

COFs as catalyst in organic methodologies

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

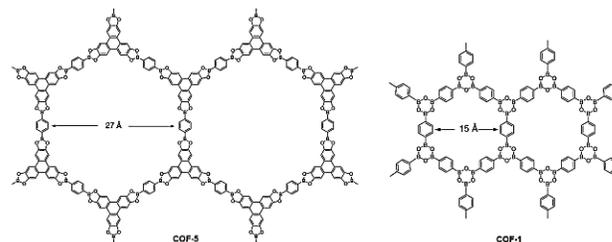
Introduction

After the groundbreaking work by Yaghi and co-workers in 2005 [1], in last years, covalent organic frameworks (COFs) (**Scheme 1**) had proven themselves as emerging class of porous materials [2]. COFs consist of atomically precise organization of organic subunits to form two- or three-dimensional porous crystalline structures through strong covalent bonds. These porous structures, entirely consist of covalent bonds between light elements such as carbon, hydrogen, boron, nitrogen and oxygen which they are joining by C-N, C=N, C=O, B-O and other chemical bonds [3-7].

In COFs, the size, symmetry and connectivity of the linkers predefine the geometry of the framework. Therefore, composition, topology and porosity of the resulting two- or three-dimensional COFs can be controlled easily by using proper precursors which enables the preparation of regular structures with adjustable chemical and physical characteristics. Some of their privileged features of COFs are including high thermal stability, low density, tunable pore size and structure, permanent porosity and high surface area [8-11].

Due to these interesting features connected with COFs, it is no wonder that these versatile compounds have found a variety of promising uses including catalysis, sensing materials, separation processes, energy and gas storage, adsorption, optoelectronics, and drug delivery [12-16].

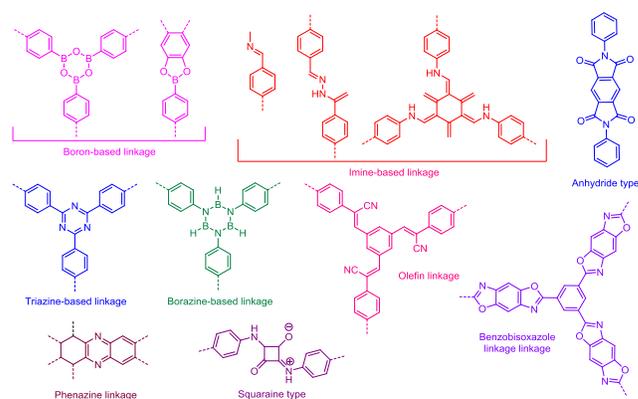
Based on applied units for the synthesis of COFs, these porous materials divided into three main classes comprising imine-based, triazine-based and boron-containing COFs. In addition to these classes several types of COFs including anhydride and squaraine types, phenazine, benzimidazole, benzobisoxazole borazine and olefin linkages have been recently reported in the literatures [12].



Scheme 1. First reported COFs by Yaghi and co-workers.

Scheme 2, represented the abovementioned common linkages which applied for the construction of COFs.

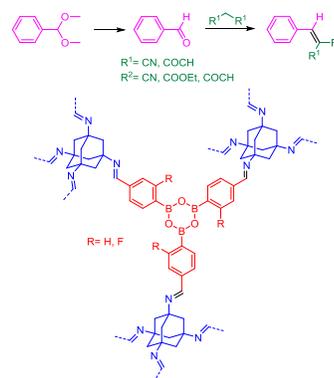
Due to the abovementioned promising features and different possible applicabilities of COFs, herein I wish to highlight their catalytic applications in organic methodologies.



