

A Review on Synthesis and Characterization of Porphyrin based Covalent Organic Framework

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ABSTRACT

Porphyrin-based covalent organic frameworks (COFs) represent an innovative class of porous crystalline materials, exhibiting remarkable photophysical, electrochemical, and catalytic properties. This review provides a comprehensive overview of the synthesis, characterization, and applications of porphyrin-based COFs, emphasizing their structural adaptability and functional diversity. By harnessing the unique attributes of porphyrins, including their π -conjugated structure and metal-coordinating capabilities, researchers have developed porphyrinic COFs with tailored two-dimensional and three-dimensional architectures. These frameworks boast exceptional thermal stability, high specific surface areas, and customizable functionalities, rendering them promising candidates for applications in catalysis, energy storage, gas adsorption, sensing, and biomedicine. Furthermore, the strategic integration of heterocyclic units and metal centers has significantly enhanced the optoelectronic and electrocatalytic capabilities

of these COFs. As research continues to address challenges related to large-scale production, dimensional optimization, and biomedical applications, porphyrin-based COFs are poised to play a transformative role in advancing material science, chemistry, and industrial domains.

Keywords: Porphyrin-based COF, Synthesis, Porous Crystalline Materials, Structural Stability, Characterization

Introduction

Porphyrin macrocycles consist of a ring of four pyrrole groups linked together by methine bridges [1] is considered by many to be the most crucial pigment found in nature [2]. Naturally occurring tetrapyrroles and related compounds, such as phthalocyanines, are typically colored and are therefore referred to as the "pigments of life" [3]. Porphyrins exhibit conformational flexibility, and their macrocycle shape can be significantly altered through metal coordination and substituent effects [4] contributed to the field of porphyrin chemistry for an impressive period of over 50 years [5]. Since their discovery in crude oils and shales as "molecular fossils" by Treibs, porphyrins have been the subject of extensive research [6]. Porphyrins, with their unique π -conjugated structure, have garnered significant attention due to their outstanding photophysical, photochemical, electrochemical, and structural characteristics [7]. Porphyrins and their derivatives are crucial for photosynthesis due to their superior light-harvesting ability in the visible spectrum [8].

The porphyrin π system has been extended through the fusion of aromatic rings, either by peripheral annulation of the pyrrole units or by introducing aryl substituents at the meso-positions, thereby altering the electronic structure of the porphyrins [9]. Porphyrin-based chromophores with conjugated molecular structures have been explored for various applications, including optical materials, nanowires and etc. [10] Porphyrins' optical spectra are highly sensitive to their frontier molecular orbitals. The optical spectra of porphyrins and their derivatives are strongly linked to their frontier molecular orbitals [11]. Variations to the porphyrin structure have been extensively explored through peripheral substitution and central nitrogen metalation in order to optimize their therapeutic potential. Porphyrins with a positive charge exhibit increased affinity for molecules bearing negative charges, including DNA and RNA in cancer cell [12]. A promising approach involves modifying the porphyrin core by substituting one or two pyrrole nitrogen atoms with other heteroatoms, such as O, S, Se, Te, Si, P, or C, resulting in heteroatom-containing porphyrins or core-modified porphyrins, whose electronic properties can be precisely tailored through structural modifications shown in Figure.1[13].

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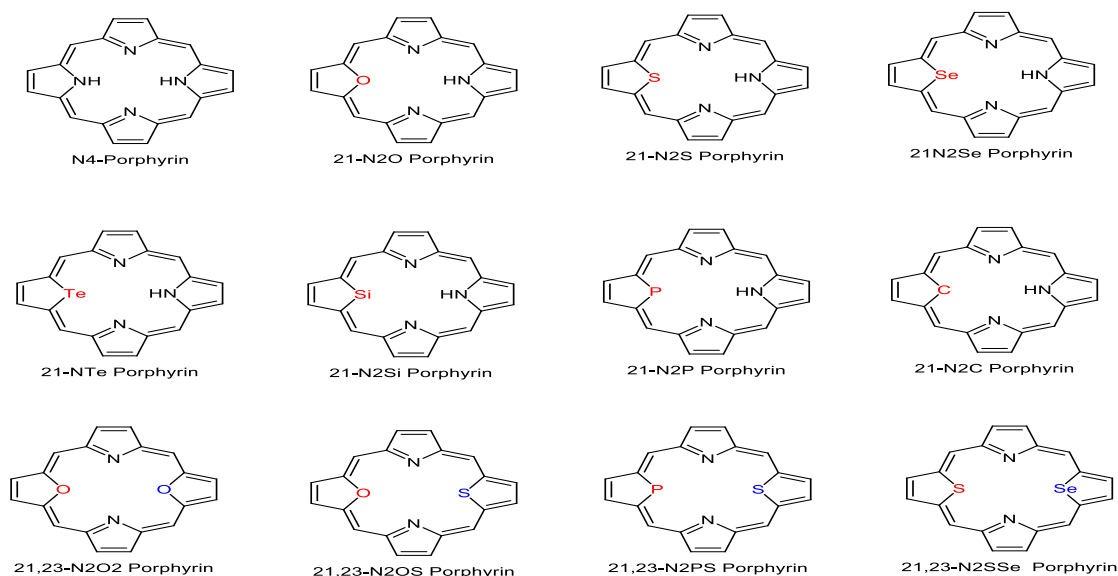


Figure 1.1 Different Types of Heteroatom-Substituted Porphyrin

Hydrophilic moieties have been incorporated into porphyrins and their derivatives to overcome their poor water solubility, which is often caused by self-aggregation of the compounds [14]. In recent years, the synthesis of porphyrin derivatives has garnered significant interest within the scientific community [15]. Porphyrin derivatives play a vital role in natural light-harvesting systems, and their exceptional chemical stability and adaptable redox properties make them crucial for various fundamental biological processes. The vital role of porphyrins in biological light-to-charge conversion has inspired the development of artificial light-harvesting systems, including dye-sensitized solar cells and organic photovoltaic (OPV) devices [16]. Porphyrin derivatives hold great promise as photosensitizers for photodynamic therapy (PDT) and photodynamic diagnosis (PDD), with some analogues already in clinical use. Our research has led to the development of pH-activatable [17]. Compounds of the porphyrin type possess a number of distinctive and significant characteristics [18]. The vital functions of these compounds have significantly impacted our existence. As a result, scientists have been drawn to studying them for centuries, seeking to comprehend the intricacies of our world [19]. Porphyrins are polar, conjugated, and highly delocalized organic molecules, characterized by their strong affinity for coordinating metal cations into stable complexes. The unique characteristics of porphyrin and its derivatives make them attractive candidates for bifunctional oxygen electrocatalysis [20].

We report the synthesis and characterization of porphyrinic COFs, where porphyrin units are covalently linked via Schiff-base reactions. 3. The linkage of a sp^3 -hybridized carbon atom from tetraphenyl methane to a planar porphyrin unit results in the formation of a diamond-like topology within the COF [21]. Covalent organic frameworks (COFs) are porous materials formed by the covalent bonding of organic molecules into well-defined geometric structures [22, 23]. As an emerging class of porous crystalline materials, COFs have attracted widespread interest due to their broad application prospects in various fields. Their unique advantages, including low density,

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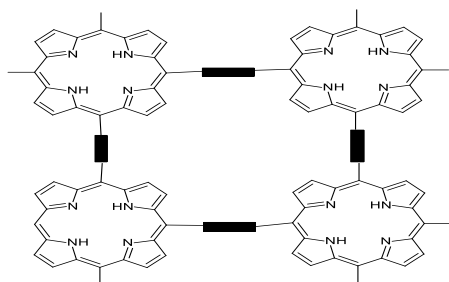
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high surface areas, and customizable properties, arise from the covalent bonding of organic building blocks comprising light elements. However, despite their potential, COFs have yet to be commercialized [24]. Porphyrin-based MOFs and COFs have been the subject of in-depth investigations, yielding innovative framework structures and showing great potential for various applications [25, 26] porphyrins exhibit a distinctive set of characteristics, including a planar conjugated structure, strong thermal and chemical stability, ease of functionalization, high mechanical strength, and superior catalytic properties [27]. Porphyrin-based porous organic frameworks (POFs) have garnered significant attention due to their scalable synthesis, exceptional chemical stability, diverse functionality, and distinctive optoelectronic properties. However, incorporating heterocyclic units into these porous networks remains a relatively unexplored area [28].

The first report of porphyrin-based crystalline covalent organic frameworks (COFs) was made by Jiang and Yaghi in 2011. Additional research demonstrated that the 2D layered structure plays a crucial role in promoting efficient charge-carrier transport [29]. Covalent Organic Frameworks (COFs) are a new type of material made from small organic building blocks. These blocks are arranged in a precise and predictable way to form two- or three-dimensional structures with strong chemical bonds. This creates materials with controlled composition, shape, and pores [30]. COFs are characterized by their highly ordered, covalently bonded architectures, which can be precisely controlled to form various topologies, including 2D layers, 3D networks, and intricate woven structures [31]. In three-dimensional COFs, the structures expand in three dimensions, generating a 3D network, whereas in two-dimensional COFs, the structures extend in two dimensions, forming a 2D plane. All known porphyrin-based COFs have either two- or three-dimensional structures. Most of these use porphyrin as a building block with C₄ symmetry to form two-dimensional COFs with square-shaped pores [32]. Utilizing metal-organic frameworks (MOFs) or covalent organic frameworks (COFs) to immobilize active metal sites or molecular catalysts, such as metal-porphyrins, has emerged as a promising strategy for the electrochemical CO₂ reduction reaction (eCO₂RR), as demonstrated by pioneering work from Yaghi, Hupp, Lan, and colleagues [33]. The ordered structure of these materials facilitates characterization through powder X-ray diffraction (PXRD) patterns. Furthermore, various physicochemical techniques can be employed to determine and elucidate their properties [34]. Porphyrin-based covalent organic frameworks (COFs) have shown promise as semiconducting organic materials for near-infrared (NIR) photodetection [35].



2D Porphyrin-based COFs

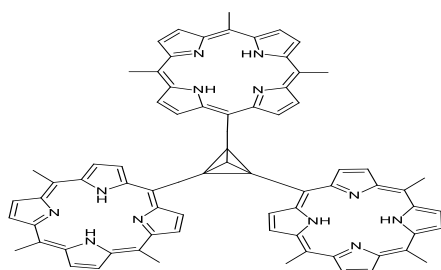
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3D Porphyrin-based COFs

Figure1.2 2D and 3D Porphyrin-based COFs

COFs possess several distinct advantages, including high specific surface areas, well-defined pore structures, extremely low densities, and easily controllable functional groups, all while maintaining excellent thermal and chemical stability [36].

The photocatalytic activity of porphyrins is uniquely sensitive to their aggregation state, making it a critical factor in their performance. With this in mind, we set out to design and synthesize 2D and 3D porphyrinic COFs, with the goal of exploring how dimensionality influences their properties and functionality [37]. In 2011, Yaghi and colleagues reported the synthesis of COF-366, a prototypical 2D porphyrin-based COF, through the condensation reaction of tetra(p-aminophenyl)porphyrin (TAPP) and terephthalaldehyde (TPA) [38]. In contrast to the synthesis of 2D COFs, which often relies on noncovalent interactions (such as π - π interactions) between adjacent layers, the formation of 3D COFs is primarily driven by the establishment of covalent bonds. Following the initial report of 3D COFs in 2007, the field remained relatively underdeveloped for several years. To tackle the longstanding challenges in this area, our group initiated research efforts in 2016 [39]. The porphyrin-based COF, TPE-Por-4, was initially expected to be synthesized through a [4 + 4] condensation reaction involving C_4 -symmetric and D_{2h} -symmetric monomers. Characterization results unequivocally revealed that TPE-Por-4 is a microporous material [40]. A porphyrin-based COF was successfully synthesized via a Schiff base reaction between tetra(4-aminophenyl)porphyrin and 4,4'-biphenyldicarboxaldehyde [41].

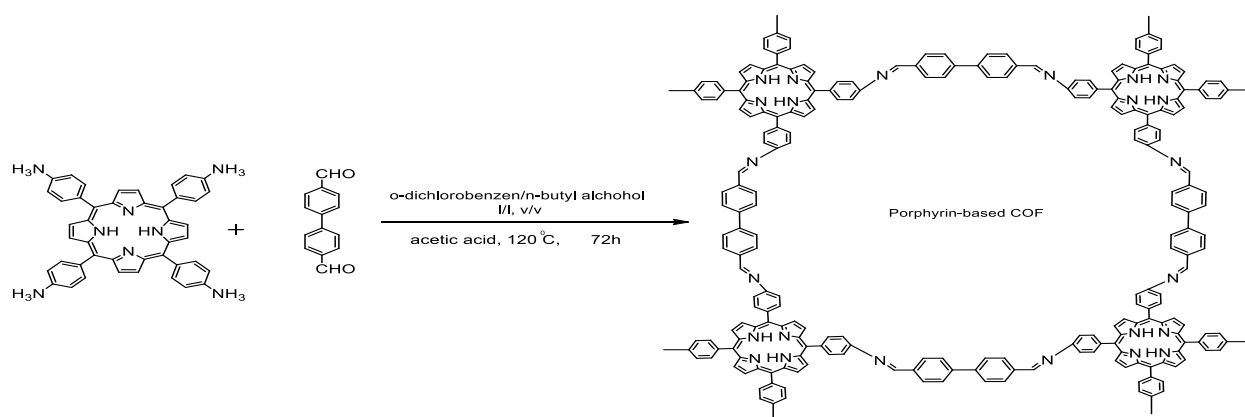


Figure 1.3 Synthetic Scheme of Porphyrin-based COF

Covalent organic frameworks (COFs) have emerged as a highly active research area in materials science and chemistry, with a plethora of publications in top-tier journals. Porphyrin-based frameworks have been the subject of intense research, yielding materials with a wide range of functional properties [42]. This approach enables the precise integration of functional modules into periodic arrays, surrounding highly ordered open pores, resulting in materials with enhanced properties [43]. COFs exhibit a wide range of potential applications, including sensing, gas adsorption and separation, catalysis, energy storage, and the development of photoelectric devices and so on. COF-based materials have the following advantages, (1) The use of diverse secondary building blocks enables precise control over the structure and function of synthesized COFs, yielding a rich array of active sites; (2) Controlling the secondary building units also facilitates the systematic tuning of active sites, enabling in-depth studies of structure-activity relationships and the optimization of electrocatalytic performance; (3) The extensive conjugation present in COFs facilitates efficient electron transport, which is advantageous for various electrocatalytic reactions [44]. Notably, the large size and irregular morphology of COFs pose significant challenges for their application in biomedical fields [45]. COFs' outstanding characteristics significantly expand their potential applications, spanning a wide range of fields [23].

Although several reviews have addressed the design, synthesis, and applications of porphyrin-based COFs, this field continues to evolve. This review article updates the current state of porphyrin-based COF synthesis, highlighting typical strategies and summarizing efficient methods for large-scale and rapid production. This review systematically explores the structure-performance relationships of various applications, including catalysis, photocatalysis, electrocatalysis, sensing, biomedicine, energy storage, gas/liquid adsorption, and membrane separation. Furthermore, this review identifies future opportunities and challenges in the field of COFs from the perspectives of chemistry, materials science, medicine, and industrial applications.

Synthesis

Synthesis of Porphyrin-COF:

In 2015, Yuxia Hou et al. reported H2P-Bph-COF by mixing of 5,10,15,20-tetra(p-amino-phenyl) porphyrin (H2TAPP) and 4,4'-biphenyldialdehyde in a solvent EtOH/mesitylene/ AcOH and was stirred for 30 minutes at room temperature. Then the mixture was sealed in a Teflon-lined container and heat at 120°C for 3 days. After this cooled to room temperature, a purple solid was collected by centrifugation, washed with N,N-dimethyl-formamide (DMF), tetrahydrofuran (THF), and acetone. dried at 80°C to yield H2P-Bph-COF as a purple powder (40.9 mg, yield 66%)[46]. In 2015, Yuxia Hou et al. also reported Pd/H2P-Bph-COF in dichloromethane Pd(OAc)₂ and H2P-Bph-COF were dissolved, stirring at room temperature for 24 hours. Then the final solid was collected by centrifugation, washed with dichloromethane, dried at 80°C to yield Pd/H2P-Bph-COF as a dark purple powder (61 mg, 84% yield [46]).

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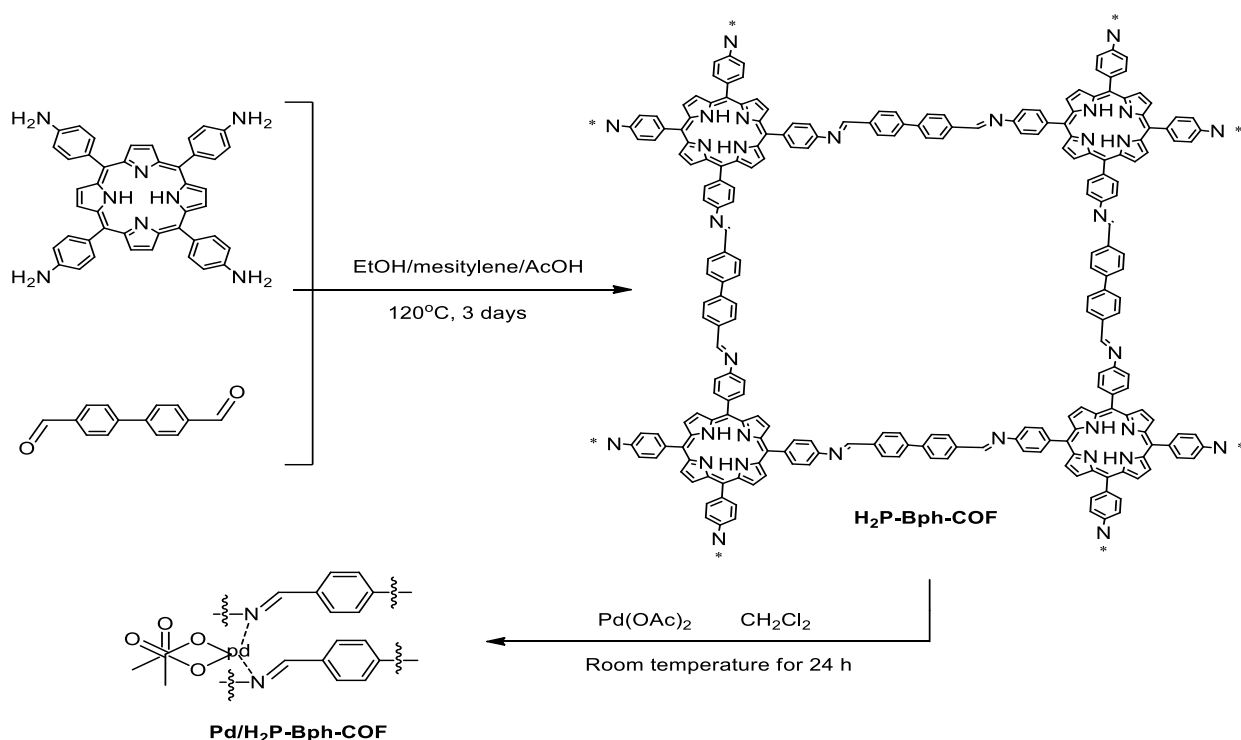


Figure 2.1 Synthetic Scheme of H₂P-Bph-COF and Pd/H₂P-Bph-COF

Characterization:

¹³C CP/TOSS NMR: 158 ppm: Imine bonds. 173 ppm: Carbonyl groups of Pd(OAc)₂. 26 ppm: Methyl groups of Pd(OAc)₂.

FT-IR: 1619 cm⁻¹: C=N stretching (imine bond). 1691 cm⁻¹: C=O stretching (attenuated). 3309 cm⁻¹: N-H stretching (attenuated).

PXRD: 2θ = 2.96°: (100) plane. 2θ = 5.93°: (200) plane. 2θ = 8.48°: (300) plane. 2θ = 24.4°: Interlayer stacking (0.36 nm).

BET Analysis: H₂P-Bph-COF: Surface area: 550 m²/g. Pore size: 2.96 nm. Pd/H₂P-Bph-COF: Surface area: 147 m²/g. Pore size: 2.96 nm (unchanged) [46].

In 2016, Huaping Liao et al. reported the isolation of Por-COF by mixing of p-PorCHO, p-phenylenediamine aqueous acetic acid, butane (solvent) and 1,2-dichlorobenzene (solvent) in a pyrex tube. The mixture was then degassed and sealed, then heat at 120°C for 3 days. The Por-COF with a 79% yields was isolated as purple solid by filtration, wash with tetrahydrofuran and acetone and at 80°C dried it [47]. In 2016, Huaping Liao et al. also synthesized the Por-COF/S composite by mixing activated Por-COF and sublimed sulfur uniformly in a mortar. Heat the mixture at 155°C for 12 hours to allow sulfur to diffuse into the nanopores. After cooling, the Por-COF/S composite was obtained [47].

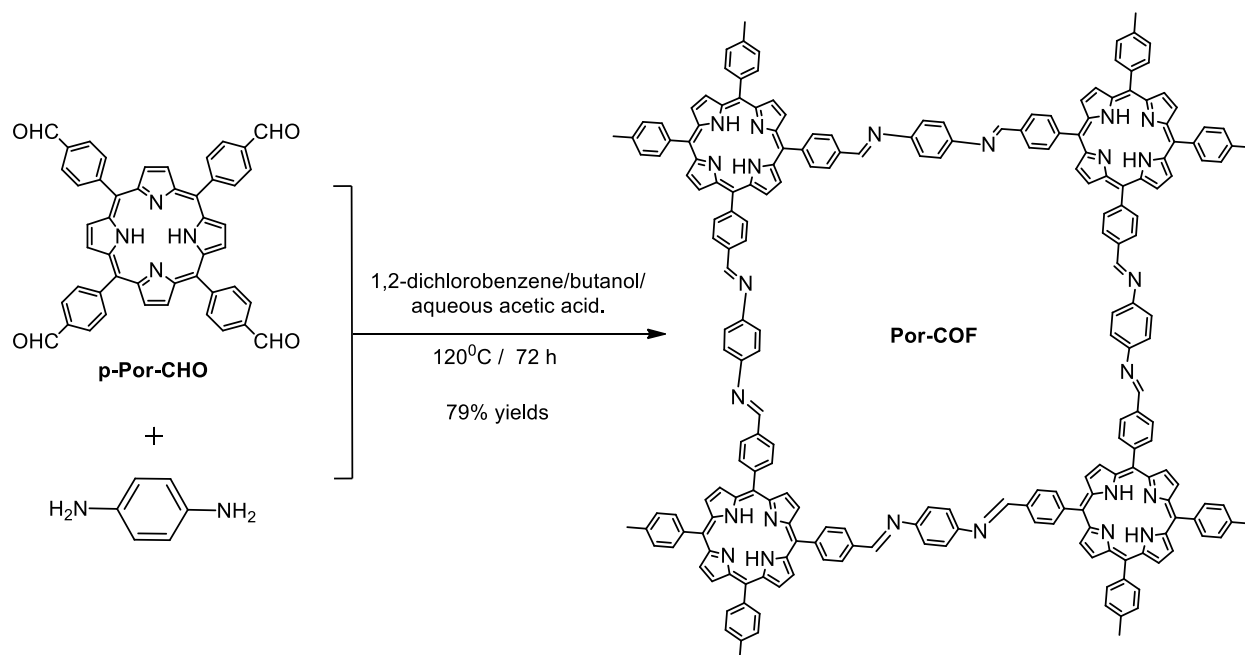


Figure 2.2 Synthetic Scheme of Por-Covalent Organic Framework

Characterization:

(FT-IR): Peak at 1618 cm⁻¹ (C=N stretching vibration of imine bonds).

¹³C (CP-TOSS) NMR: Resonance at 156.8 ppm (imine carbon atom).

X-ray Photoelectron Spectroscopy (XPS): Peaks after discharge: 160.3 eV (Li₂S), 161.9 eV (Li₂S₂). Peaks after charge: 162.4 eV (terminal sulfur), 163.9 eV (bridging sulfur). Peaks between 166–172 eV: S(IV) oxidation state and LiTFSI salt.

Powder X-ray Diffraction (PXRD): Peak at 3.5° (010 reflection). Peak at 7.2° (020 reflection).

Thermogravimetric Analysis (TGA): Stability up to 450 °C.

Nitrogen Adsorption (BET and DFT analysis): BET surface area: 1095 m²/g. Pore volume: 0.71 cm³/g. Pore size: 1.55 nm [47].

In 2016 Hui Yang et al, reported the high conductive 2D COF polyporphyrin named meso-tetrakis-(4-thiophenophenyl)porphyrin (TThP), 4-(thiophen-2-yl)benzaldehyde, pyrrole, and chloroform were mixed in a flask and purged with nitrogen. Boron trifluoride diethyl etherate (BFEE) was added, and the mixture was stirred at room temperature under nitrogen. When the aldehyde was fully consumed (monitored by TLC), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added, and the reaction continued for one hour. The reaction was quenched with triethylamine, and the solvent was evaporated. The crude product was purified by column chromatography and washed with methanol, yielding meso-tetrakis-(4-thiophenophenyl)porphyrin as a purple solid (118 mg, 10%)[48].

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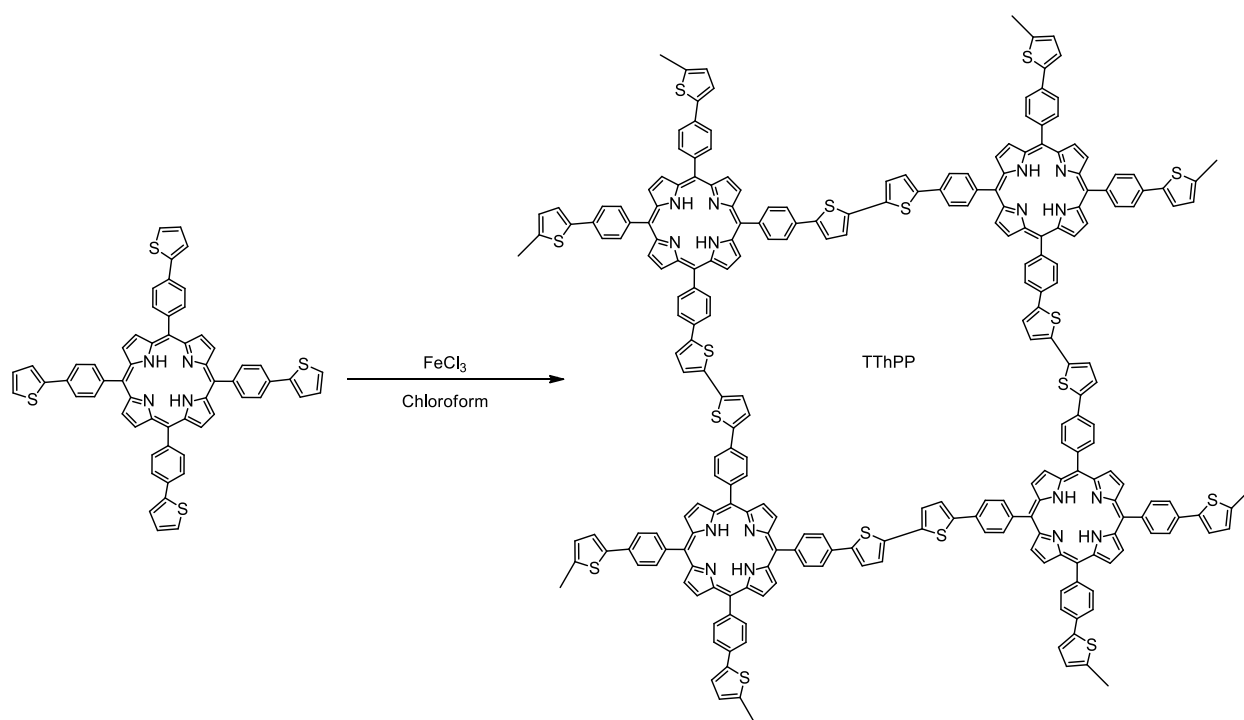


Figure 2.3 Synthetic Scheme of TThP (COF)

Characterization:

Raman Spectroscopy: Band at 1238 cm^{-1} : $\text{C}\alpha\text{--C}\alpha'$ linkage vibration, D-to-G band intensity ratio: 0.66 (high order, low defects).

ATR-IR Spectroscopy: C–C coupling absorption: 1112 cm^{-1} , C–S stretching shift: From 806 cm^{-1} to 799 cm^{-1} .

UV-Vis and Fluorescence Spectroscopy: TThP Soret band: 426 nm , shifts to 448 nm after polymerization, TThP Q-bands: 518 nm and 558 nm , shift to 558 nm and 596 nm . Fluorescence peaks: Shift from 661 nm and 720 nm to 668 nm and 725 nm .

XPS Analysis: $\text{S}2\text{p}_{1/2}$ binding energy: Shift from 165.3 eV to 165.5 eV , $\text{C}1\text{s}$ binding energy: Shift from 284.8 eV to 284.9 eV .

Morphological Characterization: TThPP film thickness (SEM): $1.2\text{ }\mu\text{m}$, Individual nanosheet thickness (AFM): 3.8 nm [48].

In 2016 Shi-Bin Ren et al, was synthesized f HBY-COF, freshly distilled pyrrole and Tetrakis(4-formyloxymethylene)methane were added to propanoic acid. Then, $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ was added into the given mixture. The mixture was re- fluxed under N_2 atmosphere for 2 days at 140°C . A black powder was obtained and washed with ethanol and tetra- hydrofuran. Finally, the obtained product (HBY-COFs) was dried and washed by Soxhlet extraction for 24 hours with dichloro- methane and methanol, respectively. Its yield reached 72% [49].

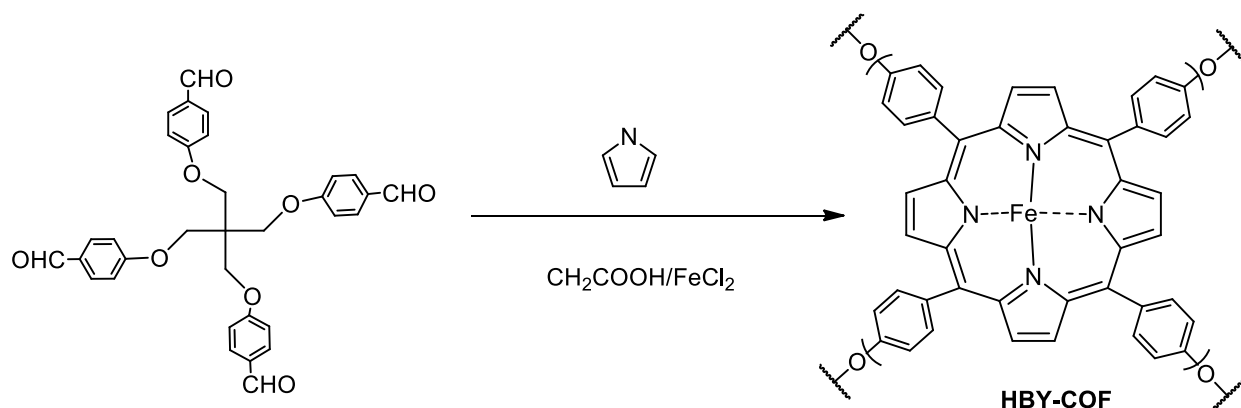


Figure 2.4 Synthetic Scheme of HBY-COF

In 2016 Shi-Bin Ren et al, was also prepared HBY-COF-900: First, HBY-COF was activated under vacuum at 150 °C. Then, 100 mg of the activated HBY-COF was placed in a tube furnace and heated under an argon atmosphere. The HBY-COF powder was heated at 6 °C/min to 300 °C for 1 hour, then at 3 °C/min to 900 °C for another hour. After cooling to room temperature, HBY-COF-900 was obtained and HBY-COF-*t* (*t*=600, 800, 1000 °C): The same procedures were followed as for HBY-COF-900 [49].

Characterization:

Raman Spectra Peaks: D band: 1328 cm⁻¹, G band: 1586 cm⁻¹, Ratio (I_D/I_G): Increases with pyrolysis temperature (indicating increased graphitization).

X-ray Photoelectron Spectroscopy (XPS): N1s Peak: Pyridinic-N: ~398.3 ± 0.1 eV, Graphitic-N: ~401.0 ± 0.1 eV, C1s Peak: ~284.5 eV (graphitic carbon)

Mössbauer Spectroscopy: Isomer Shift (IS): HBY-COF: 0.241 mm/s, HBY-COF-900: 0.443 mm/s, Assignment: Doublet (D1) corresponds to FeN₄ centers, which are identified as the catalytic active sites.

Electrochemical Characterization: Onset Potential for ORR: 0.84 V for HBY-COF-900 (close to 20% Pt/C), H₂O₂ Yield: Below 15% over the potential range of 0.4 V to 0.8 V for HBY-COF-900, Kinetic Current Density: Indicative of a four-electron ORR pathway.

Thermal Analysis: Stability: Up to ~400°C in N₂ atmosphere.

Porosity (Nitrogen Adsorption/Desorption at 77 K): Isotherm Type: IV with a hysteresis loop (medium to high-pressure regions, P/P₀ = 0.4–1.0) [49].

In 2017 Guiqing Lin et al. reported the 3D- Por-COF combines TAPM, p-Por-CHO, o-dichlorobenzene, butanol and aqueous acetic acid in a Pyrex tube. After this the mixture was then degassed and sealed, then heat at 120°C for 7 days. The 3D-Por-COF with a 72% yields was isolated as purple solid by filtration, wash with THF and dichloromethane and at 80°C dry it Shows in scheme [50].

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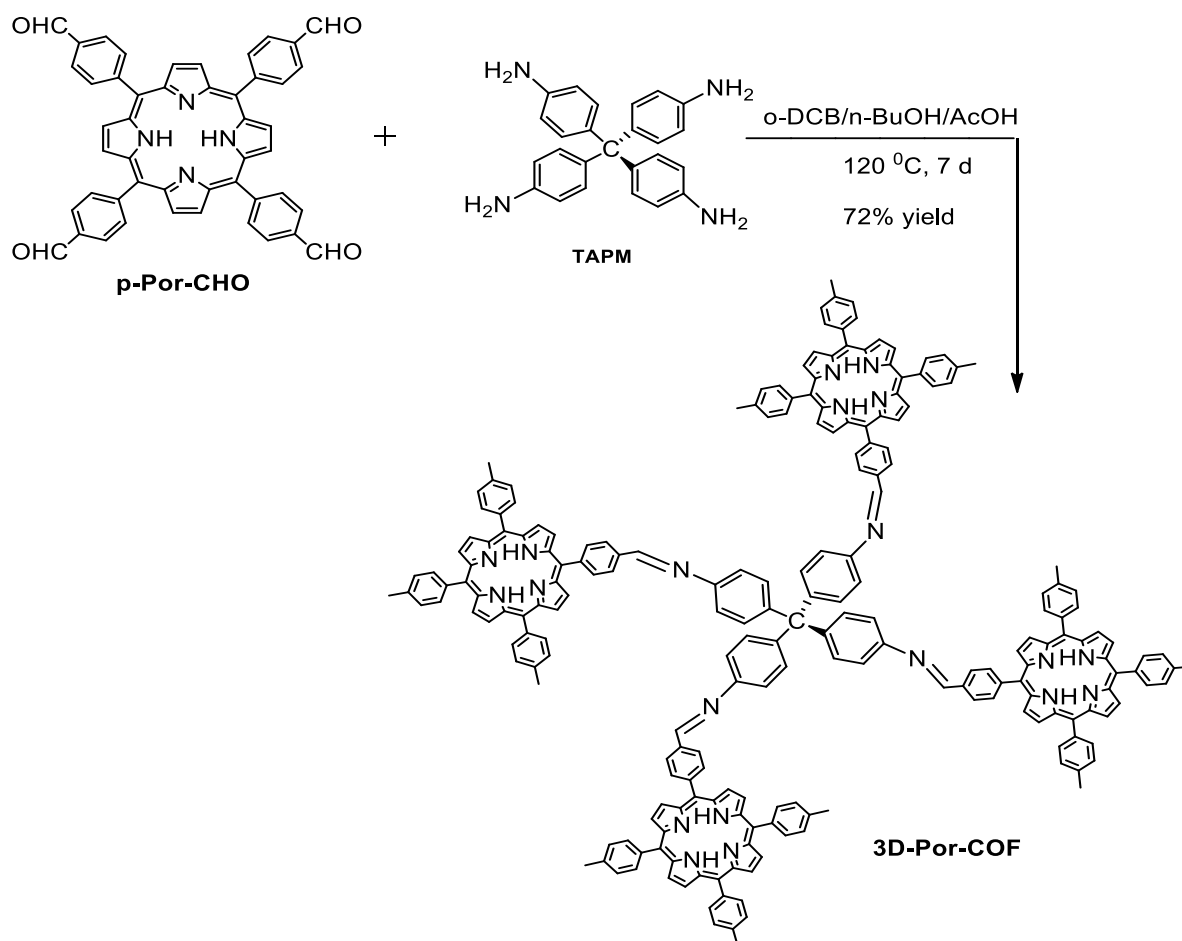


Figure 2.5 Synthetic Scheme of 3D-Por-COF

Characterization:

¹³C NMR spectroscopy: 3D-Por-COF: 158 ppm (C=N group)

FT-IR spectroscopy: 3D-Por-COF: 1627 cm⁻¹ (imine bonds), 3D-CuPor-COF: 1627 cm⁻¹ (imine bonds), 3D-CuPor-COF: disappearance of 3318 cm⁻¹ peak (N-H bond)

PXRD analysis: 3D-Por-COF: peaks at 6.82° and 8.17°, 3D-CuPor-COF: peaks at 6.80° and 7.96°

TGA analysis: Both COFs: high thermal stability up to 500 °C.

Nitrogen sorption isotherms: 3D-Por-COF: BET surface area = 1398 m²/g, 3D-CuPor-COF: BET surface area = 1335 m²/g, Pore size distributions: 3D-Por-COF: peaks at 0.60 and 1.07 nm, 3D-CuPor-COF: peaks at 0.63 and 1.18 nm [50].

In 2017 Subhajit Bhunia et al a 2D COF named SB-PORPy by mixing of dimethyl acetamide (DMAc) and *o*-dichlorobenzene (*o*-DCB). This mixture was added to 5,10,15,20-Tetrakis(4-aminophenyl)porphyrin and 1,3,6,8-tetrakis(4-formylphenyl)pyrene in a Schlenk tube with an acetic acid catalyst. The mixture was sonicated for 1 hour, degassed, sealed, and heated at 120 °C for 7-8 days. The resulting greenish-brown precipitate was collected by centrifugation, washed with THF, and dried under vacuum at 120 °C overnight, yielding SB-PORPy-COF with a 76% yield [51].

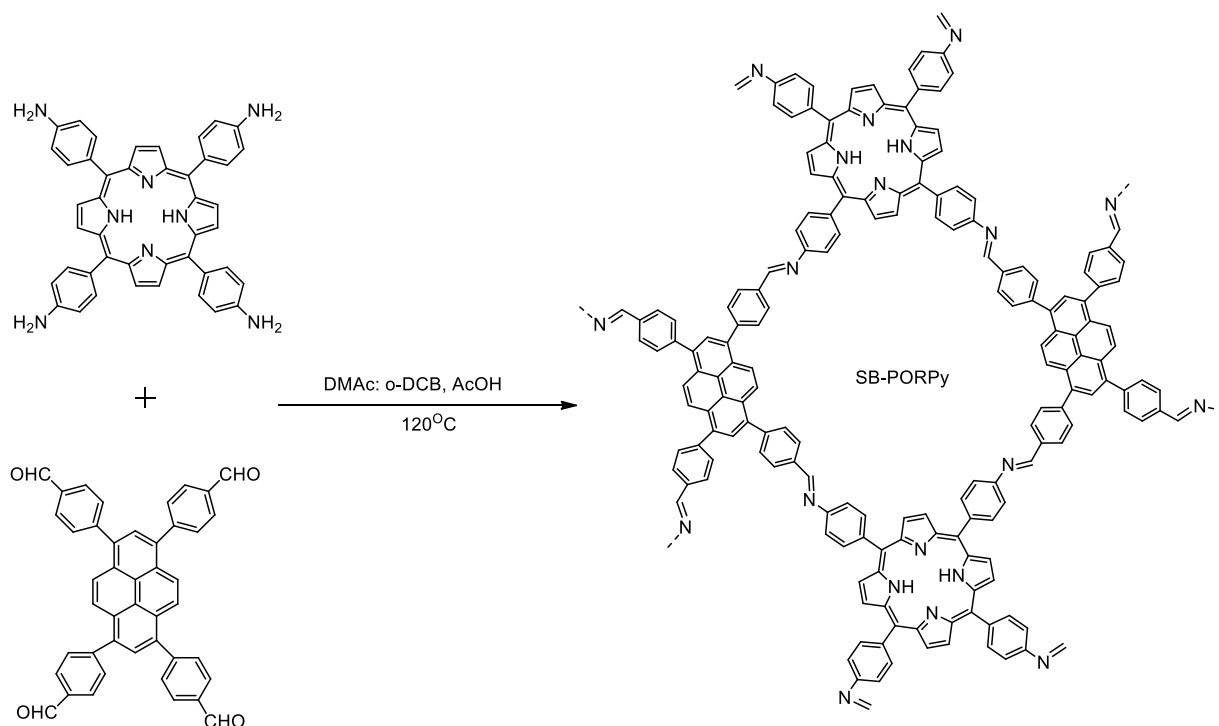


Figure 2.6 Synthetic Scheme of imine-based COF (SB-PORPy)

Characterization:

FT-IR spectroscopy: 601 cm^{-1} (C=N bond stretching modes)

^{13}C CP-MAS NMR spectroscopy: 159.7 ppm (carbon of C=N bond), 147.1 ppm (quaternary carbon of the organic framework), 119.6 ppm (methine carbon of the porphyrin macrocycle), 114.1 ppm (β -pyrrolic carbon), 131.1 ppm (pyrenyl phenyl moiety)

XPS: 399 eV (N1s), 284 eV (C1s), 398 eV (pyrrolic nitrogen), 400 eV (pyrrolic -NH peak)

PXRD analysis: Peaks at $2\theta = 4.9^\circ$ and $\sim 22^\circ$

TGA analysis: Thermal stability up to 400 $^\circ\text{C}$

N₂ adsorption/desorption isotherms: BET surface area: $\sim 869 \text{ m}^2/\text{g}$, Total pore volume: $0.51 \text{ cm}^3/\text{g}$, Pore size distribution: unimodal porosity with a single peak at 1.7 nm [51].

In 2018 Jan Hynek et al. reported isolation of 2D- Por-TTP (COF-366) dissolved 5,10,15,20-tetrakis(4-aminophenyl) porphyrin in ethanol and terephthalaldehyde in mesitylene. Mix these two solutions in a glass ampule with acetic acid. After this mixture was degassed and sealed, then heat at 120 $^\circ\text{C}$ for 72 hours. After cooling 2D- Por-TTP (COF-366), filter the purple solid product, wash with tetrahydrofuran and 1,4-dioxane for 24 hours and expected yield is 58%[21].

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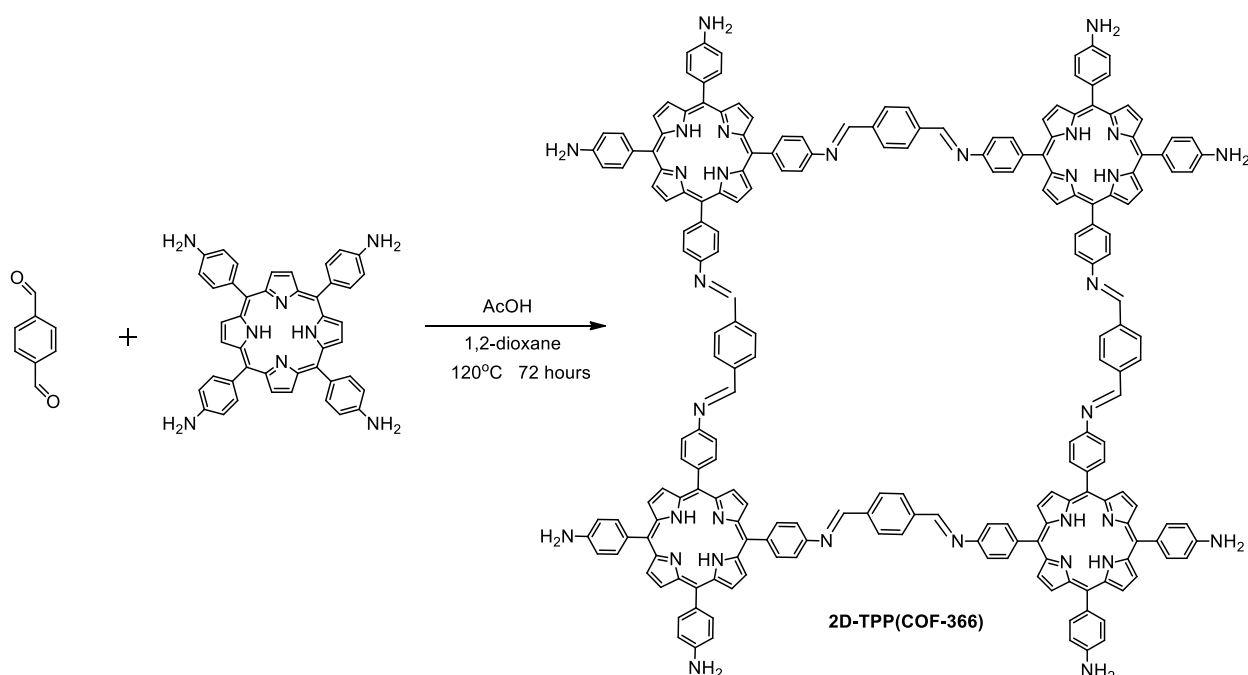


Figure 2.7 Synthetic Scheme of 2D-TPP (COF-366)

Characterization:

PXRD: 2D-TPP: 4.0° and 9.1° , corresponding to a basal spacing of $25.2 \text{ \AA}$

^{13}C CP-MAS NMR spectra: Broad signals: 110-138 ppm, Imine linkages: 158 ppm, Terminal aldehyde groups (2D-TPP): 190 ppm, Aromatic carbon atoms (3D COFs): 142 ppm, Quaternary carbon atoms (3D COFs): 65 ppm

FTIR spectra: -C=N stretching vibration: 1620 cm^{-1} , Aromatic C-H vibrations: $3024\text{--}3055 \text{ cm}^{-1}$, Pyrrole ring vibration: $794\text{--}798 \text{ cm}^{-1}$, Residual aldehyde groups: 1700 cm^{-1} , N-H vibrations: 3380 and 3470 cm^{-1} , Pyrrole N-H stretching (disappears in 3D-PdTPP): 3315 cm^{-1}

UV/vis absorption spectra: Soret bands: broadened and red-shifted compared to monomeric TPP at 413 nm , Q bands: red-shifted

O₂(1 Δg) luminescence: Band: approximately 1270 nm [21].

