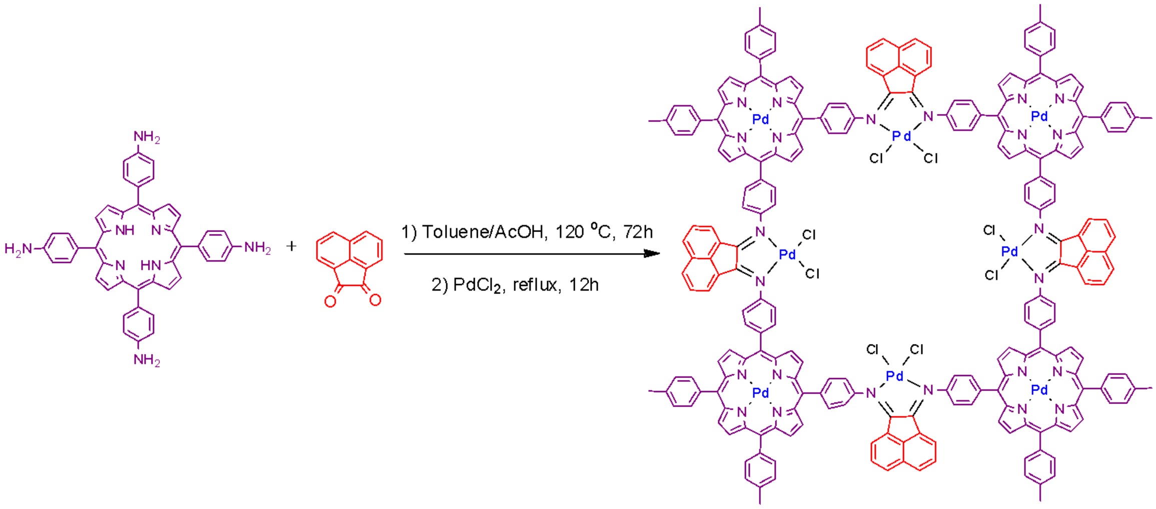
In another approach, Gu et al. constructed a novel imine-linked porphyrin COF, termed PPOP-1(Pd), first, via imine condensation of TAPP and acenaphthalenequinone followed by refluxing with $PdCl_2$ to afford PPOP-1(Pd) (scheme 7) [13]. The resulting COF contains two catalytic sites, namely, Pd(II)-porphyrin and Pd(II)-α-diimine moieties rendering it efficient for tandem catalytic reactions.



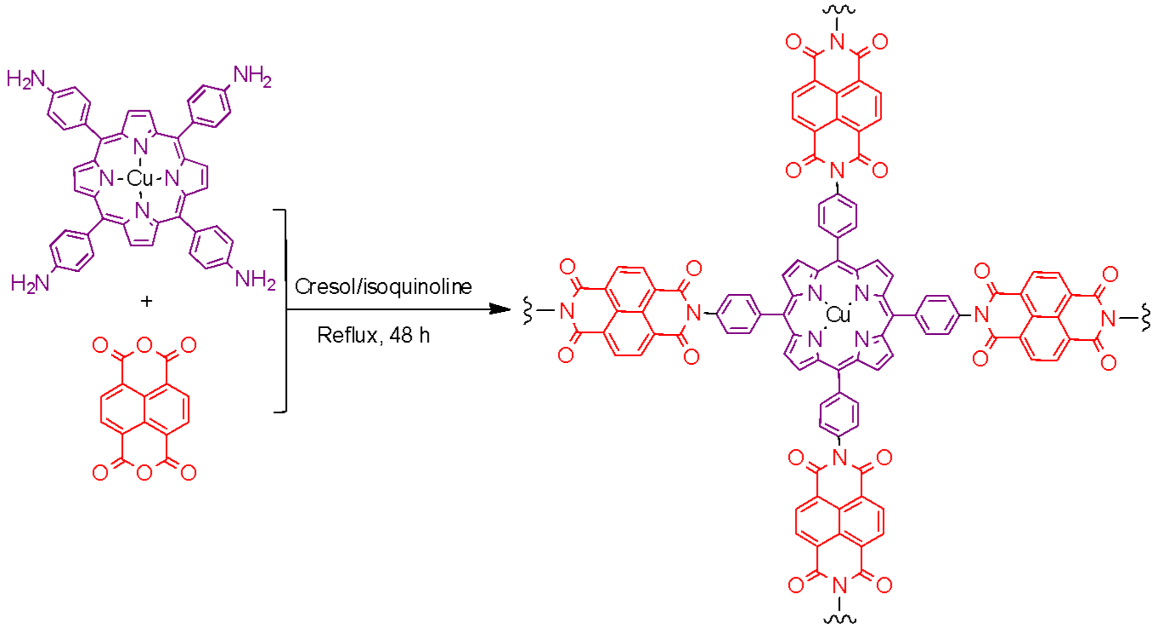
Scheme 6. Synthesis of TPE-Por-4.