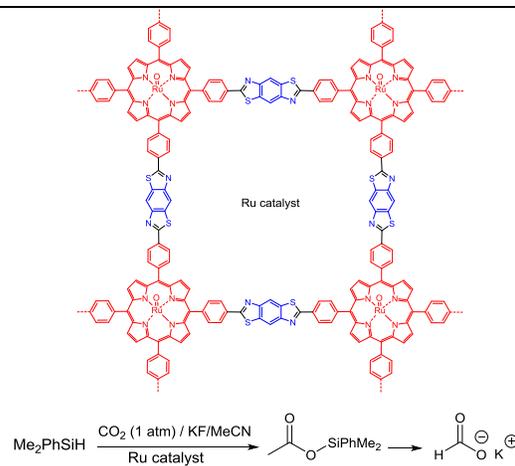
Scheme 2. Common linkage involved in COFs construction.

Abstracts

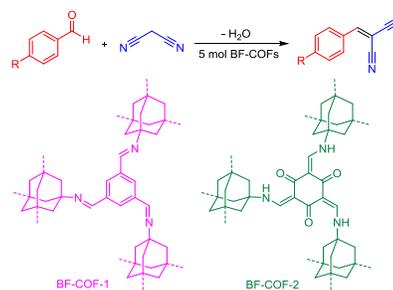
(A) In 2016, two three dimensional COFs with based on dual linkages (including boroxine and imine linkages) were reported. The resulting COFs showed high capability for gas uptake. Also, the prepared COFs applied as acid-base catalyst for one-pot cascade reactions [17].



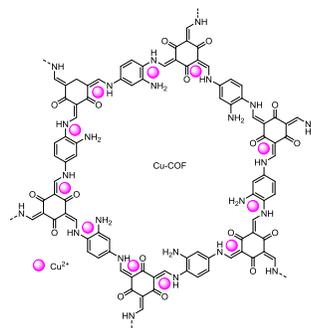
(B) McGrier and co-workers reported the synthesis of a ruthenium porphyrin-based COF. Then, the authors applied the prepared structure for the hydrosilylative reduction of CO₂ to potassium formate with good turnover number and frequency [18].



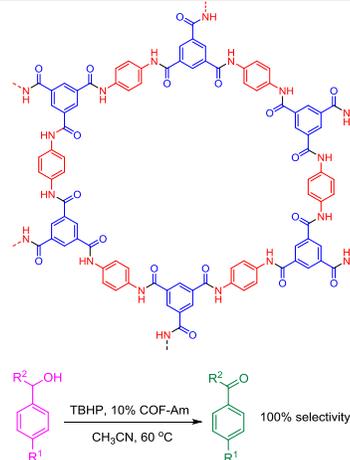
(C) In 2014, Yan and co-workers reported the rational design and synthesis two 3D base-functionalized COFs including BF-COF-1 and BF-COF-2. Also, they applied the resulting COFs as selective and recyclable catalysts in base-catalyzed Knoevenagel condensation reactions [19].



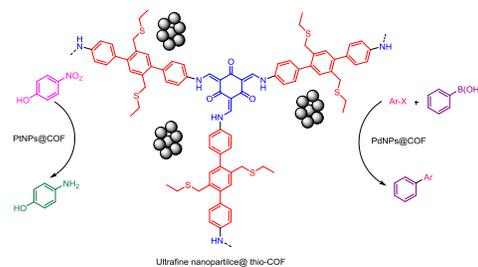
(D) An amino-functionalized COF namely TpPa-NH₂, has been synthesized and applied as a proper carrier for transition Cu(II) ion to generate a hybrid Cu-COF as catalyst. The resulting hybrid catalyst has been used in Knoevenagel condensation, oxidation of styrene and reduction of 4-nitrophenol [20].



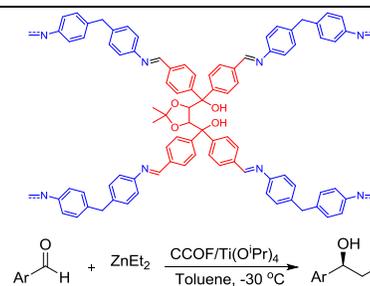
(E) In 2017, Sarma *et al.*, have been reported the synthesis and catalytic activity of a 2D COF by applying 1,3,5-benzenetricarbonyl trichloride and p-phenylenediamine as starting materials. The resulting COF has been applied as a catalyst for the selective oxidation of benzyl alcohols at 60 °C [21].