In 2019 Xu Yan et al, reported p-COF that was synthesized by a simple and facile oil-bath approach using 5,10,15,20-tetrakis(4-aminophenyl) porphyrin (TAPP) and terephthalaldehyde as monomers. Amino groups in TAPP and aldehyde groups (-CHO) in terephthalaldehyde can react with each other via nucleophilic addition-elimination to generate imine groups (C=N-) (Scheme 1). In a typical synthesis procedure, 6 mg of terephthalaldehyde was dissolved in DMSO. Then, TAPP was added to this mixture, and the reaction system was placed in an oil bath at 90°C for 2 days. The product was washed repeatedly with tetrahydrofuran and ethanol and then dried at to yield p-COF[52].

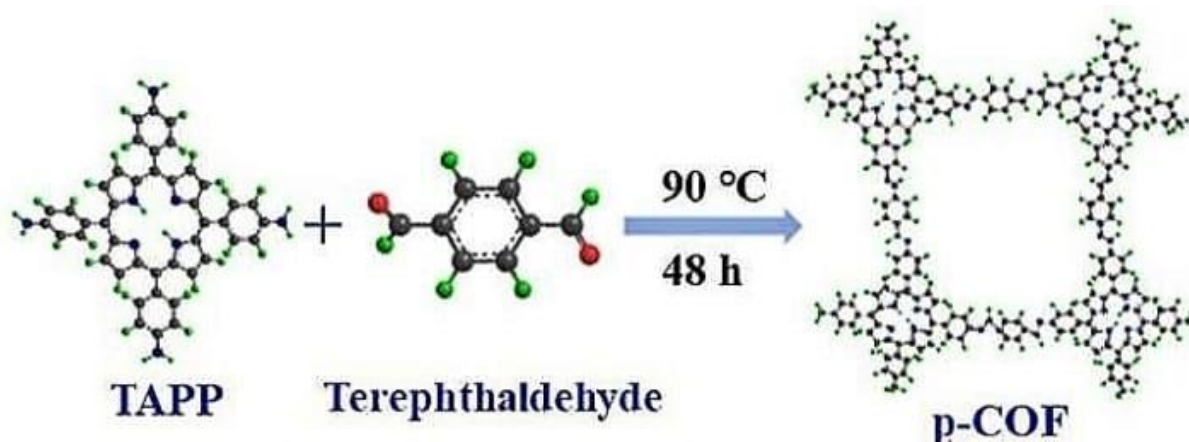


Figure 2.8 Synthetic Scheme of p-COF

Characterization:

T-IR spectroscopy: 1659 cm^{-1} (C=N- stretching of imine groups), 3432 cm^{-1} (O-H stretching mode of crystalline water), 629 cm^{-1} (-OH groups of H_2O molecules)

^{13}C NMR spectroscopy: $\delta=158.85$ (C=N), 149.82, 139.46, 130.21, and 119.49 ppm (other carbon peaks)

XPS: C 1s: 283.7 (C=C), 284.3 (C-C), 285.0 (C-N), 286.3 (C-O), 288.2 (N-C=O), and 290.7 eV ($\pi-\pi^*$), N 1s: 397.4 (atomic $\beta\text{-N}$), 399.1 (pyridinic N), 399.9 (pyrrolic N), and 402.2 eV (pyridinic -(N+ -O-)), O 1s: 531.5 (C=O) and 532.5 eV (C-O), P 2p: ~ 133.5 (P $2p_{3/2}$) and ~ 134.4 eV (P $2p_{1/2}$)

PXRD analysis: Peaks at $2\theta = 26^\circ$, 33° , and 52°

N_2 adsorption/desorption isotherms: BET surface area: $117.2\text{ m}^2/\text{g}$, Total pore volume: $0.23\text{ cm}^3/\text{g}$, Pore size distribution: narrow distribution centered at around 2 nm [52].

In 2019 Xi Zhang et al, reported p-COFs, 5,10,15,20-tetrakis(4-aminophenyl)porphyrin and 1,3-benzenedialdehyde added to a pyrex reaction tube, and the reaction tube was evacuated and sealed with a plastic plug. Then 1,4-dioxane was injected into the reaction tube and dissolved ultrasonically, and acetic acid was slowly dropped into the tube. The reaction tube was evacuated by liquid nitrogen cooling to exhaust bubbles and brought to room temperature. Subsequently, the mixture was heated at 95°C for three days followed by cooling to room temperature. Then, the resulting mixture were collected by centrifugation, and washed three times with tetrahydrofuran (THF) and N, N-dimethylformamide (DMF). After drying the resulting product was obtained as a brown solid [53].

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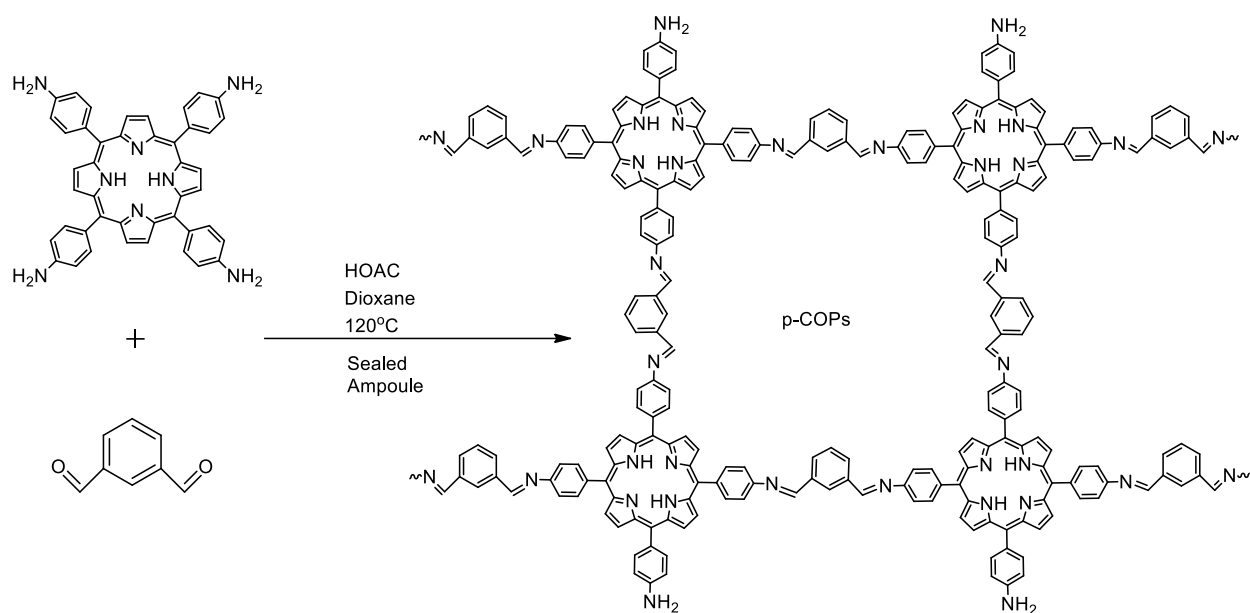


Figure 2.9 Synthetic Scheme of p-COF by condensation

Characterization:

TEM: p-COFs exhibited a thin, flat, and slightly wrinkled layer structure, **SEM:** Confirmed the shape of p-COFs, consistent with TEM results, **TEM:** NiS nanoparticles were synthesized, **TEM:** Ag nanoparticles were synthesized with an average diameter of 50-100 nm.

FT-IR: Strong C=N stretching vibration at 1616-1624 cm⁻¹, indicating imine bonds.

¹³C CP/MAS NMR: Peak at ~145 ppm corresponds to the carbon atom of the C=N bond, **¹³C CP/MAS NMR:** Signals at ~112, 122, 130, and 137 ppm attributed to carbon atoms of phenyl groups.

XRD: Strong and sharp diffraction peak (100) at 2θ = 5°, indicating an ordered crystalline COF material.

SEM: NiS, p-COFs, and AgNPs were modified on the electrode surface in a layer-by-layer manner.

[53].

In 2019 Yong Liu et al. reported porphyrin-COF-1 by mixing of TFBM, TAPP, o-dichlorobenzene solution, mesitylene and aqueous acetic acid. To insure the homogeneous dispersion sonicate for 10 minutes. After this freeze in liquid N₂, degas, seal and heat at 120°C for 7 days. Filter and wash the precipitate with N,N-dimethyl formamide. By using Soxhlet extractor for 24 hours extract with tetrahydrofuran. Dry is 80°C for 24 hours and finally obtain porphyrin-COF-1 as a dark purple powder with a 60% yield. Yong Liu et al also synthesized porphyrin-COF-2 by using TABPP following the same procedures [27].

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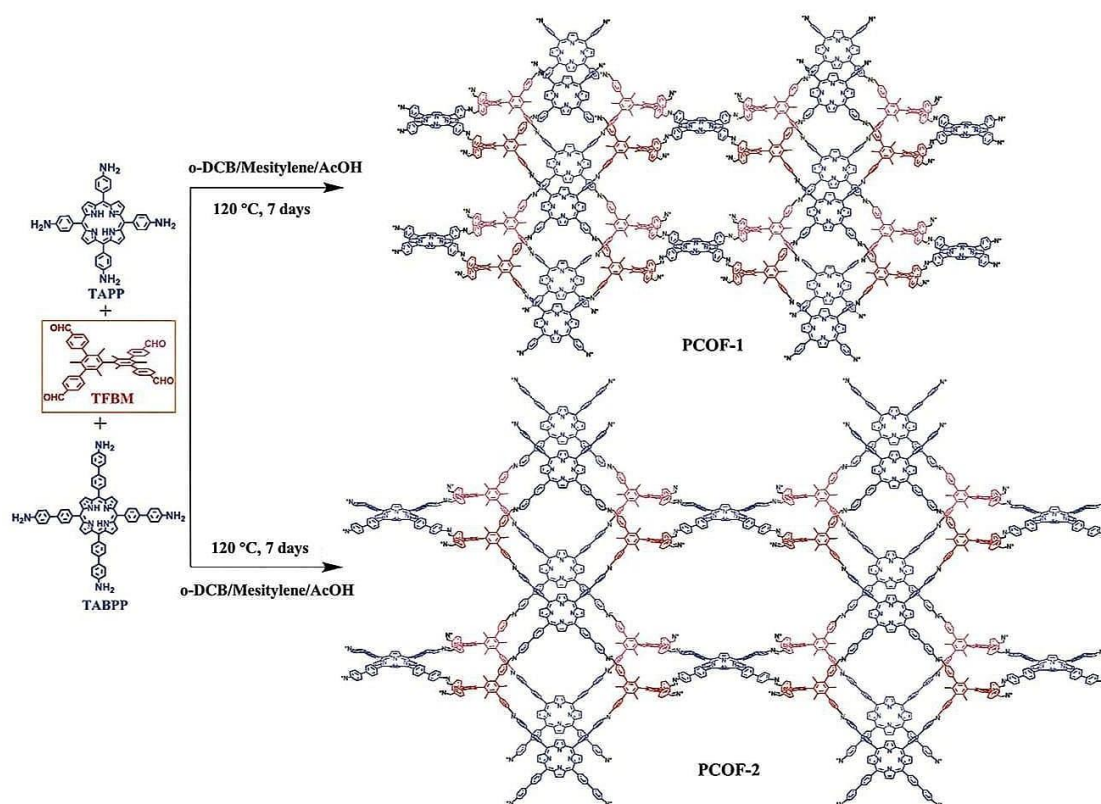
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Figure 2.10 Synthetic Scheme of PCOF-1 and PCOF-2

Characterization:

PXRD: PCOF-1 and PCOF-2 show diffraction peaks corresponding to the (010), (110), (210), (120), (212), and (312) facets.

FT-IR: Weakened signals from the C=O vibration (1701 cm^{-1}) and the appearance of the C=N bond (1622 cm^{-1}).

^{13}C CP/MAS NMR: Resonance signal at 155 ppm from the carbon in the C=N group.

SEM: PCOF-1 and PCOF-2 are agglomerates of tiny spheres.

TEM: Nanopore channels throughout the whole networks of PCOF-1 and PCOF-2.

BET Surface Area: 316 and $234\text{ m}^2\text{ g}^{-1}$ for PCOF-1 and PCOF-2, respectively.

Pore Size Distribution: 2.3 and 4.3 nm for PCOF-1, and 1.9 nm for PCOF-2.

Thermal Stability: Good thermal stability with small mass losses below 420°C .

Chemical Stability: High chemical stability in various solvents [27].

In 2019 Miao Zhang et al. reported one-dimensional COF (named COF-K) in a sealed Pyrex by mixing of 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (POR) and 3,6-diformyl-9-ethylcarbazole (DFEC) solvent used o-dichlorobenzene/n-butanol and aqueous acetic acid. To insure the homogeneous dispersion, sonicate for 10 minutes. After this degas, seal and was heat at 120°C for 3 days. A dark violet precipitate was formed by using Soxhlet extractor for 3 days extract with tetrahydrofuran. Dry it 120°C for 12 hours and One-dimensional COF dark violet powder was obtained in 69% yield Shows in scheme:3 [32].

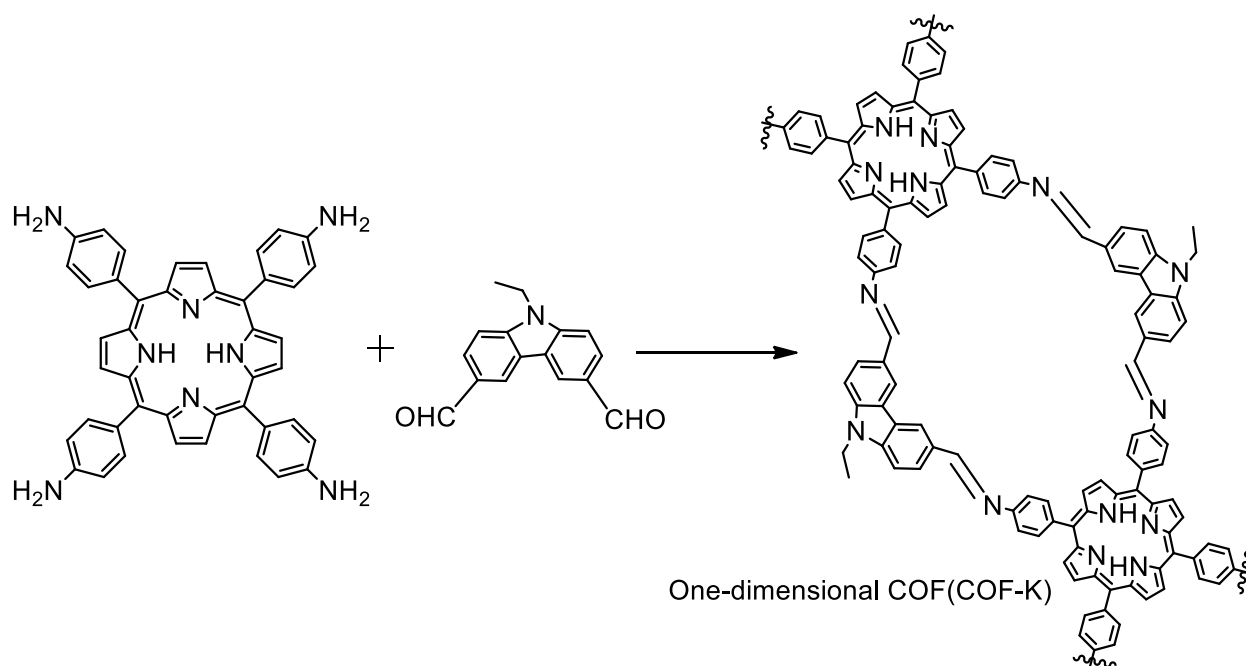


Figure 2.11 Synthetic Scheme of One-Dimensional COF (COF-K)

Characterization:

PXRD: COF-K showed a one-dimensional eclipsed structure with a triclinic P1 space group.

FT-IR: Characteristic C=N stretching vibration at 1620 cm^{-1} .

^{13}C CP-MAS solid-state NMR: Emerging characteristic signal at 160 ppm.

SEM: Flake-like morphology.

TEM: Strip-like layered-sheet arrangement morphology.

BET Surface Area: $626\text{ m}^2\text{ g}^{-1}$.

Pore Size Distribution: 1.25 nm.

Thermal Stability: Up to $480\text{ }^\circ\text{C}$.

CO_2 Adsorption Capacity: 89 mg g^{-1} at 273 K and 1 bar [32].

In 2019 Tae Wu Kim et al, reported two-dimensional Porphyrin-based-covalent organic frameworks (Por-COFs), perylene-3,4,9,10-tetracarboxylic dianhydride and 5,10,15,20-tetrakis(4-aminophenyl)-21H,23H-porphyrin were prepared separately and then linked together by the polymerization process. Perylene-3,4,9,10-tetracarboxylic dianhydride was dissolved in anhydrous pyridine. To this solution, a solution of 5,10,15,20-tetrakis(4-aminophenyl)-21H,23H-porphyrin in pyridine was added. After overnight stirring at $130\text{ }^\circ\text{C}$ in argon atmosphere, the reaction mixture was cooled down to room temperature. The reddish-purple precipitate was filtered and washed with copious amount of distilled water, methanol, and chloroform. After drying in the oven at $110\text{ }^\circ\text{C}$, pale purple solid product was obtained[54].

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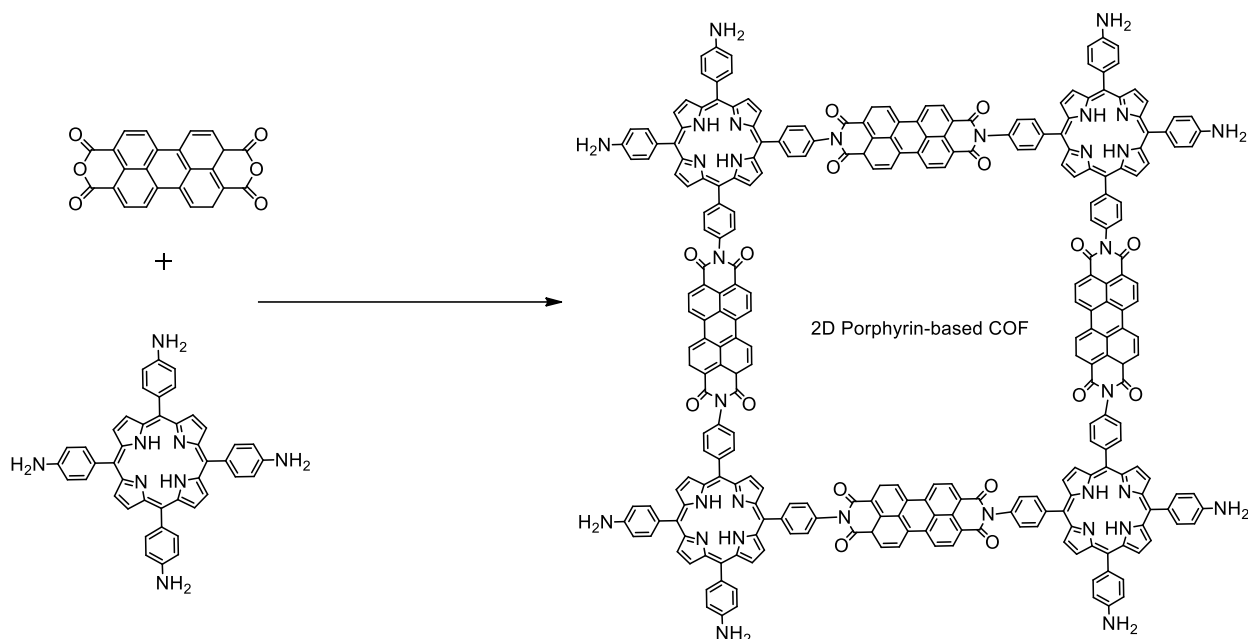


Figure 2.12 Synthetic Scheme of 2D Covalent organic framework (COF)

Characterization:

FT-IR Peaks: C=N stretching vibration: 1620 cm^{-1} , N-H stretching vibration: $3100\text{--}3400\text{ cm}^{-1}$, C=O stretching vibration: 1680 cm^{-1} , Fermi double resonance: 2808 and 2722 cm^{-1}

^{13}C CP-MAS Solid-State NMR Peaks: Characteristic signal of COF-K: 160 ppm , Carbon atom of carbonyl carbon in DFEC: 190 ppm

PXRD Peaks: (100) facet: 4.62° , (210) facet: 8.15° , (120) facet: 11.35° , (300) facet: 13.59° , (230) facet: 18.82° , (001) facet: 21.62°

Vibrational Modes: 76 cm^{-1} : Collective motions including (i) saddling motion of PDI moiety, (ii) in-plane and out-of-plane motions of free-base porphyrin moiety, and (iii) torsional motion of benzene ring that covalently links PDI and free-base porphyrin. 285 cm^{-1} : In-plane distortion of PDI moiety without any rotating motion of benzene linker and in-plane and out-of-plane motions of free-base porphyrin moiety.

Time Constants: A $\rightarrow$ B transition: 124 fs , B $\rightarrow$ C transition: 1.25 ps , Sb state decay: 179 fs , Si state decay: 173 fs , Sd state decay: 1.55 ps [54].

In 2020 Tina Skorjanc et al, reported PV-COF that was synthesized through the Zincke reaction between an amino-derivative of porphyrin and the Zincke salt. In a typical experiment, porphyrin and the Zincke salt were reacted with the mixture of ethanol and water under microwave irradiation at 90°C for 2 hours. The crude solid was purified by washing with ethanol and chloroform, and PV-COF was obtained in high yield (80 mg COF from 50 mg starting porphyrin)[55].

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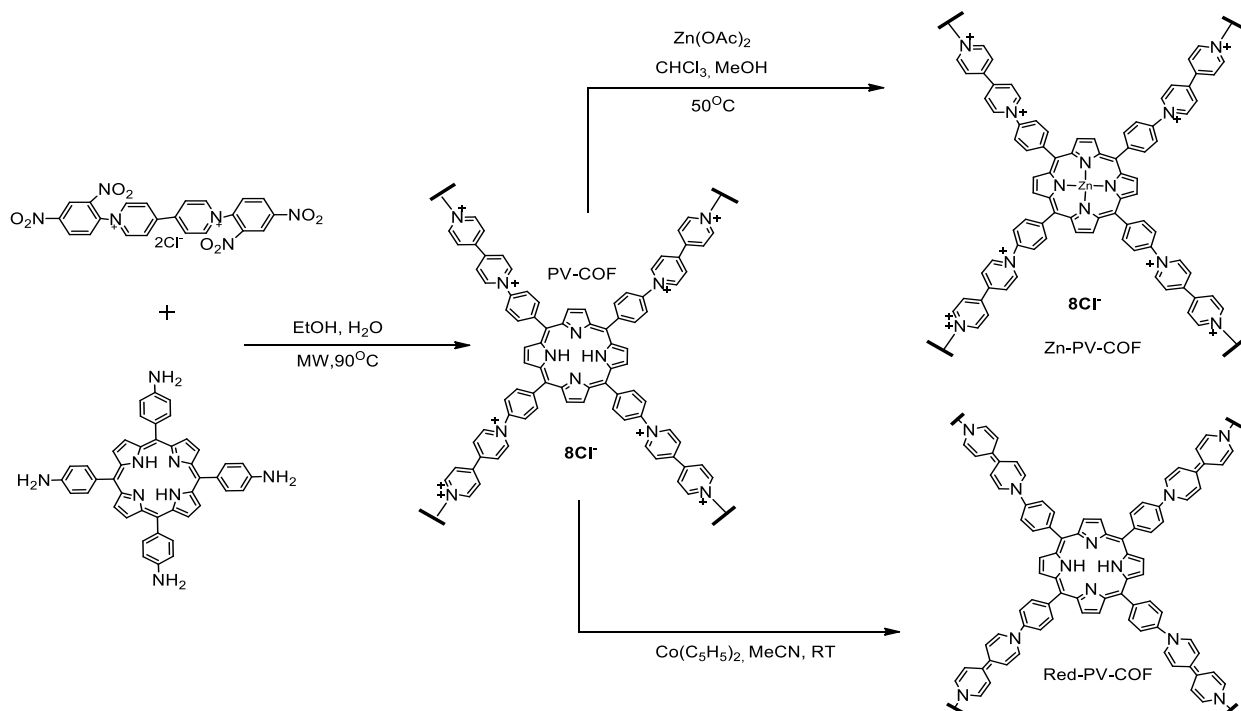


Figure 2.13 Synthetic Scheme of PV-COF (Zn-PV-COF and Red-PV-COF)

Characterization:

FT-IR Peaks: –C]N– vibration: 1603 cm⁻¹, –C]N– vibration (bipyridinium subunit): 1630 cm⁻¹, –N–H vibrations: 3100 cm⁻¹, –C–N– bonds (Zn-PV-COF): 1001 cm⁻¹

¹³C CP-MAS Solid-State NMR Peaks: Pyridyl carbon atoms (Ar–C linker): 142.56 ppm, Phenyl carbons of the porphyrin subunit (Ar–C core): 128.39 ppm, Pyrrole rings of the porphyrin moiety: 123.65 and 149.25 ppm.

PXRD Peaks: (100) plane: 3.86°, (200) plane: 7.39°, (300) plane: 10.90°[55].

In 2020 Xing Kang et al, COF-1 was synthesized via a [3 + 4] condensation reaction between NBC and H₂(TAP) in a mixture of o-DBC, n-butanol, and acetic acid at 120 °C. The product was collected by filtration, washed with anhydrous DMF and acetone, and dried to yield black-purple crystalline powders with an approximately 80% yield [56]. In 2020 Xing Kang et al, COF-2 was also synthesized under similar conditions, except using Cu(TAP) instead of H₂(TAP), yielding crimson crystalline solids with an approximate 75% yield [56].

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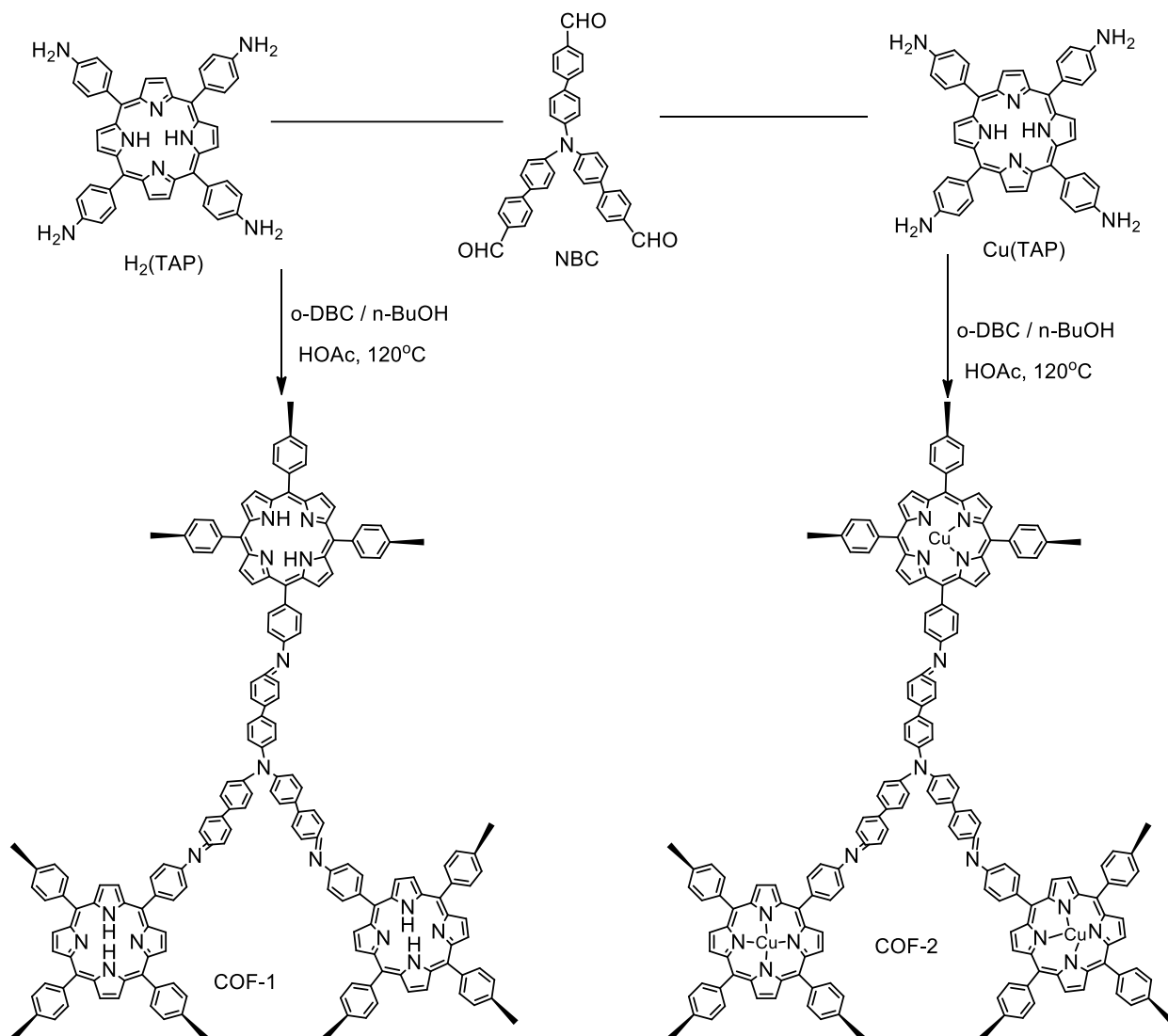


Figure 2.14 Synthetic Scheme of Porphyrin-based COF-1 and COF-2

Characterization:

FT-IR Peaks: --C=N-- vibration: 1615 and 1605 cm^{-1}

^{13}C CP-MAS NMR Peaks: Iminic carbons: 147 ppm (COF-1) and 145 ppm (COF-2)

PXRD Peaks: **COF-1:** (200) plane: 1.65°, (222) plane: 3.40°, (331) plane: 3.95°, (422) plane: 4.73°, (371) plane: 7.11°, (237) plane: 7.91°, (211) plane: 9.20°, (2 $\bar{1}$) plane: 9.89°, (541) plane: 17.1°, (312) plane: 19.9°, (041) plane: 23.1°. **COF-2:** (200) plane: 1.63°, (222) plane: 3.39°, (331) plane: 3.95°, (422) plane: 4.72°, (371) plane: 7.11°, (237) plane: 7.91°, (211) plane: 9.20°, (2 $\bar{1}$) plane: 9.89°, (541) plane: 17.1°, (312) plane: 19.9°, (041) plane: 23.1°[56].

In 2020 Lu-jie Wang et al, Synthesized TAPBB-COF, TAPP, BDB, aqueous acetic acid and o-dichlorobenzene and n-butanol were added to a glass tube. After the ultrasonic mixing was uniform, the tube was rapidly frozen in liquid nitrogen and evacuated, and then the tube was sealed. Incubate at 120°C for 3 days and cooled to

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room temperature at 120 °C for 3 days and cooled to room temperature within 12 h. The black solid was collected by filtration. After extracting with dichloromethane, it was dried in vacuum to give TAPBB-COF 0.080 g, 91.6% of yield [57].

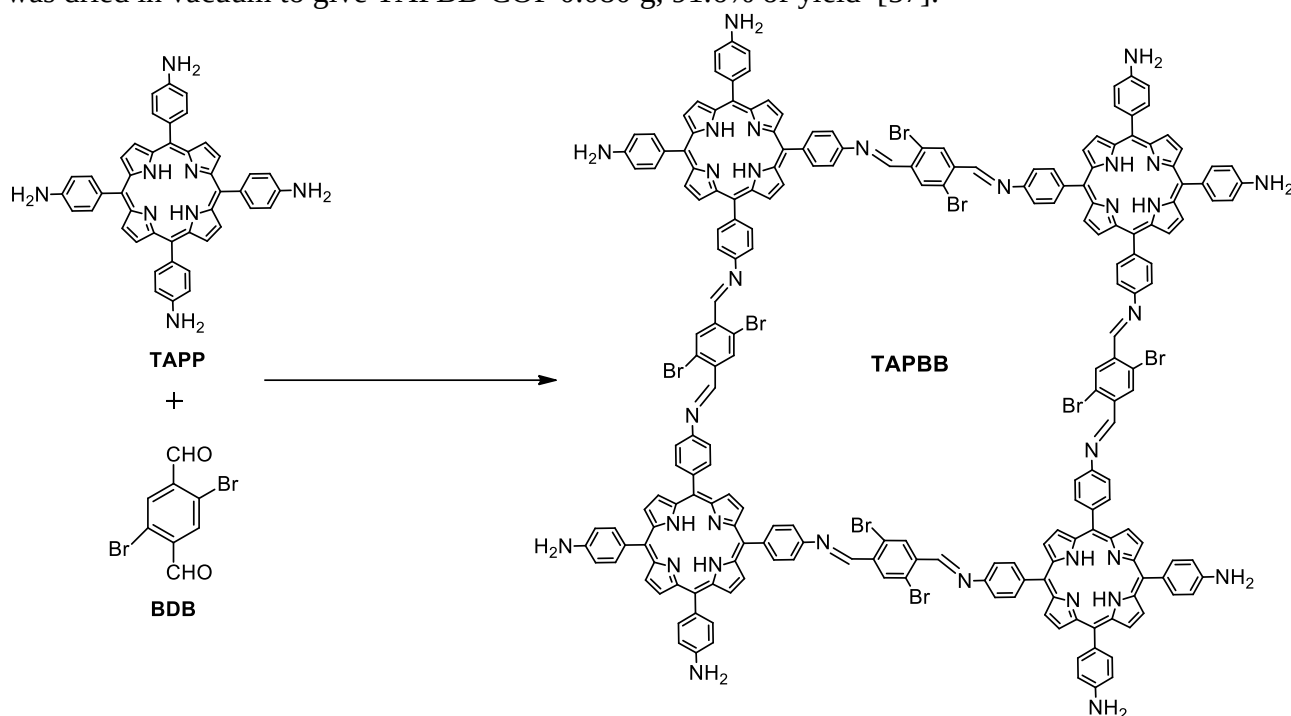


Figure 2.15 Synthetic Scheme of Porphyrin-based COF (TAPBB-COF)

Characterization:

FT-IR Peaks: C=O stretching peak of 2,5-dibromo-terephthalaldehyde (BDB): 1687 cm^{-1} , C=N stretching vibration of the Schiff base structure in TAPBB-COF: 1617 cm^{-1} , C-Br bond in TAPBB-COF: 425 cm^{-1}

^{13}C CP-MAS NMR Peaks: Iminie carbons in COF-1: 147 ppm, Iminie carbons in COF-2: 145 ppm

PXRD Peaks: TAPBB-COF: (1 0 0) face: 3.498°, (11 0) face: 4.978°, (20 0) face: 6.968°, (2 1 0) face: 7.398°, (30 0) face: 10.998°

UV/Vis Diffuse Reflectance Spectrum: COF-366 and TAPBB-COF: almost the same light absorption capacity.

Photoluminescence (PL) Spectrum: g-C₃N₄: PL emission peak at 470 nm, COF-366 and TAPBB-COF: no significant peak found.

Valence Band (VB) and Conduction Band (CB) Values: COF-366: Valence band (VB): +0.86 V, Conduction band (CB): -0.88 V. TAPBB-COF: Valence band (VB): +1.10 V, Conduction band (CB): -0.83 V [57].

In 2020 Yanjie Li et al, synthesized CorMeO-COF, a tube was loaded with H₃TPAPC, DM-CHO, n-butanol, mesitylene, and acetic acid. This mixture was sonicated, degassed, and sealed. It was then heated at 120°C for 72 hours, forming a dark solid. This solid was isolated by centrifugation, cleaned with THF, and dried, yielding a dark powder at 84.7% yield [58]. In 2020 Yanjie Li et al, also synthesized @CorMeO-COF samples, CorMeO-COF was dispersed in THF solutions with various

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metal ions (Ga(III), Al(III), Cr(III), Fe(III), or Cu(II)). The mixture was then filtered, washed with THF, and dried, yielding the M@CorMeO-COF samples [58].

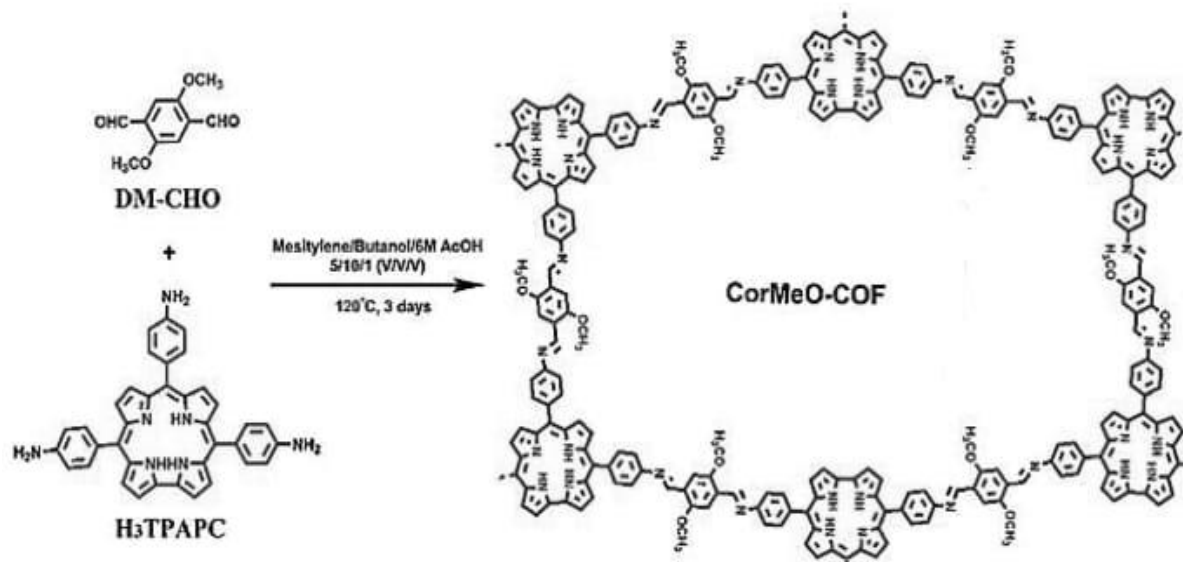


Figure 2.16 Synthetic Scheme of CorMeO-COF (Porphyrin-based COF)

Characterization:

FT-IR Peaks: C=N bond in CorMeO-COF: 1615 cm^{-1} , Out-of-plane bending vibration of original N–H in the macrocycle of CorMeO-COF: 962 cm^{-1}

PXRD Peaks: CorMeO-COF: (100) face: $2\theta = 2.46^\circ$, (110) face: $2\theta = 3.52^\circ$, (120) face: $2\theta = 5.32^\circ$, (220) face: $2\theta = 7.40^\circ$, (001) face: $2\theta = 20.10^\circ$.

XPS Peaks: Schiff-base-type N in CorMeO-COF: 398.8 eV, Corrole-type N in CorMeO-COF: 399.6 eV, Nitro-type N in Cu@CorMeO-COF: 406.3 eV, Cu $2p_{3/2}$ in Cu@CorMeO-COF: 934.7 eV, Cu $2p_{1/2}$ in Cu@CorMeO-COF: 954.5 eV, Cr $2p_{3/2}$ in Cr@CorMeO-COF: 577.1 eV, Cr $2p_{1/2}$ in Cr@CorMeO-COF: 586.5 eV.

Fluorescence Peaks: Maximum emission band of CorMeO-COF: 655 nm (excitation at 425 nm) [58].

In 2020 Yan Zhang et al synthesized H2P-DHPh COF. H2P and DHTA were placed in a glass ampule vessel, followed by the addition of a solution of o-DCB/n-BuOH/ acetic acid. The mixture was sonicated, then flash-frozen in liquid nitrogen, and degassed. sealed, then heated $120\text{ }^\circ\text{C}$ for 3 d. The resulting precipitate was filtered out, washed sequentially with THF and acetone to give a purple-colored powder, which was dried to give the desired product in 70% yield [59]. In 2020 Yan Zhang et al, also synthesized BuBr@H2P-DHPh COF. H2P-DHPh COF and potassium carbonate were weighed into a glass vial, to which dehydrated THF was added. The mixture was heated at reflux, 1,4-dibromobutane was added, and the mixture was maintained at reflux, and stirred. After cooling, the precipitate of the product was collected by filtration, washed with water and acetone. The powder was dried to give the corresponding product of BuBr@H2P-DHPh COF, quantitatively [59]. In 2020 Yan Zhang et al also synthesized AMIMBr@H2P-DHPh COF, the obtained BuBr@H2P-DHPh COF was stirred in 1-methylimidazole under nitrogen protection at $80\text{ }^\circ\text{C}$ for 4 h. After cooling down to room temperature, the solvent was removed. The residue was washed thoroughly with water

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and acetone to get the targeted product AMIMBr@H2P-DHPh COF [59].

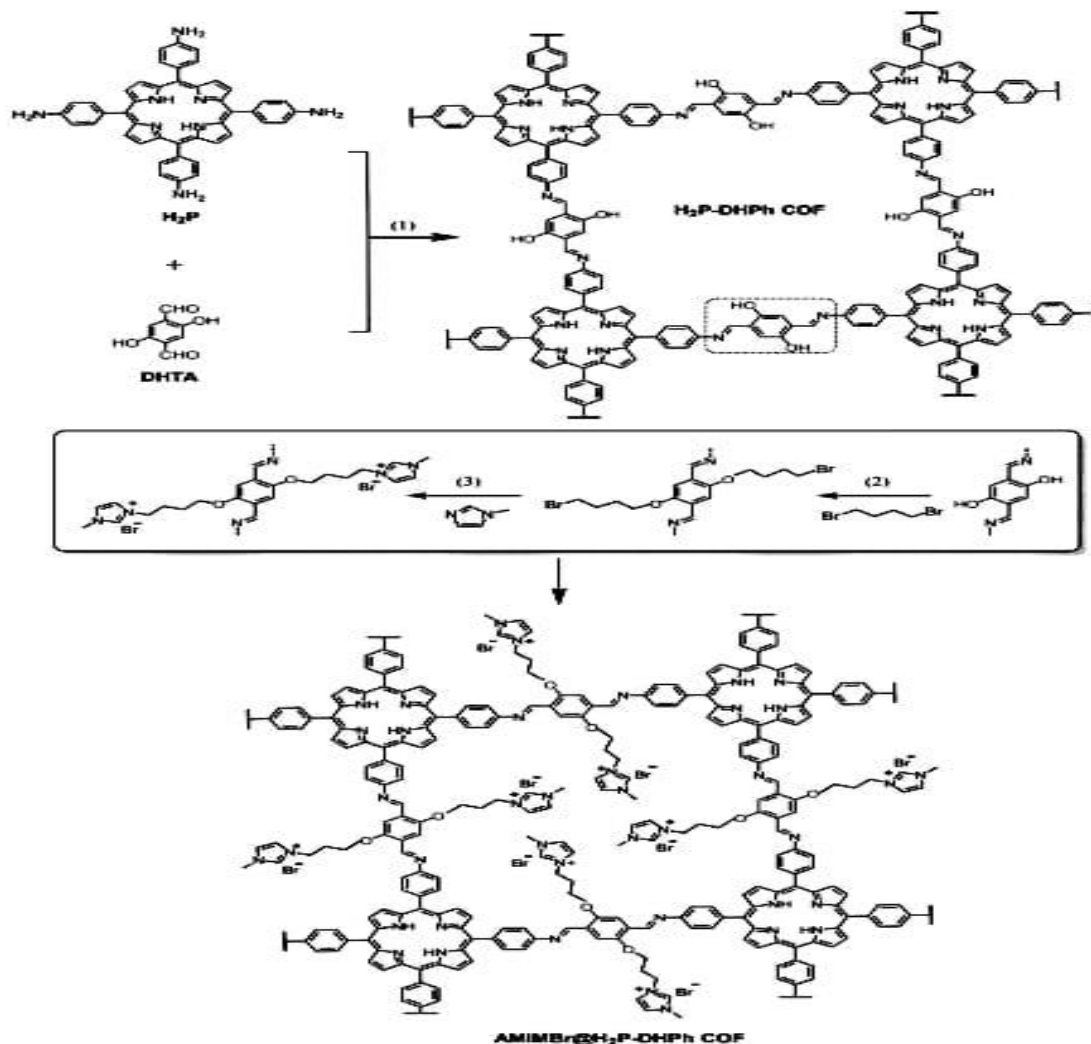


Figure 2.17 Synthetic Scheme of H₂P-DHPh COF (Porphyrin-based COF)

Characterization:

FT-IR Peaks: Imine bonds in H₂P-DHPh COF: 1620 cm⁻¹, C-Br stretching vibrations in BuBr@H₂P-DHPh COF: 660 cm⁻¹, C=C band of the 1-methylimidazole group in AMIMBr@H₂P-DHPh COF: 1556 cm⁻¹

PXRD Peaks: H₂P-DHPh COF: (100) face: 2θ = 3.5°, (200) face: 2θ = 7.1°, (001) face: 2θ = 22.9°

TGA: The COF materials showed good thermal stability, surviving up to 300 °C without decomposing [59].

