Design, Synthesis and Applications of Tetraphenylethene - Based Covalent Organic Frameworks

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Abstract. Covalent organic frameworks (COFs) as new class of crystalline organic porous materials are assembled by appropriate building blocks through covalent bonds. COFs have been utilized in many fields such as storage and separation of gases, energy storage, catalysis, proton conduction, sensing, optoelectronics and biomedicine due to their regular channels, high stability, high crystallinity and adjustable structure. In recent years, tetraphenylethylene (TPE)-based covalent organic frameworks have attracted much attention due to their obvious aggregation induced luminescence effect, simple synthesis and easy functionalization. In this paper, the construction units, topological structures, synthesis strategies and application progress of TPE-based COFs in different fields are briefly reviewed. Finally, the development and possible challenges of TPE-based COFs are prospected.

Keywords: Covalent organic frameworks; tetraphenylethylene; building blocks; topology; application.

1. Introduction

Tetraphenylethylene (TPE) is a typical aggregation induced emission (AIE) molecule [1]. Vinyl is linked to four benzene rings by a single bond, and the peripheral benzene rings are distributed in a spiral pattern. In the dilute solution state, the single molecule moves freely and can release energy through the non-radiative decay process such as rotation or vibration of the benzene ring within the molecule, so no fluorescence can be seen. However, when the molecule is in the aggregated state, the movement of the benzene ring is constrained and the energy is emitted in the form of radiation transition, thus inducing the fluorescence opening of TPE. Tetraphene has attracted much attention because of its obvious AIE effect, simple synthesis, easy functionalization and high sensitivity. In recent years, more and more tetraphene derivatives have been designed and developed, playing an important role in ion detection [2-3], biological imaging [4-6], biological and chemical sensing [7-9], light-emitting diodes [10-11], drug delivery [12-13] and other fields [14-15].

In recent years, covalent organic frames (COFs) [16-19], as a new type of porous materials, have attracted great attention due to their advantages of high crystallinity, low density, ordered pore structure, high chemical and thermal stability, large specific surface area, high porosity, and structural harmonization and easy functionalization. At present, it has shown excellent application prospects in the fields of gas storage and separation, catalysis, proton conduction, energy storage materials, optoelectronics, sensing and biomedicine [20-26]. Tetraphene and its derivatives have also been used to construct covalent organic frameworks. In this paper, we review the progress in the construction and application of tetrapyryl COFs (TP-Based COFs), including the design and synthesis of tetrapyryl COFs with different topologies, the types of reactions used to construct tetrapyryl COFs, and the design of tetrapyryl COFs with different topologies. Progress in the application of tetraphenyl-based COFs in catalysis, gas adsorption and storage, sensing, photochemistry, biomedicine and related fields. Finally, the development prospect of tetraphenyl-based COFs and the possible challenges and opportunities are pointed out.

2. Topological structure and unit of tetraphenyl COFs

Currently, there are five main tetraphenyl-based monomers used to construct COFs (Figure 1): They are tetrad (4-aminophenyl) ethylene (ETTA), tetrad (4-aldehyde phenyl) ethylene (ETBA), tetrad (4-aminophenyl) ethylene (ETTBA), tetrad (4-aldehyde biphenyl) ethylene (ETBC), and tetrad (4-boronic acid phenyl) ethylene (TPEBA). The monogeneity of tetraphenyl COFs makes people more diversified in the selection of another construction unit. Through the selection and modification of ligand types, not only the diversity and controllability of tetraphenyl COFs topology is increased, but also the adjustable pore size of COFS material is realized, and the application field of the material is more extensive.

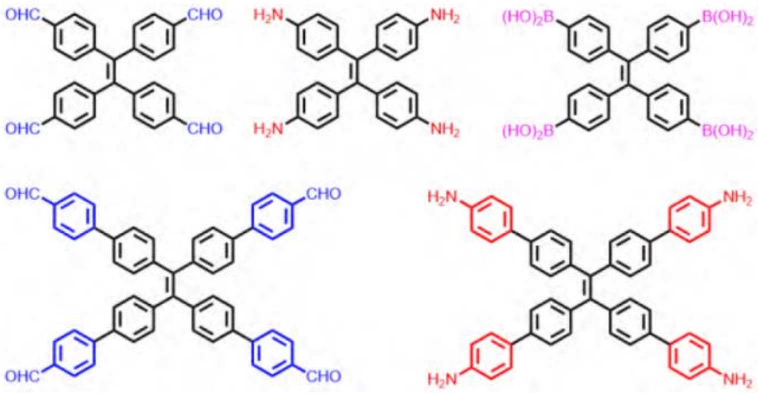

Fig 1. Monomers for use in the synthesis of TPE-based COFs.

