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Additional Information

MICROWAVE ASSYNTED SYNTHESIS OF COVALENT ORGANIC FRAMEWORKS (COFS): A REVIEW

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ABSTRACT

Covalent organic frameworks (COFs) are relatively recent materials. They have received great attention due to their interesting properties. However, the application of microwaves in their synthesis, despite its advantages such as faster and more reproducible processes, is a minority. Herein, a comprehensive compilation of the research results published in the microwave-assisted synthesis (MAS) of COFs is presented. This review includes articles of 2D and 3D COFs prepared using microwaves as source of energy. The articles have been classified depending on the functional groups including boronate ester, imines, enamines, azines, and triazines, among others. It compiles the main parameters of synthesis and characteristics of the

materials together with some general issues related with COFs and microwaves. Additionally, current and future perspectives of the topic have been discussed.

Key words: microwave assisted synthesis, covalent organic framework, COF, synthesis procedures, 2D COF

1.   Introduction

Covalent organic frameworks (COFs) were first introduced in 2005 by Yaghi and co-workers as crystalline porous organic polymers.[1,2,26] They involve organic subunits connected by strong covalent bonds building two- or three-dimensional porous crystalline structures, the skeletal structure of which is composed totally of light elements such as hydrogen, boron, carbon, nitrogen, and oxygen.[3--6]

Unlike classic covalent polymers, COFs offer an internal order, with high specific surface area and low framework density, homogeneous pore size distribution, and stable structure that gives them special applicability in a wide range of fields.[5,7] The main fields of application include gas capture,[8] separation and storage,[9--11] biomedicine,[12,13] drug delivery,[14,15] catalysis,[16,17] energy storage,[8,18] optoelectronic devices,[19] sample pretreatment,[20] chromatographic separation,[21] and sensing,[22] among other applications.[23--25]

Depending on the COFs' applicability, their porosity, functionalization, and structure must be carefully designed. Consequently, there are different synthetic perspectives including solvothermal, ionothermal, mechanochemical, sonochemical, and microwave methods for successful COF synthesis.[6] Solvothermal synthesis is the most commonly used nowadays. Indeed, the first two COFs synthetized by Yaghi and co-workers where prepared by this technique.[26] This methodology is similar to zeolite syntheses,

where the solvents are mixed with the monomers in a closed Pyrex tube and heated for the required reaction time.[27,28] However, it can take between 2 and 9 days at continuous heating at 80–120 °C until the reaction is finished, and the selection of the correct solvent is also crucial to success as it governs the solubility of reactants.[22,29] Ionothermal methodology is usually used to generate covalent triazine frameworks.[30] Unlike the classic method, instead of organic solvents the presence of an ionic liquid/molten salt (usually $ZnCl_2$), which serves as both solvent and catalyst, is required. Nevertheless, it has high drawbacks as it develops under harsh conditions (about 400 °C, high pressures, and high reaction time) and increases the risk of secondary decomposition and condensation reactions.[3,31] In order to supply these downsides, the mechanochemical method was developed. In this case, the monomers are placed in a solvent-free mortar and manually ground at room temperature.[22,32] However, until now, the mechanochemical method has not been very successful in the synthesis of COFs based on Schiff reactions.[5] By contrast, the use of microwave technology in the synthesis of COFs has been scarcely explored during the past years as an alternative of the solvothermal method despite its advantages such as the reduction of reaction times (in some cases more than 200 times faster), more reproducible processes, and isolation of cleaner products.[33]

Taking into account these outstanding features of microwave assisted synthesis (MAS), it is not then surprising that it has been used in the synthesis of diverse materials, not only inorganic, such as metallic nanoparticles,[34,35] nanoporous and mesoporous materials,[36] or metal oxides,[37] but also organic, such as polymers[38] and mixed organic-inorganic materials like metal-organic frameworks (MOFs).[39]

Over the years, the interest in finding different synthetic routes for COFs, as well as the creation of new structures and possible applications, has increased considerably. A measure of this interest could be the number of reviews written by scientists in impact journals on this topic. Before 2015, only 5 reviews on COFs had been published, increasing this number in subsequent years until reaching more than 20 reviews published only in 2019. However, none of these works deal with the microwave-assisted synthesis of COFs, despite the cited outstanding advantages. Thus, this review focuses specifically on the synthesis, characterization, and properties of the COF procedures reported under microwave irradiation up to date.