In 2020 SangWook Park et al, reported the targeted 2D BECOFs. a chloroform solution of SOS surfactant was dropped onto the water surface and a SOS monolayer was achieved with the RSO₄ - polar head groups facing the water phase after the evaporation of chloroform. Subsequently, acidic aqueous solution comprising monomer 1 and HCl was injected into water phase. Due to the electrostatic interactions between protonated porphyrin of monomer 112 and the RSO₄ - head groups of SOS, monomer

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1 was readily adsorbed underneath the SOS monolayer. Next, acidic aqueous solution comprising monomer 2 and HCl was added into the water phase and then diffused to the pre-adsorbed monomer 1. The mixed solution was treated to trigger the polycondensation reaction at the interface. After a freestanding COF film with shiny reflection was observed on the water surface. The resultant 2D BECOF-PP film on water was obtained [60].

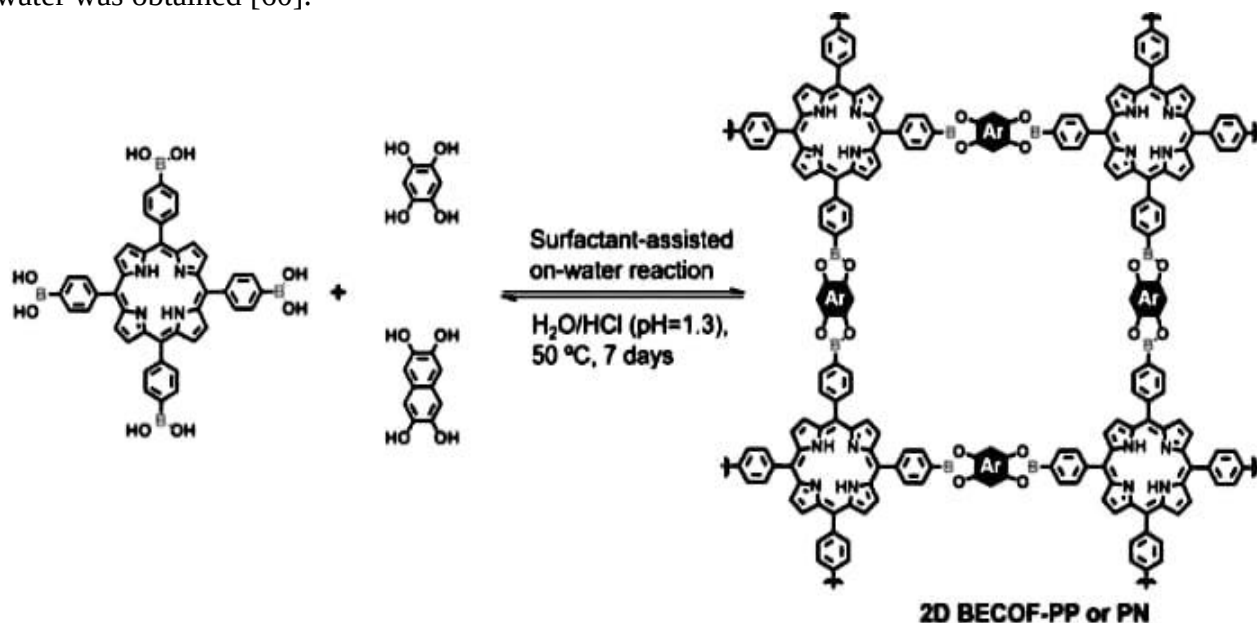


Figure 2.18 Synthetic Scheme of 2D BECOF-PP or PN (Porphyrin-based COF)

Characterization:

SAED Peaks: 2D BECOF-PP: 0.406 nm^{-1} (i.e., $a = b = 2.46 \text{ nm}$, $\gamma = 90^\circ$), 2D BECOF-PN: 0.384 nm^{-1} (i.e., $a = b = 2.60 \text{ nm}$, $\gamma = 90^\circ$)

HR-TEM: 2D BECOF-PP: long-range ordered square lattices with a size of 2.46 nm , 2D BECOF-PN: 2D extended square lattices with a size of 2.60 nm [60].

In 2021 Siqi Chang et al. reported TPE-Por-COF by adding TPE and Porphyrin to a quartz ampoule. After this add mixture of anhydrous toluene and anhydrous acetonitrile, then evacuated, sealed it, and heated at 120°C for 7 days. After the completion obtained product was cooled, washed with acetone, and then dried under vacuum at 90°C for 12 hours. Isolated yield of TPE-Por-COF of was about 78% [36].

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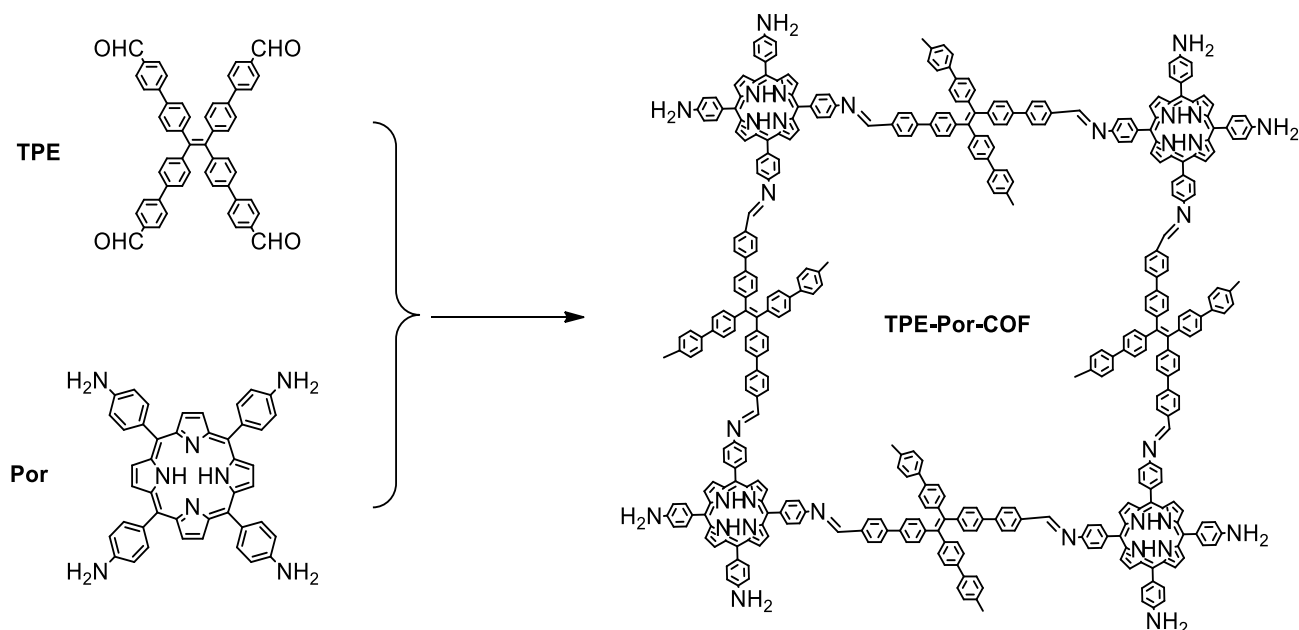
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Figure 2.19 Synthetic Scheme of TPE-Porphyrin-based COF

Characterization:

FT-IR Peaks: C=O: 1669 cm^{-1} (monomers Por and TPE), N-H2: 3194 and 3276 cm^{-1} (monomers Por and TPE), C=N (imine bond): 1650 cm^{-1} (TPE-Por-COF), C=C (benzene ring): 1576 cm^{-1} (monomers Por and TPE), 1567 cm^{-1} (TPE-Por-COF).

^{13}C NMR Peaks: C=N (imine bond): 163.7 ppm , Aromatic carbon: 145.68 - 113.25 ppm , Residual aldehyde groups: 190 ppm .

PXRD Peaks: TPE-Por-COF: 4.38° ((200) crystal plane), 3.26 , 6.12° , 8.82° , 20.06° ((110), (210), (410), (001) crystal planes).

BET Surface Area and Pore Volume: BET specific surface area: $89.14\text{ m}^2\text{ g}^{-1}$, Pore volume: $0.37\text{ cm}^3\text{ g}^{-1}$, Main pore distribution: $\sim 2.89\text{ nm}$ [36].

In 2021 Xingchun Wu et al synthesized TPE-Por-4, a mixture of 5,10,15,20-tetra-(4-aminophenyl) porphyrin, 4,4',4'',4'''-(ethene-1,1,2,2-tetrayl) tetrabenzaldehyde, acetic acid, and a solution of 1,2-dichlorobenzene and 1-butanol was prepared in a Pyrex tube. After degassing with three freeze–pump–thaw cycles, the tube was sealed and heated to 120°C for 3 days, yielding a purple precipitate. This was collected, washed with acetone and dichloromethane, and dried, producing TPE-Por-4 [40]. In 2021 Xingchun Wu et al also synthesized TPE-Por-2, the same procedure as TPE-Por-4 was followed, but starting with 5,15-di(4-aminophenyl)-10,20-diphenylporphyrin and 4,4',4'',4'''-(ethene-1,1,2,2-tetrayl) tetrabenzaldehyde. After washing and drying, TPE-Por-2 was obtained [40].

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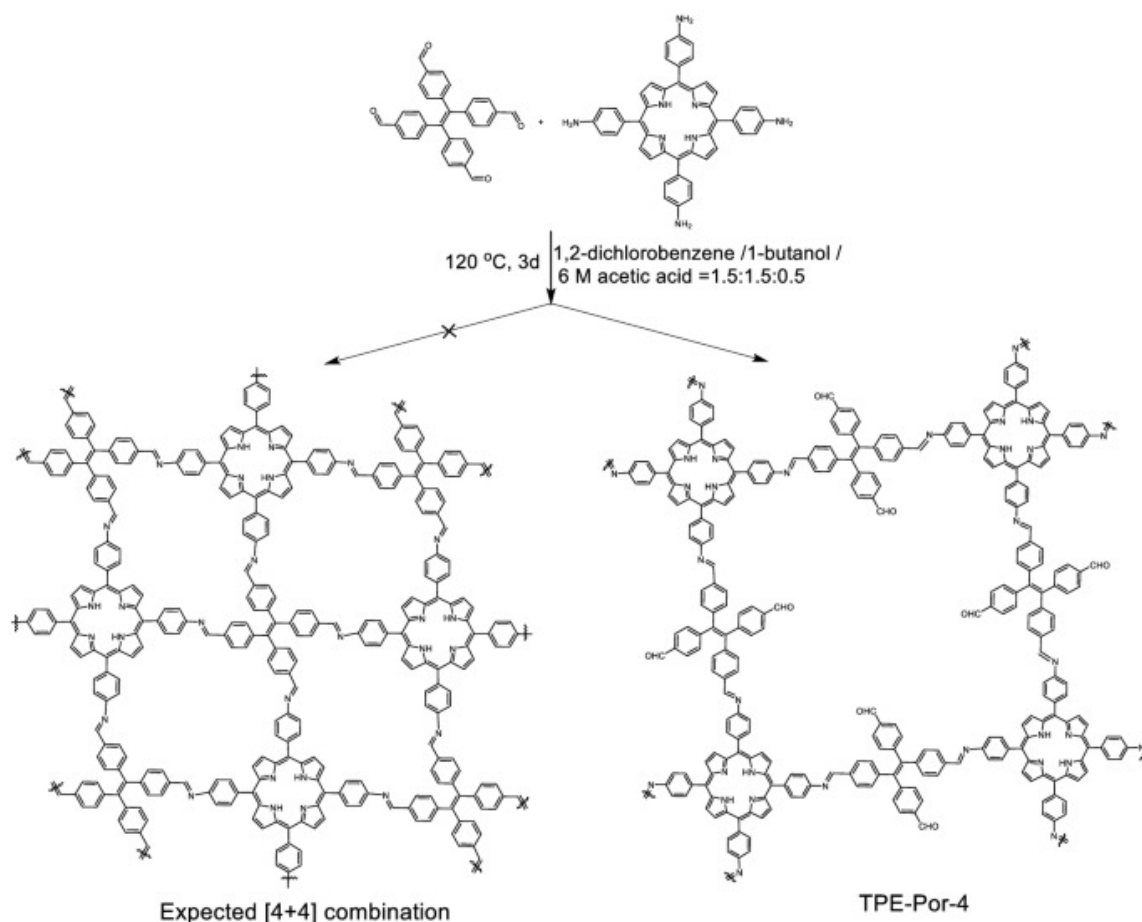


Figure 2.20 Synthetic Scheme of TPE-Por-4 (Porphyrin-based COF)

Characterization:

FT-IR Peaks: Imine linkages: 1620 cm^{-1} and 1622 cm^{-1} , Formyl group: 1697 cm^{-1} (TPE-Por-4), 1700 cm^{-1} (TPE-Por-2).

^{13}C CP/MAS NMR Peaks: Imine groups: 159.3 ppm (TPE-Por-4), 157.3 ppm (TPE-Por-2), Formyl groups: 191.7 ppm.

PXRD Peaks: TPE-Por-4: 5.52, 7.99, 11.18, and 19.69

Photoluminescence Peaks: TPE-Por-4: 686 nm (in tetrahydrofuran), 663-677 nm (in aqueous solution at different pH), TPE-Por-2: 672 nm (in tetrahydrofuran), Monomers TPE, Por-2, and Por-4: 400-640 nm, 692 nm, and 702 nm, respectively [40].

In 2021 Chen Yu et al, synthesized porphyrin-based COF, TAPP and 4,4'-biphenyldicarboxaldehyde were combined with o-dichlorobenzene, n-butyl alcohol, and acetic acid in a Pyrex tube. After sonication, the mixture was flash frozen in liquid nitrogen, followed by three freeze-pump-thaw cycles, then vacuum-sealed. The sealed tube was heated to 120 °C in an oil bath for reaction three days. The product was collected by centrifugation and further purified by washing with methanol and methylene chloride [41].

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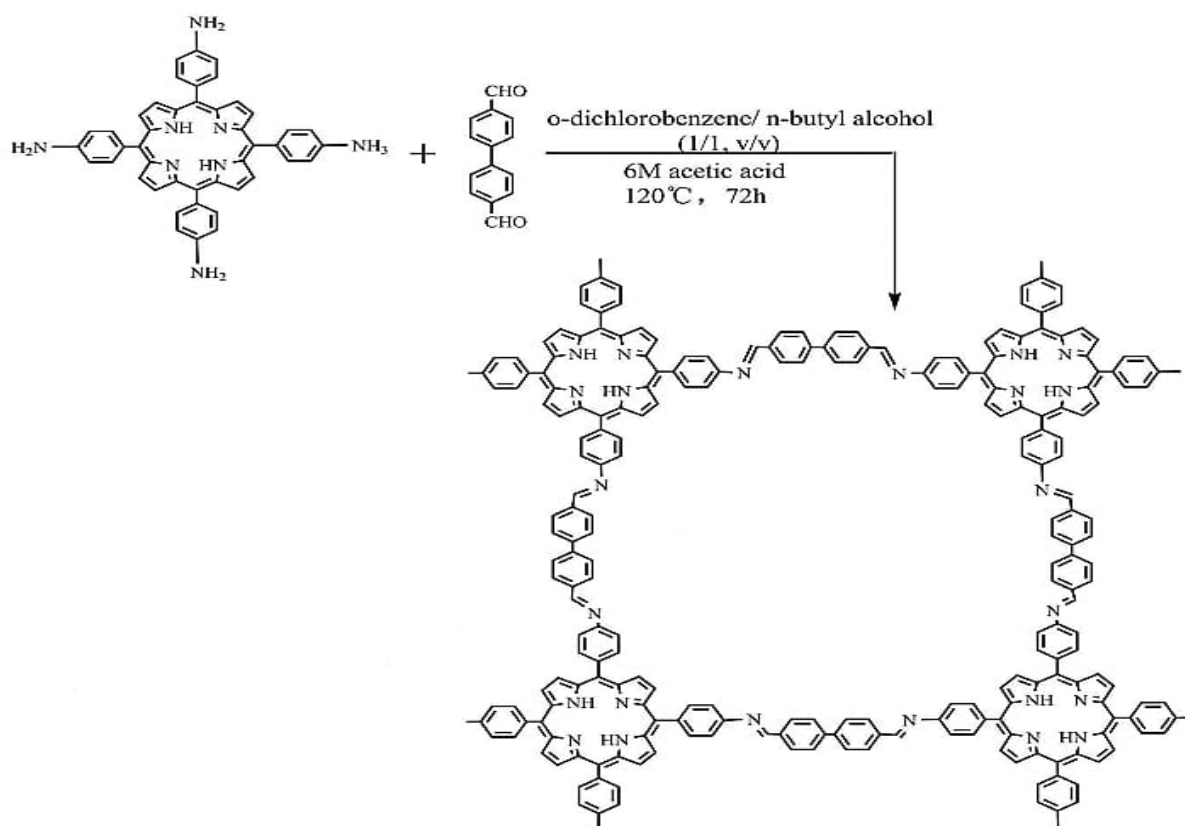


Figure 2.21 Synthetic Scheme of porphyrin-based COF

Characterization:

FESEM (Fiber Coating Morphology): Coating thickness: $\sim 25 \mu\text{m}$

PXRD (Crystalline Nature): Diffraction peaks at $2\theta = 6^\circ$ ((220) plane), Broad reflection around $2\theta = 21^\circ$ (π - π stacking and 2D crystalline structure)

Nitrogen Adsorption-Desorption Isotherms: BET surface area: $566 \text{ m}^2/\text{g}$, Pore volume: $1.07 \text{ cm}^3/\text{g}$ and Average pore width: 8.7 nm

FT-IR (Chemical Structure): 3442 cm^{-1} : N-H stretching vibration, 966 cm^{-1} : Porphyrin skeleton vibrations, 1622 cm^{-1} : C=N stretching vibration and $1468, 1500, 1602 \text{ cm}^{-1}$: Benzene skeleton vibrations

TGA (Thermal Stability): Stable up to 400°C , Significant weight loss observed above 400°C [41].

In 2021 Jing Cui et al, synthesized the p-COF network using a solvothermal method. To prepare it, PDA and TAPP were dissolved in ethanol and 1,3,5-trimethylbenzene mixture with acetic acid as a catalyst. After ultrasonic treatment for 20 min, the reaction continued at 120°C for 72 h. The resulting product was then washed several times with 1,3,5-trimethylbenzene and ethanol, and dried [61].

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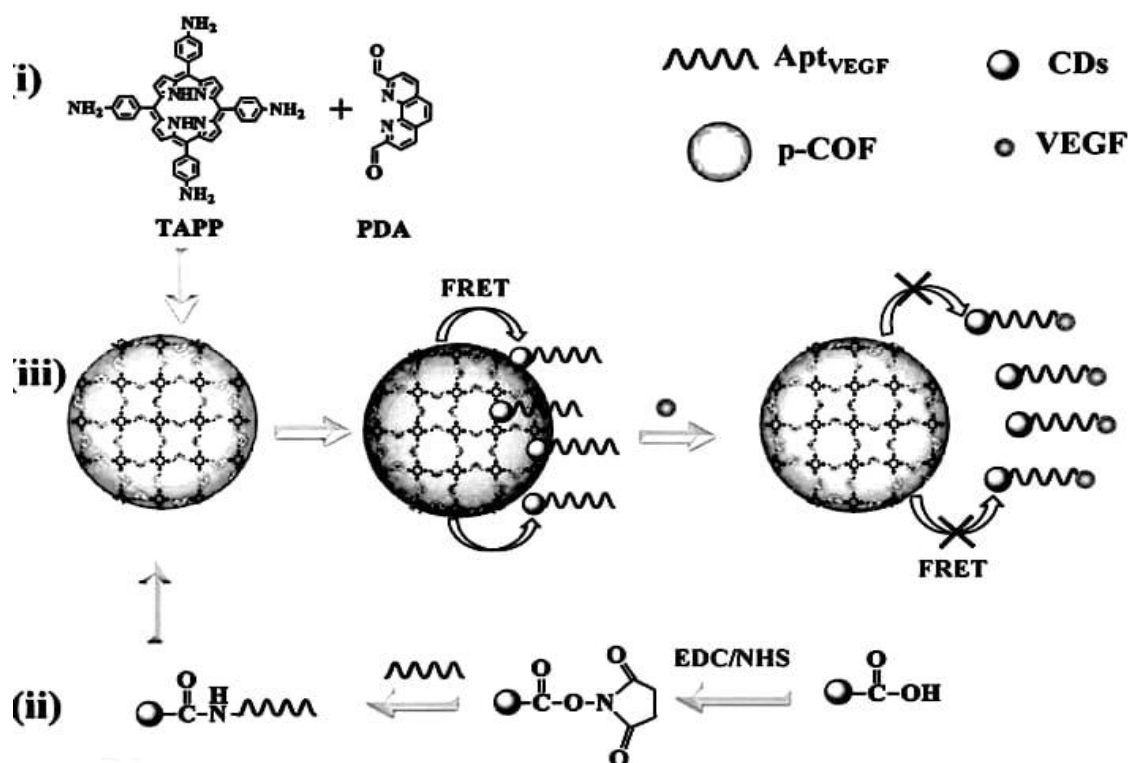


Figure 2.22 Synthetic Scheme of p-COF network (Porphyrin-based COF)

Characterization:

3442 cm^{-1} (N–H stretching vibration), 966 cm^{-1} (porphyrin skeleton vibrations), 1622 cm^{-1} (C=N stretching vibration), 1468 cm^{-1} (benzene skeleton vibrations), 1500 cm^{-1} (benzene skeleton vibrations), 1602 cm^{-1} (benzene skeleton vibrations), 6° ((220) plane, PXRD) [61].

In 2022 Yaling Li et al, synthesized TADP–COF, 5,10,15,20-Tetrakis(4-aminophenyl)porphyrin (TAPP), 2,5-dihydroxyterephthalaldehyde(Dha), and 1,4-phthalaldehyde(PA) were mixed in a glass ampule with a solution of 1,2-dichlorobenzene(o-DCB) and n-butanol. The mixture was sonicated, flash frozen with liquid nitrogen, and acetic acid was added. The system was degassed by freeze-pump-thaw cycles, sealed, and heated at 120 C for 3 days. The resulting purple COF powder was filtered, washed with THF, DMF, and acetone, and dried, yielding 83% [62].

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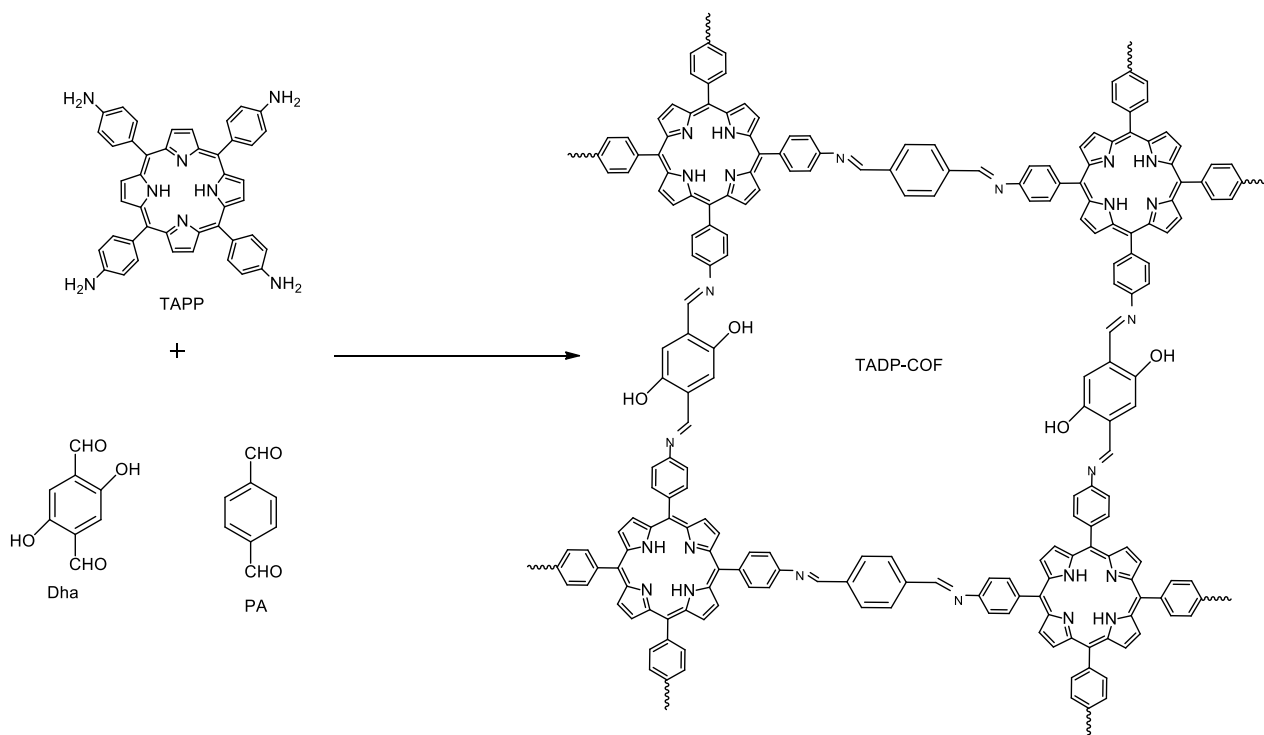


Figure 2.23 Synthetic Scheme of TADP-COF (Porphyrin-based COF)

Characterization:

FT-IR Peaks: -NH₂: ~3352 and 3316 cm⁻¹, -CHO: ~1660 cm⁻¹, C=N linkages: ~1612 cm⁻¹, Imine linkage: 1605 cm⁻¹

¹³C Solid-State NMR Peak: Carbon of the imine linkages: ~150.4 ppm.

XPS Peaks: N 1s: TADP-COF: 398.1, 399.2, and 400.1 eV, Cu(II)@TADP-COF: 398.9 eV and Pd(II)/Cu(II)@TADP-COF: 398.6 and 400.0 eV. 2. O 1s: TADP-COF: 532.9 eV, Cu(II)@TADP-COF: 532.6 eV and Pd(II)/Cu(II)@TADP-COF: 531.5, 532.5, and 534.3 eV. Cu 2p: Cu(II)@TADP-COF: shifted downfield. Pd 3d: Pd(II)/Cu(II)@TADP-COF: shifted downfield.

PXRD Peaks: TADP-COF: 3.4, 6.9, and 23.5, Cu(II)@TADP-COF and Pd(II)/Cu(II)@TADP-COF: similar to TADP-COF [63].

In 2023 Ting He et al, synthesized COF1 by reacting 5,5'-(porphyrin-5,15-diyl)diisophthalaldehyde (P-CHO) with 4,4'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)dianiline (Bt-NH₂) in a 1,2-dichlorobenzene and 1-butanol, using acetic acid as a catalyst at 120 °C for 3 days, giving an 88% yield. By replacing Bt-NH₂ with different amines—4,4'-(pyridazine-3,6-diyl)dianiline (Pz-NH₂), [1,1':4',1''-terphenyl]-4,4''-diamine (TP-NH₂), or 2',5'-dimethoxy-[1,1':4',1''-terphenyl]-4,4''-diamine (DMTP-NH₂)—under the same conditions, COF2, COF3, and COF4 were obtained. COF5 was produced using a different aldehyde, 5,5'-(10,20-bis(perfluorophenyl)porphyrin-5,15-diyl)diisophthalaldehyde (PF₅-CHO)[64].

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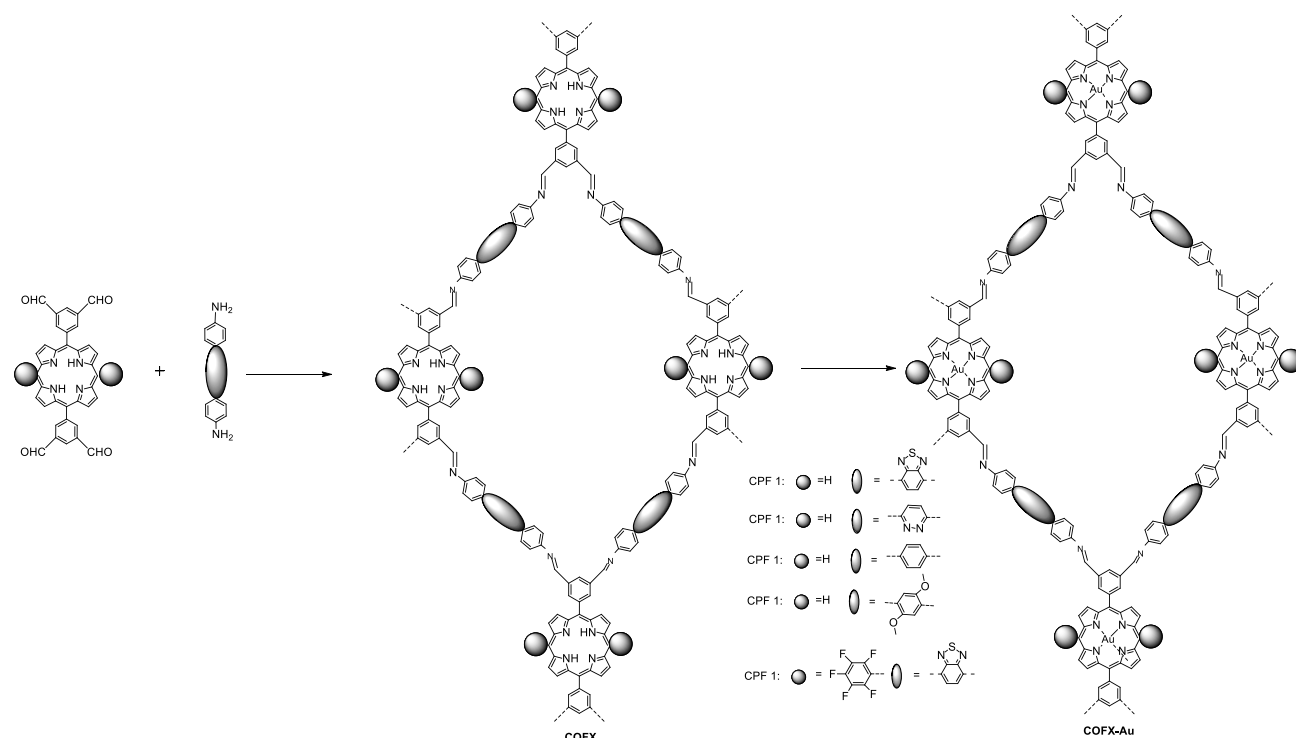


Figure 2.24 Synthetic Scheme of COFX and COFX-Au (Porphyrin-based COF)

Characterization:

FT-IR Peaks: N–H stretching vibration: $3400\text{--}3500\text{ cm}^{-1}$, C=N stretching vibration: 1620 cm^{-1} , N–H stretching vibration: 3430 cm^{-1} , H–N–H bending vibration: 1480 cm^{-1} , H₂N–NH₂ stretching vibration: 1145 cm^{-1}

PXRD Peaks: OF1: 3.0° , 3.8° , 6.0° , 7.6° , and 27.2°

UV-Vis absorption edge: 700 nm

Optical band gaps (E_g): 1.51–1.54 eV

Photoluminescence (PL) peaks: 640–680 and 690–730 nm [64].

In 2023 Sara Oudi et al, synthesized Porph-UOZ-COF, 7 mg of DHPP and DBBA were added to a Pyrex vial containing a mixture of 1,4-dioxane and mesitylene. The vial was degassed under vacuum and heated in an oil bath at 120°C for 5 days. The solid product was collected by centrifugation, washed several times with acetone, and dried [65].

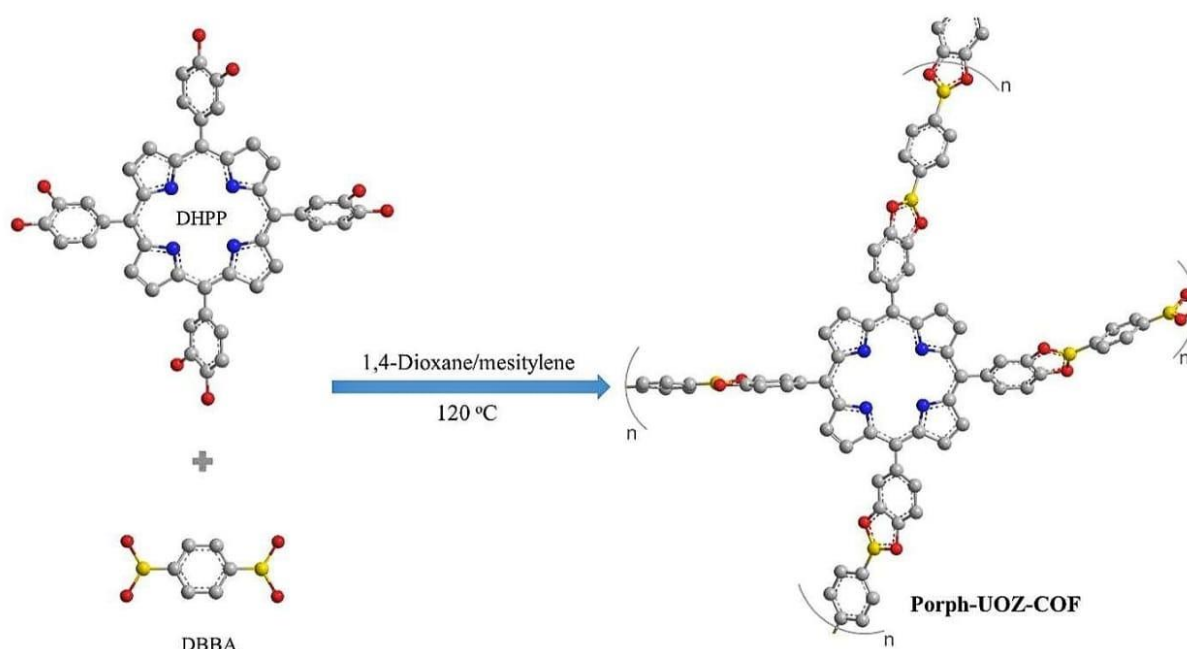


Figure 2.25 Synthetic Scheme of Porph-UOZ-COF (Porphyrin-based COF)

Characterization:

FT-IR Peaks: C-O bonds: 1115 cm^{-1} , B-O stretching: 1344 cm^{-1}

PXRD Peaks: Porph-UOZ-COF: 7.5° and 21°

XPS Peaks: C 1s: 284.6, 285.2, and 288.2 eV, N 1s: 400.1 eV, O 1s: 532.1 and 533.2 eV, B 1s: 191.7 eV [65].

In 2023 Wenyan Ji et al, synthesized COFs, TAPP and dialdehyde monomers were mixed with a solvent containing aqueous acetic acid. The mixture was sonicated in Pyrex tube, which was then degassed, flame-sealed, and heated at 120°C for 72 h. The resulting precipitate COF, including DEG-HEP-COF, DEG-COF, HEP-COF, and DEG+HEP-COF was collected [66].

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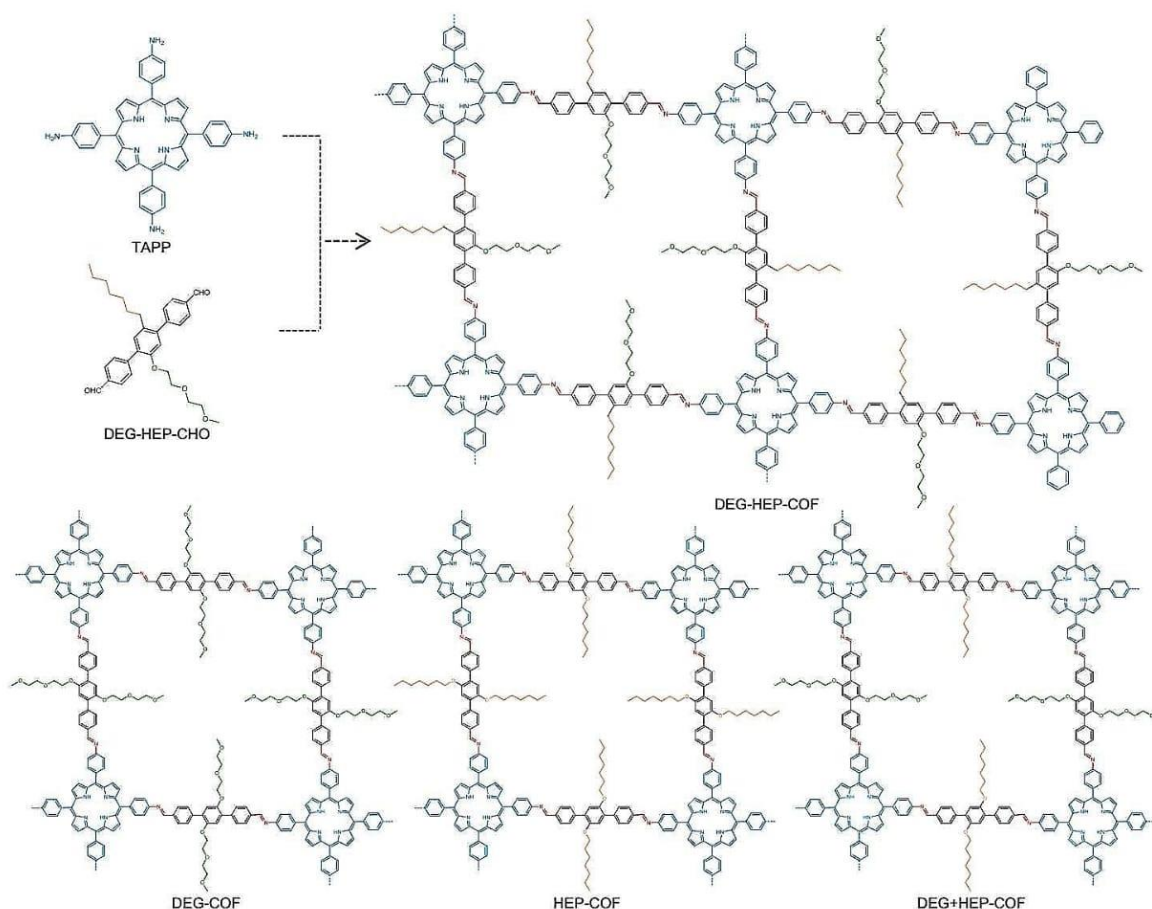


Figure 2.26 Synthetic Scheme of DEG-HEP-COF, DEG-COF, HEP-COF, and DEG+HEP-COF (Porphyrin-based COFs)

Characterization:

FT-IR Peaks: C=N bond: 1601 cm^{-1} , C-O bonds: 1115 cm^{-1} , B-O stretching: 1344 cm^{-1} , N-H and C=O bonds: 3320 and 1690 cm^{-1}

PXRD Peaks: DEG-HEP-COF: 3.2° (110 facet), 3.7° (020 facet), 4.7° (120 facet), 5.4° (200 facet), 6.1° (210 facet), 6.5° (220 facet), 7.3° (001 facet), and 7.9° (111 facet). DEG-COF: 3.2° . HEP-COF: 5.9° and 20.7° . DEG+HEP-COF: 3.4° , 6.7° , 7.4° , and 23.2° .

Solid-State ^{13}C NMR Peaks: Carbon in C=N bond: 158 ppm, Aromatic carbons in benzene ring and porphyrin: 152, 149, 140, 132, 129, 119, and 115 ppm, Alkoxy carbon (C-O): 56–72 ppm, Alkyl carbon (C-C): 11–31 ppm [66].

In 2023 Wen-Yan Li et al, synthesized disulfide-COF, named DSPP-COF, by reacting 5,10,15,20-tetrakis(4-formylphenyl)porphyrin (TFPP) with 4-(2-(4-aminophenyl)disulfanyl)benzenamine (APDSBA) under solvothermal conditions at 120°C , for 3 days. The reaction was carried out in a mixture of 1,2-dichlorobenzene, n-butanol (n-BuOH), and acetic acid (HOAc) at specific temperature, yielding 79% [67].

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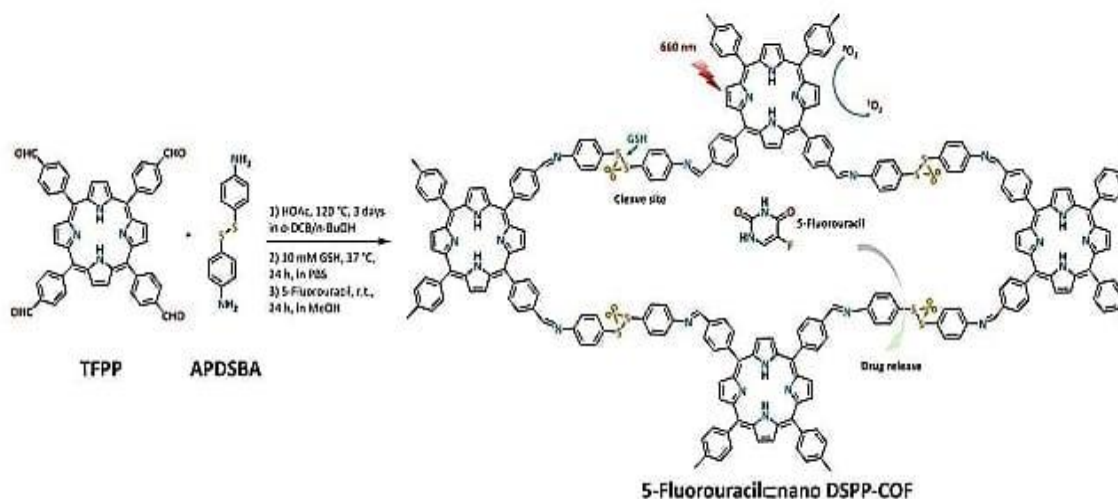


Figure 2.27 Synthetic Scheme of DSPP-COF (Porphyrin-based COF)

Characterization:

FT-IR Peaks: C=N bond: 1601 cm^{-1} , C-O bonds: 1115 cm^{-1}

PXRD Peaks: DSPP-COF: 4.4° , 6.2° , and 8.6°

Solid-State ^{13}C NMR Peaks: Carbon in C=N bond: 158 ppm, Aromatic carbons in benzene ring and porphyrin: 152, 149, 140, 132, 129, 119, and 115 ppm, Alkoxy carbon (–C–O–): 56–72 ppm, Alkyl carbon (–C–C–): 11–31 ppm [67].

2.2. Synthesis of Metal-Porphyrin based-COF:

In 2015 Venkata S, et al. reported PyP COF by mixing of meso-Tetra(4-aminophenyl)porphineCu(II) and naphthalenetetracarboxylic dianhydride. The mixture was stirred at 0°C in 20 mL m-cresol under N_2 flow until all the solids dissolved. The mixture was heated to r.t, and stirred at this temperature overnight. f isoquinoline was added and stirred at 80°C for four hours, 180°C for 16 h. The reaction mixture was cooled down, and the precipitate was isolated by filtration, washed with DMF. Then the solid was grounded into a fine powder, which was subsequently washed copiously with methanol/acetone to give a purple powder. Yield: 64% [68].

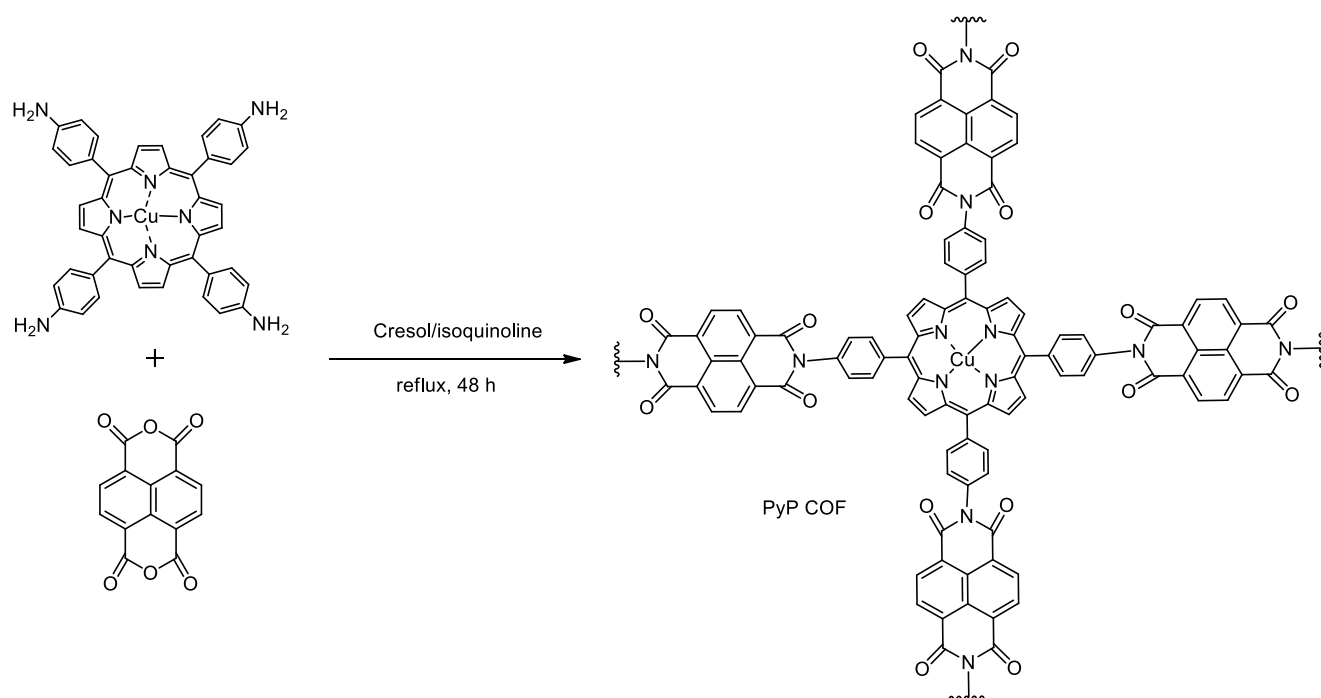


Figure 2.28 Synthetic Scheme of PyP COF (Metal-Porphyrin-based COF)

Characterization:

FT-IR Peaks: N–H stretching frequencies: disappeared, N–Cu vibration band: 995 cm^{-1} , C=O group: 1780 and 1716 cm^{-1} , C–N–C linkages: 1349 cm^{-1}

UV-Vis Peaks: Soret band: $420\text{--}454\text{ nm}$, Q bands: 560 , 590 , and 620 nm .