COFs materials are frame materials formed by covalent bond connection, and the reaction follows the principle of dynamic covalent chemistry (DCC) [27], which usually relies on the covalent bond to continuously "formation-fracture-formation" in the material preparation process to achieve self-repair, so as to obtain an orderly arrangement of structures. At present, the bonding modes of tetraphenyl-based COFs materials are relatively limited, mainly including: borate bond, imide bond, imide bond, hydrazone bond, azine bond and acetal amine bond. These bonding methods are based on reversible reactions: self-condensation of boric acid, condensation of aldehyde group with amino group to form imide bond, reaction of anhydride with amino group to form imide bond, reaction of aldehyde group with hydrazine to form hydrazone bond, reaction of aldehyde group with hydrazine to form azine bond, reaction of secondary amine with aldehyde to form acetal amine bond.

Two-component tetraphenyl COFs are formed by condensation of tetraphenyl units with C4 symmetries and ligands with C2, C3, or C4 symmetries through [4+2], [4+3], or [4+4] to obtain two-dimensional or three-dimensional COFs. Among them, two-dimensional COFs include kagome, sql, mtf, tth, bex and cpi [28] topologies, while three-dimensional COFs include ffc, fjh and pts topologies. Two topological types of tetraphenyl COFs can be obtained by the [4+2] condensation reaction, namely, two-well kagome and single-well sql. For example, Jin et al. [29] chose ETBA monomer and linear connector 4,4' -diphenylacetonitrile to synthesize ETTF-DABP-COF when studying the strategy of synthesis of crystalline porous covalent organic framework by topological template polymerization. The COF has both triangular and hexagonal channels. The two apertures are approximately 1.3 and 3.7 nm, respectively. Chen et al. [30] designed and synthesized several groups of novel COFs based on the construction strategy of nonlinear edges and suitable high-symmetry vertices. Among them, two COFs of sql topology were synthesized with different tetraphenyl monomers, both of which had only rhomboid channels with pore sizes of 15.7 and 10.4 A respectively. Tetraphenyl COFs obtained by [4+3] condensation have the richest topology. In 2020, Nguyen et al. [31] synthesized COF-432 using ETTA and 1,3, 5-triformylbenzene (TFB) as monomers, with A void square mesh mtf topology, and a single layer consisting of two square pore diameters of about 10.0 and 21.0 A. The layers are interleaved to form A one-dimensional cylindrical pore structure with a diameter of about 7.5 A. In the same year, Xiong et al. [32] used ETBC and 2,4, 6-tri (4-aminophenyl) -1,3, 5-triazine to form two three-dimensional COFs with ffc topology. This topology also appears in the tetraphenyl COFs synthesized by Kang et al. [33] using ETBC as the reaction monomer. In 2020, the Yaghi's group [34] realized the integration of ETTA and 1,3, 5-trimethyl-2,4,6-tri (4-formylphenyl) benzene (TTFB) into the same COF by designing building units, and obtained COF-790 with a pore size of 21.5A and fjh topology. [4+4] reactions typically use ETTA, ETTBA, and ETBC as reaction monomers, which are condensed with another monomer to obtain tetrapyryl COFs with 2D sql and kagome topologies and 3D pts topologies. At present, ETBC can react with tetra-(p-aminophenyl) p-phenylenediamine [35], TTBA can react with porphyrinyl monomer [36], ETTA and ETBC can react with each other [37], and can also be linked with porphyrin-containing (TAPT), to obtain two-dimensional COF with bex topology. In addition to two-dimensional COFs, three-dimensional tetraphenyl COFs have been successfully obtained by the [4+3] reaction. As early as 2018, Lan et al. [33] used ETTA as one of the monomers for the synthesis of COF, and 1,3, 5-tri (p-formylphenyl) benzene (TFPB) or tri (4-benzoyl) amine (TFPA) as the other monomer, the monomer reaction of syn-group and pyrene group [36,38,39]. ETTA can also react with carbazoly-containing monomers [38], and the COFs obtained above are all sql topologies. In addition, the two-dimensional COFs formed by the [4+4] reaction are also connected by borate ester bonds and have a kagome topology [40]. In 2019, Liu et al. [41] used ETTBA and o-phenanthroline complexes as monomers to obtain COF-500 with pts topology with interlocking structure. In 2022, Peng et al. [42] obtained the COF OF the topological structure of pts using the supercritical solvent thermal synthesis method. Compared with two-component tetraphenyl COFs, the research of three-component tetraphenyl COFs is still relatively small, and there is a huge space for development. In 2015, Chen et al. [43] obtained the COF of single-hole sql topology through the condensation of C4, C2 and C4 monomers, and its aperture distribution was 1.8 nm. Later, Pang [44] and Dong et al. [45], based on the heterostructural mixing method, connected ETTA or ETBC as one of the monomers through the [4+2+2] reaction with two other monomers with C2 symmetry and different lengths, and successively obtained multiple COFs of the three-pore kagome topology. In 2019, Yaghi research group [46] made a new discovery by connecting hexagonal hexaphenylbenzene (HAPB), tetragonal ETTA and triangular TFPB together through imine bonds to prepare a two-dimensional porous COF with an unprecedented tth topology, called COF-346. Strategies and the method for the synthesis of tetraphenyl COFs are similar to those for the synthesis of other COFs materials. There are mainly six kinds: (1) one-step solvothermal method: the monomer powder and the appropriate solvent are placed in the heat-resistant glass tube, the air in the tube is removed by three freeze-pumping methods, and then the glass tube is heated and sealed and heated to a certain temperature at a high vacuum temperature, the reaction is 1 to 10 days, and the COFs material is finally obtained. (2) Two-step solvothermal method [47]: The condensation of monomers and the crystallization of frames are divided into two steps and carried out under different solvent conditions. This method can improve the crystallinity of COFs, and is feasible for materials with good crystallinity but not easy to repeat. (3) Alcohol-assisted hydrothermal polymerization [48]: Water and alcohol are used instead of commonly used high-boiling solvents and toxic catalysts, and imine-COFs are converted into imido-COFs by changing the chemical bond. This method is environmentally friendly and environmentally friendly. (4) supercritical solvothermal method [42]: Instead of the organic solvent used in the traditional solvothermal synthesis method, supercritical CO_2 with close to zero surface tension and very low viscosity was used as the solvent to achieve the ultra-fast generation of micron-scale three-dimensional COF single crystals within 1 to 5 min for the first time, breaking through the current difficulty in the rapid synthesis of high crystal or even single crystal three-dimensional COFs. (5) Room temperature solution synthesis method [49]: The mixed system of monomer powder and solvent was stood at room temperature for 72 h to obtain SCOFs in the diameter range of 200-300 μm. This method is simple and direct, and the SCOFs obtained have high yield, good crystallinity, large and uniform size, and high thermal stability. (6) Heating reflux method: In 2022, Li et al. [50] added ETBC and 1, 4-dioxane acetonitrile (PDAN) to the mixed solvent of 1,4-dioxane and KOH, and then heated the mixture at 110 ℃ under argon atmosphere for 72 h to obtain a COF material with yellow luminescence.