2.   Structural and synthetic characteristics of COFs

As noted above, covalent organic frameworks are a class of crystalline porous polymers. They integrate organic subunits, composed from light-weight elements such as H, B, C, N, O, and Si, into 2D or 3D structures linked by strong covalent bonds.[40] COFs allow a predictable design over composition, topology, and porosity of the structure by simply varying the units involved. In this way, many COFs develop highly desirable properties such as a well-defined porosity, large surface areas, low mass density, excellent hydrothermal stability, and wide functional variety.[41] But excellent properties are not only limited to those related with the backbone constituents, because COFs can be further functionalized postsynthetically.[42]

In general, COFs can be classified attending to two structural parameters: type and topology of formed bonds.[33]

2.1. Linkages

The covalent bonds of COFs can be formed between a wide variety of functional groups. Figure 1 contains the monomers used in the materials contained in the review. In most cases, a condensation reaction, in which a small molecular byproduct (e.g., water) is generated, takes place [5] (Figure 2). Although many types of covalent bonds, either homo- or heteroatomic, have been reported for the synthesis of COFs, most COFs synthesized to date can be categorized into three categories, namely boron-containing COFs, nitrogen-containing COFs, and silicon-containing COFs.[43] In particular, the most common linkages formed, and the functional groups in which these can be found, are B<C->O (boroxine, boronate ester), B<C=>N (borazine), C<C->N (β-ketoenamine, imide, and amide), C<C=>N (imine, triazine), N<C=>N (azodioxy), and B<C->O<C->Si (borosilicate), among others. Depending on the type of bond formed, the chemical and thermal stability will vary. For instance, imine linkages (formed by the condensation reaction of an aldehyde and an amine) usually show improved chemical stability in the presence of alcohols, water, or acids compared with that of boronate ester-linked COFs.[44] Moreover, in general, triazines (formed by the condensation of nitrile groups) are even more stable than imines.

2.2. Topology

Compared with other porous solids, COFs have the distinct feature that their frameworks can be designed in a predictable manner at three different structural levels: pore design, framework design and both pore and framework complementary design.[44] The position of the reactive functional groups in the former subunits controls the growth of the elementary polygons, leading to the generation of 2D or 3D COFs (Figure 3). Moreover, the produced pore size can be also calculated attending to

the dimension of the organic building blocks. Therefore, not only the primary-order structure but also higher-order structures can be designed in advance attending to topology diagrams: it guides the integration of organic building blocks into polygons, and their extended growth producing the crystalline network of COFs. The only requirement subunits have to meet is to possess rigid structures and specific geometries.[44]

Despite the huge number of organic molecules and functional groups forming COFs, all of them can be categorized in a very short number of topologies.[45] For 2D COFs, there are five possible topologies (hexagonal, tetragonal, rhombic, trigonal, and dual pore kagome; Figure 3). In the case of 3D topologies, there are many more possibilities.[33]

2.3. Preparation Methods

As stated above, COFs are constructed by covalently linked organic molecules. These molecules are not linked together forming an amorphous structure but forming a crystalline molecular network. The structural extended order is possible thanks to the dynamic covalent chemistry (DCC) process taking place during the synthesis of COFs.[46] DCC relies on the reversible formation of covalent bonds between molecules. This equilibrium provides COFs a way to remediate kinetically generated defects, in such a way they can be repaired, allowing the formation of highly ordered frameworks.

However, reversibility does not guarantee structural order by itself. Other features, such as structural rigidity and suitable synthetic conditions (temperature, time, concentration, catalyst, etc.), must be also considered in order to avoid the formation

of amorphous structures.[47] Selection of optimal synthesis parameters is a key factor for the preparation of COFs frameworks, and this is never a trivial issue. In general, thermodynamic control can be favored at high temperatures and/or long reaction times.[5] These are usually provided in solvothermal synthesis, and that is why this is the most frequently used method for COFs preparation.[4]

Microwave synthesis is a suitable alternative to the solvothermal methods because it provides a way to quickly synthesize COFs under solvothermal conditions. Not only saving time, but an increased yield, better crystallinity, and higher Brunauer-Emmett-Teller (BET) surface area in COFs synthesis have been reported.[48] In fact, microwave synthesis has been used in organic chemistry for many decades (since 1986) in order to save time.[49,50] In the following section, the general features of microwave-assisted synthesis will be treated more in depth.