Solid-State ^{13}C NMR Peaks: N–C=O imide bonds: $\delta = 151\text{ ppm}$, Aromatic carbon atoms of PyP: $\delta = 131.3$ and 93.7 ppm .

TGA: 10% weight loss at 370°C , Gradual decomposition at 500°C

Gas Adsorption Peaks: N_2 uptake: $423\text{ m}^2\text{ g}^{-1}$ (BET surface area), Pore size distribution: $6\text{ \AA}$ and $11\text{ \AA}$, Pore volume: $0.1\text{ cm}^3\text{ g}^{-1}$, CO_2 uptake: $3.4\text{ wt\%}$ at $273\text{ K}/1\text{ bar}$, H_2 uptake: $0.4\text{ wt\%}$ at $77\text{ K}/1\text{ bar}$, CH_4 uptake: $0.32\text{ wt\%}$ at $273\text{ K}/1\text{ bar}$ [68].

In 2015 Xiong Chen et al. synthesized the metal-porphyrin-based covalent organic frameworks (COFs) by solvothermal polycondensation using 5,10,15,20-tetrakis(4'-tetraphenylamino) metalloporphyrins (MP, where $\text{M} = \text{Cu}$, Ni , or Zn) as vertices and various aldehydes as edges, such as 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzaldehyde (PyTTBA), 2,3-dihydroxyterephthalaldehyde (2,3-DHTA), 3,7-dihydroxynaphthalene-2,6-dicarbaldehyde (DHNADCA), or [2,2'-bipyridine]-5,5'-dicarbaldehyde (2,2'-BPyDCA), in the presence of aqueous acetic acid at 120°C . This method produced eight different metal-porphyrin-based COFs, including MP-PyTTPh, MP-2,3-DHPh ($\text{M} = \text{Cu}$, Ni , and Zn), CuP-DHNAPh, and CuP-BPyPh COFs, were synthesized all in high yields [69].

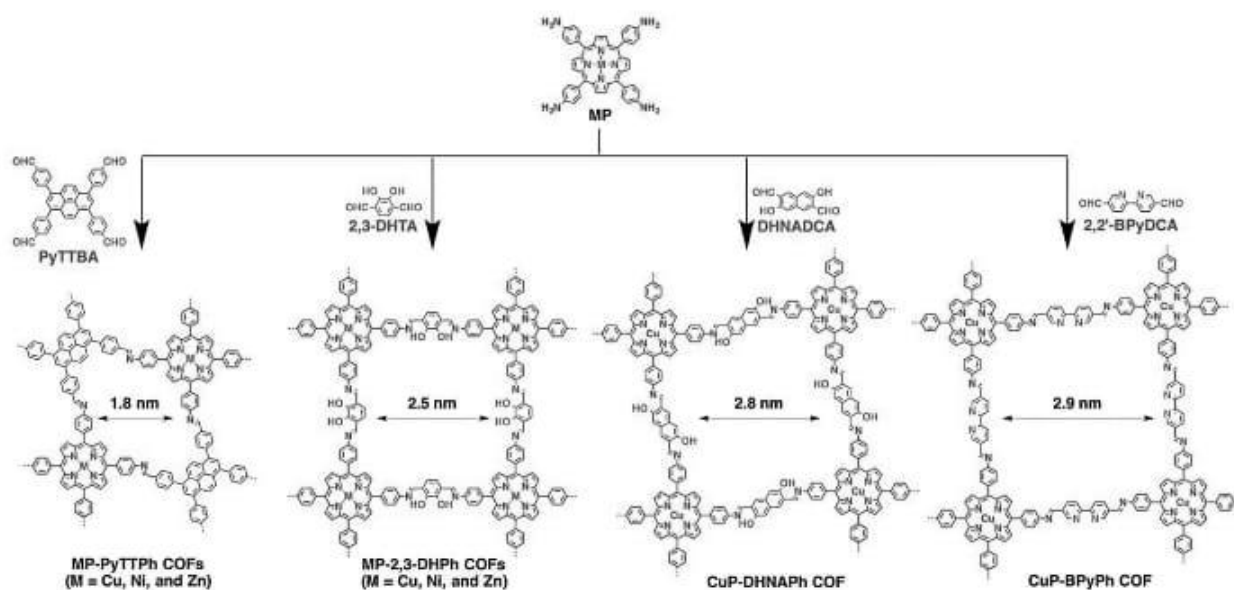


Figure 2.29 Synthetic Scheme of MP-PyTTPh, MP-2,3-DHPH, CuP-DHNAPh, and CuP-BPyPh COFs

Characterization:

FT-IR Peaks: C=N bonds: 1616-1624 cm^{-1}

UV-Vis Peaks: Soret bands: CuP-PyTTPh COF: 451 nm, NiP-PyTTPh COF: 449 nm, ZnPPyTTPh COF: 459 nm, CuP-2,3-DHPH COF: 479 nm, NiP-2,3-DHPH COF: 452 nm, ZnP-2,3-DHPH COF: 476 nm, CuP-DHNAPh COF: 456 nm, CuP-BPyPh COF: 455 nm. Q bands: Enhanced absorption in the long-wavelength visible and near-infrared regions.

XRD Peaks: CuP-PyTTPh COF: 4.82, 9.68, and 22.65°, CuP-2,3-DHPH COF: 3.48, 7.00, 10.54, and 23.18°, NiP-2,3-DHPH COF: 3.48, 7.02, and 22.64°, ZnP-2,3-DHPH COF: 3.46, 6.96, 8.52, and 21.64°, CuP-DHNAPh COF: 3.18, 6.46, 9.92, and 22.74°, CuP-BPyPh COF: 2.96, 6.08, 9.02, and 23.06°

BET Surface Areas and Pore Volumes: CuP-PyTTPh COF: 1127 $\text{m}^2 \text{g}^{-1}$, 0.82 $\text{cm}^3 \text{g}^{-1}$, NiP-PyTTPh COF: 1070 $\text{m}^2 \text{g}^{-1}$, 0.76 $\text{cm}^3 \text{g}^{-1}$, ZnP-PyTTPh COF: 1026 $\text{m}^2 \text{g}^{-1}$, 0.75 $\text{cm}^3 \text{g}^{-1}$, CuP-2,3-DHPH COF: 1099 $\text{m}^2 \text{g}^{-1}$, 0.78 $\text{cm}^3 \text{g}^{-1}$, NiP-2,3-DHPH COF: 854 $\text{m}^2 \text{g}^{-1}$, 0.60 $\text{cm}^3 \text{g}^{-1}$, ZnP-2,3-DHPH COF: 1064 $\text{m}^2 \text{g}^{-1}$, 0.77 $\text{cm}^3 \text{g}^{-1}$, CuP-DHNAPh COF: 1656 $\text{m}^2 \text{g}^{-1}$, 1.38 $\text{cm}^3 \text{g}^{-1}$, CuP-BPyPh COF: 883 $\text{m}^2 \text{g}^{-1}$, 0.64 $\text{cm}^3 \text{g}^{-1}$ [69].

In 2015 Qipu Lin et al. reported the PCN-FeCo/C (Atropurpureus powder of PCN-FeCo) (Metal-Porphyrin-based COFs) by reacting 5,10,15,20-tetrakis(4-iodophenyl)-porphyrin-iron (TIPP-Fe) and 5,10,15,20-tetrakis(4-ethynylphenyl)porphyrin-cobalt (TEPP-Co) in a mixture of anhydrous THF and triethylamine. Add tris(dibenzylideneacetone)dipalladium(0) and triphenylarsine as catalysts. the solution was Stirred under an argon atmosphere at 50 °C for 72 hours, the precipitate was filtered, washed by using Soxhlet extraction. The required solid was immersed in pyridine for 12 hours, then filter again. Heated the final solid under argon to the desired temperature at a slow rate and maintain it for 4 hours. Atropurpureus

powder of PCN-FeCo (Metal-Porphyrin-based COFs) was obtained in 97% yield [70].

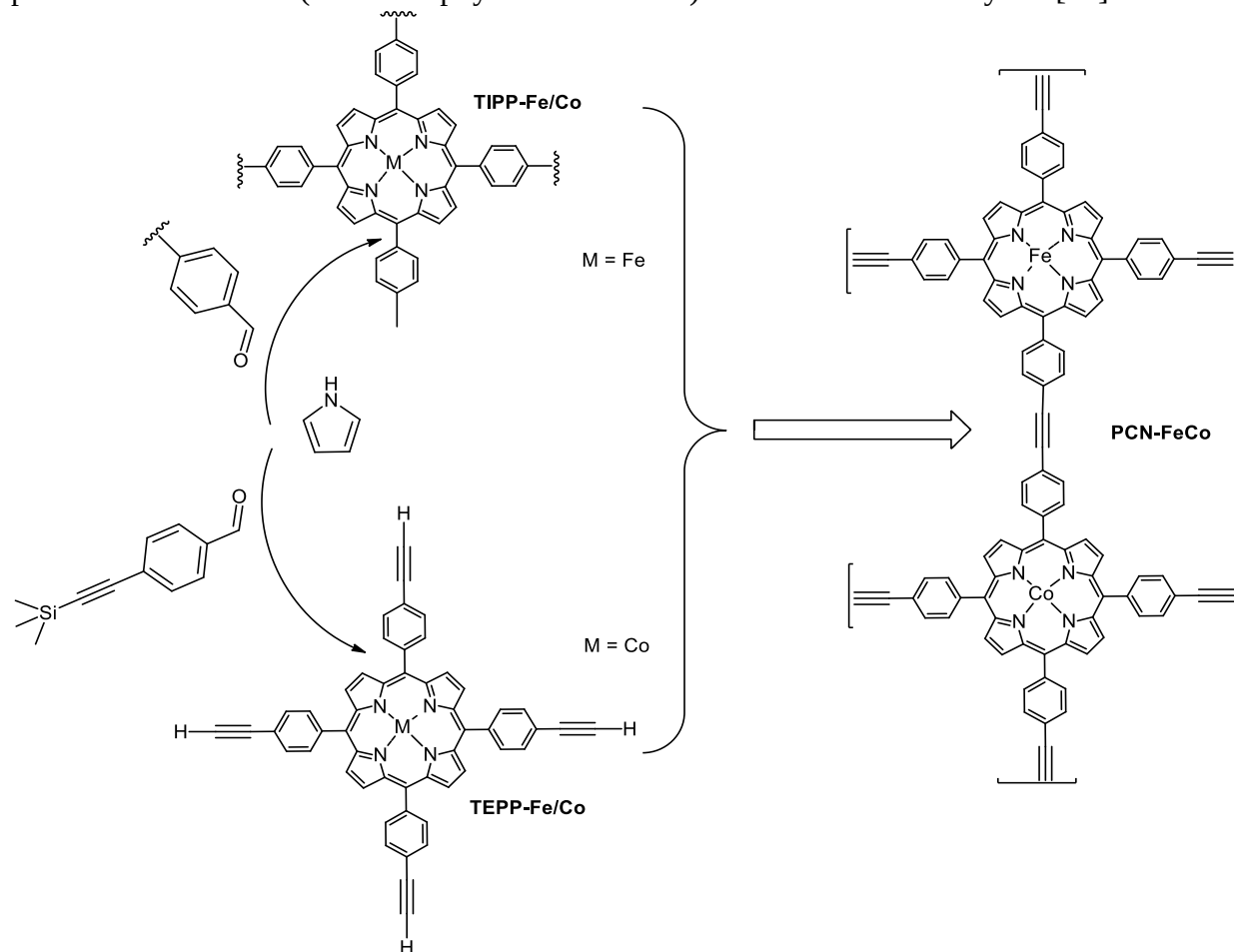


Figure 2.30 Synthetic Scheme of Porphyrinic conjugated network PCN-FeCo (Metal-Porphyrin-based COF)

Characterization:

NMR Peaks: Solid-state ^{13}C NMR spectrum: Phenylene moiety and porphyrin macrocycle: 149.65, 140.52, 130.23, and 120.53 ppm, Acetylene group: 91.60 ppm.

BET Surface Areas and Pore Volumes: PCN-FeCo/C: $930 \text{ m}^2 \text{ g}^{-1}$

CO_2 Uptake: PCN-FeCo/C: 71.3 and $46.1 \text{ cm}^3 \text{ g}^{-1}$ at 273 and 298 K, respectively.

Isosteric Heat of Adsorption (Qst): PCN-FeCo/C: Up to 36.7 kJ mol^{-1} at zero coverage.

XPS Peaks: N 1s spectrum: Pyridinic nitrogen species: 398.5 eV, Metal-coordinated nitrogen species: 399.6 eV, Graphitic nitrogen species: 400.8 eV. Fe 2p spectrum: $3p_{3/2}$ peak: 710.8 eV. Co 2p spectrum: $3p_{3/2}$ peak: 780.6 eV. C 1s peak: Graphitic carbon: 284.9 eV [70].

In 2017 Guiqing Lin et al. reported the 3D- Por-COF combines also Synthesized of 3D-CuPor-COF. It was prepared using the same synthetic protocol of 3D-Por-COF, except starting from and p-CuPor-CHO. After washing and drying, 3D-CuPor-COF was isolated as a bright red powder in 89% yield [50].

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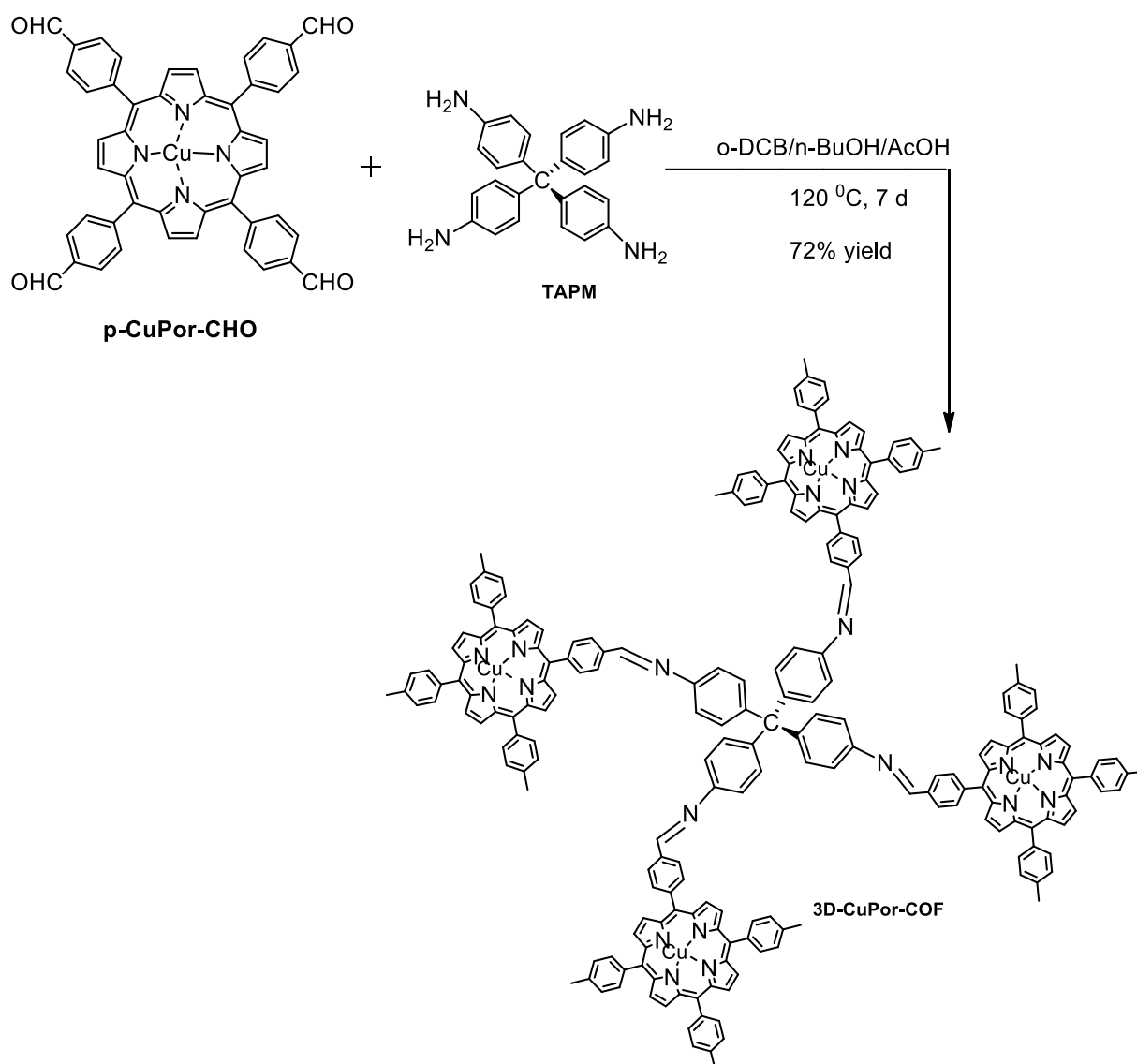


Figure 2.31 Synthetic Scheme of 3D-CuPor-COF (Metal-Porphyrin-based COF)

Characterization:

FT-IR Peaks: Imine bonds: 1627 cm^{-1} , N-H bond (porphyrin ring): 3318 cm^{-1}

NMR Peaks: ^{13}C cross-polarization with total suppression of sidebands NMR spectroscopy: - C=N group: 158 ppm.

PXRD Peaks: 3D-Por-COF: 6.82° and 8.17° and 3D-CuPor-COF: 6.80° and 7.96°

BET Surface Areas and Pore Volumes: 3D-Por-COF: $1398\text{ m}^2\text{ g}^{-1}$ and 3D-CuPor-COF: $1335\text{ m}^2\text{ g}^{-1}$

Pore Size Distributions: D-Por-COF: 0.60 and 1.07 nm and 3D-CuPor-COF: 0.63 and 1.18 nm [50].

In 2017 Kaikai Xu et al, reported COF-366-Co(1) that was synthesized by metallating of free base polymeric porphyrin COF-366 with $\text{Co}(\text{OAc})_2$. COF-366 and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ were added to ethanol and refluxed for 12 hours. After cooling, the mixture was filtered, and the filter cake was washed with ethanol. The final product

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was dried. Elem. Anal. calcd (%) for COF-366-Co(1) [71]. In 2017 Kaikai Xu et al, was also synthesized COF-366-Zn following the synthetic procedure used for COF-366-Co(1) except that $\text{Co(OAc)}_2 \cdot 2\text{H}_2\text{O}$ (1.0 g) was replaced by $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$ and ethanol was replaced by methanol. Elem. Anal. calcd (%) for COF-366-Zn [71].

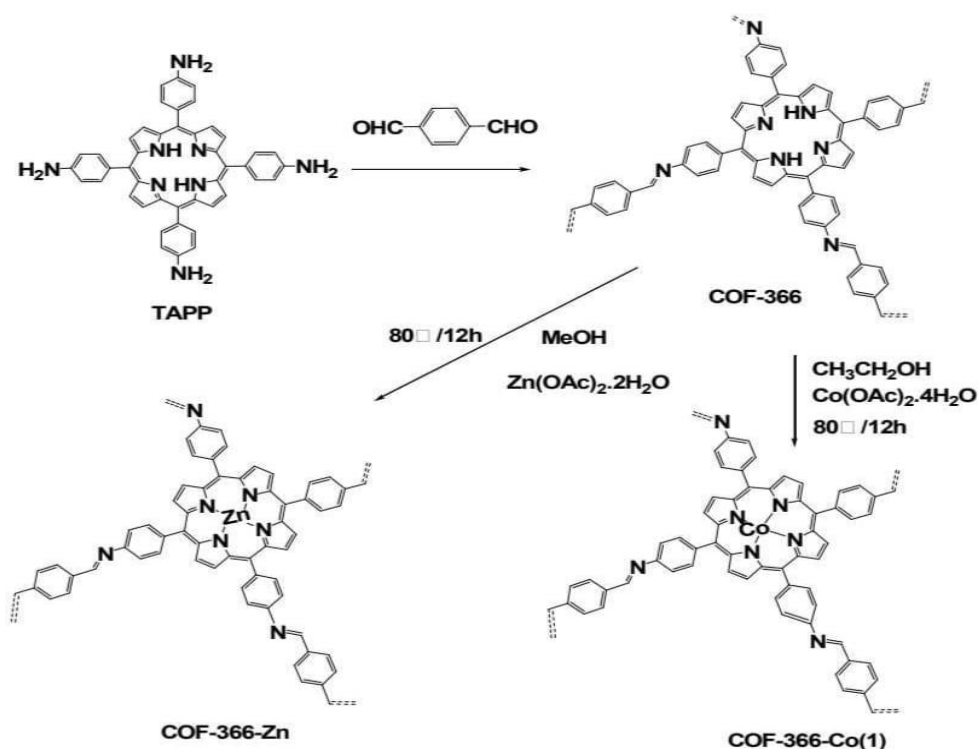


Figure 2.32 Synthetic Scheme of COF-366-Co(1) and COF-366-Zn (Metal-Porphyrin-based COFs)

In 2017 Kaikai Xu et al, was also synthesized COF-SQ, TAPP and squaric acid were mixed in n-butanol and o-dichlorobenzene, degassed in a stainless-steel autoclave, and heated at 120°C for 3 days. The resulting precipitate was filtered, washed with THF and acetone, and vacuum-dried at -60°C for 24 hours, yielding a dark purple powder [71].

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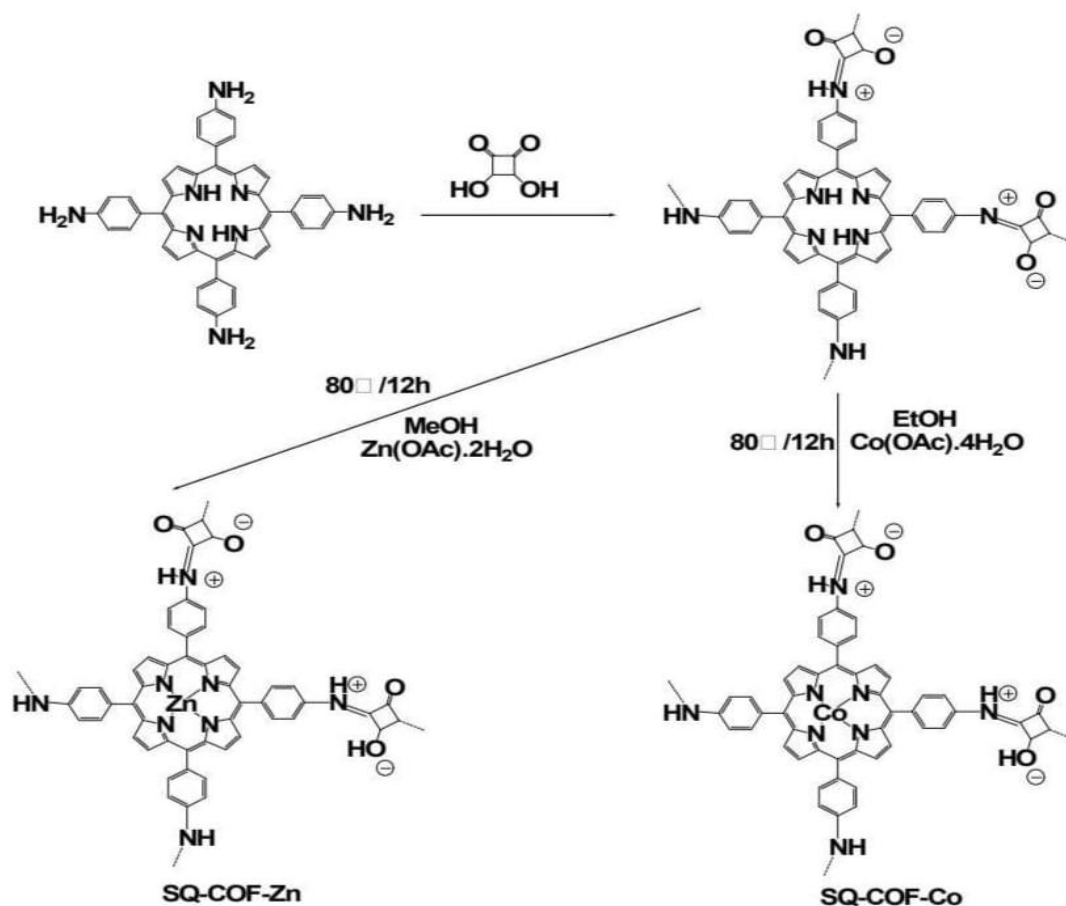


Figure 2.33 Synthetic Scheme of SQ-COF-Zn and SQ-COF-Co (Metal-Porphyrin-based COF-SQ)

Characterization:

TGA: Temperature range: 25–900 °C, Ramp rate: 5 °C/min., Atmosphere: Air, 40 mL/min flow rate

FT-IR: Range: 4000–400 cm⁻¹

PXRD: Radiation: Cu Kα (40 kV, 30 mA), 2θ range: 2°–60°, Scanning speed: 1.504 sec/step, Step increment: 0.2°

Gas Adsorption Measurements (BET): Isotherm: N₂ adsorption/desorption, Instrument: Micromeritics ASAP2020, Degassing: 24 h at 130 °C under vacuum, Testing conditions: Liquid nitrogen at 77 K

Catalysis Study: Catalyst: COF-366-Zn (and Co variant), Co-catalysts: TPPB, TBAB, PTAT, DMAP, Solvent: Acetonitrile (CH₃CN), Conditions: Temperature: 120 °C, Pressure: CO₂, 1.5 MPa, Time: 4 h, Reactant: 1,2-Epoxybutane (1.2 mL), Catalyst amount: 40 mg, Co-catalyst amount: 0.2 mmol

DFT Calculations: Software: Gaussian 09, Method: B3LYP with SCRF (PCM for CH₃CN), Basis sets: C, H, O, N: 6-311G+ (d,p), Zn, Co: LanL2dZ ECP [71].

In 2018 Christian S. et al. reported cobalt-porphyrin derived COFs by mixing of 5,10,15,20-tetrakis(4-aminophenyl) porphyrinato]cobal, BDA, 2,5-dimethoxyterephthalaldehyde/2-fluoroterephthalaldehyde/2,3,5,6-

tetrafluoroterephthalaldehyde, 1,2- dichlorobenzene, butanol, and aqueous acetic acid. Then sonicated, frozen, evacuated, sealed and then reaction was heated at 120°C for 72 hours. a dark purple precipitate was formed in the tube, which is filtered, washed with methanol, acetone in the Soxhlet extractor then washed with liquid CO₂ Finally the product was evacuated at 100 °C for 18 hours under low pressure. Finally yield was 24.18mg (~90% of Co(TAP)).For thin films, a HOPG substrate was included and washed with acetone and methanol Shows in scheme:6[22].

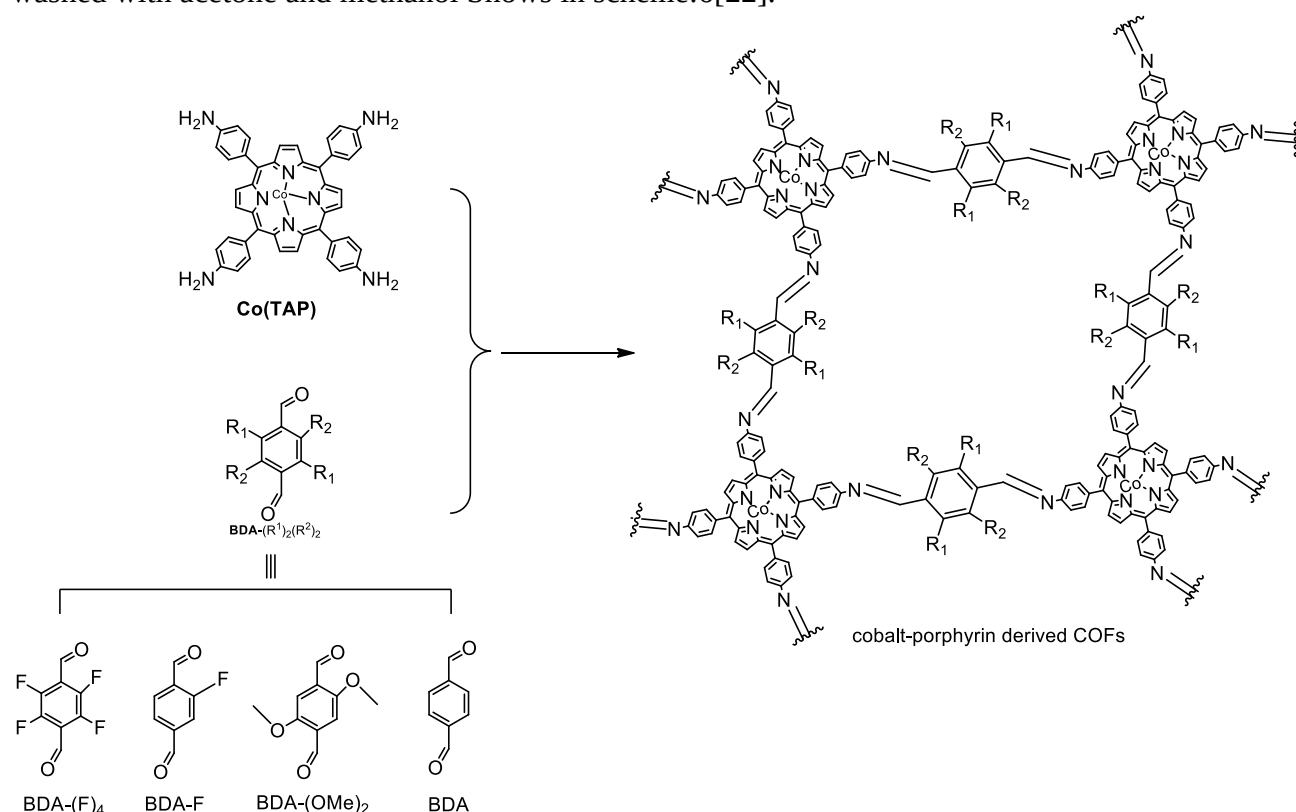


Figure 2.34 Synthetic Scheme of cobalt-porphyrin derived COFs (Metal-Porphyrin-based COF)

Characterization:

XAS Peaks: 777 eV and 779 eV

PXRD Peaks: 2θ from 2 ~ 60°

FT-IR Peaks: 4000-400 cm⁻¹

NMR Peaks: ¹³C cross-polarization with total suppression of sidebands NMR spectroscopy: 158 ppm [22].

In 2018 Zhihui Dai et al, reported Fe-COF. FeSO₄·7H₂O and COF-366 were dissolved in a mixture of dichloromethane and methanol. The mixture was stirred continuously for 36 hours at room temperature. The resulting solid product was separated by centrifugation, washed with dichloromethane and methanol, and then drying in order to obtain product (Fe-COF, brown powder, 18 mg, 80% yield)[72].

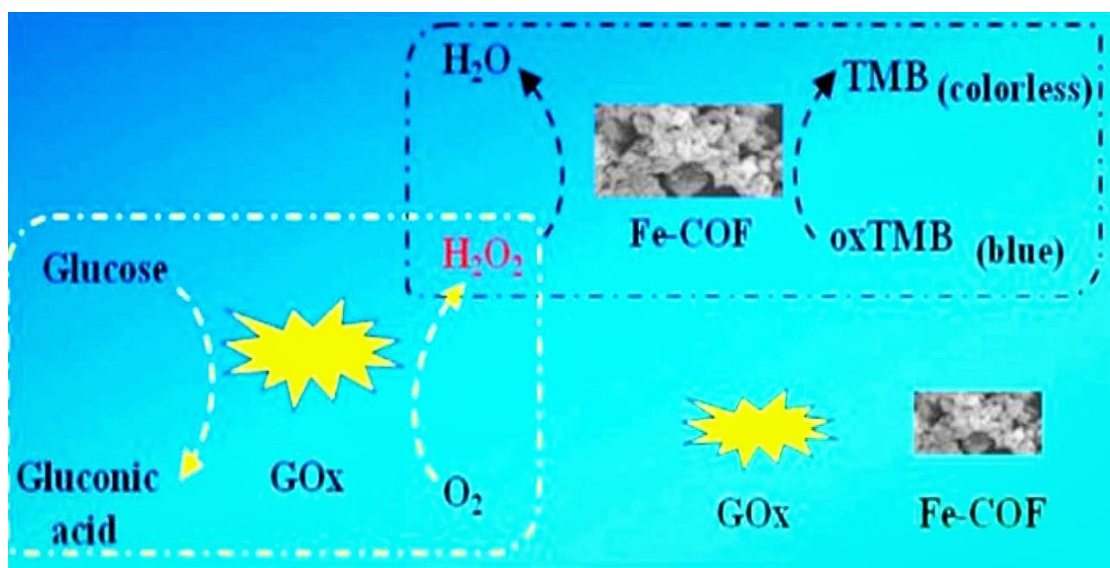


Figure 2.35 Synthetic Scheme of Fe-COF (Metal-Porphyrin-based COF)

Characterization:

XRD Peaks: 2θ of 3.5°

XPS Peaks: Fe 2p peaks at 724.2 eV and 712.2 eV (Fe(III)) and Fe 2p peaks at 722.6 eV and 709.6 eV (Fe(II)).

UV-Vis Peaks: 652 nm (oxidation product of TMB) and 508 nm (iron ions in the supernatant of Fe-COF) [72].

In 2019 Xionghui Ma et al, reported Zr-amide-Por-based 2D COF, the TcPP was refluxed in thionyl chloride at 70°C for 3 h under a N₂ atmosphere until the suspension became a dark red/brown solution. Removed excess thionyl chloride to obtain TcPP chloride. The chlorinated product was dissolved in dichloromethane for the organic phase preparing. And it was poured into a glass cylinder at room temperature, under nitrogen atmosphere. Then the solution was covered with pure water to create a two-phase system. Gently to the water phase an aqueous solution of ZrCl₄ and o-PD was added. Keeping undisturbed the reaction system for 12 hours, a bottle green film of Zr-amide-Por-based 2D COF was generated at the interface. The obtained product was centrifuged and washed with ethanol, and was then vacuum-dried overnight

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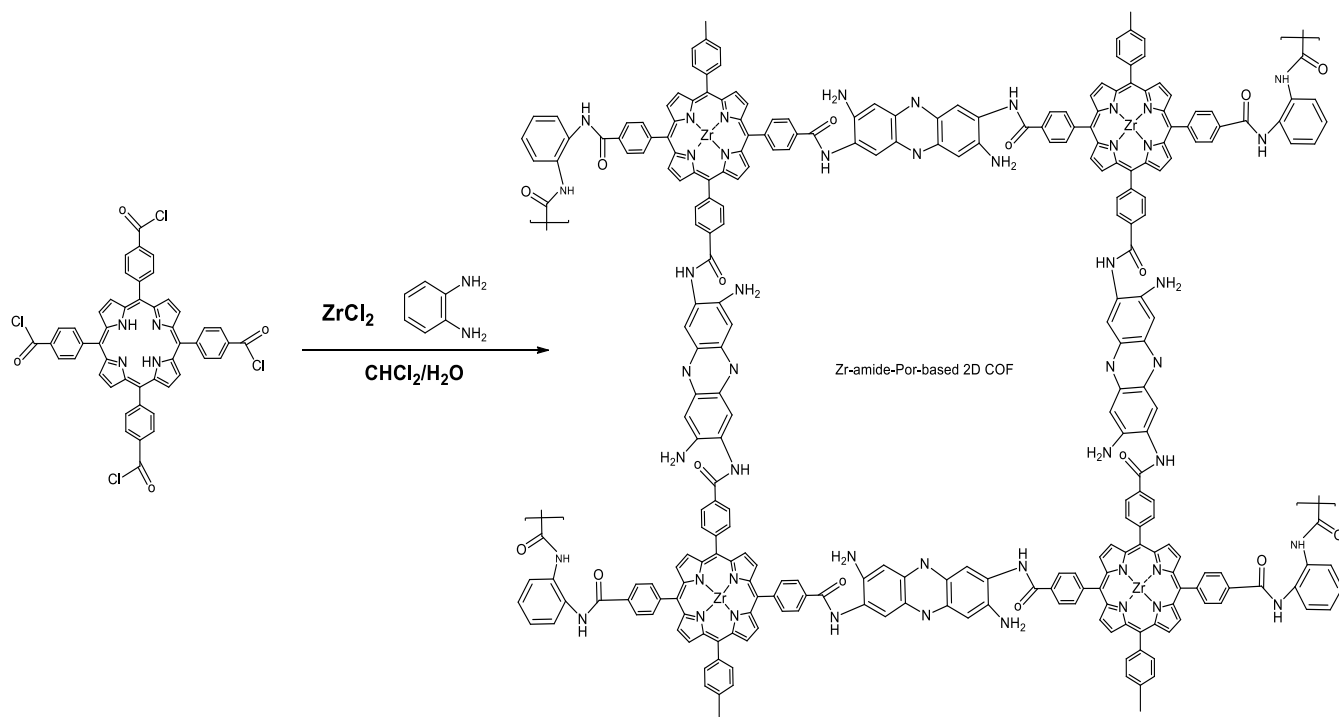


Figure 2.36 Synthetic Scheme of Zr-amide-Por-based 2D COF(Metal-Porphyrin-based COF)

Characterization:

FT-IR Peaks: 1660 cm^{-1} (carbonyl stretch) and 1532 cm^{-1} (amide II band).

XPS Peaks: C 1s peak at 284.0 eV (C–C), C 1s peak at 285.0 eV (C–H/C–C), C 1s peak at 288.0 eV (C–N bonds), N 1s peak at 397.6 eV (pyrroles of the porphyrin unit), O 1s peak at 531.2 eV (N–C–O in the amide), O 1s peak at 532.6 eV (partly unreacted –COOH in the TcPP) and Zr3d peak at 184.9 eV (Zr–N coordination).

XRD Peaks: 2θ of 3.4° ((110) facet) and 2θ of 7.5° ((220) facet) [73].

In 2019 Yong Liu et al. synthesized porphyrin-COF-1 and synthesized porphyrin-COF-2 and also reported PCOF-1-Fe, PCOF-2-Fe, PCOF-1-Co and PCOF-2-Co. synthesized PCOF-1-Fe by dispersion of PCOF-1 and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in DMF under a nitrogen atmosphere and refluxed for 6 hours. After cooling down to room temperature, powder was obtained by centrifuging. The resulting precipitate was washed with deionized water, anhydrous methanol, DMF, and anhydrous THF and finally dried at 80°C under vacuum for 12 hours to obtain PCOF-1-Fe. Yield: 75%. PCOF-2-Fe was synthesized using PCOF-2 following the same procedures which is used for the preparation of PCOF-1-Fe. Yield: 69%. PCOF-1-Co was synthesized using PCOF-1 and excess $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ following the same procedures which is used for the preparation of PCOF-1-Fe. Yield: 73%. PCOF-2-Co was synthesized using PCOF-2 and excess $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ following the same procedures which is used for the preparation of PCOF-1-Fe. Yield: 79%. Characterization and Scheme already shows [27].

In 2020 Yan Lu et al. reported COF-Based Catalysts with Isolated Cobalt Porphyrin Units (called COF-366-Co@CNT) by mixing of Co(TAPP),

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terephthalaldehyde and CNTs dispersion in ethanol with solvent o-dichlorobenzene and n-butanol and catalyzed by aqueous acetic acid in a Pyrex tube. After this the mixture was sonicated for 15 minutes, frozen in liquid nitrogen, degassed, by butane flame in vacuum and heated at 120°C for 3 days. The resulting 366-Co@CNT washed with DCM, ethanol, tetrahydrofuran, and acetone. Then dried to obtain COF366-Co@CNT as a black solid with 17.5 mg and 77% yield[74].

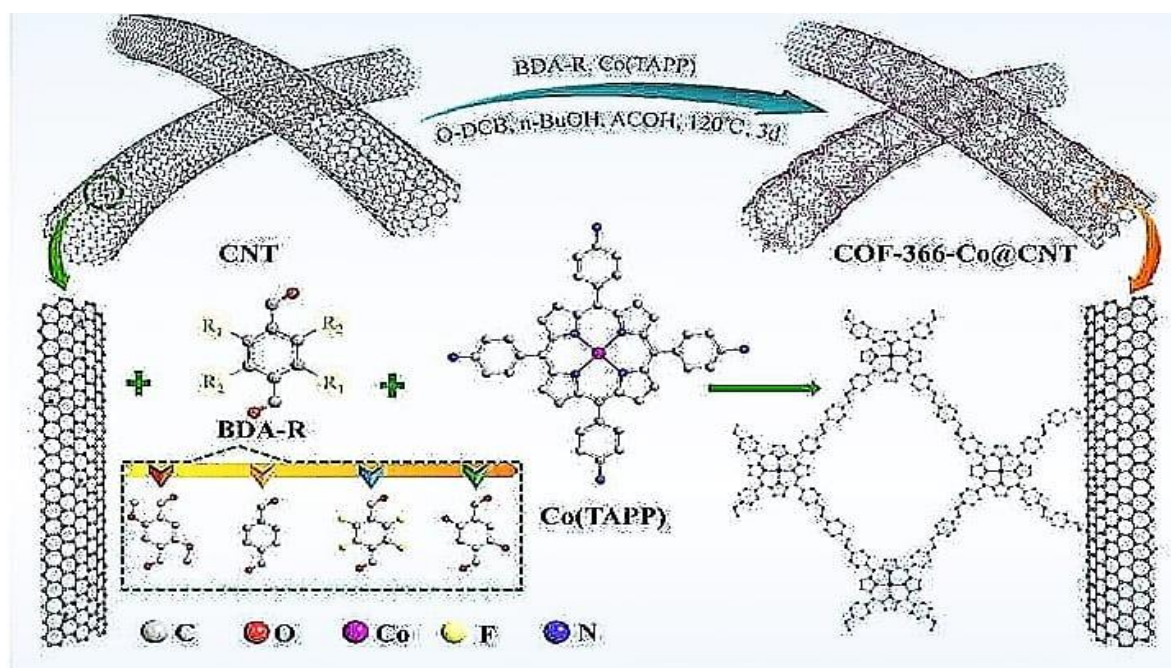


Figure 2.37 Synthetic Scheme of COF-366-Co@CNT (Metal-Porphyrin-based COF)

Characterization:

PXRD patterns: COF-366-(OMe)₂-Co: (100) and (200) reflection planes and COF-366-(OMe)₂-Co@CNT: (100) and (200) reflections.

FT-IR spectroscopy: COF-366-(OMe)₂-Co: 1618 cm⁻¹ (C=N linkages) and COF-366-(OMe)₂-Co@CNT: 1576 and 1382 cm⁻¹

XPS: COF-366-(OMe)₂-Co: 781 eV (Co 2p_{3/2} spectra, Co²⁺ oxidation state) and COF-366-(OMe)₂-Co@CNT: 781 eV + 0.52 eV (Co 2p_{3/2} spectra, Co²⁺ oxidation state).

Raman spectroscopy: COF-366-(OMe)₂-Co@CNT: ID/IG = 1.03 [74].

In 2020 Xiaoyi Xu et al. synthesized TAPP-TFPP-COF by mixing of Zn-TAPP and Zn-TFPP were mixed in a solution of n-BuOH, o-DCB, and acetic acid in a Pyrex tube. The mixture was degassed, then sealed and heated at 120°C for 72 hours. The precipitate was collected by centrifugation and washed with acetone and THF. The deep-brown powder was dried under vacuum at 120°C for 12 hours, yielding TAPP-TFPP-COF with an isolated yield of 82% [35]. In 2020 Xiaoyi Xu et al. also synthesized I₂-doped TAPP-TFPP-COF Dissolve iodine in n-hexane to make a solution. Immerse of activated TAPP-TFPP-COF in the iodine solution for 36 hours. Filter the resulting black powder and was washed it with n-hexane until the filtrate is colorless. I₂-doped TAPP-TFPP-COF was dried in an oven at 80°C overnight. Isolated yield: 95% [35].