3. Covalent organic frameworks for application

3.1. covalent organic frameworks for catalysis

As a catalyst, COFs materials have obvious advantages [51]: the regular pores of COFs materials are conducive to material transport; COFs are easy to functionalize and introduce various functional groups into the structure, which can increase the catalytic reaction site. The application of tetraphenyl COFs in catalysis mainly focuses on photocatalytic hydrogen evolution reaction, photocatalytic CO_2 reduction reaction and photocatalytic organic reaction. Photocatalytic water decomposition for hydrogen production can achieve low-cost, large-scale, efficient and clean conversion of solar energy into hydrogen energy [52, 53]. Xu et al. [54] used ETBC and porphyrinyl groups as building units to prepare high crystalline TP-COF. Under visible light conditions, Pt (5 wt %) was used as auxiliary catalyst and TEOA (20 vol %) as sacrifice agent, and the hydrogen evolution rate was 58.4 $\mu mol\cdot g^{-1}\cdot h^{-1}$. After 30 h cycle experiment, the catalytic activity of the COF did not change significantly, and the stability was good. In 2017, Sick et al. [55] reported a compact oriented BDT-Etta COF film made from the condensation of ETTA and benzo [1,2-b:4,5-b'] dithiophen-2,6-diformaldehyde (BDT) for the first time, using the COF film as a photoelectrode for water decomposition without the use of auxiliary catalysts or sacrifice agents. The resulting COF film thickness is 100 nm and the current density is 1.5 $\mu A\cdot cm^{-2}$ at 0.2 V (vs RHE). In addition, when the surface of COF film is coated with Pt nanoparticle catalyst, the current density at 0.1V is 1.1 $\mu A\cdot cm^{-2}$, while the current density at 0.3V is 4.3 $\mu A\cdot cm^{-2}$. Compared with the COF film without catalyst at the same potential, the photocurrent increases by 4 times. In 2019, Rotter et al. [56] proposed a new and improved method, using electrophoretic deposition (EPD) to prepare films with or without Pt nanoparticle catalysts, respectively, and compared the performance of COF films made in 2017. The results show that with catalyst, the current density of the film obtained by EPD method increases 117 times, reaching 128.9 $\mu A\cdot cm^{-2}$. The improvement of photoelectric properties directly indicates that electrophoretic deposition is an important complementary method for the preparation of COF films. In 2022, Yu et al. [57] designed and synthesized D-A type COF, which is widely used in catalytic degradation and has a hydrogen evolution rate of up to 7204.3 $\mu mol\cdot g^{-1}\cdot h^{-1}$. It was more than 10 times that of PEBP-COF (217.1 $\mu mol\cdot g^{-1}\cdot h^{-1}$) without D-A structure in the control group.