2.2. Imide-linked porphyrin COFs.

Polyimide (PI) polymers are known for their excellent chemical and thermal stabilities. Typically, imidization reaction involves the condensation of an amine and an anhydride. The imidization reaction has been exploited to construct various porphyrin COFs in which TAPP (amine monomer) was employed as a node and the anhydride monomer as a linker. For instance, Echegoyen et al. reported the synthesis of a polyimide porphyrin COF via the condensation of Cu (II)-TAPP and naphthalene tetracarboxylic dianhydride in m-cresol/isoquinoline mixture (scheme 8) [14]. The resulting polyimide porphyrin COF exhibited adsorption capacity of 3.5 wt% for CO_2, 0.32 wt% for CH_4 at 273K, 1bar, and 0.4 wt% for H_2 at 77 K/1 bar.

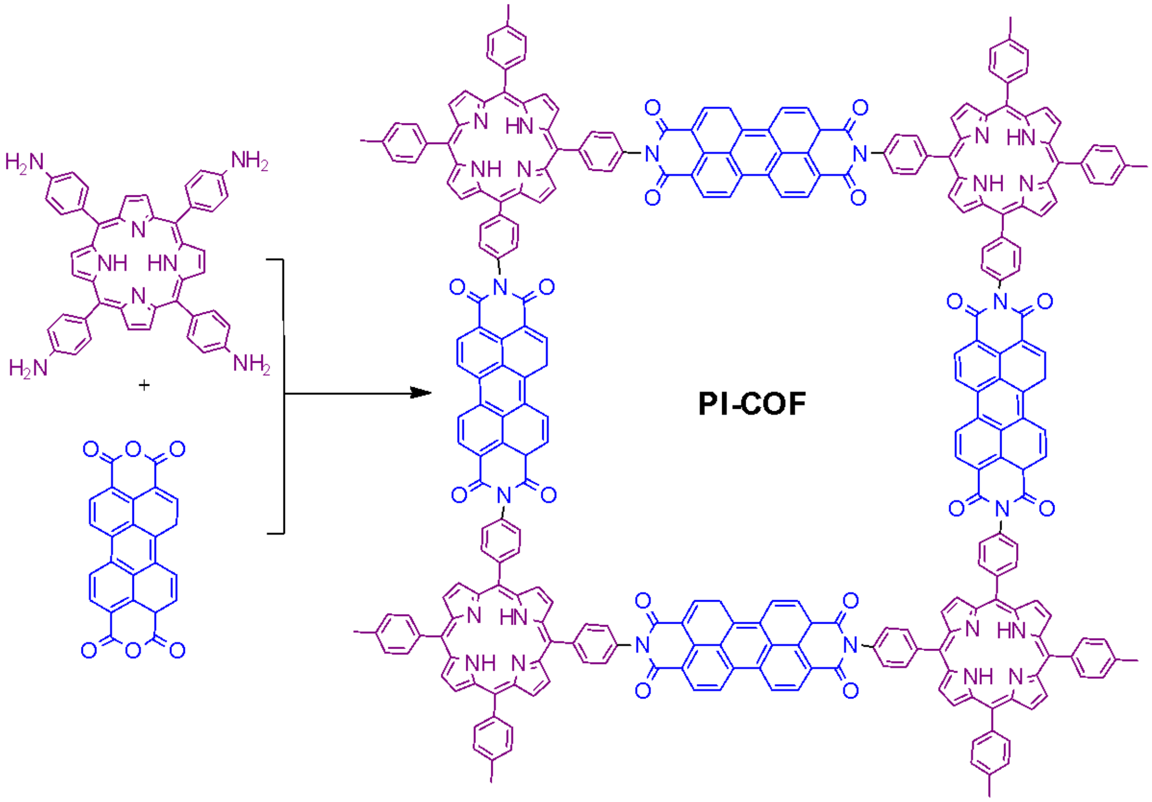


Scheme 7. Synthesis of PPOP-1(Pd).