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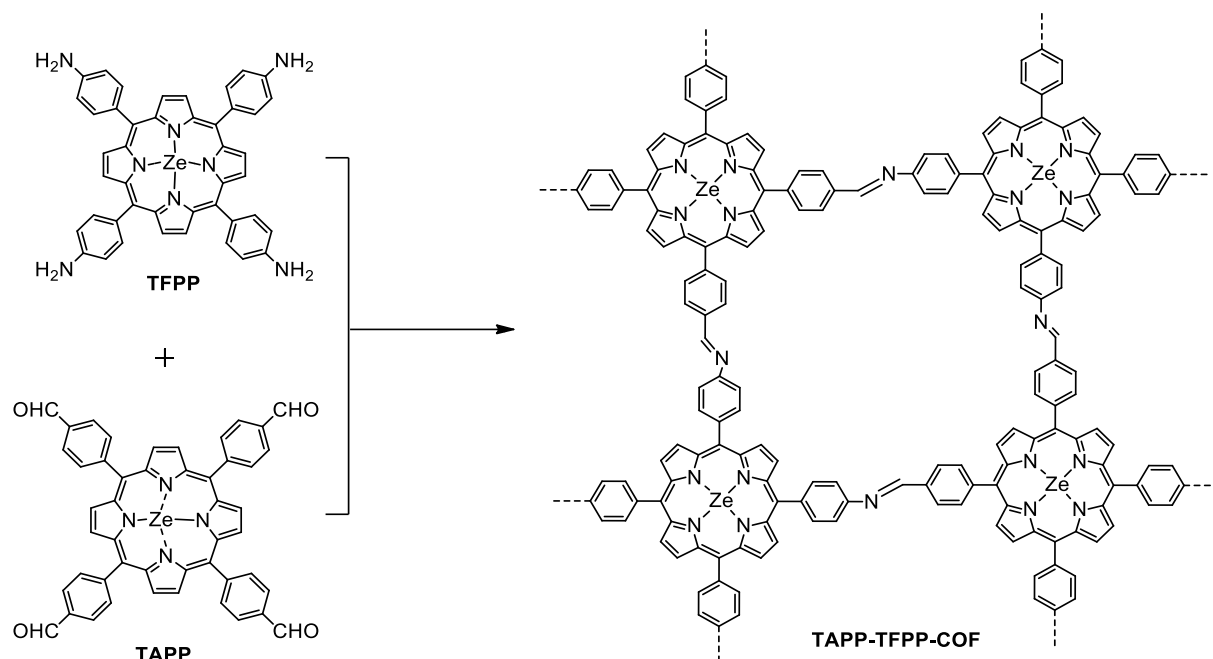


Figure 2.38 Synthetic Scheme of TAPP-TFPP-COF (Metal-Porphyrin-based COF)

Characterization:

PXRD Peaks: 4.62°, 9.24°, 13.82° and 22.54°

FT-IR Peaks: 1602 cm⁻¹ (imine bond)

Solid-State ¹³C (CP-MAS) NMR Spectroscopy Peaks: 158.75 ppm, 151.25 ppm, 144.32 ppm, 134.15 ppm, 131.57 ppm, 120.67 ppm, 113.54 ppm and 192 ppm (satellites, -CHO groups).

Raman Spectroscopy Peaks: 167 cm⁻¹ (I₅-ions), 112 cm⁻¹ (perturbed asymmetric I₃-ions and di-iodine molecules), 144 cm⁻¹ (perturbed asymmetric I₃-ions and di-iodine molecules) and 164 cm⁻¹ (perturbed asymmetric I₃-ions and di-iodine molecules) [35].

In 2020 Yi Xie et al, synthesized COFp-por NH₂-BTA by mixing p-por NH₂ and BTA. They were dissolved in a mixture of o-DCB and n-BuOH, then sonicated to form a uniform solution. Afterward, the mixture was heated at 120°C for 72 hours with the addition of M HAc. A black-violet solid, COFp-por NH₂-BTA, was obtained as the final product [75]. In 2020 Yi Xie et al also synthesized COFp-Fepor NH₂-BTA using a post-modification method. In this process, the prepared COFp-por NH₂-BTA material is combined with FeCl₂·4H₂O powder, then heated and stirred. Upon cooling, a precipitate forms, which is collected by centrifugation with DMF and methanol. Finally, the brown-black product is dried in a vacuum freeze dryer [75]. In 2020 Yi Xie et al also prepare COFp-por NH₂-BTA/GCE and COFp-Fepor NH₂-BTA/GCE, COFp-por NH₂-BTA or COFp-Fepor NH₂-BTA suspension is applied to a polished GCE surface and dried [75].

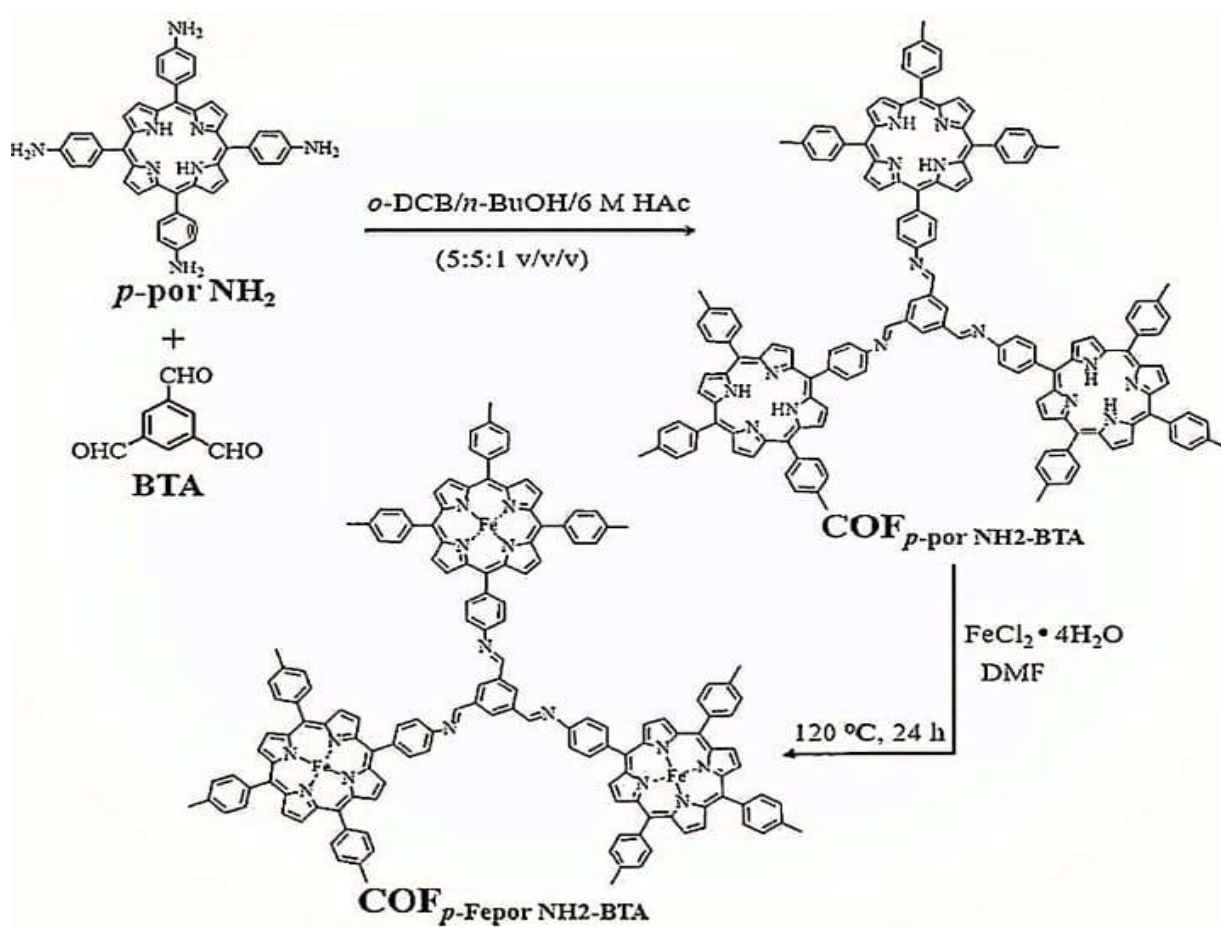


Figure 2.39 Synthetic Scheme of COF_p-por NH₂-BTA (Porphyrin-based COF) and COF_p-Fepor NH₂-BTA (Metal-Porphyrin-based COF)

Characterization:

FTIR Peaks: 1620 cm⁻¹ (C=N), 1700 cm⁻¹ (CHO bond), 3353 cm⁻¹ -3440 cm⁻¹ (N-H bond) and 1000 cm⁻¹ (Fe-N coordination).

XRD Peaks: 5.0°, 8.29°, and 20.27° (COF_p-por NH₂-BTA) and 7.71°, 11.80°, 20.01°, and 26.7° (COF_p-Fepor NH₂-BTA)

XPS Peaks: 284.79 eV (C 1s), 399.25 eV (N 1s), 710.77 eV (Fe 2p), 709.92 eV and 711.39 eV (Fe 2p_{3/2}), 718.82 eV and 724.21 eV (Fe³⁺ and Fe 2p_{1/2}), 398.86 eV and 400.5 eV (FeN and pyrrolic N) [75].

In 2020 Yaxin Zhao et al, synthesized Fe-PorCOF, iron(II) chloride tetrahydrate and PorCOF were added into N,N-dimethylformamide. The mixture was heated at 80°C in an oven and kept at the same temperature for 24h. Fe-PorCOF powder was collected via filtration and washed with N,N-dimethylformamide and acetone, and dried [76].

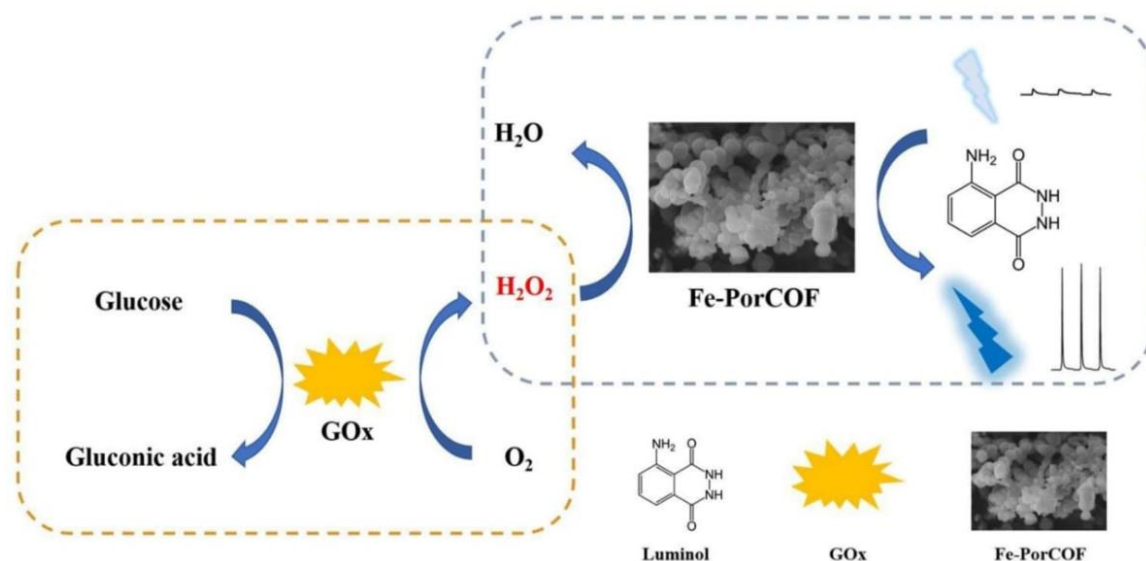


Figure 2 40 Synthetic Scheme of Fe-PorCOF (Metal-Porphyrin-based COF)

Characterization:

FTIR Peaks: 3333 cm^{-1} (N–H stretching band of TAPP), 2864 cm^{-1} (C–H stretching bands of terephthaldehyde), 1684 cm^{-1} (C=O stretching bands of terephthaldehyde) and 1018 cm^{-1} and 1092 cm^{-1} (symmetrical stretching bands of Fe-PorCOF) [76].

In 2020 Haowei Lv et al, synthesized H2P-TPE-COF, a Pyrex tube was loaded with H2TAP and TPE in a solution of o-dichlorobenzene, n-butanol, and acetic acid. After three freeze-pump-thaw cycles, the tube was vacuum-sealed and heated at $120\text{ }^{\circ}\text{C}$ for 7d. The resulting dark-red precipitate was filtered, washed with THF and acetone, extracted. Finally, it was dried, yielding H2P-TPE-COF [77]. In 2020 Haowei Lv et al, also synthesized NiP-TPE-COF and CoP-TPE-COF, the same procedure used for H2P-TPE-COF was followed, except that H2TAP was replaced by NiTAP and CoTAP respectively [77].

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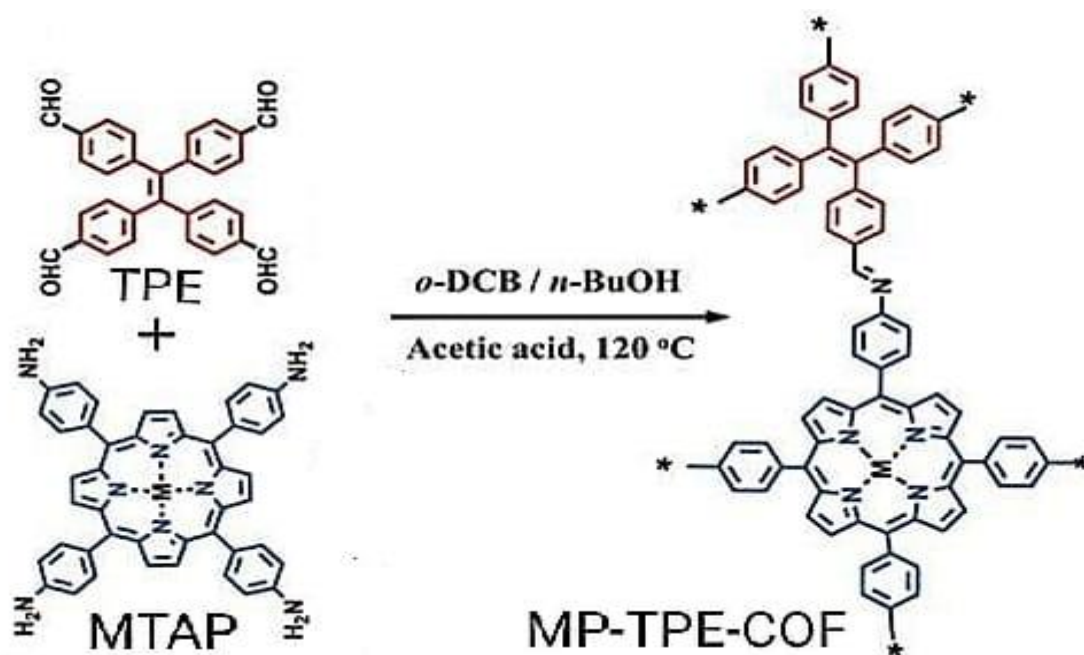
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Figure 2.41 Synthetic Scheme of H2P-TPE-COF (Metal-Porphyrin-based COF)

Characterization:

FTIR Spectroscopy: Carbonyl peak of TPE: 1695 cm^{-1} , N–H stretching bands of H2TAP/NiTAP: $3,100\text{--}3,400\text{ cm}^{-1}$, C=N stretching vibration peak: $1,626\text{ cm}^{-1}$

XPS Spectroscopy: Binding energy peaks for iminic, pyrrolic, and imine nitrogen atoms in H2P-TPE-COF: 398.02, 399.93, and 399.04 eV, respectively, Binding energy peaks for nitrogen atoms in NiP-TPE-COF: 398.64 and 399.04 eV and Binding energy peaks for Ni 2p in NiP-TPE-COF: 855.34 and 872.39 eV

Solid-State ^{13}C NMR Spectroscopy: Characteristic signal of C=N bond: 158.8 ppm and Peaks for aromatic carbon atoms: 108–154 ppm

PXRD Patterns: Diffraction peaks for H2P-TPE-COF: 5.3° and 10.9° (indexed to (110) and (220) crystal facets, respectively) and Diffraction peaks for NiP-TPE-COF: 5.4° and 11.2° (indexed to (110) and (220) crystal facets, respectively).

UV-Vis Spectroscopy: Q-bands for H2P-TPE-COF and NiP-TPE-COF: typical four Q-bands (blue shift observed for NiP-TPE-COF due to metalation of porphyrin units)

In Situ FTIR Spectroscopy: Asymmetric stretching band for molecular CO_2 : $2,335\text{ cm}^{-1}$ and Adsorption peak for CO_2 on NiP-TPE-COF: $2,364\text{ cm}^{-1}$ [77].

In 2020 Yun-Nan Gong et al synthesized COF-367- Co^{II} , A mixture of Co^{II} -TAP, 4,4'-biphenyldicarboxaldehyde), 1,2- dichlorobenzene, ethanol, 3-aminopropyltriethoxysilane and aqueous acetic acid was added into a Pyrex tube, which was sonicated. This mixture was flash frozen (liquid N_2 bath). Then the tube was evacuated to an internal pressure of 50 mtorr and sealed off. The reaction was proceeded at 120°C for 72 h. After cooling down, the dark purple product was collected by filtration and washed with acetone, followed by soaking in acetone. Finally, the product was evacuated to yield the activated sample of COF-367- Co^{II} [78]. In 2020 Yun-Nan Gong et al also synthesized COF-367- Co^{III} following the same procedures as COF-367- Co^{II} except for the addition of Co^{III} -TAP instead of Co^{II} -TAP. The COF-367 was

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synthesized following the same procedures as COF-367-Co^{II} except for the addition of H₂TAP and BPDA respectively, instead of a mixture of Co^{II}-TAP and BPDA. The COF-366 was synthesized following the same procedures as COF-367-Co^{II} except for the addition of H₂TAP and 1,4- benzenedicarboxaldehyde respectively, instead of the mixture of Co^{II}-TAP and BPDA. The COF-366-Co^{II} was synthesized following the same procedures as COF-367-Co^{II} except for the addition of BDA instead of BPDA [78].

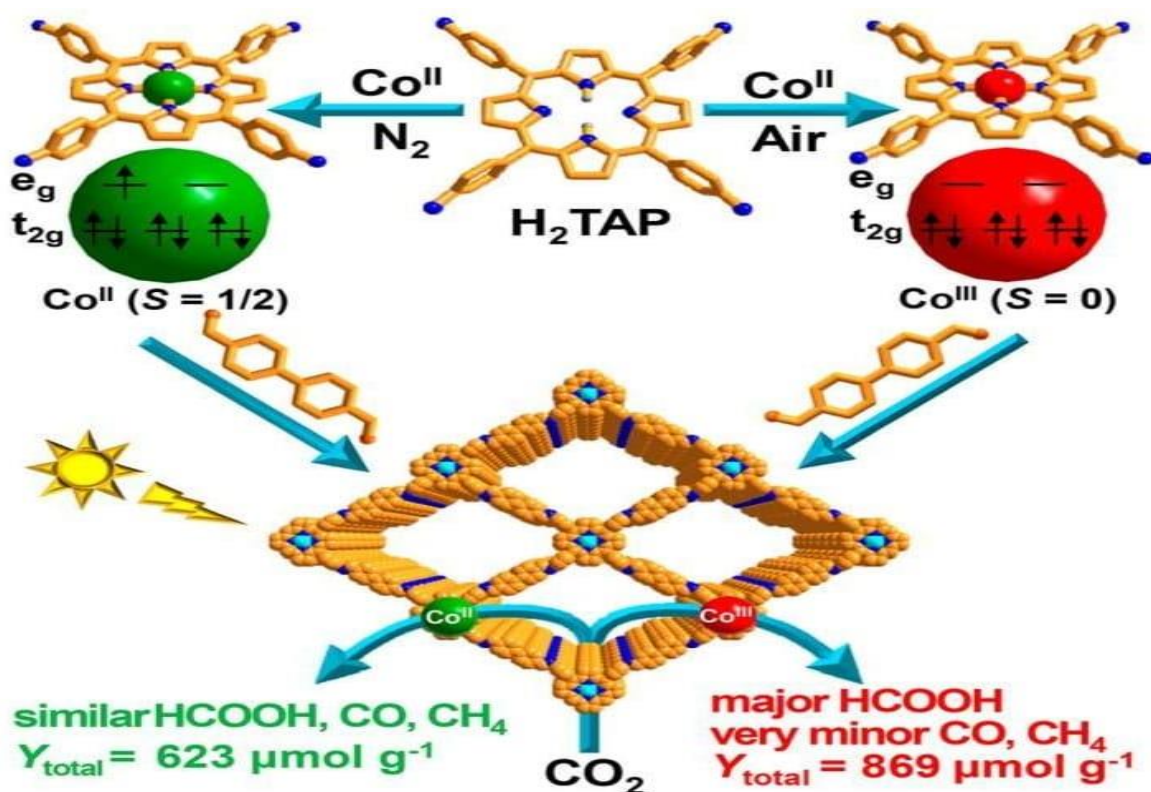


Figure 2.42 Synthetic Scheme of COF-367-Co^{II} and COF-367-Co^{III} (Metal-Porphyrin-based COF)

Characterization:

UV-vis spectra: COF-367-CoII: 430 nm and COF-367-CoIII: 453 nm (blue-shifted by 23 nm compared to COF-367-CoII)

FT-IR spectra: Imine C=N stretching band: 1622 cm⁻¹ and C-N stretching vibration band: 1262 cm⁻¹

XPS spectra: Co 2p_{1/2}-2p_{3/2} spin-orbit level energy spacing: COF-367-CoII: 16 eV, COF-367-CoIII: 15 eV and Cl 2p signal peak: 197.3 eV

EPR spectra: COF-367-CoII: strong signal at g = 2.30 and COF-367-CoIII: no signal at g = 2.30

N₂ sorption: BET surface areas: COF-367: 442 m²/g, COF-367-CoII: 580 m²/g and COF-367-CoIII: 489 m²/g. Pore size distributions: 12 to 25 Å.

Solid-state UV-vis-NIR spectra: COF-367-CoII: band gap energy (E_g) = 1.03 eV and COF-367-CoIII: band gap energy (E_g) = 1.10 eV

Mott-Schottky measurements: Flat band potentials: COF-367-CoII: -0.96 V vs NHE

and COF-367-CoIII: -0.84 V vs NHE

DFT calculations: CO₂ adsorption energy: COF-367-CoII: 0.05 eV and COF-367-CoIII: 0.11 eV. HCOOH adsorption energy: COF-367-CoII: 0.47 eV and COF-367-CoIII: 0.93 eV [78].

In 2021 Aisan Khaligh et al, synthesized COF-TPP-CB[6], two starting materials, CB6(O-P)_n and TPP-Zn-4N₃, were dissolved in DMSO and combined. The mixture was heated at 120 °C for 30 min, and a copper sulfate and sodium ascorbate solution were added to initiate the reaction. The reaction ran at 120 °C for 96h, monitored by FT-IR, until the azide band disappeared, indicating completion. The resulting brownish solid was filtered, washed with water and chloroform to remove impurities, and dried to yield 150 mg of COF-TPP-CB[6] powder [79].

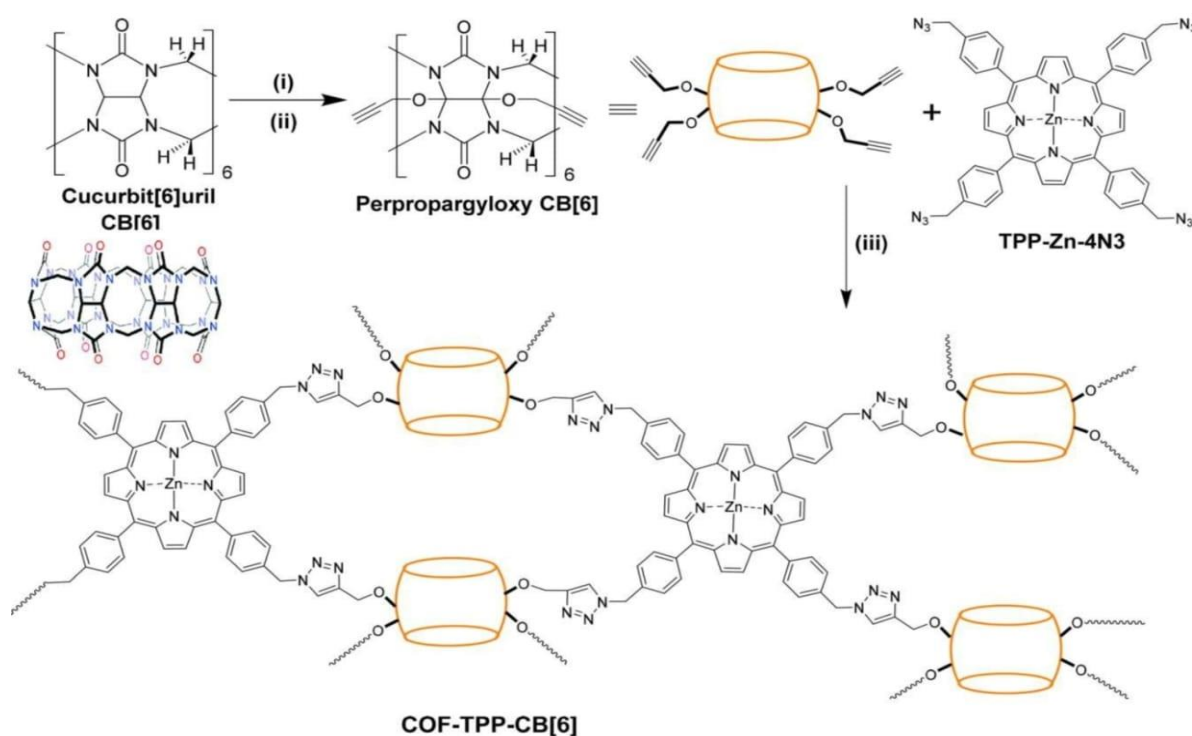


Figure 2.43 Synthetic Scheme of COF-TPP-CB[6] (Metal-Porphyrin-based COF)

Characterization:

NMR: ¹H NMR: characteristic signals for the protons of CB[6], porphyrin, and phenyl units.

FT-IR: 2158 cm⁻¹: alkyne stretching signal (C≡C), 3258 cm⁻¹: alkyne stretching signal (-C≡C-H), 1735 cm⁻¹: carbonyl signal, 2095 cm⁻¹: azide signal and 379 cm⁻¹: Tafel slope of COF-TPP-CB[6]-TiO₂

XPS: C 1s: 285.49, 286.40, 287.45, and 288.90 eV (C=C, C-C, C-N, C-O, C=O, and N-C=O bonds), N 1s: 397.75 eV (Zn-N), 399.04 eV (pyrrolic-N), 400.17 eV (triazole-N and amine-N), and 401.35 eV (graphitic-N), O 1s: 531.75 and 533.26 eV (C-O and C=O bonds) and Zn 2p: 1044.49 and 1021.41 eV (Zn 2p_{1/2} and 2p_{3/2})

SEM/EDX: Elemental mapping: C, N, O, and Zn

TEM: Average particle size: 40-50 nm

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XRD: Crystalline structure with well-defined diffraction peaks at $2\theta = 8.2^\circ$, 18.1° , 22.1° , and 28.3° [79].

In 2021 Luo-Gang Ding et al, Synthesized COF-PI-1. A mixture of Dha, Tph, Bim-Br, $\text{BF}_3 \cdot \text{OEt}_2$, DDQ, and acetic acid in o-DCB/n-BuOH was heated at 120°C for 7 days in a N_2 atmosphere. After cooling, the solids were collected by centrifugation and successively washed with DMF, THF, and ethanol and then dried to afford COF-PI-1 as a dark red crystalline solid in 81% yield [80]. In 2021 Luo-Gang Ding et al, also synthesized COF-PI-2. A mixture of COF-PI-1 and cobalt(II) acetate was stirred in DMF for 24 h at 80°C under a N_2 atmosphere. The solids were collected by centrifugation and sequentially washed with DMF and acetone and then dried to afford COF-PI-2 [80]. In 2021 Luo-Gang Ding et al, Fabricated COF-PI-2@Chitosan Aerogel-Based Cup-like Reactor, crystalline COF-PI-2, glass beads, and 1,4-butanediol diglycidyl ether were added into acidic aqueous solution of chitosan with ultrasonic shaking to afford a homogeneous suspension. The obtained solution was immediately transferred into the “split-flask” quartz mold and allowed to stand for ca. 12 h until a robust hydrogel was formed. After freezing at -18°C , the frozen sample was freeze-dried at -50°C for 24 h in a freeze-dryer. After thorough washing with ethanol to remove residual acetic acid, the obtained COF-PI-2@chitosan aerogel-based cuplike reactor was applied to catalysis [80].

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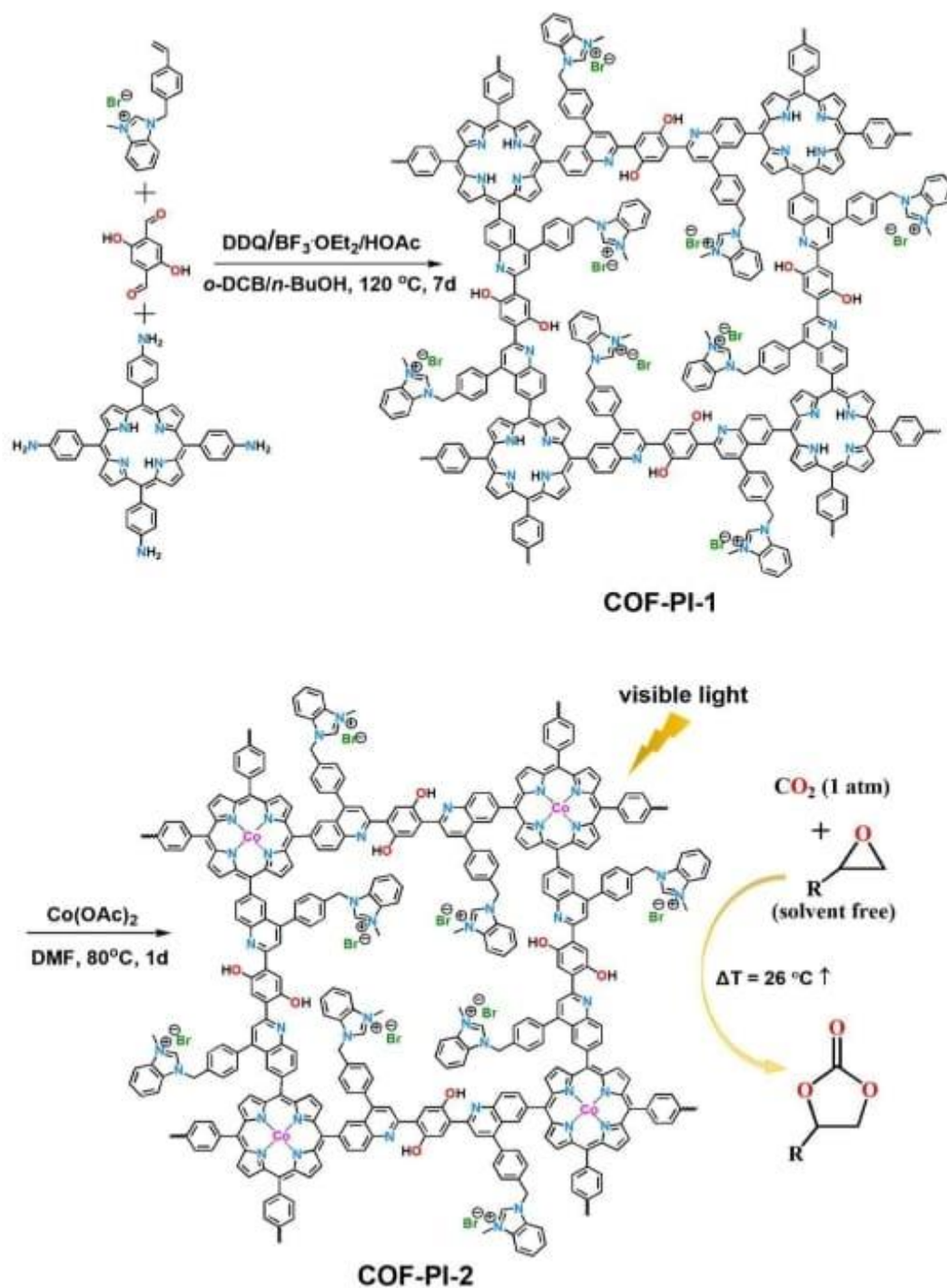


Figure 2.44 Synthetic Scheme of COF-PI-1 and COF-PI-2 (Metal-Porphyrin-based COF)

Characterization:

FT-IR: N–H vibration peaks: 3352 and 3213 cm⁻¹, C=O vibration peak: 1669 cm⁻¹ and C=N groups: 1589 and 1531 cm⁻¹

Solid-state ¹³C-NMR: 2-quinolyl carbon: 156.9 ppm

PXRD: Prominent peaks: 3.5, 4.9, 6.9, and 22.3, Corresponding facets: (100), (110), (200), and (001)

N₂ adsorption–desorption: N₂ adsorption capacity: 251.9 cm³ g⁻¹ (COF-PI-1), 247.8 cm³ g⁻¹ (COF-PI-2), BET surface area: 420.6 m² g⁻¹ (COF-PI-1), 409.1 m² g⁻¹ (COF-PI-2) and Average pore size distribution: 1.0 nm

XPS: N 1s peaks: 400.0 and 398.1 eV (COF-PI-1), 398.6 eV (COF-PI-2) and Co 2p_{1/2} and Co 2p_{3/2} peaks: 796.6 and 781.3 eV [80].

In 2021 Zhijian Gan et al, A series of COF-366-Co@CNT-x compounds is synthesized by adjusting the mass ratio of COF monomers to MWCNTs. For COF-366-Co@CNT-1.4, 3 mg each of MWCNTs and TAPP are combined in n-butyl alcohol and orthodichlorobenzene and sonicated. Acetic acid is added, followed by a TA solution, and sonicated again. This mixture is transferred to a glass tube, degassed, and heated at 120°C for 72 hours. After washing and drying, cobalt ions are introduced by combining the COF-366@CNT with cobaltous acetate in methanol, refluxing at 80°C, then washing and drying [81].

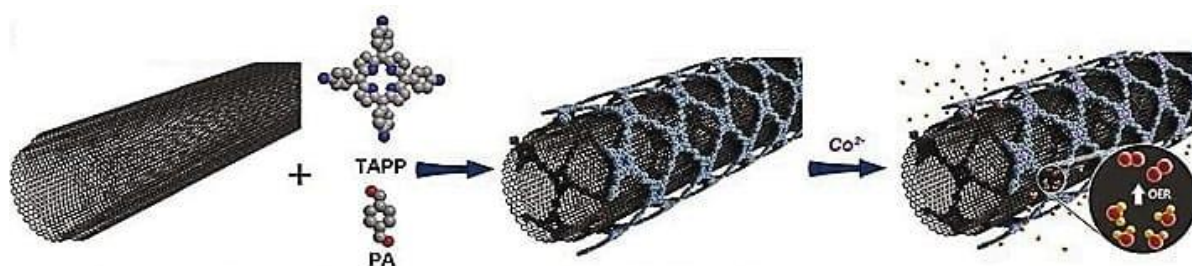


Figure 2 45 Synthetic Scheme of COF-366-Co@CNT-x (Metal-Porphyrin-based COF)

Characterization:

NMR: ¹H NMR: characteristic signals for the protons of CB[6], porphyrin, and phenyl units.

FT-IR: 2158 cm⁻¹: alkyne stretching signal (C≡C), 3258 cm⁻¹: alkyne stretching signal (-C≡C-H), 1735 cm⁻¹: carbonyl signal, 2095 cm⁻¹: azide signal, 379 cm⁻¹: Tafel slope of COF-TTP-CB[6]-TiO₂, 1620 cm⁻¹: C-N vibration peak, 1300 cm⁻¹: C-N vibration peak, 2952, 2922, and 2852 cm⁻¹: stretching vibrations of C-H bond in the benzene ring and 1697 cm⁻¹: C-O bond (almost vanished for COF-366-Co@CNT).

XPS: C 1s: 285.49, 286.40, 287.45, and 288.90 eV (C=C, C-C, C-N, C-O, C=O, and N-C=O bonds), N 1s: 397.75 eV (Zn-N), 399.04 eV (pyrrolic-N), 400.17 eV (triazole-N and amine-N), and 401.35 eV (graphitic-N), O 1s: 531.75 and 533.26 eV (C-O and C=O bonds), Zn 2p: 1044.49 and 1021.41 eV (Zn 2p_{1/2} and 2p_{3/2}) and Co 2p: 781.2 eV (Co 2p_{3/2}) and 796.8 eV (Co 2p_{1/2}).

Raman: 1006 cm⁻¹: vibration of phenyl, 1356 cm⁻¹: vibration of C-N, 1625 cm⁻¹: vibration of C-N, 399 cm⁻¹: Co-N bond, 565 cm⁻¹: CoOOH, 440 cm⁻¹: Eg, and 595 cm⁻¹: F_{2g} (Co-O stretching) vibrational modes of Co(OH)₂

PXRD: 3.5°, 4.4°, 7°, and 8.7°: diffraction peaks corresponding to (100), (110), (200), and (210) facets [81].

In 2021 Yite Li et al, reported the pre-designed GFeF nanozyme was made in three steps. First, iCOF nanoparticles were synthesized by heating a mixture of TPyP,

p-xylylene dibromide, and polyvinylpyrrolidone in NMP under nitrogen at 80 °C for 24 hours. These nanoparticles were washed with NMP, dispersed in methanol, and then chelated with ferrous chloride at room temperature to form Fe-iCOF. Finally, Fe-iCOF was mixed with glucose oxidase in water and centrifuged to produce the GFeF nanozyme [82].

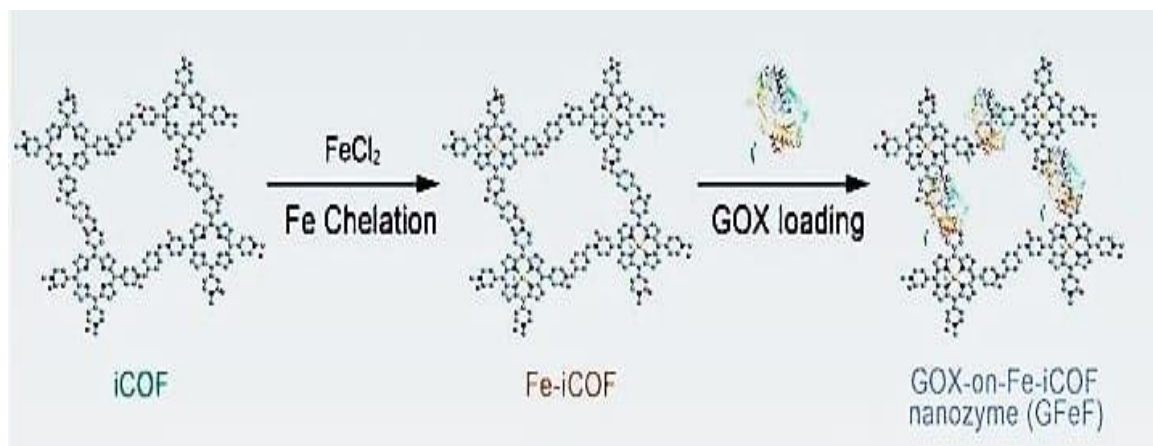


Figure 2 46 Synthetic Scheme of pre-designed GFeF nanozyme (Metal-Porphyrin-based COF)

Characterization:

ζ potential value of iCOF: 25 mV, ζ potential value of Fe-iCOF: 33 mV, ζ potential value of GFeF: ≈ 35 eV.

UV-vis absorption of iCOF, Fe-iCOF, and GFeF: similar, Diffraction peaks of iCOF: 5.65° and 17.55° .

^{13}C NMR chemical shifts of iCOF: Aromatic carbons of TPyP and p-Xylylene dibromide: 100-160 ppm, Alkyl carbon: 65 ppm

XPS peaks of Fe-iCOF: Fe 2p $_{1/2}$: 725.2 eV, Fe 2p $_{3/2}$: 711.8 eV and C 1s: 284.65, 285.9, 288.05 eV

FTIR peaks of GFeF: -C=N: 3358 cm^{-1} and -C=O: 1680 cm^{-1} [82].

In 2022 Mingbo Lv, We synthesized a metalloporphyrin-based donor-acceptor (D-A) covalent organic framework (COF) called Zn-Por-TT using Zinc (II) 5,10,15,20-tetrakis(para-aminophenyl) porphyrin (Zn-TAPP) as the acceptor and thieno[3,2-b]thiophene-2,5-dicarbaldehyde (TT) as the donor through a solvothermal method at 120 °C for 3 day. To confirm the role of Zn $^{2+}$ as the active site and the importance of D-A interactions, we also synthesized a metal-free Por-TT COF and COF-366-Zn. The Zn-Por-TT COF was obtained as a dark purple powder with a 75% yield [83].

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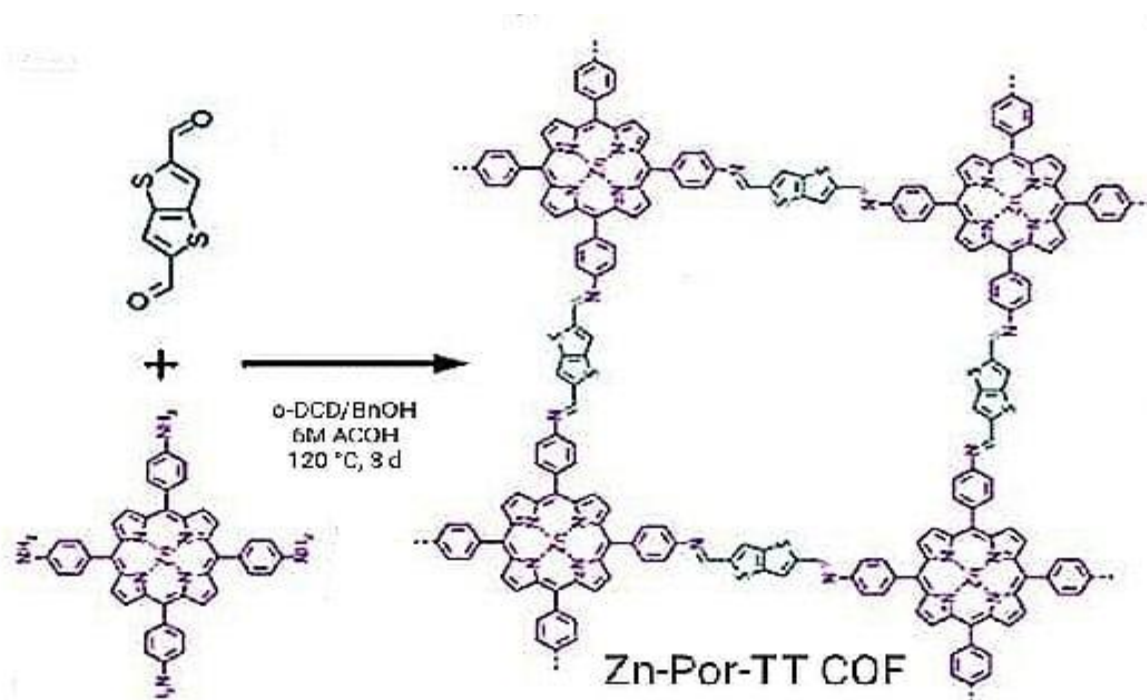
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Figure 2.47 Synthetic Scheme of Zn-Por-TT COF (Metal-Porphyrin-based COF)

Characterization:

FT-IR Peaks: -NH_2 : ~ 3352 and 3316 cm^{-1} , -CHO : $\sim 1660\text{ cm}^{-1}$ and C=N linkages : $\sim 1612\text{ cm}^{-1}$

^{13}C Solid-State NMR Peak: Carbon of the imine linkages: $\sim 150.4\text{ ppm}$

XPS Peaks: Zn 2p: 1021.59 eV (Zn 2p $_{2/3}$) and 1044.60 eV (Zn 2p $_{1/2}$)

PXRD Peaks: Zn-Por-TT COF: 3.3° , 6.6° , 7.2° , 9.8° , 10.7° , and 22.2°

UV-Vis DRS: Zn-Por-TT COF: absorption edge at $\sim 700\text{ nm}$, band gap of $\sim 1.8\text{ eV}$ [83].

In 2022 Liang Zhang et al, synthesized COF-618-Cu, a Pyrex tube was filled with L-BT, TAPP-Cu, *o*-dichlorobenzene, *n*-butanol, and aqueous acetic acid. The mixture was sonicated to dissolve the components. The solution was quickly frozen using liquid nitrogen and was sealed with a flame. After warming to room temperature, the tube was heated. The product was then filtered and washed with dioxane and acetone [84].