3.2. covalent organic frameworks for adsorption

Adsorption and separation depend on the pore size, pore type and pore environment of COFs, and can realize adsorption and separation of specific molecules after designing COFs into specific materials. The adsorption of gases, organics, metal ions, etc., proves that COFs materials are powerful tools for mitigating environmental and energy problems. In 2019, Liu et al. [58] designed and synthesized a COF-etta-2, 3-DHA that integrated ETTA and 2, 3-dihydroxy-*p*-phenyldialdehyde (2, 3-DHA). It shows very good stability in neutral, acidic and alkaline solutions, and the intramolecular hydrogen bond interaction gives it this high stability against hydrolysis. Because there are a large number of accessible ortho-dihydroxyl binding sites in COF, Cd^{2+} can be better adsorbed in aqueous solution. It can be seen from the adsorption-time curve that the adsorption capacity in the neutral solution increases rapidly in the early stage, and the absorption capacity of cadmium is 39.6 $mg\cdot g^{-1}$ at 1 min and 95.6 $mg\cdot g^{-1}$ at 20 min. After 60 min, it becomes stable and reaches the saturation adsorption capacity of 116 $mg\cdot g^{-1}$, with remarkable absorption effect. The adsorption effect is better in alkaline solution (when pH = 12, the adsorption capacity is close to 120 $mg\cdot g^{-1}$), and the effect is worst in acidic solution. This was one of the highest values of Cd^{2+} adsorption reported at that time. In the study of Gao et al. [59], ETBA and ETTA were used as monomers for imide condensation, and the obtained TPE-COF-I had a complete network structure because both amino and aldehyde groups of the two monomers participated in the reaction, while TPE-COF-II had a blocked network structure because two aldehyde groups of monomers ETBA did not participate in the reaction. Larger than surface area, adsorption of CO_2 With a capacity of 118.8 $cm^3\cdot g^{-1}$, this was one of the most powerful COFs materials reported at the time to adsorb carbon dioxide. The COFs mentioned by Tian et al.

[60] have two different shapes and sizes of micropores: The quadrilateral micropores and non-equilateral hexagonal micropores have good adsorption capacity for CO_2 and H_2, with CO_2 absorption rate of 19.8 wt% (273 K,1 bar) and H_2 absorption rate of 1.79 wt% (77 K,1 bar).

3.3. covalent organic frameworks for sensor

The tetraphenyl-based COFs sensor overcomes the aggregation-induced fluorescence quenching caused by electrostatic interaction and other factors, and has a high quantum yield and can emit strong fluorescence in the aggregation state, which has the advantage of detecting various substances with the naked eye, and improves the sensitivity of the analytical test. Nitro-explosives, such as 2,4, 6-trinitrophenol (TNP), 2,6-Dinitrotoluene (DNT), 2-nitrophenol (NP), often used in the pharmaceutical industry, fireworks, military, will not only cause environmental pollution, but more importantly, will produce strong stimulation to the eyes, skin, organs of workers, resulting in irreversible damage. Therefore, rapid, efficient and sensitive detection of explosives has important practical significance for environmental protection, anti-terrorism and stability maintenance, and national defense. In 2012, Zhang et al. [61] reported for the first time the use of microwave assisted synthesis of high-fluorescence COF for explosive sensing. In this way, *p*-phenyldiformaldehyde and melamine are condensed to form COF nanoparticles, called SNW-1. Its fluorescence can be quickly quenched by TNP, DNT, nitrobenzene (NB) and other nitro aromatic explosives, among which the quenching effect on TNP is the strongest, and the detection limit of the sensor is as low as the ppb level. Since then, there have been more and more researches on the application of COFs in the field of explosive sensing. In 2018, Gao et al. [62] selected ETBA and 1,3,6, 8-tetri (4-aminophenyl) pyrene units to synthesize Py-TPE COF nanoparticles