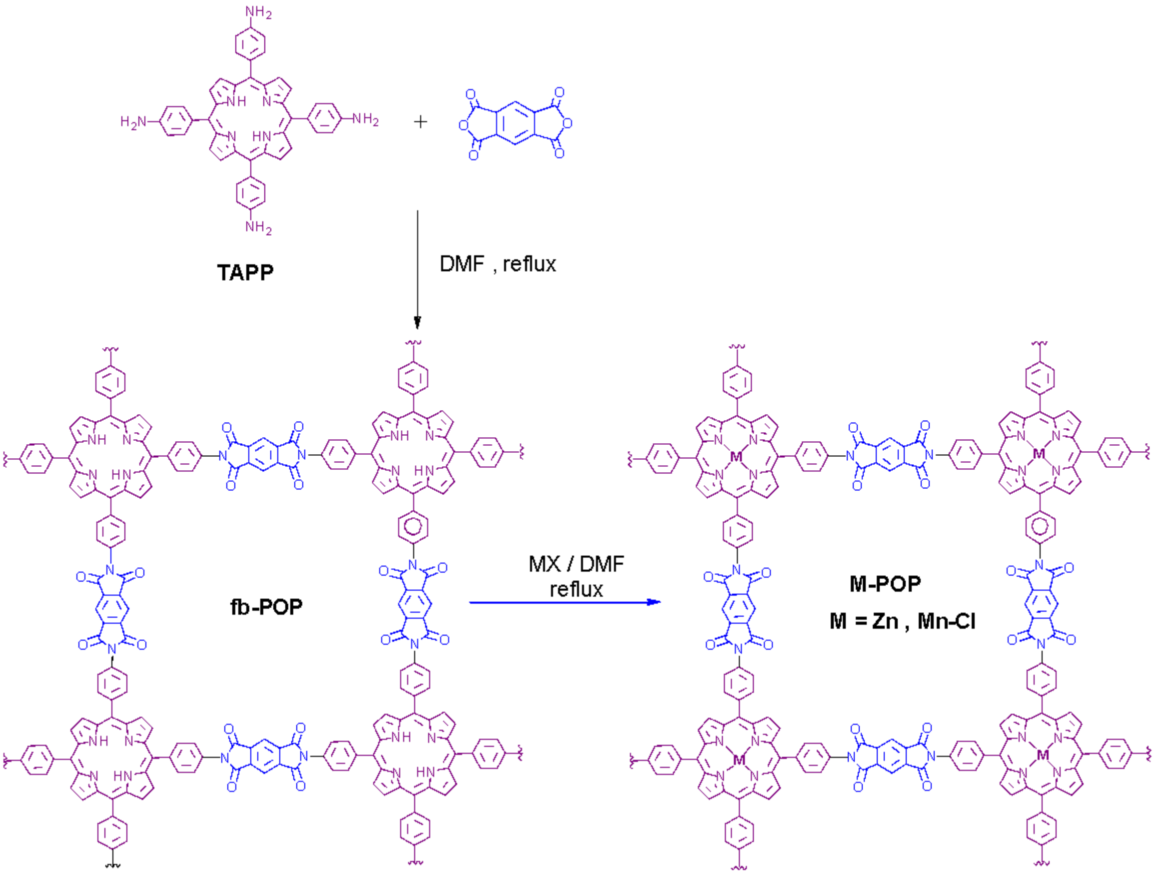
Scheme 8. Synthesis of Cu(II)-TAPP and naphthalene tetracarboxylic dianhydride based COF.

Another polyimide porphyrin COF, termed PI-COF, was constructed by Xian et al. via the imidization reaction of TAPP and perylenetetracarboxylic dianhydride (PTCA) (scheme 9) [15]. The resulting PI-COF possesses porous crystalline and excellent thermal stability. Furthermore, it exhibits a strong fluorescence which was attributed to the existence of a p-n heterojunction between TAPP and PTCA building units. The fluorescence was enhanced upon the exfoliation of PI-COF to few layered PI covalent organic nanosheets (PI-CONs). The latter was employed as a fluorescent probe to detect TNP with high sensitivity and selectivity.



Scheme 9. The synthesis of PI-COF.