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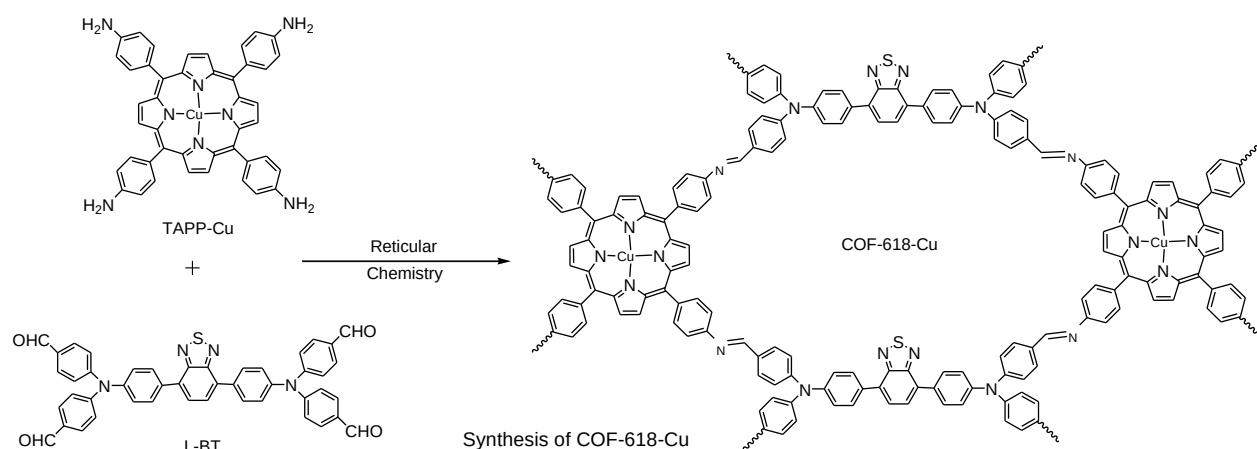


Figure 2.48 Synthetic Scheme of COF-618-Cu (Metal-Porphyrin-based COF)

Characterization:

NMR Spectrum: Imine bond: 154 ppm

XPS: Imine bond: 398.08 eV

IR Spectrum: Imine bond: 1597 cm^{-1}

PXRD: Sharp peaks indicate high crystallinity and Pawley refinement results: Rwp = 1.67%, Rp = 0.99%

Brunauer–Emmett–Teller Surface Areas: COF-618-Cu: 1440 $\text{m}^2 \text{g}^{-1}$ [84].

In 2022 Hui-Chao Ma et al, synthesized (R)-CuTAPBP-COF as a black-purple crystalline solid by directly polymerizing the chiral (R)-BINOLPA-DA monomer with Cu(II)-TAPP through imine condensation. This process was done under solvothermal conditions (EtOH/mesitylene/HOAc, 120°C, 72 hours) and yielded 58% [85].

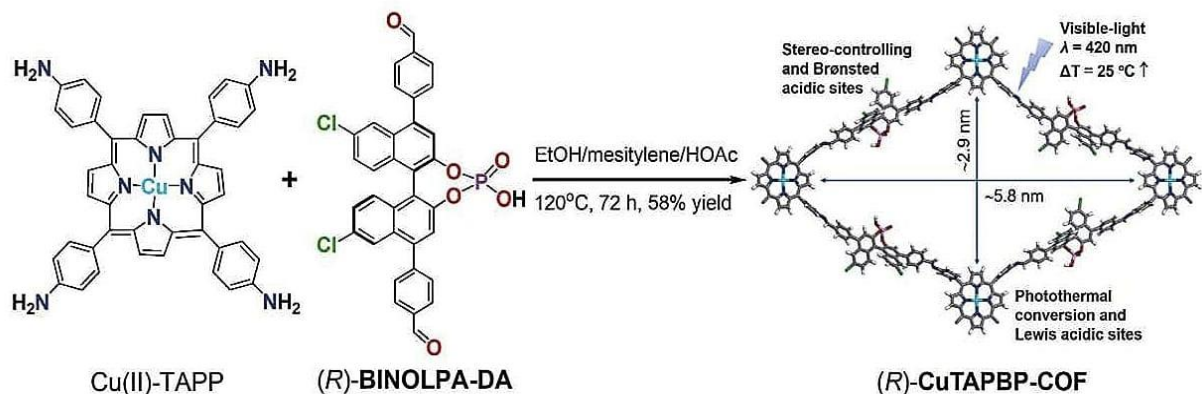


Figure 2.49 Synthetic Scheme of (R)-CuTAPBP-COF (Metal-Porphyrin-based COF)

Characterization:

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FT-IR Peaks: -NH₂: ~3352 and 3316 cm⁻¹, -CHO: ~1660 cm⁻¹, C=N linkages: ~1612 cm⁻¹ and Imine linkage: 1605 cm⁻¹

¹³C Solid-State NMR Peak: Carbon of the imine linkages: ~150.4 ppm

XPS Peaks: N 1s: TADP-COF: 398.1, 399.2, and 400.1 eV, Cu(II)@TADP-COF: 398.9 eV and Pd(II)/Cu(II)@TADP-COF: 398.6 and 400.0 eV. O 1s: TADP-COF: 532.9 eV, Cu(II)@TADP-COF: 532.6 eV and Pd(II)/Cu(II)@TADP-COF: 531.5, 532.5, and 534.3 eV. Cu 2p: Cu(II)@TADP-COF: shifted downfield. Pd 3d: Pd(II)/Cu(II)@TADP-COF: shifted downfield.

PXRD Peaks: (R)-CuTAPBP-COF: 2.7, 4.7, 5.4, 6.5 and 7.7°[85].

In 2022 Yaling Li et al, also synthesized Cu(II)@TADP-COF, copper acetate monohydrate was dissolved in methanol, and TADP-COF was added. The mixture was stirred for 24 h at 50°C, washed thoroughly with water and methanol. Cu(II)@TADP-COF was then activated under vacuum overnight at 90°C. The process yielded a dark-purple powder with 91% efficiency [63]. Synthesized Pd(II)@TADP-COF, palladium acetate was dissolved in dichloromethane, and TADP-COF was added. The mixture was stirred for 24 h at room temperature, washed thoroughly with water and methanol and Pd(II)@TADP-COF was then activated under vacuum overnight at 90°C. The process yielded a dark-purple powder with 94% efficiency [63]. Synthesized Pd(II)/Cu(II)@TADP-COF, Cu(II)@TADP-COF was treated with palladium acetate dissolved in dried dichloromethane. The mixture was stirred for 24 h at room temperature, the precipitate was collected by filtration, washed with dichloromethane, and then dried. The resulting dark-purple Pd(II)/Cu(II)@TADP-COF powder was obtained with 93% yield. Structure and Characterization already shows [63].

In 2022 Zou Bin et al, synthesized COF-366-Zn, terephthalaldehyde and ZnTAPP were dissolved in n-butanol. Then, 1,2-dichlorobenzene, aniline, and aqueous acetic acid were added, and the mixture was sonicated. The reaction solution was poured into a metal reaction kettle, degassed, and sealed. The reaction was conducted at 120 °C for 72 h. Afterward, the product was filtered, washed thoroughly with tetrahydrofuran, and then extracted with acetone at 80 °C for 24 h. The final product was dried [86]. In 2022 Zou Bin et al, also synthesized COF-366-Zn/GO/Nafion/GCE biomimetic enzyme biosensor, COF-366-Zn (ZnTPP, ZnTMPP, or ZnTHPP) and graphene oxide were dissolved in PBS (pH 7.0). The mixture was sonicated for 15 min to obtain the COF-366-Zn/GO composite dispersion. Then, the solution was pipetted onto a pre-treated glassy carbon electrode (GCE) and dried. After drying, Nafion was added dropwise and dried to obtain the COF-366-Zn/GO/GCE (ZnTPP/GO/GCE, ZnTMPP/GO/GCE, or ZnTHPP/GO/GCE) biomimetic enzyme modified electrode [86].

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Figure 2.50 Synthetic Scheme of COF-366-Zn, COF-366-Zn/GO/Nafion/GCE, COF-366-Zn/GO/GCE and COF-366-Zn/GO (Metal-Porphyrin-based COF)

Characterization:

XPS: C 1s: 287.6 eV (C=N-C bonds), O 1s: 532.4 eV (C-O-C bond on GO), N 1s: 398.4 eV (C-N=C bond) and Zn 2p: 1021.0 eV and 1044.1 eV (Zn 2p_{3/2} and Zn 2p_{1/2} transitions)

FT-IR: Absorption peak: 1670 cm⁻¹ (C=N bond in COF-366-Zn)

XRD: Strong diffraction peak: $2\theta = 4.02^\circ$ (characteristic of COF-366-Zn)

Cyclic Voltammetry: Redox peak currents: COF-366-Zn/GCE: $I_{pa} = 31.90 \mu A$, $I_{pc} = 29.90 \mu A$ and COF-366-Zn/GO/GCE: $I_{pa} = 45.23 \mu A$, $I_{pc} = 41.19 \mu A$

Electrochemical Impedance Spectroscopy (EIS): Charge transfer resistance (R_{ct}): Bare GCE: high R_{ct} , COF-366-Zn/GCE: lower R_{ct} and COF-366-Zn/GO/GCE: lowest R_{ct} [86].

In 2023 Si-Wen Ke et al, synthesized Ni-TAPP-2H, a Pyrex tube was filled with 2H-TAPP, Ni(bded)₂, 1,4-dioxane, mesitylene, and aqueous acetic acid. The mixture was sonicated for 15 min. After freezing, the tube was sealed and heated at 120°C for 72 hours. The resulting dark purple precipitate was collected by filtration, washed with methanol (CH₃OH) and tetrahydrofuran (THF), and extracted with THF. Finally, the product was dried to yield the activated Ni-TAPP-2H [87]. In 2023 Si-Wen Ke et al, also synthesized Ni-TAPP-Co followed the same procedure as Ni-TAPP-2H, with the only difference being the use of Co-TAPP instead of 2H-TAPP [87].

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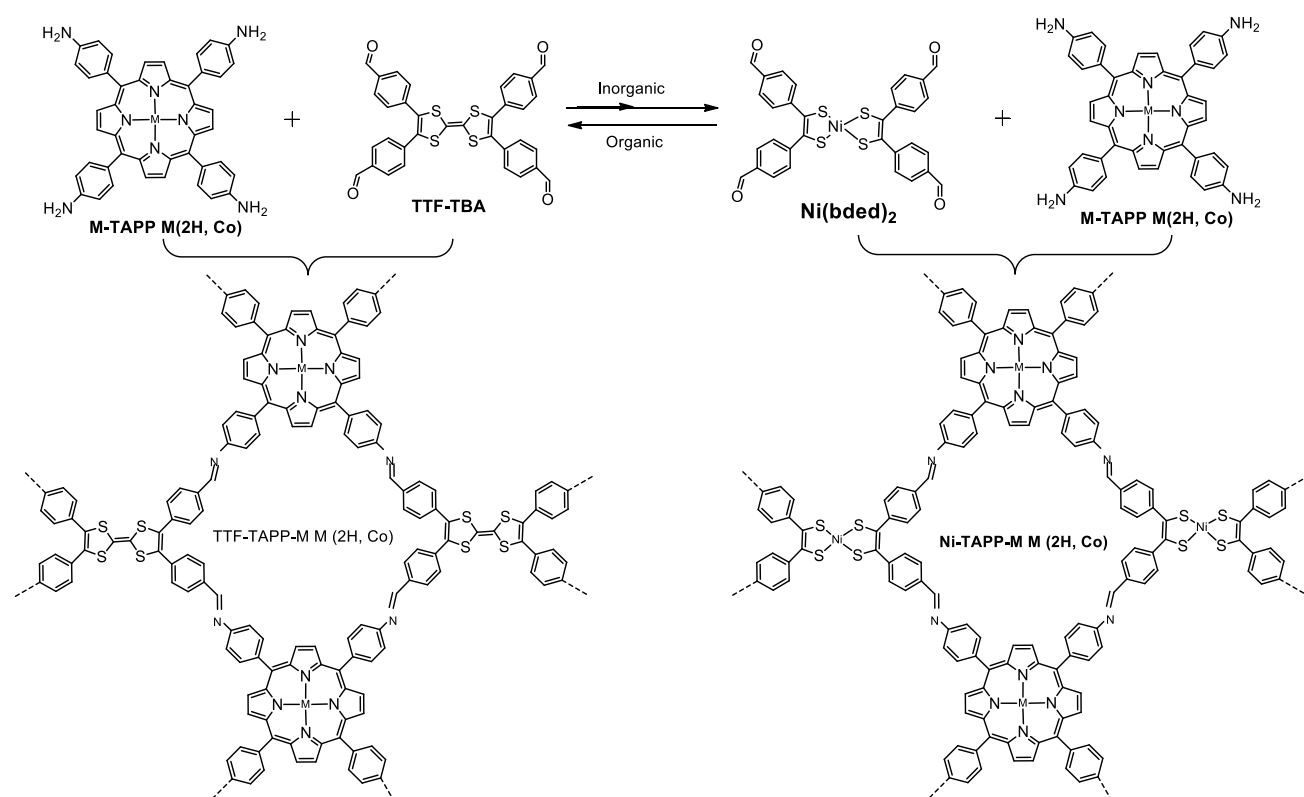


Figure 2.51 Synthetic Scheme of Ni-TAPP-2H and TTF-TAPP-M (Metal-Porphyrin-based COF)

Characterization:

PXRD Peaks: Ni-TAPP-Co: 5.17°, 5.84°, 10.36°, 11.69°, and 21.77°

FT-IR Peaks: Ni-TAPP-2H and Ni-TAPP-Co: 1621 cm⁻¹ (C=N bonds), Ni(bded)₂: 1701 cm⁻¹ (C=O stretching band), Ni(bded)₂: 3200-3500 cm⁻¹ (N-H stretching bands)

Raman Peaks: Li2O2: 793 cm⁻¹

UV-Vis Peaks: Ni-TAPP-2H and Ni-TAPP-Co: edge at 1800 nm

XPS Peaks: Ni-TAPP-2H: ΔGads = -2.02 eV (*LiO2 binding free energy on Ni sites), TTF-TAPP-Co: ΔGads = -1.98 eV (*LiO2 binding free energy on Co sites), Ni-TAPP-Co: ΔGads = -2.05 eV (*LiO2 binding free energy on Ni sites), ΔGads = -2.01 eV (*LiO2 binding free energy on Co sites) [87].

In 2023 Ting He et al, also reported COF1-Au by treating COF1 with potassium tetrachloroaurate (KAuCl₄) in N,N-dimethylformamide (DMF) at 85 °C for 24 hours. After the reaction, the mixture was cooled, and the product was isolated. The Au content in COF1-Au was determined to be 0.9 wt% by inductively coupled plasma optical emission spectroscopy (ICP-OES). Other COF-Au systems (COF2-Au, COF3-Au, COF4-Au, and COF5-Au) were prepared similarly by replacing COF1 with the corresponding COF and treating with KAuCl₄ under the same conditions .Figure and Characterization shows already above[64].

In 2023 Suleman Suleman et al, synthesized MPor-Dha COFs, cobalt meso-tetra(4-hydrazidocarbonylphenyl) porphyrin (CoPor) and 2,5-dihydroxyterephthalaldehyde (Dha) were mixed with mesitylene, N-methyl-2-

pyrrolidone (NMP), and acetic acid. The mixture was sonicated to form a uniform solution, then evacuated and flame-sealed, heated at 120 °C for 3 days. The resulting product was collected by filtration and washed with DMF, ethanol, and methanol to yield CoPor-Dha [88]. In 2023 Suleman Suleman et al, also synthesized NiPor-Dha and CuPor-Dha were prepared using nickel or copper porphyrin with the same procedure but using DMF as the primary solvent. The products were washed with DMF, tetrahydrofuran, and methanol [88].

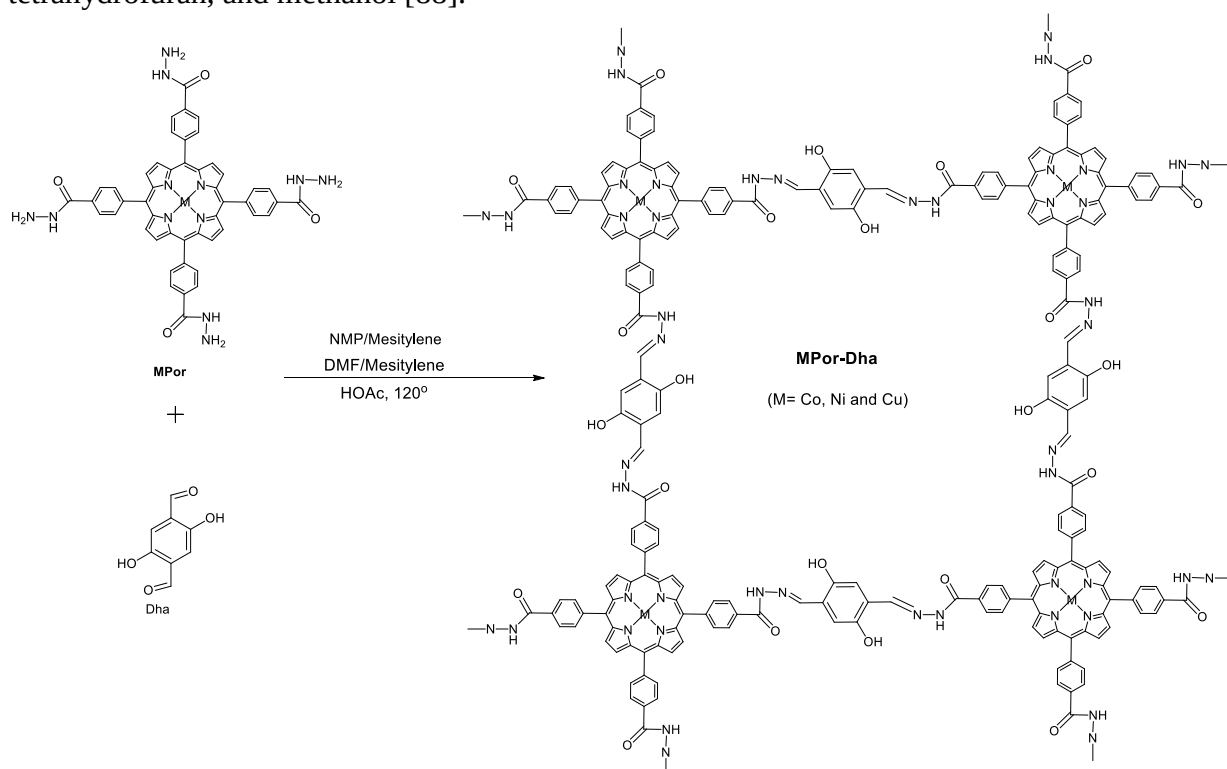


Figure 2.52 Synthetic Scheme of MPor-Dha COFs (Metal-Porphyrin-based COF)

Characterization:

FT-IR: HC=O stretching bands: 1670 cm^{-1} (disappeared after COF formation) and C=N stretching vibrations: 1654-1656 cm^{-1} (formed after COF formation)

PXRD: Strong peak: 2.9° (diffraction of (100)) and Prominent peaks: 5.8° and 8.8° (diffractions of (200) and (300), respectively)

BET surface area: CoPor-Dha: 118 $\text{m}^2 \text{g}^{-1}$, NiPor-Dha: 150 $\text{m}^2 \text{g}^{-1}$ and CuPor-Dha: 286 $\text{m}^2 \text{g}^{-1}$ [88].

In 2023 Ting He et al, synthesized ZnP-Pz-DHTP-COF by reacting zinc porphyrin (ZnP), pyrazine-2,5-dicarbaldehyde (PzDA), and 2,5-dihydroxyterephthalaldehyde (DHTA) in under solvothermal conditions, achieving an 86% yield [89]. In 2023 Ting He et al, also synthesized hydrophobic ZnP-Pz-COF by polymerizing ZnP with PzDA, yielding 88%. A non-crystalline control (ZnP-Pz-DHTP-POP) was made in 81% yield, and another control, ZnP-TP-DHTP-COF, was synthesized by using a phenyl linker instead of pyrazine, yielding 85%, synthesized hydrophilic ZnP-Pz-PEO-COF with a 96% yield by reacting ZnP-Pz-DHTP-COF with 1-bromo-2-(2-methoxyethoxy)ethane in the presence of K_2CO_3 in DMF at 85°C.

Similarly, ZnP-Pz-PEO-POP and ZnP-TP-PEO-COF were prepared in 98% and 96% yields, respectively, using the same reagent to modify ZnP-Pz-DHTP-POP and ZnP-TP-DHTP-COF [89].

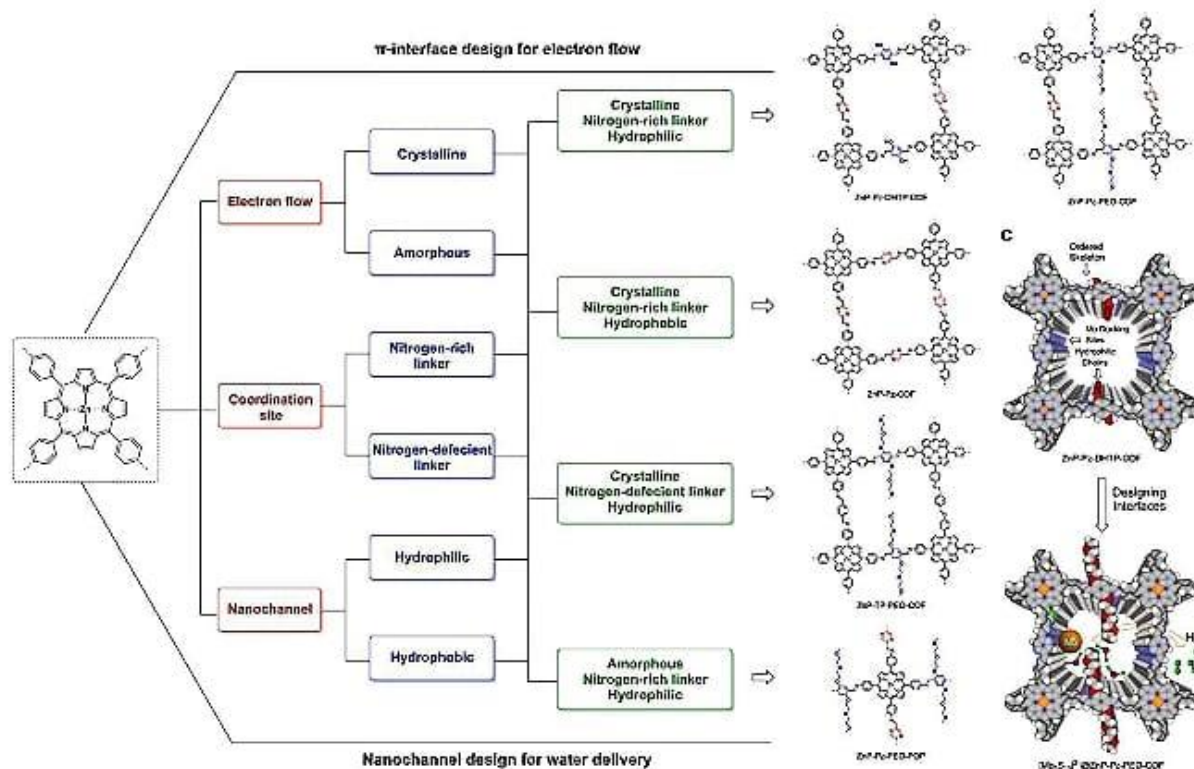


Figure 2.53 Synthetic Scheme of ZnP-TP-PEO-COF, ZnP-Pz-DHTP-POP and ZnP-TP-DHTP-COF (Metal-Porphyrin-based COF)

Characterization:

PXRD Peaks: ZnP-Pz-DHTP-COF: 3.4°, 6.8°, 10.2°, 24.5°, ZnP-Pz-PEO-COF: 3.4°, 6.8°, 8.6°, 24.5° and [Mo3S13]2- @ZnP-Pz-PEO-COF: 10.5°, 16.3°, 24.5°, 27.3°

FT-IR Peaks: C=N stretching bands: 1612 cm⁻¹, Alkyl C-H stretching bands: 2874 cm⁻¹ (ZnP-Pz-PEO-COF) and C-O-C stretching bands: 1100 cm⁻¹ (ZnP-Pz-PEO-COF)

Solid-State 13C CP/MAS NMR Peaks: Methyl groups: 58 ppm (ZnP-Pz-PEO-COF) and Methylene groups: 71 ppm (ZnP-Pz-PEO-COF)

XPS Peaks: Mo-N bond: 398.0 eV ([Mo3S13]2- @ZnP-Pz-PEO-COF), Mo 3d_{5/2}: 230.0 eV ([Mo3S13]2- @ZnP-Pz-PEO-COF) and Mo 3d_{3/2}: 233.0 eV ([Mo3S13]2- @ZnP-Pz-PEO-COF) [89].

In 2023 Xi Tian et al, synthesized NiPc-DFP COF, NiPc-8NH₂ and 2,6-diformylphenol were mixed with mesitylene, 1,4-dioxane, and triethylamine in a Pyrex tube. After sonication for approximately 30 min, the mixture was frozen using liquid nitrogen, degassed, heated at 80 °C and left undisturbed for 72 h and the resulting dark green solid was filtered, washed with methanol, DMF, DCM, and THF and further purified. The product was dried, yielding 40.5 mg of activated material [90]. In 2023 Xi Tian et al, also synthesized NiPc-DFP-Co COF, NiPc-DFP COF and Co(Ac)₂ were added to methanol and stirred for 24 h,. The mixture was then filtered, washed thoroughly with methanol and water, and evacuated at 80 °C under dynamic vacuum

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overnight, yielding a dark green solid. Using the same process but replacing $\text{Co}(\text{Ac})_2$ with $\text{Ni}(\text{Ac})_2$, NiPc-DFP-Ni COF was synthesized as a dark green solid [90]. CoPc-DFP COF followed the same procedure as NiPc-DFP COF, except that NiPc-8NH₂ was replaced with CoPc-8NH₂ [90]. CoPc-DFP-Co COF, CoPc-DFP COF and $\text{Co}(\text{Ac})_2$ were added to methanol and stirred for 24 h. The mixture was then filtered, washed thoroughly with methanol and water and evacuated at 80 °C under dynamic vacuum overnight, yielding a dark green solid. Using the same process but replacing $\text{Co}(\text{Ac})_2$ with $\text{Ni}(\text{Ac})_2$, CoPc-DFP-Ni COF was synthesized as a dark green solid [90].

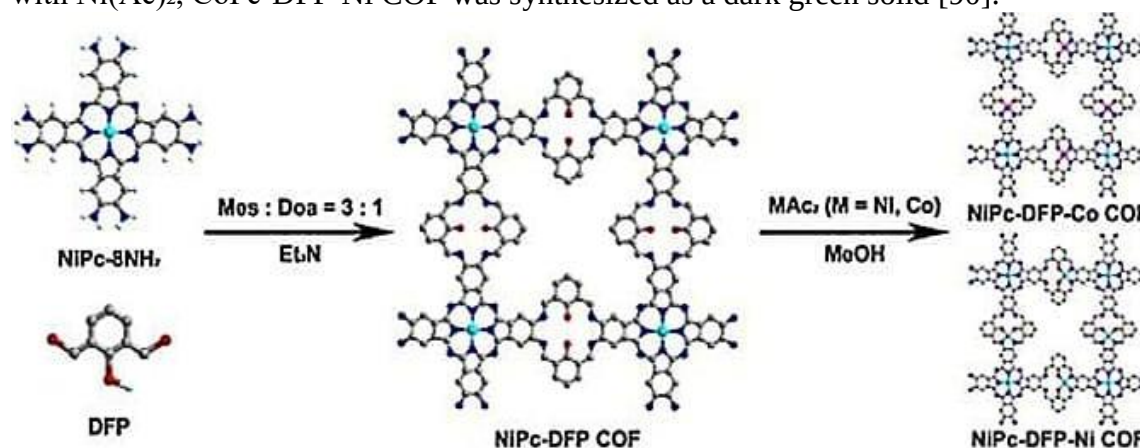


Figure 2.54 Synthetic Scheme of NiPc-DFP COF, NiPc-DFP-Co COF and NiPc-DFP-Ni COF (Metal-Porphyrin-based COF)

Characterization:

PXRD: Strong peak: 4.39° (diffraction of (011)) and Prominent peaks: 8.74° (diffraction of (031))

FT-IR: HC=O stretching bands: 1675 cm⁻¹ (disappeared after COF formation), N–H stretching band: 3199–3350 cm⁻¹ (disappeared after COF formation), C=N stretching vibration band: 1619 cm⁻¹ (appeared after COF formation) and C=N groups with metal coordination: 1594 cm⁻¹

XPS: N 1s spectrum: 398.6 eV (C–N=C) and 400.6 eV (C=N–Ni), Ni 2p spectrum: 855.6 eV (Ni 2p_{3/2}) and 873.0 eV (Ni 2p_{1/2}) and Co 2p spectrum: +2 oxidation states

UV–vis absorption spectra: Visible light absorption: NiPc-DFP COF and NiPc-DFP-M COF (M = Ni and Co) present visible light absorption ability [90].

In 2024 Hugo Veldhuizen et al, synthesized COFs using metalloporphyrins with four amino groups and terephthalaldehyde linkers under solvothermal conditions. They created five COFs by varying the nickel-to-zinc ratios: Ni100/Zn0, Ni75/Zn25, Ni50/Zn50, Ni25/Zn75, and Ni0/Zn100. Interestingly, the Ni50/Zn50 COF also produced formate (43% efficiency) and methane (14% efficiency) at 150 mA/cm², showing a unique catalytic synergy between the two metals [91].

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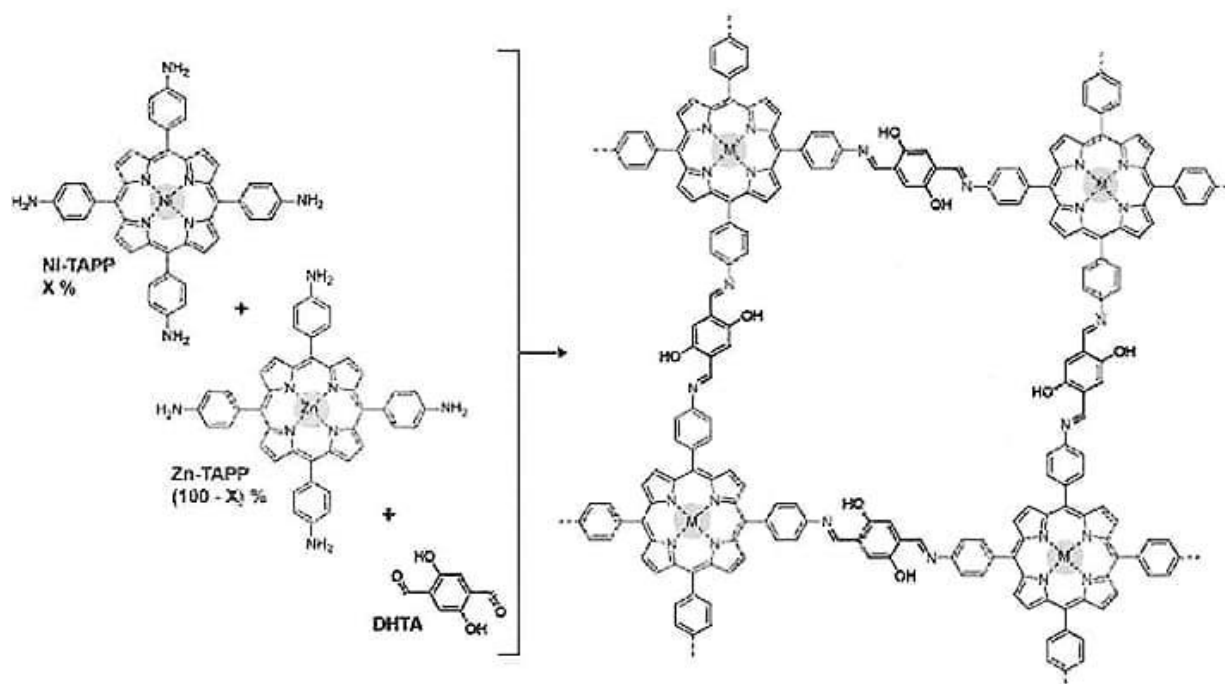


Figure 2.55 Synthetic Scheme of Metal-Porphyrin-based COF on the bases of Ni-TAPP, Zn-TAPP and DHTA

Characterization:

FT-IR: 1618 cm^{-1} and 1390 cm^{-1} : formate species after catalysis

XPS: 294.4–294.7 eV: potassium (K 2p) after catalysis, 397.5–397.8 eV and 398.7–399.3 eV: nitrogen, indicating stability of porphyrin ring and imine polymer backbone

PXRD: 2.45 nm: in-plane distance, 0.4 nm: interlayer distance

Nitrogen Adsorption Isotherms and BET Analysis: Micropore volume: 0.17–0.25 $\text{cm}^3 \cdot \text{g}^{-1}$, Small mesopore volume: 0.06–0.13 $\text{cm}^3 \cdot \text{g}^{-1}$, Ni₅₀/Zn₅₀ COF: BET surface area of 1180 $\text{m}^2 \cdot \text{g}^{-1}$, total pore volume of 0.67 $\text{cm}^3 \cdot \text{g}^{-1}$

Tafel Slopes: 212 mV/dec (Ni₇₅/Zn₂₅), 184 mV/dec (Ni₅₀/Zn₅₀), 92 mV/dec (Ni₂₅/Zn₇₅), 385 mV/dec (Ni₀/Zn₁₀₀)

Gas Chromatography and Faradaic Efficiencies (FE): Ni₅₀/Zn₅₀ at –0.6 V vs RHE: FECO = 69%, FE_{formate} = 10%, total FE = 79%, Ni₅₀/Zn₅₀ at 100 mA cm^{-2} (MEA setup): FE_{formate} = 40%, FE_{CH₄} = 11%, Ni₅₀/Zn₅₀ at 150 mA cm^{-2} (MEA setup): FE_{formate} = 43%, FE_{CH₄} = 14%

Binding Energies from DFT Calculations: CO binding enthalpy: –33.8 kJ/mol for Ni(II)-TPP, –29.1 kJ/mol for Zn(II)-TPP [91].

In 2024 Hong-Jing Zhu et al, synthesized BPy-CoPor, Co-TAPP and BPy were mixed with benzyl alcohol, o-dichlorobenzene, and acetic acid in a Pyrex tube. The mixture was sonicated, flash-frozen, and degassed and heated d at 120 °C and allowed to stand undisturbed for 72 h. The product was filtered, washed with THF and acetone, and as evacuated at 70 °C under vacuum overnight to obtain the activated sample [92]. In 2024 Hong-Jing Zhu et al, also synthesized lose-DAE-BPy-CoPor, a THF dispersion of open-DAE-BPy-CoPor was exposed to UV light (~365 nm) for 3 hours [92].

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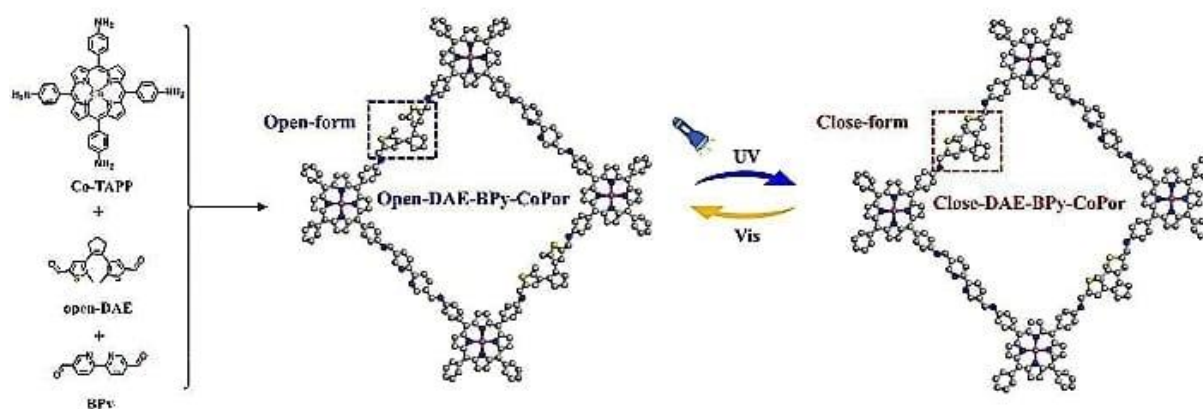
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Figure 2.56 Synthetic Scheme of BPy-CoPor (Metal-Porphyrin-based COF)

Characterization:

XPS: 780.2 eV: Co 2p_{3/2}, 795.67 eV: Co 2p_{1/2}, 164.3 eV: S 2p_{3/2} for open-DAE-BPy-CoPor

- 164.7 eV: S 2p_{3/2} for close-DAE-BPy-CoPor

PXRD: 3.0°: (100) facet, 6.1°: (020) facet

N₂ Adsorption Isotherms and BET Analysis: 899.4 m² g⁻¹: BET surface area of open-DAE-BPy-CoPor, 605.2 m² g⁻¹: BET surface area of close-DAE-BPy-CoPor, 0.67 cm³ g⁻¹: total pore volume of open-DAE-BPy-CoPor

XANES: 7715.3 eV: pre-edge peak for open-DAE-BPy-CoPor and close-DAE-BPy-CoPor

EXAFS: 1.43 Å: Co-N scattering path for open-DAE-BPy-CoPor, 1.93 Å: Co-N bond length for close-DAE-BPy-CoPor [92].

In 2024 Enbo Zhou et al, synthesized CoTPP-CoBpy₃ COF, by sonicating 5,10,15,20-tetrakis(4-aminophenyl)-21H,23H-porphine, 2,2'-bipyridyl-5,5'-dialdehyde, 2,2'-bipyridine, and cobalt(II) acetate tetrahydrate in a mixture of o-dichlorobenzene and n-butanol. Acetic acid was added, and the mixture was flash-frozen, degassed, sealed, and heated at 120°C for 3 days. The resulting precipitate was filtered, washed with water, tetrahydrofuran, and ethanol, then dried, yielding deep-red CoTPP-CoBpy₃ (bulk) powder [93]. In 2024 Enbo Zhou et al, also synthesized CoTPP-Bpy COF, 5,10,15,20-tetrakis(4-aminophenyl)-21H,23H-porphine cobalt(II) and 2,2'-bipyridyl-5,5'-dialdehyde were sonicated in a mixture of DCB and n-butanol. After adding acetic acid, the mixture was flash-frozen, degassed, sealed and heated at 120°C for 3 days. The resulting precipitate was filtered, washed with water, tetrahydrofuran, and ethanol, and then dried, yielding black CoTPP-Bpy powder with a 92% isolated yield [93]. Synthesized CoTPP-CoBpy₃ nanosheets by sonication in a mixture of ethanol and water. The nanosheets were then collected by high-speed centrifugation to remove excess solvent. Finally, the collected nanosheets were dried, yielding a reddish-brown loose powder [93]. Synthesized Co^{II}(bpy)₃(OAc)₂, a mixture of Co(OAc)₂·4H₂O and 2,2'-bipyridine was dissolved in methanol and refluxed. The resulting solution was cooled and then remove the solvent. The orange powder-like Co^{II}(bpy)₃(OAc)₂ was obtained [93].

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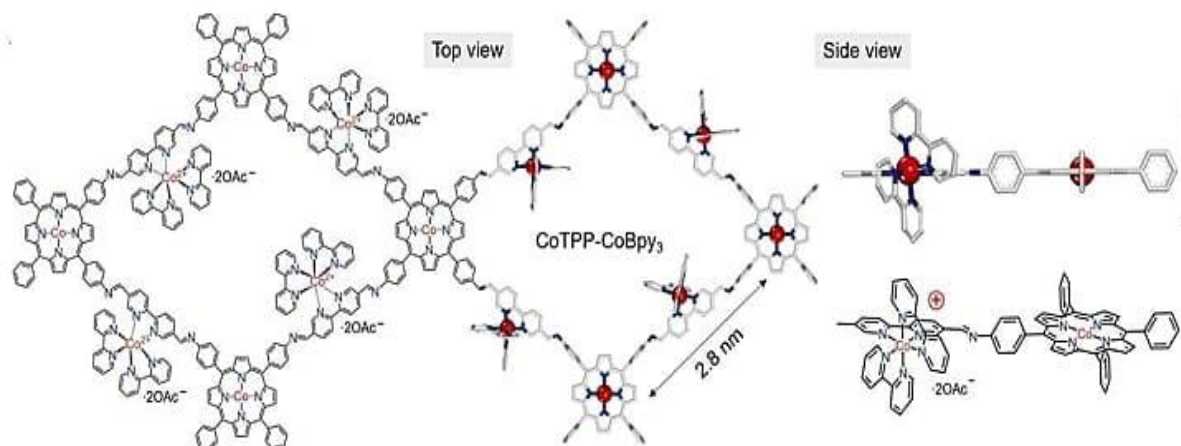
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Figure 2.57 Synthetic Scheme of CoTPP-CoBpy₃ (Metal-Porphyrin-based COF)

Characterization:

PXRD: 3.1° ((110) facet), 4.0° ((020) facet) and 6.2° ((220) facet)

FTIR: 1623 cm⁻¹ (C=N stretching), 1588 cm⁻¹ (C=N stretching) and 1662 cm⁻¹ (coordination of Co complex moiety)

UV-vis: 445 nm (Soret band of CoTPP), 600 nm (Q bands of CoTPP) and 525 nm (shoulder peak of OAc₂)

Photoluminescence: 525 nm (photoluminescence quenching)

XPS: 398.6 eV (N 1s spectrum, C=N=C), 400.6 eV (N 1s spectrum, C=N-Ni), 855.6 eV (Ni 2p spectrum, Ni 2p_{3/2}) and 873.0 eV (Ni 2p spectrum, Ni 2p_{1/2})

In situ ATR-IR: ~1000 cm⁻¹ (prominent peak indicating surficial superoxide, Co-O₂ ·) [93].

2.3. Synthesis of Porphyrin COFs with Tunable Content of Hydrogen-Bonding Structures:

In 2015 Xiong Chen et al. synthesized 2D- Porphyrin COFs (MP-DHPh_xCOFs) mix dihydroxyterephthalaldehyde (DHTA) and terephthalaldehyde (TA) in different molar ratios and combine this monomer with 5,10,15,20-tetrakis(4'-tetraphenylamino) porphyrin derivatives (MP; M = Cu, H₂, and Ni). Use a solvent mixture of o-dichlorobenzene and n-butanol under solvothermal conditions produces the MP-DHPhX COFs in 68–83% isolated yields [94].

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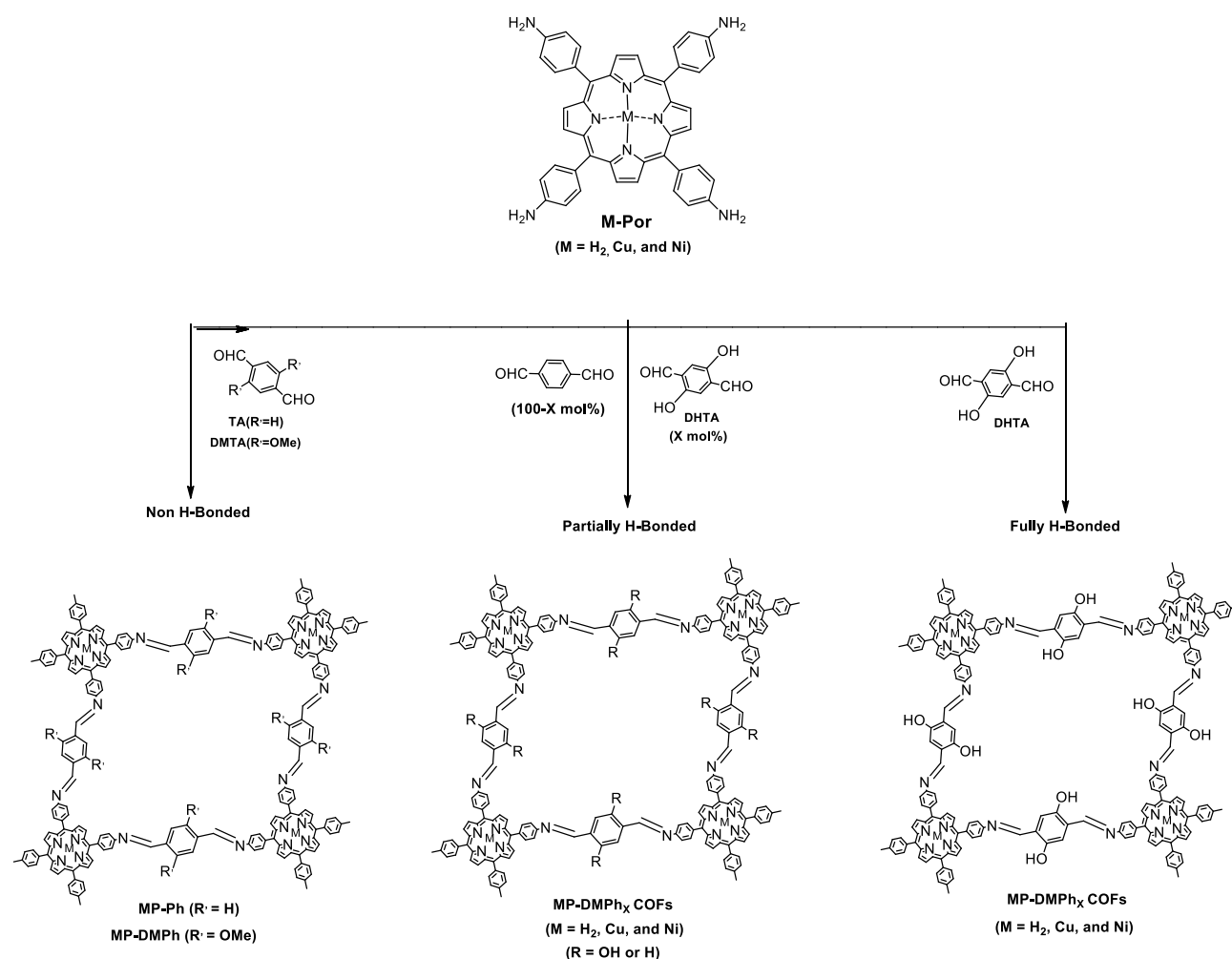


Figure 2.58 Synthetic Scheme of Porphyrin COFs with Tunable Content of Hydrogen-Bonding

Characterization:

PXRD Peaks: 3.5° (100 facet), 7.2° (200 facet) and 22.9° (001 facet)

FTIR Peaks: 1612 cm⁻¹ (C=N stretching band of CuP-DHPh COF), 1622 cm⁻¹ (C=N vibration band of amorphous CuP-Ph polymer) and 1616 cm⁻¹ (C=N vibration band of CuP-DHPh_X COFs)

UV-vis Peaks: 494 nm (Soret band of CuP-DHPh COF), 505 nm (Soret band of H₂P-DHPh COF) and 250-600 nm (continuous absorbance of NiP-DHPh COF)

Other Peaks: 1270 nm (fluorescence of singlet oxygen) [94].