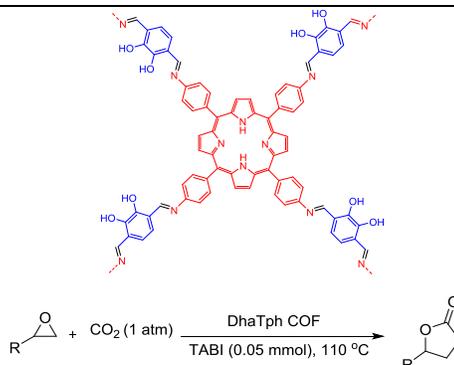
(F) A thioether-containing COF has been designed, synthesized and applied for the growth of ultrafine metal nanoparticles of Pt and Pd. Also, the authors reported the catalytic performance of the described COF for reduction of nitrophenol and Suzuki-Miyaura coupling reaction under mild conditions [22].



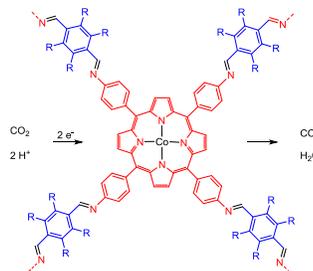
(G) In 2016, Cui and co-workers have reported the construction of 2D COFs containing chiral functionalities. Also, the authors reported the catalytic application of prepared homochiral COFs as an efficient and recyclable heterogeneous catalyst for the asymmetric addition of diethylzinc to aldehydes [23].



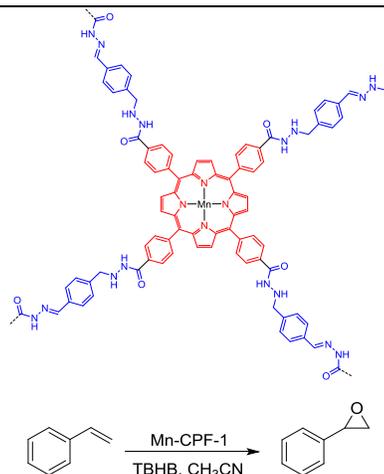
(H) In another investigation, Bhanage *et al.* reported the synthesis of two imine-linked catechol porphyrin-based COFs and applied them as an organocatalyst for the chemical fixation carbon dioxide to yields the related cyclic carbonates [24]. Also, similar work has been reported by Wang *et al.* in 2017 [25].



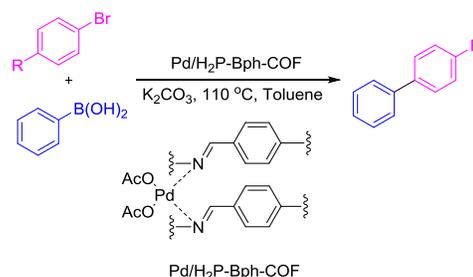
(I) In 2015, Yaghi and co-workers reported the catalytic application of COF-366-Co and COF-367-Co films for aqueous reduction of carbon dioxide to carbon monoxide through a high active and selective manner [26,27].



(J) In another work, Jiang *et al.* reported the synthesis of porphyrin-based COFs containing manganese(III) ions. The prepared structures have been shown promising catalytic activity towards the epoxidation of alkenes [28]. Also, another porphyrin-based COF has been synthesized and applied as an organocatalyst for Michael addition reaction [29].



(K) In 2015, Jiang *et al.* reported the construction of an imine-linked porphyrin-based COF. They then applied the resulting COF for the synthesis of a Pd-immobilized catalyst and reported its catalytic performance in Suzuki cross-coupling reactions [30]. Also, a multifunctional COF bearing Pd(0) nanoparticles has been reported as a catalyst for C-H activation reactions [31]. In another work, Jia and co-workers reported the synthesis, characterization, and catalytic performance of a phosphomolybdic acid-functionalized COF in olefin epoxidation [32].



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