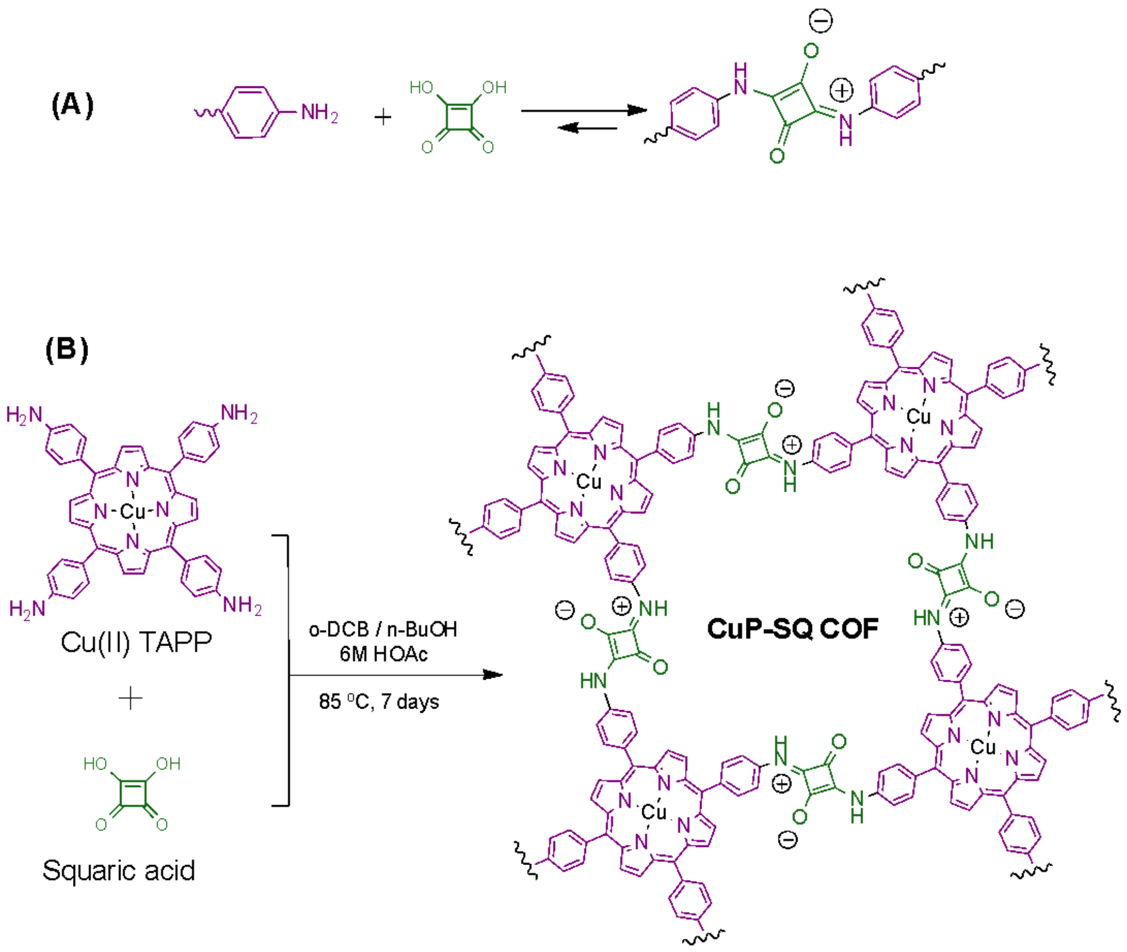
Recently, Fathalla reported the synthesis of new porphyrin COFs through the condensation between TAPP and pyromellitic dianhydride (scheme 10) [16]. Furthermore, the post-synthetic metallation of the free-base porphyrin macrocycles of the resulting COF with either Zn or Mn metals afforded the metallo-porphyrin COF analogues in excellent yields. The metalated analogues showed higher CO_2 uptake capabilities compared to the free-base COF. In addition, Mn^{III}-COF was found to be an effective catalyst for the selective epoxidation of styrene to the corresponding epoxide.



Scheme 10. Synthesis of TAPP and pyromellitic dianhydride based COFs.

2.3. Miscellaneous TAPP based COFs.

Even though the imine and imide bond formation are the most common synthetic approaches to construct TAPP-based COFs. There have been other synthetic strategies that were employed to assemble COFs using TAPP building units. For instance, Jiang et al. harnessed squaraine chemistry to assemble a novel COF (CuP-SQ-COF) through the condensation between Cu-TAPP and squaric acid (scheme 11) [17]. The reported COF are highly stable in solvents and has a zigzagged conformation which prevents the side slippage of the layered structure. In addition, it exhibits a very broad rang of light absorption.



Scheme 10. Synthesis of CuP-SQ COF.

3. Conclusion.

Owing to its potential applications in many fields as well as predictable structures and pore functionality, COFs have gained considerable attention over the past decade. Porphyrin-containing COFs have been relatively well-explored and proven to be attractive materials in terms of stability and promising applications. Specifically, tetra(4-aminophenyl)porphyrin (TAPP) has been one of the most used building units in constructing various COFs. This review summarized the synthetic approaches employed so far to assemble COFs based on TAPP. The amino groups of TAPP rendering it an attractive building unit for the formation of imine- and imide-linked COFs.