The tetrahydrofuran solution of the particles exhibited the highest photoluminescence quantum yield (PLQY) among the known imine-COFs at that time, reaching 21.1%. Under the same conditions, the quenching percentage of TNP reached 95.5%, while the quenching degree of PL for other explosives was very small, indicating that the COF had excellent selectivity for TNP. In 2019, Faheem et al. [63] synthesized dual-fluorescent DL-COF by assembling ETTA and conjugated plane 9, 10-anthracene dialdehyde as monomers. It has high sensitivity and excellent selectivity for nitroaromatic explosives with a detection limit of ppb level, which is superior to many nitroaromatic fluorescence sensors based on COFs and MOFs. Fe^{3+} is also an important biological metal ion, is the main component of hemoglobin, involved in the transport of oxygen in the human body, iron deficiency is very easy to cause anemia. The COF constructed by Cui et al. [64] not only can effectively adsorb CO_2 and volatile organic compounds, but also has the ability to specifically sense Fe^{3+} ions. Its fluorescence intensity is almost non-fluorescent after adding Fe^{3+}. The percentage of emission and quenching is close to 99.6%, and the detection limit is 3.07 $\mu mol \cdot L^{-1}$. At the same time, the cycle performance and stability were excellent. After 5 cycles, the quenching percentage did not change much, and the morphology and structure of COF remained unchanged before and after the cycle. Hg^{2+} is a highly toxic element, if absorbed by the human body, it will lead to chronic poisoning, causing substantial damage to the organs, nervous system, endocrine system. Zheng et al. synthesized sulfur-containing COF with ETBC and 4, 4 '-dithianiline, and the sulfur active site was embedded in the pore wall with uniform distribution. As a sensitive sensor for selective detection of toxic mercury ions, its response to Hg^{+} and Hg^{2+} can be directly observed with the naked eye. The detection limits were 1.22 ppb and 38.7 ppb, respectively.

3.4. covalent organic frameworks for others

The rigid structure and regular channels of COFs give them excellent photoelectric properties, but because of the anisotropy of COFs growth, they usually exist in a solid powder state and cannot be well processed into photoelectric devices. In 2020, Xiong et al. [32] selected photoactive monomer ETBC and monomer TAPT to synthesize Cupr-based single layer graphene by chemical vapor deposition. COF was grown in situ to form an ordered COF-graphene heterostructure, and the photodetector was prepared with the COF-graphene heterostructure. The optical responsiveness at

473 nm is as high as 3.2×107 A·W^{-1}, with a response time of about 1.14 ms. Peng et al. [42] successfully synthesized a series of three-dimensional single crystal CFS by supercritical solvothermal method, including sc-COFTPE synthesized by ETBC and tetra-(4-aminophenyl) methane (TAM), and applied it to the field of polarization optics.

4. Summary

Tetraphenyl compounds provide a unique building block for the synthesis of COFs, and also enrich the content of COFs. This review summarizes the development of tetraphenyl-based COFs and their applications in many fields such as adsorption, catalysis, sensing, photochemistry and biomedicine. At present, the construction of tetraphenyl COFs monomer types is still relatively scarce, and most tetraphenyl COFs are two-component, and the development of three-component monomer COFs is still very few, which limits the development of different tetraphenyl COFs to a certain extent. As mentioned in the previous article, the introduction of functional groups [or substituents and the change of solvent conditions are flexible strategies to develop tetraphenyl-based COFs with novel topologies and porous structures, and the development of more diverse tetraphenyl-based CFS in the future is still a key breakthrough. Since the two monomers used have been reported to contain tetraphenyl groups, whether there is interaction or synergistic effect between the two monomers, so as to construct tetraphenyl COFs with mixed bonds and its application performance still need to be further studied. In summary, tetraphenyl-based COFs show strong application potential and development prospects in various fields. In the future, attention should be paid to enriching the structural diversity of tetraphenyl-based COFs and improving their application performance.

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