2.4. synthesis of core-shell structured Fe₃O₄@COFs nanospheres:

IN 2019 Juan Zhang et al. reported the core-shell Fe₃O₄@COFs nanospheres by Placing of TAP, 4,4'-biphenyldicarboxaldehyde, and Fe₃O₄-NH₂ into a Pyrex tube. Solvents was used 1,2-dichlorobenzene, butanol, and acetic acid into the tube. Sonicate the mixture for 15 minutes. the tube was degassed. Sealed the tube under vacuum and heated setup at 120°C and let it react for 3 days. After the reaction is complete, a dark purple precipitate was form in the tube. Use an external magnetic field to collect the

precipitate. Then, the wet solid was moved to a Soxhlet extractor and heated to reflux in methanol and acetone, respectively, for 24 hours to get the required product which is the core-shell $\text{Fe}_3\text{O}_4@\text{COFs}$ nanospheres [95].

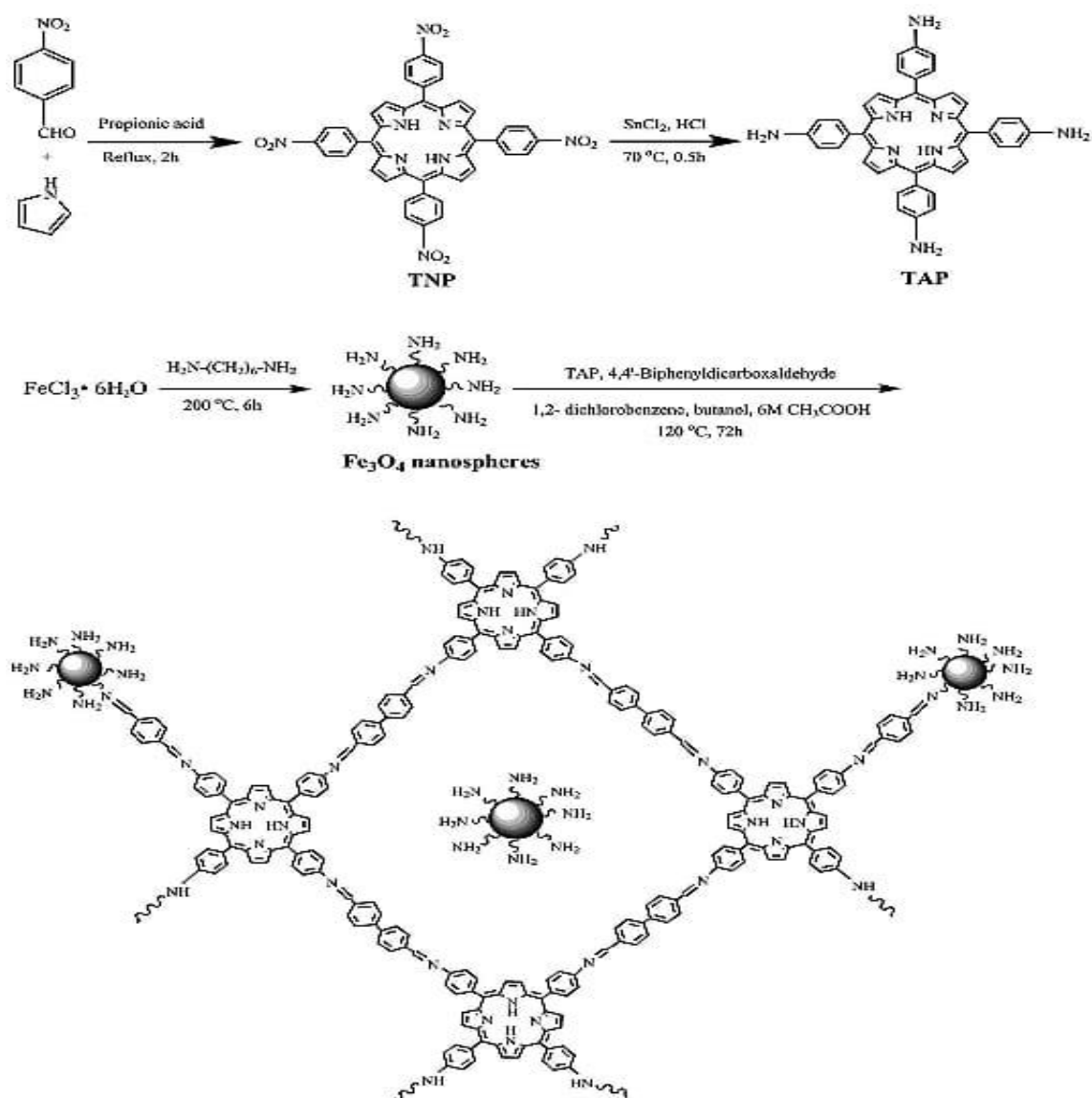


Figure 2.59 Synthetic Scheme of core-shell $\text{Fe}_3\text{O}_4@\text{COFs}$ nanospheres (Porphyrin-based COF)

Characterization:

FT-IR: 587 cm^{-1} : Fe-O-Fe vibration on core of Fe_3O_4 , 1000 cm^{-1} : Porphyrin skeleton vibrations, 1625 cm^{-1} : C=N stretching vibration of the COF coating, 1490 , 1554 , 1600 cm^{-1} : Benzene skeleton vibrations, 3443 cm^{-1} : N-H stretching vibration

XRD: Diffraction peak positions consistent with JCPDS card (19-0629)

VSM: M_s value of 42 emu g^{-1} for $\text{Fe}_3\text{O}_4@\text{COFs}$ nanospheres, M_s value of 74 emu g^{-1} for Fe_3O_4 nanospheres [95].

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<http://amresearchreview.com/index.php/Journal/about>**2.5. Synthesis of A₂B₂-Por-COF by the self-condensation of A₂B₂-Por monomer:**

In 2019 Wenjing Hao et al. reported A₂B₂-Por-COFs were readily synthesized by the compound A₂B₂-Por (4',4'''-(10,20-bis(4-aminophenyl)porphyrin-5,15-diyl)bis([1,1'-biphenyl]-4-carbaldehyde)) by self-condensed in a single solvent system with acetic acid as a catalyst. The reaction mixture was refluxed for 7 days. After this period, dark-purple crystalline A₂B₂-Por-COFs were obtained with high yields of 82–87% [29].

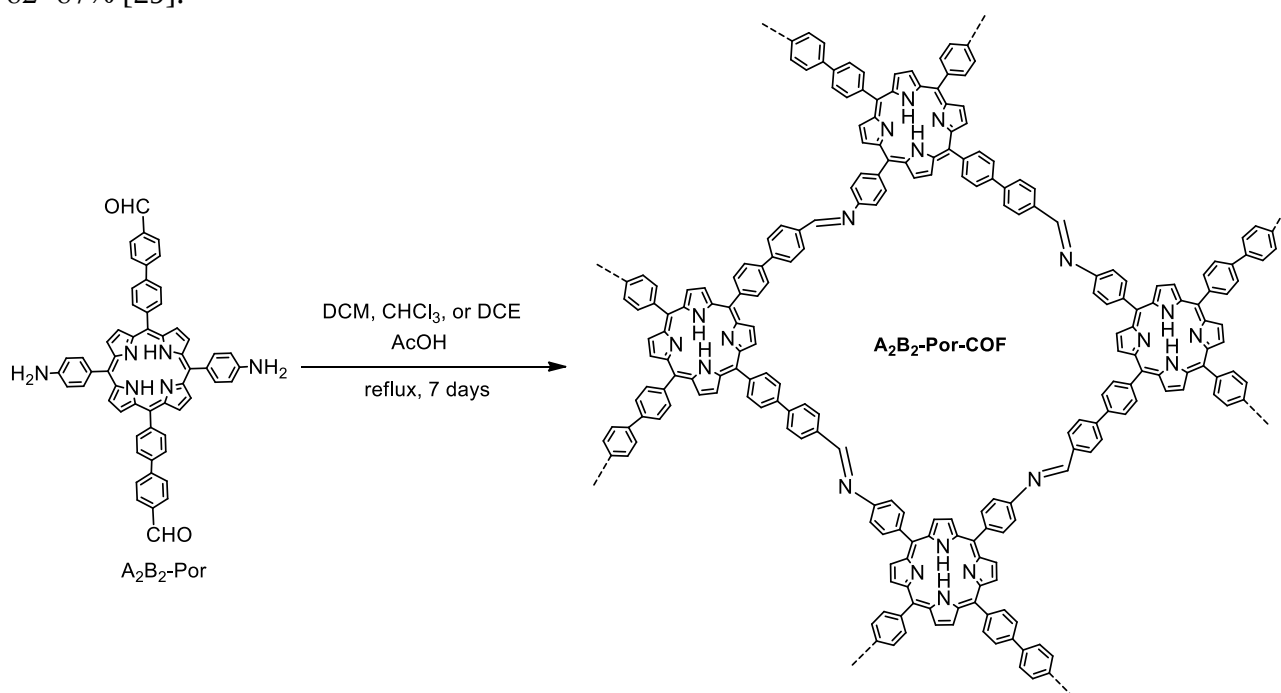


Figure 2.60 Synthetic Scheme of A₂B₂-Por-COF by the self-condensation of A₂B₂-Por monomer (Porphyrin-based COF)

Characterization:

FTIR Peaks: 1600 cm⁻¹ (C=N imine linkages) and 1696 cm⁻¹ (C=O band of the formyl groups)

¹³C Solid-State NMR Peaks: 165 ppm (carbon of the C=N bond), 150 ppm (carbon of pyrrole ring) and 120-140 ppm (other aromatic carbons)

PXRD Peaks: 3.75° ((110) facet), 7.55° ((220) reflection), 11.35° ((330) reflection), 15.10° ((440) reflection) and 20.30° ((001) reflection) [29].

2.6. Synthesis of MPor-DETH-COFs (M=H₂, CO, Ni, Zn):

In 2021 Rufan Chen et al, was synthesized H₂Por-DETH-COF, A pyrex tube was charged with p-Por-CHO, DETH, 1,2-dichlorobenzene, butanol and aqueous acetic acid. After being degassed, sealed, and heated at 120 °C for 3 days. The resulting precipitate was collected by centrifugation, exhaustively washed by Soxhlet extractions with THF and DCM for 24 h, dried under vacuum at 80 °C. The H₂Por-DETH-COF was isolated as brown powders in 88% yield[96]. In 2021 Rufan Chen et al, was also synthesized CoPor-DETH-COF, A pyrex tube was charged with p-CoPor-CHO, DETH, 1,2-dichlorobenzene, butanol and aqueous acetic acid. After being degassed, sealed and heated at 120 °C for 7 days. The resulting precipitate was collected by

centrifugation, exhaustively washed by Soxhlet extractions with THF and DCM for 24 h, dried under vacuum at 80 °C. The CoPor-DETH-COF was isolated as dark red powders in 85% yield[96]. In 2021 Rufan Chen et al, was also synthesized NiPor-DETH-COF. A pyrex tube was charged with p-NiPor-CHO, DETH, 1,2-dichlorobenzene, butanol and aqueous acetic acid. After being degassed, sealed and heated at 120 °C for 7 days. The resulting precipitate was collected by centrifugation, exhaustively washed by Soxhlet extractions with THF and DCM for 24 h, dried under vacuum at 80 °C. The NiPor-DETH-COF was isolated as red powders in 86% yield[96]. In 2021 Rufan Chen et al, was also synthesized ZnPor-DETH-COF. A pyrex tube was charged with p-ZnPor-CHO, DETH, 1,2-dichlorobenzene, butanol, and aqueous acetic acid. After being degassed, sealed and heated at 120 °C for 7 days. The resulting precipitate was collected by centrifugation, exhaustively washed by Soxhlet extractions with THF and DCM for 24 h, dried under vacuum at 80 °C. The ZnPor-DETH-COF was isolated as green powders in 85% yield[96]

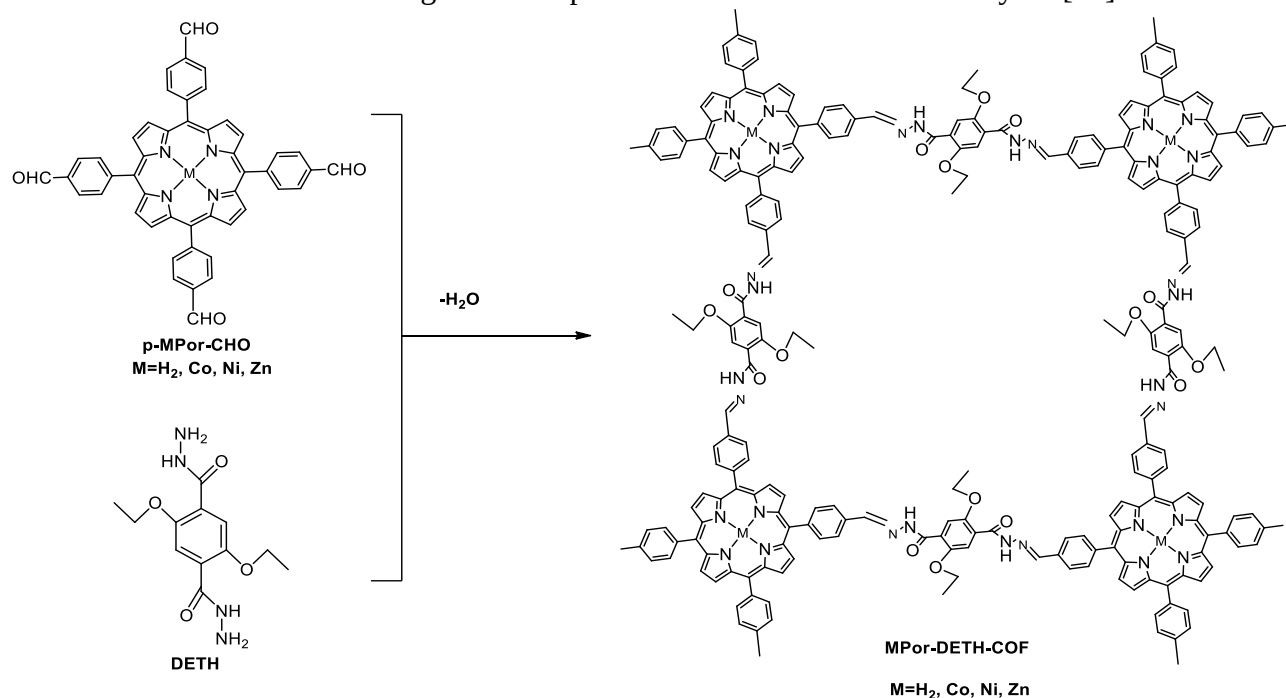


Figure 2.61 Synthetic Scheme of Synthesis of MPor-DETH-COFs ($M = H_2, Co, Ni, Zn$) (Porphyrin-based COF)

Characterization:

FTIR Peaks: 1670–1660 cm^{-1} (C=N bond)

PXRD Peaks: 3.0° ((110) crystal facet), 6.1° ((220) reflection)

N₂ Sorption Peaks: Pore size: 2.4 nm [96].

2.7. Synthesis of Por-based-COF composite:

In 2017 Quan Zuo et al, first time reported Co-porphyrin-based COF-rGO (CoCOF-Py-rGO) framework that was synthesized by stacking Co-Por-COF onto rGO sheets functionalized with a pyridine-containing dye (G-dye). Co-Por-COF was created by polymerizing cobalt(II) porphyrin and terephthalaldehyde. The pyridine ligand acted

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as structural nodes, coordinating with cobalt ions to form a 3D structure, while also enhancing solubility and preventing aggregation. Various amounts of G-dye were added to the Co-Por-COF precursors to produce CoCOF-Py-nrGO composites[97].

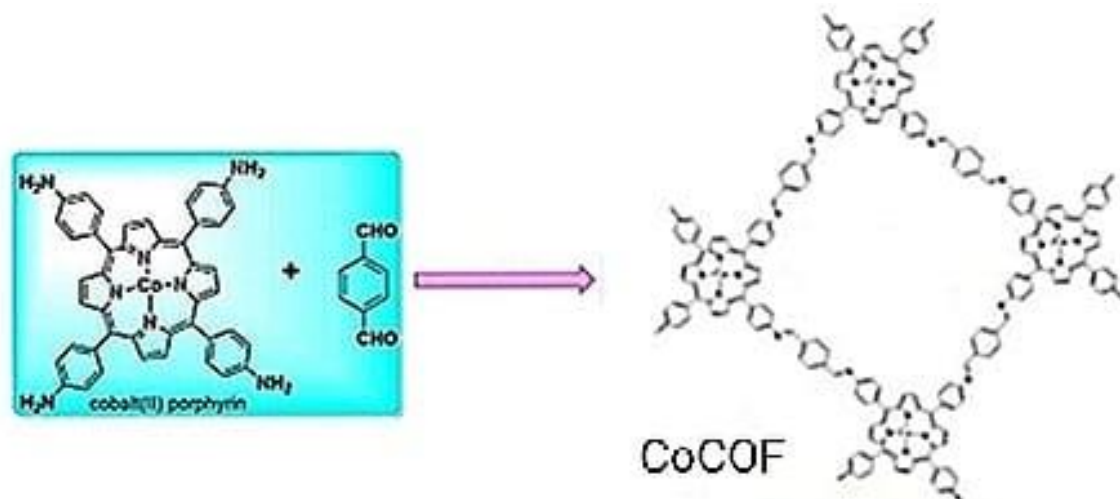


Figure 2.62 Synthetic Scheme of Por-based-COF composite

Characterization:

FTIR Peaks: 1734 cm^{-1} (carboxylic species (C=O)), 1624 cm^{-1} (skeletal ring stretch vibration peak), 1550 cm^{-1} (skeletal ring stretch vibration peak), 1400 cm^{-1} (hydroxyl species (OH deformation)), 1330 cm^{-1} (C–N of pyridine group), 1230 cm^{-1} (the C–OH stretching), 1061 cm^{-1} (C–O–C stretching), 1008 cm^{-1} (C=N stretch of Schiff base group) and 1700 cm^{-1} (Co–N stretching from the metalation of porphyrin ring)

PXRD Peaks: 3.0° ((110) crystal facet), 3.4° (characteristic XRD peaks of CoCOF), 4.1° (characteristic XRD peaks of CoCOF), 6.1° ((220) reflection), 6.9° (characteristic XRD peaks of CoCOF) and 8.5° (characteristic XRD peaks of CoCOF)

UV-Vis Peaks: 432 nm (Soret band (B-band)), 521 nm (Q-bands), 575 nm (Q-bands), 595 nm (Q-bands) and 665 nm (Q-bands)

Raman Peaks: 1575 cm^{-1} (characteristic G band) and 1335 cm^{-1} (characteristic D band)

XPS Peaks: 398.6 eV (pyridinic N), 399.2 eV (CoNX) and 399.9 eV (pyrrole N) [97].

In 2019 Yuxia Hou et al, reported CuPor-Ph-COF/g-C₃N₄ composites, were made using a simple LAG method. First, g-C₃N₄ and terephthalaldehyde were mixed in a mortar with a few drops of an o-dichlorobenzene/n-butanol solution and a drop of acetic acid. The mixture was ground for 30 minutes. Then CuTAPP was added and ground for another 60 minutes. Different amounts of CuTAPP were used to make various composites. The resulting red powder was washed trichloromethane and methanol and dried, and labeled based on the CuTAPP percentage. Pure CuPor-Ph-COF was also made under the same experimental conditions [98].

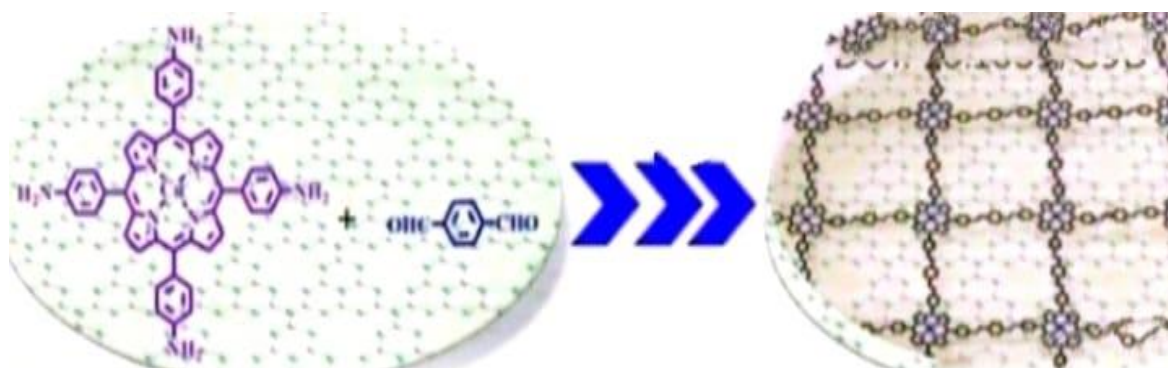


Figure 2.63 Synthetic Scheme of CuPor-Ph-COF/g-C₃N₄ composites

Characterization:

FTIR Peaks: 1612 cm⁻¹ (imine (–C=N) stretching vibration of the linker) and 1000 cm⁻¹ (characteristic metalloporphyrin band)

PXRD Peaks: 2θ = 3.5° ((100) plane of the square lattice, with a d value of 25 Å), 2θ = 7.1° ((200) diffraction), 2θ = 22° ((001) diffraction).

UV-Vis Peaks: 430 nm (Soret band (B-band)), 500–700 nm (Q-bands)

XPS Peaks: 935 eV (Cu2p_{3/2} 2+ oxidation state, characteristic of copper metalloporphyrin), 398.6 eV (pyridinic N), 399.2 eV (CoNX) and 399.9 eV (pyrrole N) [99].

2.8. Synthesis of CuP-DMNDA-COF and CuP-DMNDA-COF/F:

In 2017 Yuxia Hou et al, Synthesized of CuP-DMNDA-COF, CuTAPP and DMNDA) were dissolved in o-dichlorobenzene/n-butanol/6M AcOH and sonicated for 20 min to ensure a homogenous dispersion. Then the mixture was transferred to Teflon-lined stainless-steel container and reacted at 120°C for 72 h. After the reactor was cooled to room temperature, a purple powder formed was isolated by centrifugation and washed with tetrahydrofuran, chloroform, and acetone to remove the adsorbed guest molecules such as oligomer and unreacted starting materials, then dried at 80°C under vacuum for 12 h to yield CuP-DMNDA-COF as a purple powder, 98.2 mg (71.1 %)[100]. In 2017 Yuxia Hou et al, also synthesized CuP-DMNDA-COF/Fe, FeCl₃, CuP-DMNDA-COF, and 18 mL of acetone were added to a 50 mL of roundbottom flask and stirred for 24 h at room temperature. The resulting black precipitate was filtered, washed with acetone, and then dried at 60°C under vacuum for 12 h to yield CuPDMNDA-COF/Fe[100].

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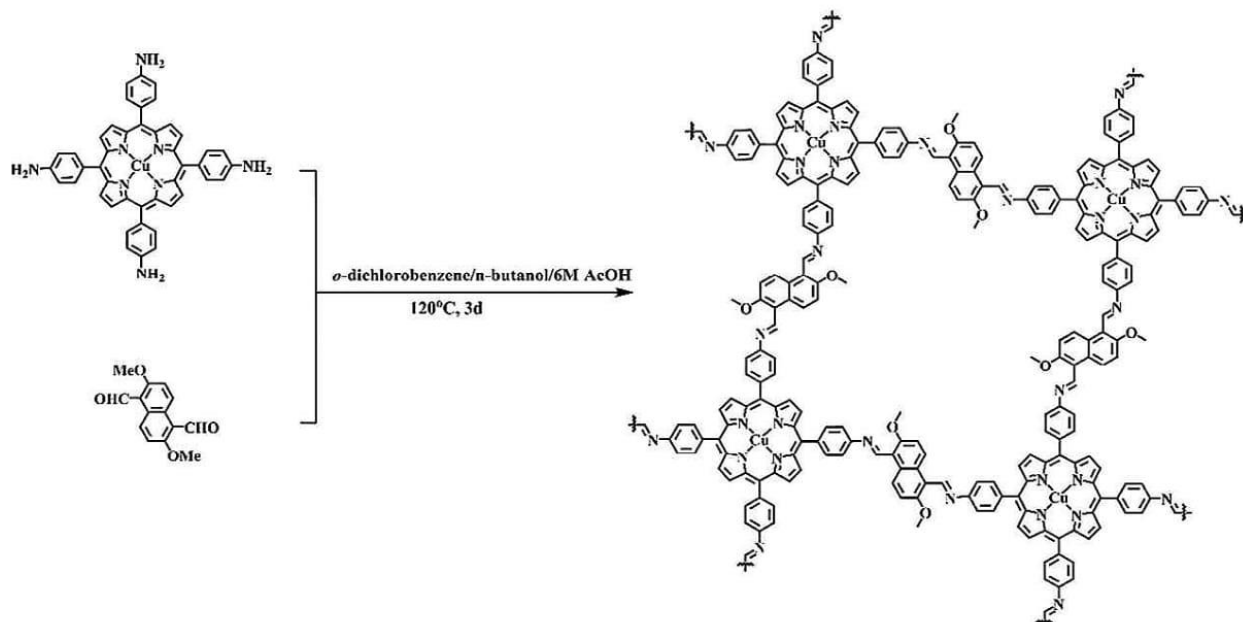
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Figure 2.64 Synthetic Scheme of CuP-DMNDA-COF and CuP-DMNDA-COF/F (Porphyrin-based COF)

Characterization:

FT-IR Peaks: 1586 cm^{-1} : C=N stretching, 1663 cm^{-1} : C=O stretching, 3357 cm^{-1} : N-H stretching, 815 cm^{-1} : Fe-O stretching vibration (in RhB-treated CuP-DMNDA-COF/Fe)

UV-Vis Peaks: 420 nm: Soret band, 515-590 nm: Q bands, 554 nm: main RhB absorption band

PXRD Peaks: $2\theta = 3.43^\circ$ (corresponding to 2.57 nm), $2\theta = 4.96^\circ$ (corresponding to 1.78 nm), $2\theta = 6.85^\circ$ (corresponding to 1.29 nm), $2\theta = 7.33^\circ$ (corresponding to 1.20 nm)

^{13}C CP/TOSS NMR Peaks: 158.6 ppm: carbon atom of the C=N bond [100].

2.9. Synthesis of the one-pot synthesis of Porphyrin Covalent Organic Framework (POF):

In 2019 Bo-Quan Li et al, reported the one-pot synthesis of POF by one-pot method. BDA was first dissolved in propionic acid. Then were added TFA and NBZ as the catalyst and the oxidant. After that, pyrrole was added into solution, which turned into deep purple. The mixture was heated 130 °C under continuous stirring for 12 h and cooled to room temperature overnight to afford a dark suspension. The product was filtered and washed with ethanol, chloroform, and ethanol to remove unreacted reagents and small porphyrin molecules. POF was finally obtained as black powders after being dried at 60 °C for 24 h. The actual output of POF is 2.17 g and the yield is 95%[101].

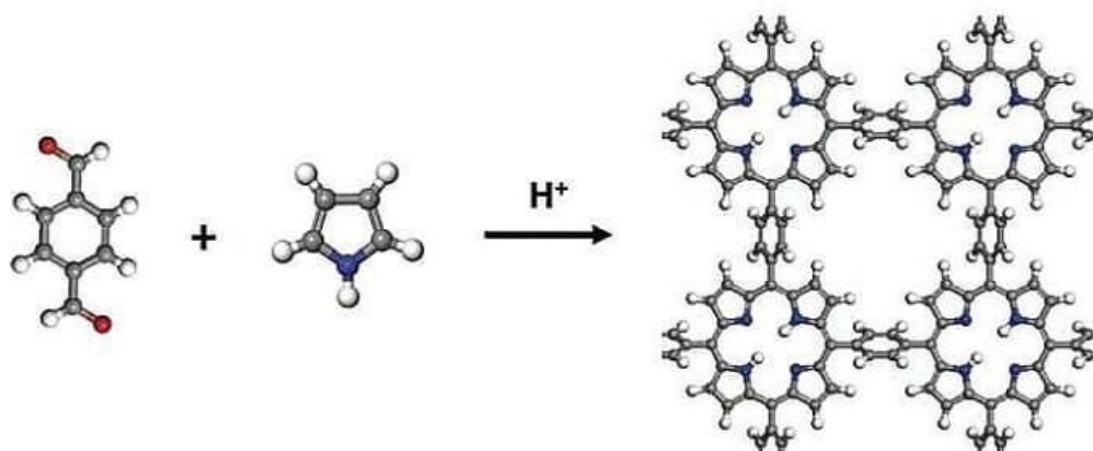


Figure 2.65 Synthetic Scheme of one-pot synthesis of Porphyrin Covalent Organic Framework (POF)

Characterization:

FTIR Peaks: 1586 cm^{-1} (C=N stretching), 1663 cm^{-1} (C=O), 3357 cm^{-1} (N-H), 1700 cm^{-1} (carbonyl groups), 1600 cm^{-1} (C=C stretching vibration)

PXRD Peaks: $2\theta = 3.43^\circ$ ((100) plane), $2\theta = 4.96^\circ$ ((110) plane), $2\theta = 6.85^\circ$ ((200) plane), $2\theta = 7.33^\circ$ ((210) plane), $2\theta = 13^\circ$ (POF peak), $2\theta = 22^\circ$ (POF peak), $2\theta = 11^\circ$ ((101) plane), $2\theta = 22^\circ$ ((002) plane)

UV-Vis Peaks: 430 nm (Soret band), 500-700 nm (Q-bands)

XPS Peaks: 398.5 eV (pyridinic N), 400.1 eV (pyrrolic N), 401.2 eV (quaternary N), 405.6 eV (absorbed N), 935 eV ($\text{Cu}2p_{3/2}$)

NMR Peaks: 120.5 ppm (porphyrin), 135.6 ppm (benzene linkages) [101].

2.10. Synthesis of $\text{FeSn}_2@\text{FeSnOx}@S\text{-N-C}$:

In 2019 Xiaoying Zhang et al, synthesized $\text{FeSn}_2@\text{FeSnOx}@S\text{-N-C}$ (Fe-Sn-CPFs) by heating Fe-Sn-CPFs under N_2 atmosphere with a heating rate of $2^\circ\text{C}/\text{min}$. The resulting material was then leached with KOH solution to remove unstable Sn-based species, yielding $\text{FeSn}_2@\text{FeSnOx}@S\text{-N-C-n}$. For comparison, they also synthesized single metal-based Fe-S-N-C-n and Sn-S-N-C-n, as well as metal-free S-N-C-n, by modifying the heating conditions for Fe-CPFs, Sn-CPFs, and CPFs, respective[102].

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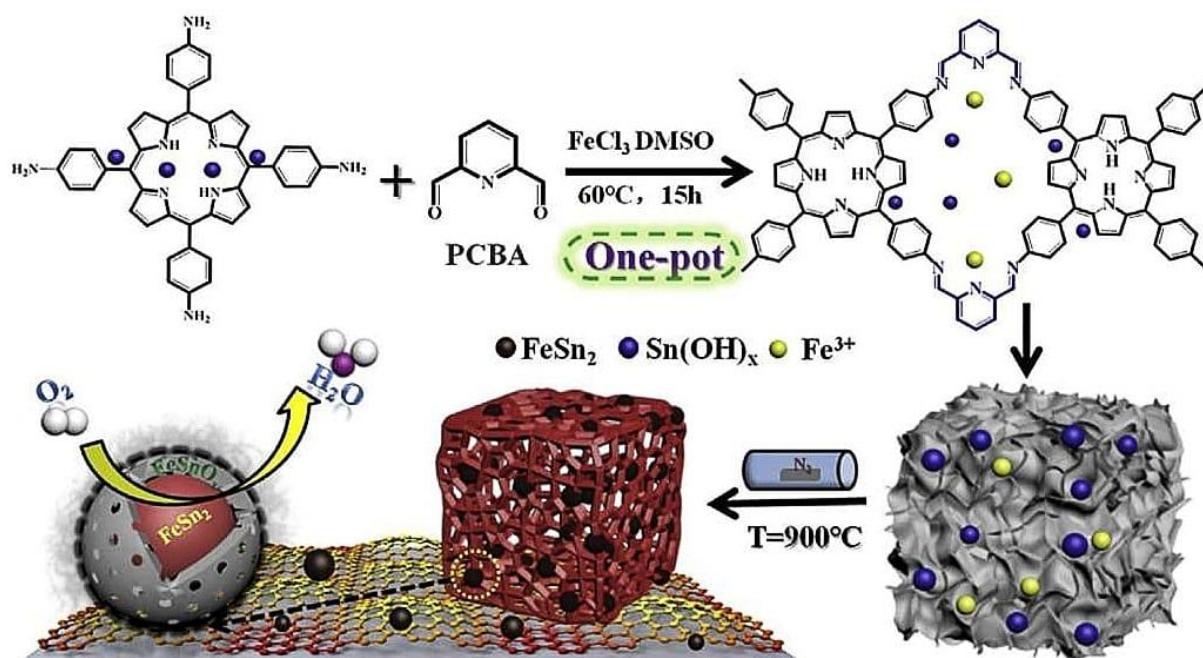


Figure 2.66 Synthetic Scheme of FeSn₂@FeSnO_x@S-N-C (Porphyrin-based COF)

Characterization:

FTIR Peaks: 1586 cm⁻¹ (C=N stretching), 1663 cm⁻¹ (C=O), 3357 cm⁻¹ (N-H), 1700 cm⁻¹ (carbonyl groups), 1600 cm⁻¹ (C=C stretching vibration), 653 cm⁻¹ (attributing to stretching vibration of O—Sn—O)

PXRD Peaks: 2θ = 3.43° ((100) plane), 2θ = 4.96° ((110) plane), 2θ = 6.85° ((200) plane), 2θ = 7.33° ((210) plane), 2θ = 13° (POF peak), 2θ = 22° (POF peak), 2θ = 11° ((101) plane), 2θ = 22° ((002) plane), 2θ = 33 (002), 35 (211), 39.1 (112), 43.8 (310), 61.1 (411), 67.3 (402), and 71 (004) (cubic FeSn₂ alloys)

UV-Vis Peaks: 430 nm (Soret band), 500-700 nm (Q-bands), 377 nm (Soret band), 500-700 nm (Q bands)

XPS Peaks: 398.5 eV (pyridinic N), 400.1 eV (pyrrolic N), 401.2 eV (quaternary N), 405.6 eV (absorbed N), 935 eV (Cu2p_{3/2}), 711 eV (Fe(III) and Fe(II) ions), 708 eV (Fe (0) species), 487.1 and 495.2 eV (Sn(OH)_x species), 486.8 and 495.2 eV (Sn 3d_{5/2} and 3d_{3/2}), 531.5 eV (metal-O species), 399.8 eV (pyrrolic N of porphyrin rings or a few of Fe-N_x species), 398.4, 399.6, 400.9 and 402.9 eV (pyridinic N, pyrrolic N, graphitic N, and N oxides) [102].

2.11. Synthetic routes of the Zn-ZnDETPP, Co-CoDETPP, and Zn-CoDETPP polymers:

In 2019 Zhuqing Chen et al. synthesized 5,15-Di(4-[(trimethylsilyl)ethynyl]phenyl)-10,20-diphenylporphyrin (DETPP-TMS) by reacting 5,15-Dibromo-10,20-diphenylporphyrin with 4-[(trimethylsilyl)ethynyl]phenylboronic acid pinacol ester in THF. They added K₂CO₃ and Pd(PPh₃)₄, stirred for 12 hours at 65°C, and purified the product by column chromatography, yielding 208 mg (76%) of DETPP-TMS as a purple solid[103]. In 2019 Zhuqing Chen et al, also synthesized 5,15-Di(4-ethynylphenyl)-10,20-diphenylporphyrin (DETPP) by desilylating 5,15-Di(4-

[(trimethylsilyl)ethynyl]phenyl)-10,20-diphenylporphyrin with K_2CO_3 in a CH_2Cl_2/CH_3OH mixture. They stirred for 3 hours at room temperature, monitored by TLC, and then purified the product by column chromatography, yielding 547 mg (95%) of DETPP as a purple solid[103]. In 2019 Zhuqing Chen et al, synthesized Cobalt(II) 5,15-Di(4-ethynylphenyl)-10,20-diphenylporphyrin (CoDETPP) by reacting 5,15-Di(4-ethynylphenyl)-10,20-diphenylporphyrin with cobalt(II) acetate tetrahydrate in a $CHCl_3/CH_3OH$ solution. They stirred for 12 hours at $65^\circ C$, then purified the product by column chromatography, yielding 85 mg (79%) of CoDETPP as a purple solid[103]. In 2019 Zhuqing Chen et al, also Zhuqing Chen et al. synthesized Zinc(II) 5,15-Di(4-ethynylphenyl)-10,20-diphenylporphyrin (ZnDETPP) by reacting 5,15-Di(4-ethynylphenyl)-10,20-diphenylporphyrin with zinc(II) acetate dihydrate in a $CHCl_3/CH_3OH$ solution. They stirred for 12 hours at $65^\circ C$ and then purified the product by column chromatography, yielding 94 mg (87%) of ZnDETPP as a purple solid [103]. In 2019 Zhuqing Chen et al, also synthesized Zinc(II)-Cobalt(II) 5,15-Di(4-ethynylphenyl)-10,20-diphenylporphyrin (Zn-Co DETPP) by coupling Zinc(II) 5,10,15,20-tetrakis-(4'-bromophenyl)porphyrin with Cobalt(II) 5,15-di(4-ethynylphenyl)-10,20-diphenylporphyrin in NEt_3/THF . They degassed the mixture, added PPh_3 , $Pd(OAc)_2$, and CuI , and stirred for 12 hours at $76^\circ C$. After filtration, washing, and Soxhlet extraction, the product was dried in a vacuum oven to yield Zn-CoDETPP [103]

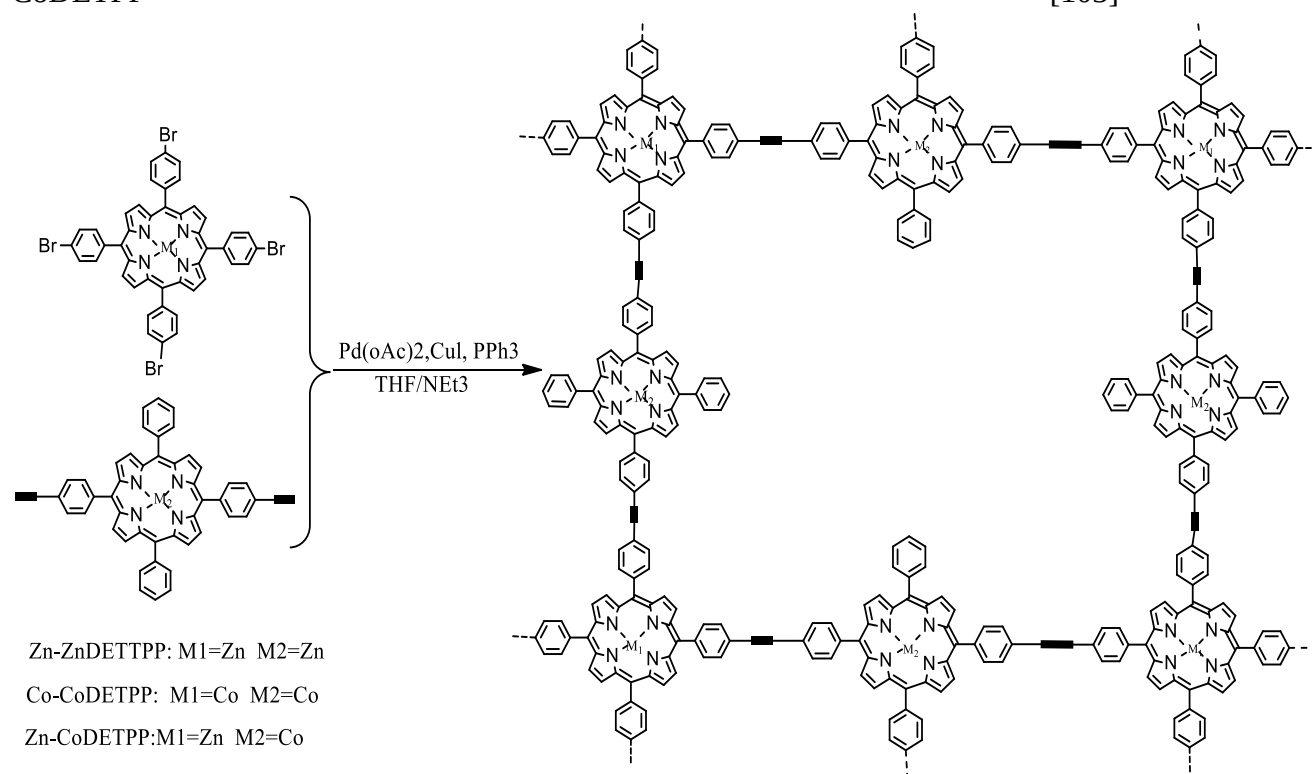


Figure 2.67 Synthetic Scheme of Metal-CoDETPP polymers (Porphyrin-based COF)

Characterization:

FTIR Peaks: $\sim 700\text{--}800\text{ cm}^{-1}$ (external plane bending vibrations of C–H in benzene)

and pyrrole rings), $\sim 1350\text{ cm}^{-1}$ (pyrrole rings vibrations), $\sim 1600\text{ cm}^{-1}$ (benzene rings vibrations), 3290 cm^{-1} (stretching vibration peaks of C–C–H), 2107 cm^{-1} (stretching vibration peaks of C–C)

Raman Peaks: $\sim 1490\text{ cm}^{-1}$ (stretching vibration of enyne), $\sim 1349\text{ cm}^{-1}$ (defect D-band), $\sim 1573\text{ cm}^{-1}$ (broad G-band)

XPS Peaks: 1021.8 eV (Zn $2p_{3/2}$), 1044.9 eV (Zn $2p_{1/2}$), 779.9 eV (Co $2p_{3/2}$), 795.7 eV (Co $2p_{1/2}$), 1022.0 eV (Zn $2p_{3/2}$) in Zn-CoDETPP, 1045.0 eV (Zn $2p_{1/2}$) in Zn-CoDETPP, 779.7 eV (Co $2p_{3/2}$) in Zn-CoDETPP, 795.5 eV (Co $2p_{1/2}$) in Zn-CoDETPP

XAS Peaks: 795.8 eV (Co L-edge spectra before visible light irradiation), 795.3 eV (Co L-edge spectra after 15 min light irradiation), 794.5 eV (Co L-edge spectra after 30 min irradiation [103].

2.12 Donor-acceptor covalent organic frameworks of porphyrin:

In 2020 Nanfeng Xu et al, synthesized PD-COF-23 and PD-COF-23-Ni, In a pyrex tube, 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (TAPP) and DPP-CHO was dissolved in a mixture of n-butanol and mesitylene. Then, aqueous acetic was added. The reaction mixture was sonicated to get homogeneous solution. The reaction vessel was degassed and heated. The obtained dark precipitate was collected by filtration and washed with THF and acetone. The powder obtained was exchanged by acetone and dried to get PD-COF-23 as dark powder (9.4 mg, 52%) [104]. In 2020 Nanfeng Xu et al also synthesized PD-COF-23-Ni was processed similarly to PD-COF-23 using NiTAPP instead of TAPP, affording PD-COF-23- Ni as red powder (6.2 mg, 34%) [104].