4. References

[1] R. Liu, K. T. Tan,Y. Gong, Y. Chen, Z. Li, S. Xie, T. He, Z. Lu, H. Yanga and D. Jiang. Covalent organic frameworks: an ideal platform for designing ordered materials and advanced applications. Chem. Soc. Rev. 50 (2021) 120-242.

[2] D. Jiang. Covalent Organic Frameworks: An Amazing Chemistry Platform for Designing Polymers. Chem. 6 (2020) 2461-2483.

[3] K. Geng, T. He, R. Liu, S. Dalapati, K. T. Tan, Z. Li, S. Tao, Y. Gong, Q. Jiang, and D. Jiang. Covalent Organic Frameworks: Design, Synthesis, and Functions. Chem. Rev. 120 (2020) 8814–8933.

[4] H. Furukawakyle, C. O'keeffeand and O. M. Yaghi. The Chemistry and Applications of Metal-Organic Frameworks. Science 341 (2013) 6149.

[5] Q.-Y. Liu, J.-F. Li and J.-W. Wang. Research of covalent organic frame materials based on porphyrin units. J Incl Phenom Macrocycl Chem. 95 (2019) 1–15.

[6] A.P. Côté, I. A. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi. Porous, crystalline, covalent organic frameworks. Science 310 (2005) 1166–1170.

[7] S. Wan, F. Gándara, A. Asano, H. Furukawa, A. Saeki, S.K. Dey, L. Liao, W.W. Ambrogio, Y.Y. Botros, X. Duan, S. Seki, J.F. Stoddart and O.M. Yaghi. Covalent organic frameworks with high charge carrier mobility, Chem. Mater. 23 (2011) 4094–4097.

[8] S. Kandambeth, D.B. Shinde, M.K. Panda, B. Lukose, T. Heine and R. Banerjee. Enhancement of chemical stability and crystallinity in porphyrin containing covalent organic frameworks by intramolecular hydrogen bonds. Angew. Chem. Int. Ed. 52 (2013) 13052–13056.

[9] B. Gole, V. Stepanenko, S. Rager, M. Grüne, D.D. Medina, T. Bein, F. Würthner and F. Beuerle. Microtubular self-assembly of covalent organic frameworks. Angew. Chem. Int. Ed. 57 (2018) 846–850.

[10] X. Xu, S. Wang, Y. Yue, and N. Huang. Semiconductive Porphyrin-Based Covalent Organic Frameworks for Sensitive Near-Infrared Detection. ACS Appl. Mater. Interfaces 12 (2020) 37427–37434.

[11] Y. Li , J. Zhang, K. Zuo, Z. Li, Y. Wang, H. Hu, C. Zeng, H. Xu, B. Wang and Y. Gao. Covalent Organic Frameworks for Simultaneous CO_2 Capture and Selective Catalytic Transformation. Catalysts 11 (2021) 1133.

[12] X. Wu1, X. Zhang, Y. Li, B. Wang, Y. Li and L. Chen. A porphyrin-based covalent organic framework with pH-dependent fluorescence. J. Mater. Sci. 56 (2021) 2717–2724.

[13] R. Shen, W. Zhu, X. Yan, Ta. Li, Yo. Liu, Y. Li, S. Daia and Z.-G. Gu. A porphyrin porous organic polymer with bicatalytic sites for highly efficient one-pot tandem catalysis. Chem. Commun. 55 (2019) 822-825.

[14] V. S. P. K. Neti, J. Wang, S. Deng, and L. Echegoyen. Synthesis of a Polyimide Porous Porphyrin Polymer for Selective CO2 Capture. J. Chem. (2015) Article ID 281616: http://dx.doi.org/10.1155/2015/281616.

[15] C. Zhang, S. Zhang, Y. Yan, F. Xia, A. Huang, and Y. Xian. Highly Fluorescent Polyimide Covalent Organic Nanosheets as Sensing Probes for the Detection of 2,4,6-Trinitrophenol. ACS Appl. Mater. Interfaces 19 (2017) 13415−13421.

[16] M. Fathalla. Synthesis, CO_2 Adsorption and Catalytic Properties of Porphyrin-Pyromellitic Dianhydride Based Porous Polymers. Macromol. Res. 29 (2021) 321–326.

[17] A. Nagai, X. Chen, X. Feng, X. Ding, Z. Guo, and D. Jiang. A Squaraine-Linked Mesoporous Covalent Organic Framework. Angew. Chem. 125 (2013) 3858 –3862.