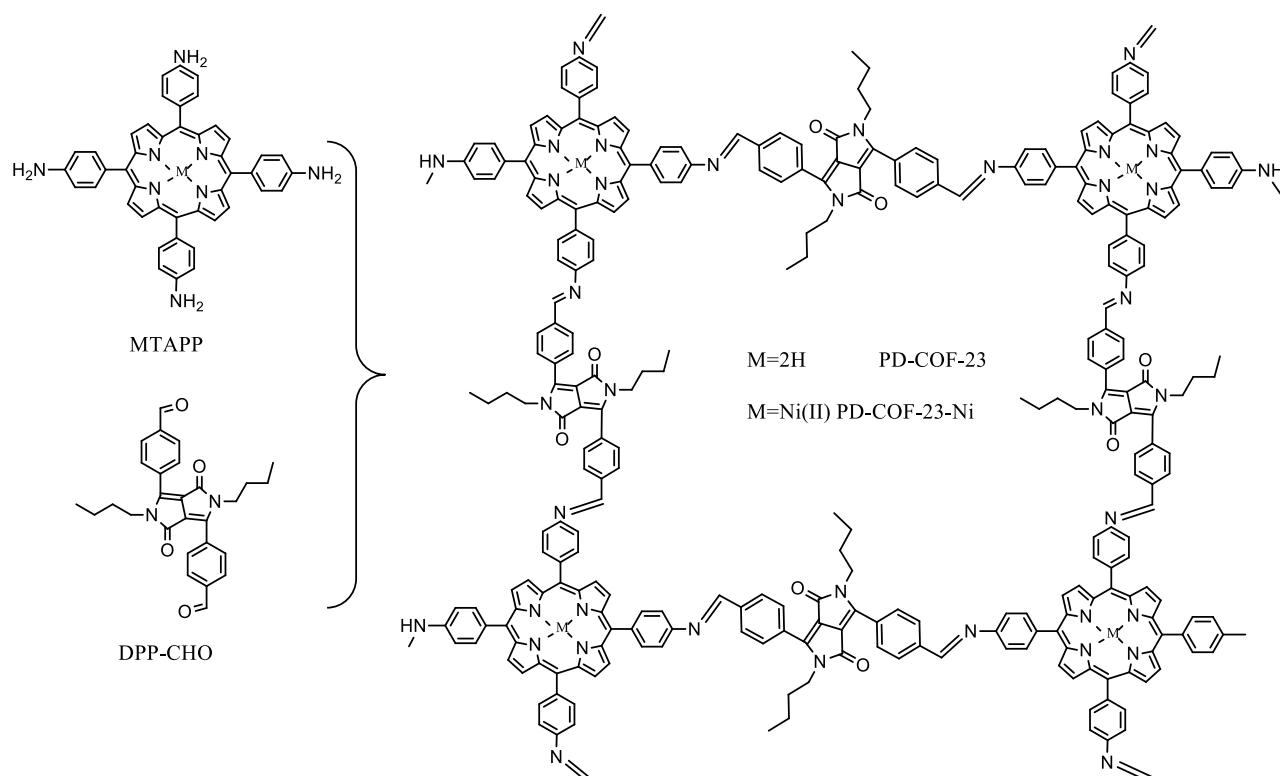


Figure 2.68 Synthetic Scheme of PD-COF-23 and PD-COF-23-Ni (Porphyrin-based COF)

Characterization:

FTIR Peaks: 1612 cm^{-1} (C=N stretching mode)

PXRD Peaks: 2.65° (110 plane), 2.73° (200 plane), 5.30° (220 plane), 7.98° (330 plane), 2.64° (110 plane) for PD-COF-23-Ni, 2.75° (200 plane) for PD-COF-23-Ni, 5.28° (220 plane) for PD-COF-23-Ni, 7.92° (330 plane) for PD-COF-23-Ni

UV-Vis Peaks: 743 nm (absorption edge) for PD-COF-23, 727 nm (absorption edge) for PD-COF-23-Ni

XPS Peaks: 400.02 eV (pyrrolic N), 401 eV (pyrrolic NH), 401.7 eV (imine C=N), 401.9 eV (N-Ni), 856.7 eV (Ni 2p_{3/2}), 874.7 eV (Ni 2p_{1/2})

NMR Peaks: 120.5 ppm (porphyrin), 135.6 ppm (benzene linkages), 164 ppm (C=N bond), 180-200 ppm (aldehyde signal, not present) [104].

In 2021 Yifan Zhu et al, in this study, designed, synthesized, and applied two types of 2D porphyrin-based COFs, named RICE-1 and RICE-2, for use in PET-RAFT polymerization. The COFs were constructed from a porphyrin derivative (TTAP) with a C₄ geometry, combined with two different aldehyde-based monomers, ETDA and BDTA, which have specific geometries (C₂/D₂). This structural design allowed the creation of highly crystalline materials suitable for targeted applications [105].

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the tube was flash frozen and flame sealed. Then the reaction was heated and kept for 3 days, the precipitate was separated by filtration, and transferred to a Soxhlet extractor and washed thoroughly with dioxane and acetone. Finally, the product was evacuated [106].



Figure 2.70 Synthetic Scheme of TT-Por(Co)-COF (Porphyrin-based COF)

Characterization:

PXRD: Peaks: 3.38° (100), 6.67° (200), 7.63° (020), Unit cell parameters: $a = 26.34 \text{ \AA}$, $b = 25.60 \text{ \AA}$, $c = 5.09 \text{ \AA}$, $\alpha = 115.69^\circ$, $\beta = 89.79^\circ$, $\gamma = 90.88^\circ$, Pore size: 2.0 nm (theoretical along the c-axis) and Layer stacking distance: 3.51 Å

FT-IR: - C=N imine stretching vibration band: 1583 cm^{-1} , - C=O stretching vibration band (disappeared post-polymerization): 1653 cm^{-1}

Solid-state ^{13}C NMR: - C=N chemical shift values: TT-Por(Co)-COF: 146.8 ppm and TT-Por(2H)-COF: 147.8 ppm

Inductively Coupled Plasma (ICP) Spectroscopy: Cobalt (Co) content: 4.16 wt%

Elemental Analysis (EA): Sulfur (S): 8.37 wt% and Nitrogen (N): 9.86 wt%

N_2 Adsorption–Desorption Isotherms: BET surface area: TT-Por(Co)-COF: $748 \text{ m}^2/\text{g}$, TT-Por(2H)-COF: $628 \text{ m}^2/\text{g}$. Pore size distribution: TT-Por(Co)-COF: 1.2–1.9 nm and TT-Por(2H)-COF: 1.1–2.2 nm. CO_2 adsorption capacity: TT-Por(Co)-COF: $12 \text{ cm}^3/\text{g}$ and TT-Por(2H)-COF: $14 \text{ cm}^3/\text{g}$

X-ray Absorption Spectroscopy (XAS): Co K-edge position: Between Co(0) and Co(II) and Co–N scattering path (EXAFS): 1.50 Å

XPS: Co2p binding energies: Co $2p_{3/2}$: 780.31 eV (TT-Por(Co)-COF), Co $2p_{1/2}$: 795.60 eV (TT-Por(Co)-COF) and S $2p_{3/2}$ binding energy: 164.33 eV (TT-Por(Co)-COF)

Conductivity: TT-Por(Co)-COF: $1.38 \times 10^{-8} \text{ S/m}$ and COF-366-Co: $6.5 \times 10^{-9} \text{ S/m}$

Carrier Mobility (μ): TT-Por(Co)-COF: $0.18 \text{ cm}^2/\text{V}\cdot\text{s}$ and COF-366-Co: $0.06 \text{ cm}^2/\text{V}\cdot\text{s}$

FECO: TT-Por(Co)-COF: 91.4% at -0.6 V vs RHE and COF-366-Co: 67.3% at -0.6 V vs RHE

Maximum CO Partial Current Density: TT-Por(Co)-COF: $7.28 \text{ mA}/\text{cm}^2$ at -0.7 V vs RHE [106].

2.13. Preparation of porphyrin-based COF fiber:

In 2020 Yuan Tian et al, synthesized TFPA-TAPP-COF coated fiber, two oversaturated solutions containing TFPA and TAPP in a mixed solvent of n-butanol, 1,2-dichlorobenzene and acetic acid were prepared, named solution A and solution B, respectively. The functionalized SSWs were immersed into the solution A for 15 min under magnetic stirring, followed by washing with absolute ethanol. The wires were placed in solution B at room temperature and were washed with clean absolute ethanol. Finally, the as-prepared wires were dried in hot air. The above steps were repeated until reaching the desired thickness. Finally, the prepared fibers were assembled to microsyringe and conditioned under nitrogen in the GC injection port until a stable baseline was obtained [107].

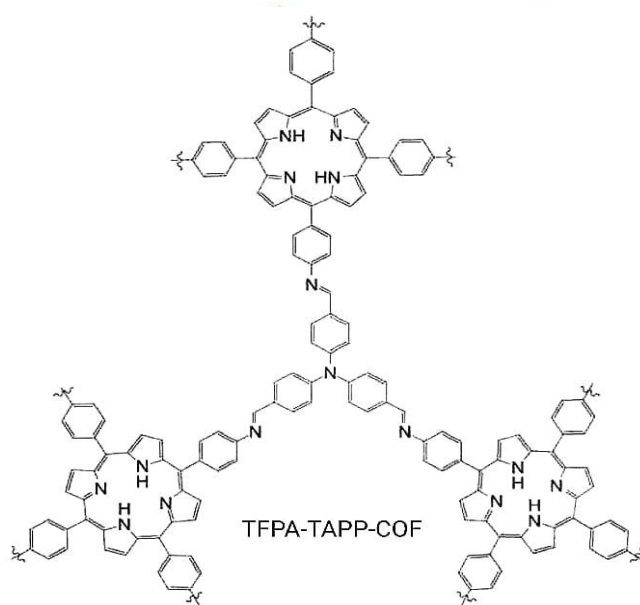
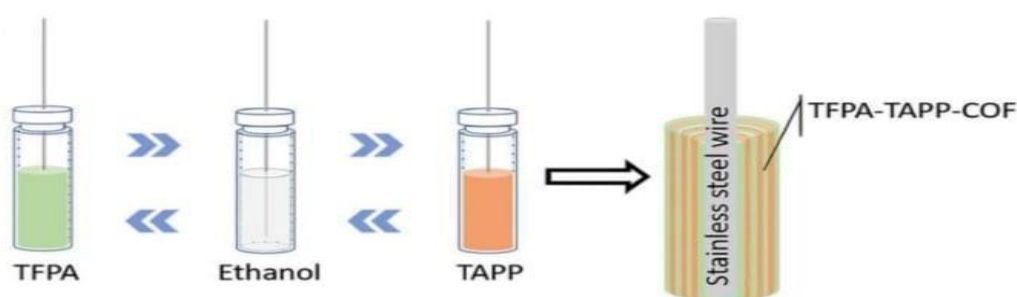


Figure 2.71 Synthetic Scheme of TFPA-TAPP-COF (porphyrin-based COF fiber

Characterization:

IR Spectroscopy: TAPP: N-H stretching: 3364 cm^{-1} , 3429 cm^{-1} , C=N (pyrrole) stretching: 1468 cm^{-1} , C-N (amino) stretching: 1285 cm^{-1} and N-H (amino) bending: 1512 cm^{-1}

TFPA: C=O bond stretching: 1688 cm^{-1} (before reaction)

TFPA-TAPP-COF: C=N (Schiff base) stretching: 1620 cm^{-1}

SEM: Coating surface: porous structure and Coating thickness: approximately $5\text{ }\mu\text{m}$

(after 60 cycles)

Thermogravimetric Analysis: Initial weight loss: 390°C

Thermal stability: good stability under normal experimental conditions [107].

In 2021 Chen Yu et al, synthesized porphyrin-based COF fiber, a stainless-steel wire was cut, roughened on one end, and cleaned with ethanol and ultrapure water in an ultrasonic bath. Silicone sealant was diluted with cyclohexane, and the roughened wire tip was dipped in this mixture, then coated with the porphyrin-based COF. The coated wire was oven-dried to remove any remaining solvent. Finally, it was mounted on an SPME device and pre-treated in a GC injector with nitrogen flow before use. Structure and characterization already shown [41].

2.14. Preparation of Porphyrin based-COFs film:

In 2021 Chuanrui Zhao et al, synthesized the TAPP-COF thin films using a liquid/liquid interface growth method. First, TPA was dissolved in methylene chloride with sonication, then topped with water as a spacer layer. Separately, TAPP and of PTSA were dissolved in a mixture of water and acetonitrile, which was slowly added above the spacer water layer. After allowing the mixture to sit undisturbed, TAPP-COF thin films formed at the interface. The water layer helped prevent early mixing and slowed diffusion, enhancing film crystallinity [108].

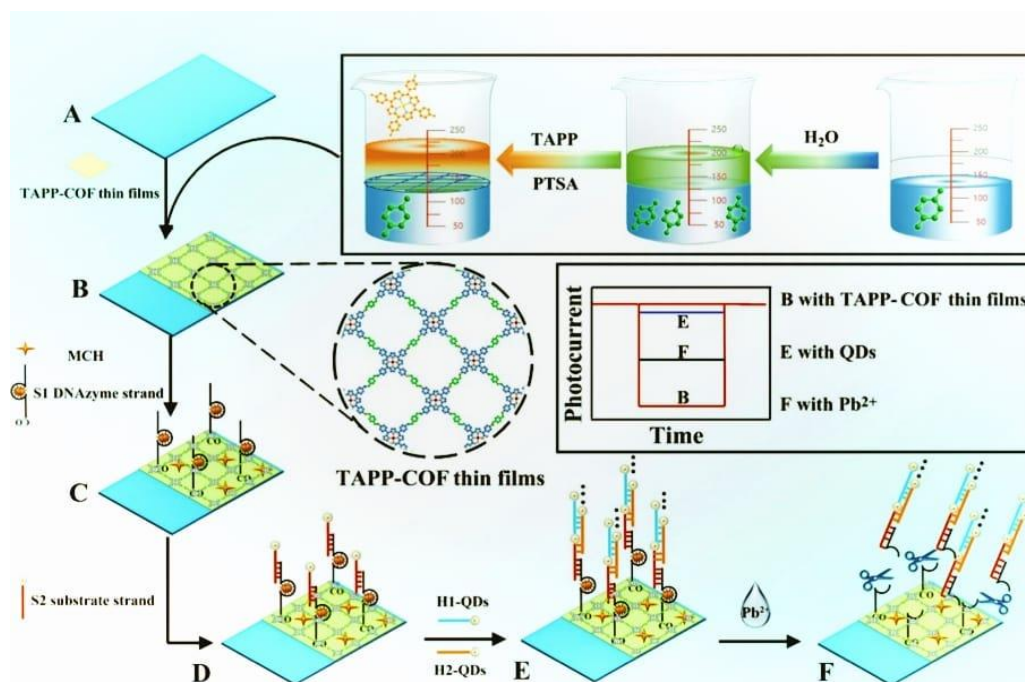


Figure 2.72 Synthetic Scheme of TAPP-COF thin films (Porphyrin based-COFs film)

Characterization:

FT-IR Spectroscopy: 1264 cm⁻¹: C=N stretching of imine functions, 3435 cm⁻¹: Amino group of TAPP (sharply weakened) and 1515 cm⁻¹: C=C stretching of benzene rings of TPA

Raman Spectroscopy: 1691 and 1702 cm⁻¹: Aldehyde stretching vibrations of TPA (absent in TAPP-COF thin films), 1527 cm⁻¹: Vibration mode of phenyl ring, 1599

cm^{-1} : Vibration mode of porphyrin ring and Shift from 1542 and 1605 cm^{-1} to 1527 and 1599 cm^{-1} (intermolecular interactions in polymer network)

XRD: $2\theta = 3.51^\circ$ (2.51 nm): Strong diffraction peak from (100) plane, 1.25 nm : (200) facet, 0.42 nm : (600) facet and 0.31 nm : (800) facet [108].

In 2023 Neha Chaki Roy et al, the experimental work involves the chemical vapor deposition (CVD) of COF366-QDs thin films using TAPP and BDA as precursors. These precursors are sealed in separate bubblers filled with THF. The deposition is performed, with N_2 gas purged before and after the process to remove unreacted species. The gaseous precursors are introduced into the chamber for 5 minutes, reacting in the presence of N_2 carrier gas, and depositing on Si and $\text{SiO}_2\text{-Au/Si}$ substrates. After deposition, the furnace is cooled. AFM images reveal changes in surface topology at different growth times [109].

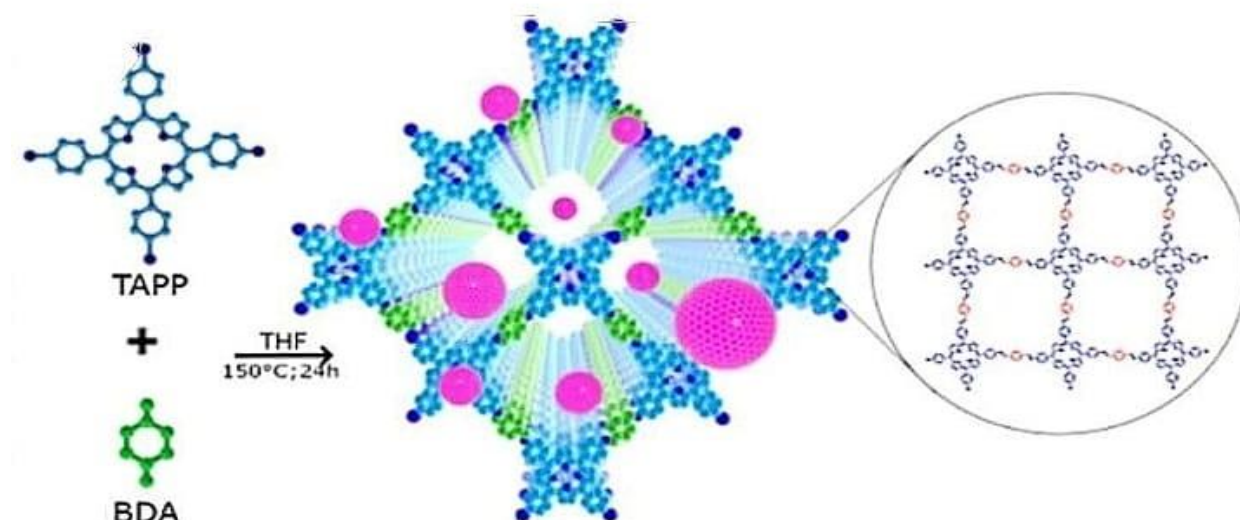


Figure 2.73 Synthetic Scheme of COF366-QDs thin films (Porphyrin-based COFs films)

Characterization:

PXRD: $2\theta = 3.7^\circ$: (100) facet, $2\theta = 6.7^\circ$: (200) facet and $2\theta = 16.7^\circ$: (001) facet

FTIR: 1590 cm^{-1} : $\text{C}=\text{N}$ stretching indicating imine group formation, 1258 cm^{-1} : Characteristic $\text{C}=\text{N}$ stretching and $3200\text{--}3500 \text{ cm}^{-1}$: Amino group range reduction after COF formation

UV-Vis Diffuse Reflectance Spectroscopy: 470 nm : Soret band and 575 nm : Q band

XPS: 398.6 eV (N 1s): Indicative of $\text{C}=\text{N}$ bonding, 397.7 eV : non-protonated nitrogen structure, 400.3 eV : Ph-NH_2 of porphyrin, 284.7 eV : $\text{C}=\text{C}$ bond in C 1s spectrum and 285.8 eV : C-N bond in C 1s spectrum

Atomic Force Microscopy (AFM): Average thickness: $\sim 112 \text{ nm}$ and Size distribution: 0.5 nm to 2.2 nm (QDs)

High-Resolution Transmission Electron Microscopy (HRTEM): QD diameter: $\sim 2.5\text{--}3 \text{ nm}$ [109].

In 2023 Yani Wang et al, synthesized 2D polysulfide porphyrin covalent

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organic framework film(S-Py-COF), A flask was filled with thionyl chloride and meso-Tetra(4-carboxyphenyl) porphyrin. The mixture was heated. After the reaction, the product was dried. Next, the linkers and dichloromethane were added (linkers to porphyrin). The mixture was stirred, then filtered. The solid collected was washed with dichloromethane and dried. The linkers used included 1,2-ethanedithiol, 1,3-propanedithiol, 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol, Bis(2-mercaptoethyl) sulfide, and 3,6-dithia-1,8-octanedithiol [110].

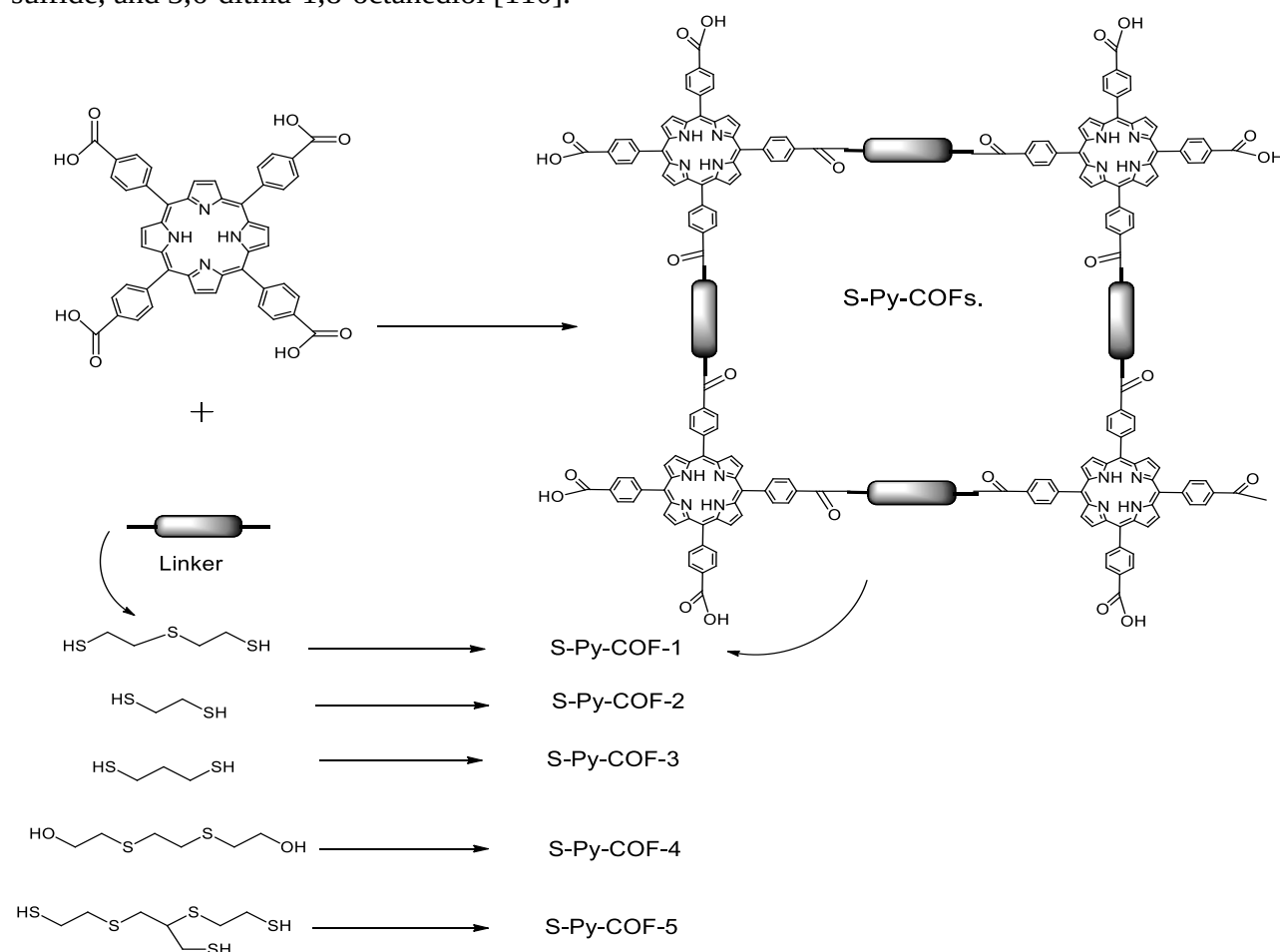


Figure 2.74 Synthetic Scheme of 2D-S-Py-COF (Porphyrin-based COF films)

Characterization:

FT-IR Peaks: C=N stretching vibration: 1602 cm⁻¹, C-S- stretching vibrations: 655 cm⁻¹, CH₂-S- swinging vibrations: 1228 cm⁻¹

TGA: Stability: Up to 300°C, Weight loss: Below 80°C due to organic solvent volatilization

Porosity and Surface Area: Pore sizes: 2.74-3.40 nm, Specific surface area (S^{BET}): 8.1502 m²/g, total pore volume: 0.033015 cm³/g

SEM/TEM Observations: Morphology: Even surfaces with nanosheet morphologies, Size range: Hundreds of nanometers to micrometers

Elemental Mapping and Adsorption Confirmation: Elemental distribution: Homogeneous distribution of C, N, and S, Post-adsorption mapping: Confirmed

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presence of Au [110].

2.15. Preparation of two metal sites in Porphyrin-based M-COFs.

In 2023 Jiawen Li et al, synthesized Co-Por, H₂-Por, cobalt acetate tetrahydrate, methanol, N,N'-dimethylformamide, and chloroform were added round-bottom flask under nitrogen. The mixture was refluxed under nitrogen. After the reaction, the dark green mixture was washed with water. The lower layer was centrifuged, and the precipitate was dried, yielding Co-Por (104.7 mg, 47.6%) as a dark purple solid [111]. In 2023 Jiawen Li et al, also synthesized Co-PorBpy, Co-Por, DFBpy, 1,2-dichlorobenzene, n-butanol, and aqueous acetic acid solution were added Pyrex tube. The mixture was sonicated frozen in a liquid nitrogen bath, and flame-sealed, then heated. After the reaction, the precipitate was filtered, washed with acetone, and dried, yielding a brown powder [111]. Synthesized Co-PorBpy-Co, Co-PorBpy was added to a methanol solution containing cobalt acetate tetrahydrate and stirred. The resulting precipitate was filtered, washed thoroughly with methanol, and dried, yielding a black powder [111]. Synthesized o-PorBpy-Ni, the method was the same as for Co-PorBpy-Co, but cobalt acetate tetrahydrate was replaced with nickel acetate tetrahydrate. The resulting precipitate was filtered, washed thoroughly with methanol, and dried, yielding a black powder [111]. Synthesized o-PorBpy/CNT, the procedure was the same as for Co-PorBpy, except that CNT was added to the precursors to achieve a 1:1 mass ratio of MCOF to MCNT [111]. Synthesized o-PorBpy-Co/CNT, Co-PorBpy/CNT was added to a methanol solution containing cobalt acetate tetrahydrate and stirred. The resulting precipitate was filtered, washed thoroughly with methanol, and dried, yielding a black powder [111].

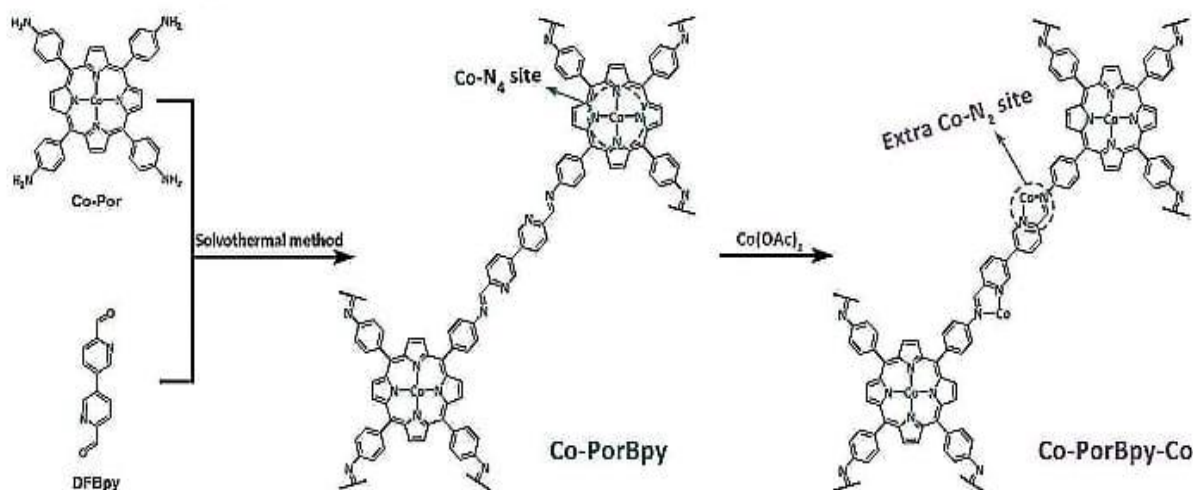


Figure 2.75 Synthetic Scheme of Co-PorBpy and Co-PorBpy-Co (Two metal sites in Porphyrin-based M-COFs)

Characterization:

FT-IR Peaks: C=N stretching vibration: 1602 cm⁻¹, NH₂ groups: 3273 cm⁻¹ (initially present, later reduced), CHO groups: 1641 cm⁻¹ (initially present, later reduced), S=O stretching vibrations (COF-PtaDha-SO₃K): Not present in this work

Solid-State ¹³C NMR: C=N signal: 162.0 ppm

PXRD Peaks: Diffraction peaks: 3.04°, 3.50°, 6.09°, and 6.99°, allocated to (110),

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(020), (220), and (040) facets, respectively.

XPS Peaks: Co 2p spectra: 795.7 and 780.3 eV (Co-PorBpy), 796.4 and 780.7 eV (Co-PorBpy-Co), N 1s spectra: 398.8 and 399.9 eV (Co-PorBpy-Co), C 1s spectra: 284.6, 285.2, 285.8, and 289.3 eV (Co-PorBpy), 284.6, 285.2, 285.8, and 288.0 eV (Co-PorBpy-Co) [111].

2.16. Preparation of Fabrication of the Free-Standing Porphyrin based-COFs

In 2024 Weipeng Xian et al, synthesized the free-standing COF-PtaDha membrane through acid-catalyzed interfacial polymerization of Pta and Dha. A solution of Dha in ethyl acetate-mesitylene was carefully layered on top of a phosphate-acetic acid aqueous solution. The COF-PtaDha membrane was then obtained by washing thoroughly with water and acetone then dried [112]. In 2024 Weipeng Xian et al, also synthesized Free-Standing COF-PtaDha-SO₃K Membrane, the free-standing COF-PtaDha membrane was treated with KOH ethanol solution and then thoroughly washed with ethanol. The resulting membrane was soaked in 1,3-propane sultone ethanol solution. During this process, 1,3-propane sultone facilitated ring opening, and the phenol oxygen anion nucleophilically attacked the α position of the sultone oxygen, incorporating alkyl chains with terminal potassium-sulfonate groups (–SO₃K) into the membrane's pore channels. The COF-PtaDha-SO₃K membrane was then washed with water and acetone, rinsed with water and dried [112].

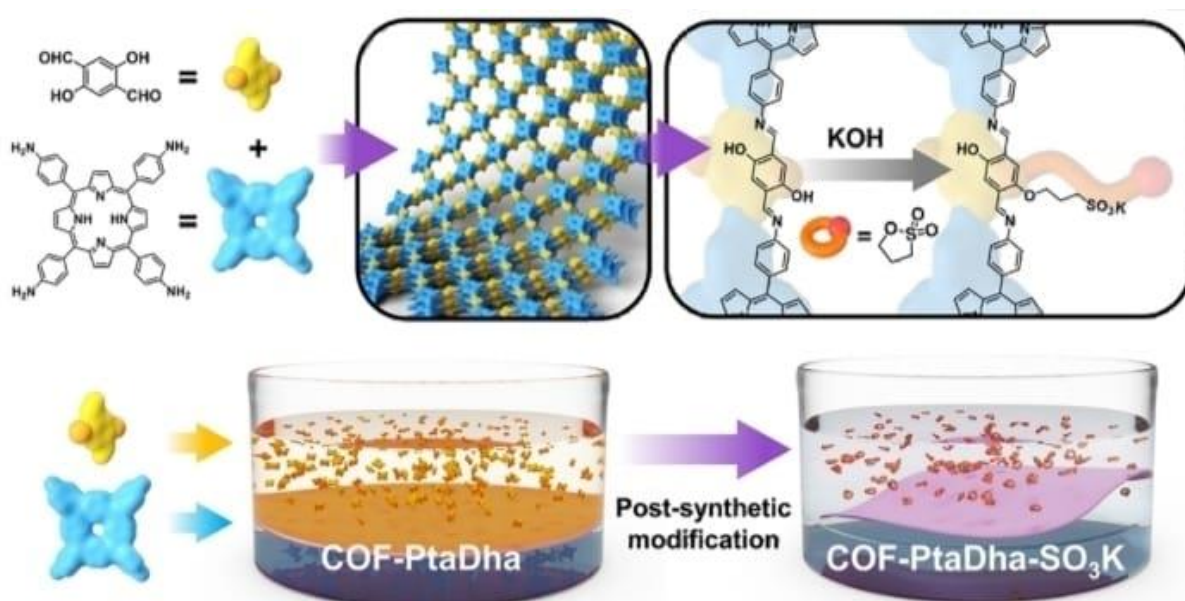


Figure 2.76 Synthetic Scheme of COF-PtaDha and COF-PtaDha-SO₃K (Fabrication of the Free-Standing Porphyrin based-COFs)

Characterization:

FT-IR Peaks: C=N stretching vibration: 1602 cm⁻¹, NH₂ groups: 3273 cm⁻¹ (initially present, later reduced), CHO groups: 1641 cm⁻¹ (initially present, later reduced), S=O stretching vibrations (COF-PtaDha-SO₃K): 1210 cm⁻¹ and 1035 cm⁻¹

Solid-State ¹³C NMR: C=N signal: 162.0 ppm

PXRD: Sharp reflections: indicative of a highly crystalline material

UV-Vis Spectroscopy: Optical bandgap: 1.46 eV (derived from the Tauc plot)

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BET Surface Area: COF-PtaDha membrane: 775 m²/g, Pore size distribution: centered at 2.1 nm, COF-PtaDha-SO₃K membrane: 85 m²/g (lower than the pristine membrane)
XPS: Sulfur signals: S 2p_{1/2} at 169.5 eV and S 2p_{3/2} at 167.7 eV (confirming sulfonate anion presence) [112].

2.17. Porphyrin-based Covalent organic framework nanoparticles:

In 2020 Bing-Jian Yao et al, synthesized Fe₃O₄@DhaTph nanoparticles a solution containing Tph, 2,5-dihydroxyterephthaldehyde (Dha), and Fe₃O₄ particles modified with BPEI/PVP in a solvent mixture (1,2-dichlorobenzene and 1-butanol in equal parts) was prepared. Then, acetic acid was added. This mixture was stirred and then sealed and heated at 120 °C in the sealed tube for three days in an inert (oxygen-free) environment. Afterward, the mixture was centrifuged, and the solvent was replaced with acetone. Finally, the product was dried, resulting in an 86% yield of Fe₃O₄@DhaTph nanoparticles as a dark brown powder [113]. In 2020 Bing-Jian Yao et al, also synthesized Fe₃O₄@DhaTph-Lipase Microsphere, a lipase solution is added to PBS buffer containing Fe₃O₄@DhaTph particles. The mixture is stirred at 25 °C with 500 rpm until adsorption is saturated for 6h. The Fe₃O₄@DhaTph-lipase composite is then separated and washed with PBS to remove loosely bound lipase. It is further washed with ethanol and hexane before being dried under vacuum at room temperature overnight for catalytic testing. The enzyme loading on Fe₃O₄@DhaTph-lipase is determined to be 33 wt % [113].

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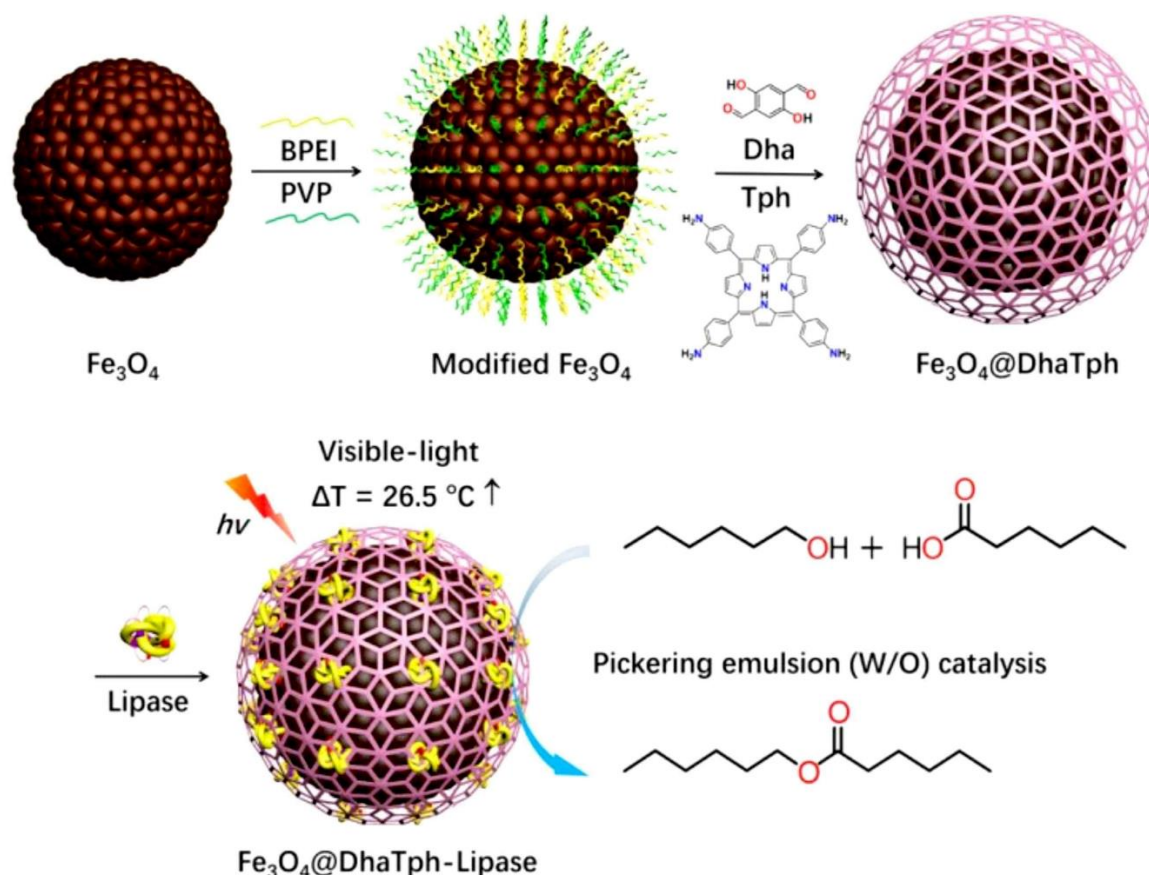
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Figure 2.77 Synthetic Scheme of Fe₃O₄@DhaTph nanoparticles (Porphyrin-based COF)

Characterization:

PXRD patterns: DhaTph COF: 3.4° and 6.9° ((100) and (200) reflection planes) and Fe₃O₄: 30.3° and 35.3° ((220) and (311) reflection planes)

FT-IR spectroscopy: Fe–O–Fe: 590 cm⁻¹ and C=N: 1614 cm⁻¹

UV-vis spectroscopy: Lipase: 562 nm, Porphyrin Soret band: ca. 428 nm and Weak Q bands: 540–702 nm

Barrett–Joyner–Halenda (BJH) analysis: Pore sizes of DhaTph: 2.01 nm, Pore sizes of Fe₃O₄@DhaTph: 1.17 nm and Pore sizes of Fe₃O₄@DhaTph-lipase: 1.17 nm.

TGA: Thermal stability of Fe₃O₄@DhaTph-lipase: up to 200 °C

BET surface area: Fe₃O₄@DhaTph-lipase: 244.9 m² g⁻¹, Fe₃O₄@DhaTph: 350 m² g⁻¹, DhaTph COF: 581.7 m² g⁻¹ and Fe₃O₄: 86 m² g⁻¹[113].

In 2019 Dianwei Wang et al, reported Preparation of COF-366 and COF-366 NPs (Tetra (p-amino-phenyl) porphyrin) (TAPP) was synthesized by Terephthaldehyde, TAPP, EtOH mesitylene were put in a Pyrex tube aqueous acetic acid was added. The tube was heated at 120 °C for 72 h, after frozen with liquid N₂, evacuated and flame sealed. The purple product was isolated by filtration. For further purification, the purple product was eluted with tetrahydrofuran (THF), followed by stirring with THF for 24 h. COF-366 NPs were prepared by ultrasonic dispersion. Firstly, COF-366 was dispersed in DMF with ultrasonic dispersion, then, phosphate

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buffer saline (PBS) was added drop by drop. DMF was removed by dialysis against PBS for 24 h in the dark[114].

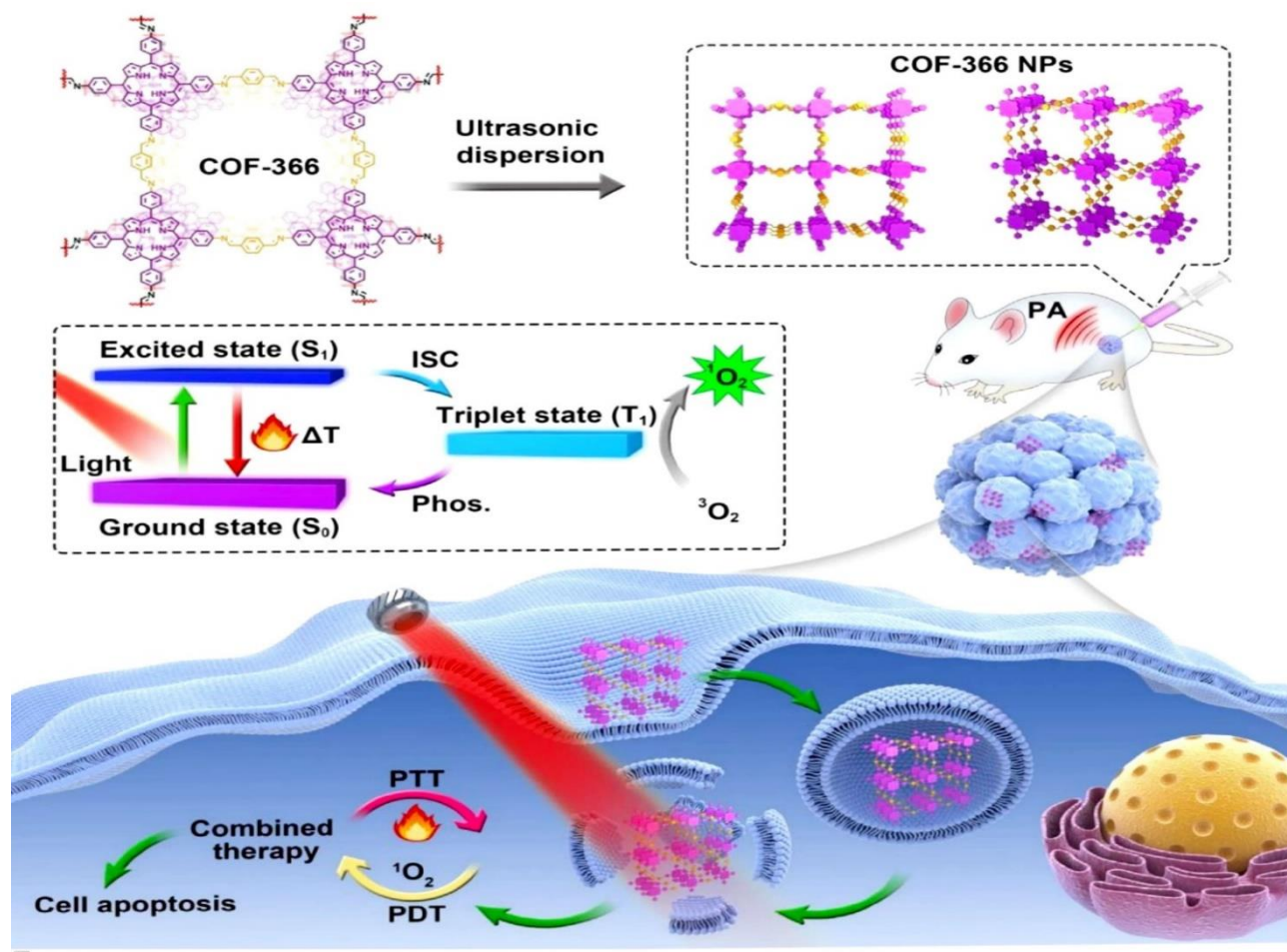


Figure 2.78 Synthetic Scheme of COF-366 and COF-366 NPs (Tetra (p-amino-phenyl) porphyrin) (TAPP)

Characterization:

FT-IR Peaks: 1115 cm^{-1} (vibrational C-O bonds) and 1344 cm^{-1} (B-O stretching within the C2O2B ring).

XPS Peaks: C 1s peak at 284.6 eV (sp² C (-C=C-)), C 1s peak at 285.2 eV (sp³ C (-C-C-)/-C-N-), C 1s peak at 288.2 eV (-C=O functionalities), N 1s peak at 400.1 eV (pyrroles of the porphyrin monomers), O 1s peak at 532.1 eV (-C-O species), O 1s peak at 533.2 eV (-C=O groups) and B 1s peak at 191.7 eV (B atoms in the pentagonal C2O2B ring).

Solid-State ¹¹B NMR Peaks: Peaks at 1.2 and 1.5 nm (C2O2B ring) and Peaks above 45 nm (B3O3 ring).

XRD Peaks: 2θ of 7.5°, 2θ of 21°[114].

3. Conclusion:

Porphyrin-based COFs are new materials with great possibilities. They can be used in

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many areas, such as energy storage, medicine, and more. Scientists have made progress in creating COFs with specific properties. They can control things like pore size, stability, and function. However, there are still challenges to overcome. These include making COFs on a large scale, being environmentally friendly, and finding new ways to make them. By working together and using new techniques, scientists can unlock the full potential of COFs. This will lead to new discoveries and innovations.

Porphyrin-based COFs have great potential:

Porphyrin-based COFs are innovative materials that have shown promising results in various fields, including catalysis, energy storage, and medicine. They have unique properties that make them useful for these applications.

Easier, more eco-friendly production methods:

Currently, producing COFs on a large scale can be challenging and may harm the environment. Future research should focus on developing simpler, more sustainable methods for producing COFs. This could involve using greener solvents, reducing energy consumption, or finding alternative synthesis routes.

Improving stability and flexibility:

While COFs have shown great potential, they can be brittle and prone to degradation. Improving their stability and flexibility will make them more practical for real-world applications. This could involve modifying their chemical structure or finding ways to incorporate them into composite materials.

Exploring new materials and design tools:

To further enhance the performance of COFs, researchers can explore new combinations of materials and use advanced design tools. This could involve combining COFs with other materials, such as metals or polymers, or using computational models to design new COF structures with improved properties.

Turning research into real-world solutions:

Ultimately, the goal of COF research is to develop practical solutions for real-world problems. By addressing the challenges mentioned above, researchers can help turn COFs into useful materials that can benefit society.

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