3.   General notions of microwave assisted synthesis.

3.1 Interaction between MW and matter.

Microwaves (MWs) are a form of electromagnetic radiation lying between infrared and radiofrequencies. To date, they have been mostly been applied for transmission of information, but also for heating.[51] In fact, MWs were initially applied for radar detection purposes during the Second World War, and MW heating was discovered by chance in 1946 by Percy Spencer when he realized that MWs could interact with matter and melt the chocolate bar he took in his pocket. This fact prompted him to launch the first commercial microwave oven in 1952.[52] Although the frequency range of MW encompasses between 300 MHz and 300 GHz (wavelengths from 1 m to 1 mm, respectively), not every frequency is allowed for heating purposes in order to

avoid interferences with telecommunication, wireless networks, and cellular phones.[53] The most widely available for Industrial Scientific and Medical (ISM) purposes are 915 MHz, 2.45 GHz, and 5.85 GHz. In particular, the frequency of 2.45 GHz is used in all household and chemical synthesis microwave ovens.

Heating by MWs is based on the ability of matter to absorb and to convert them into heat. But not all the materials behave in this way in presence of an electromagnetic field. We can find three general types of behavior. (1) Transmission: some materials, like teflon, glass, or air, are transparent to MWs. Therefore, they are employed as containers to carry out chemical synthesis in MW reactors. (2) Reflection: conductive materials like metals do not allow electromagnetic waves to pass through them and are reflected. This kind of materials are used for the walls of the ovens. (3) Absorption: electromagnetic energy is absorbed to some extent by the material and converted into heat.

Furthermore, in agreement with their electromagnetic character, MWs present an electric and a magnetic component, perpendicular to each other and to the propagation direction. The electric and magnetic fields generated by MWs can interact with matter in a different way, thus causing different effects. As the magnetic contribution to heating is usually very small, the magnetic heating is usually not considered. The complex permittivity ε^* is defined as a measure of the ability of a material to absorb and store potential energy. It has two components: the permittivity ε', also known as the dielectric constant, describes the ability of a material to act as a capacitor storing the energy. The other component, the loss factor ε'', reflects the ability of the material to dissipate energy. Neither of these parameters is constant, as

they all depend on chemical composition and structure, temperature, and frequency.[54]

Nonmagnetic materials are primarily heated by its interaction with the electric field (heating through dielectric loss). At the microwave frequencies, this can take place mainly by two different mechanisms (Figure 4).[55] The first one is dipolar polarization. This mechanism only affects polar compounds, that is, molecules with a permanent dipole moment. When in presence of an electric field (E-field), dipoles try to align themselves with the external field by rotation. However, the frequency of microwaves is too high. For example, when a commercial magnetron of 2.45 Hz is used, wave oscillations occur 4.9×109 times per second. As dipoles are not able to respond to the oscillating field at the same rate, a phase lag is produced, causing the dipoles to mutually collide and generating heat. The second referred heating mechanism is ionic conduction. This one takes place when mobile charge carriers (electrons, ions, etc.) move back and forth through the material under the influence of the microwave E-field. The induced electric current collides with neighboring molecules or atoms, thus creating an electrical resistance that further heats the material.

As already stated, the magnetic field (H-field) also interacts with matter and promotes heating, but this contribution is negligible for most non-magnetic materials. Despite this fact, and the relatively low number of papers ascribing the microwave heating effect to the H-field component, recent findings show the contribution of multiple mechanisms to microwave magnetic heating, among which eddy current losses, hysteresis loss, magnetic resonance loss, and residual losses are mentioned.[56] In short, these losses are only important when conductor and semiconductor magnetic materials (like ferrite materials) are exposed to an alternating magnetic field.

Furthermore, some literature has referred to "microwave effects" to describe some controversial phenomena associated with microwave irradiation that cannot be easily explained attending to differences in temperature profile between microwave and conventional heating.[57] These non-thermal effects include an enhanced reaction rate, improved product yields and mechanical properties, reduced processing/curing time, reduced activation energy, and different reaction pathways.[58] However, these seem to be derived from an incomplete understanding of the actual electromagnetic theory, in which an accurate mechanism of microwave interactions with matter is still not effectively explained by existing theories.[59]

3.2. Microwave ovens

A typical microwave instruments consist, at least, of four components: a microwave source, an antenna, a waveguide, and a cavity. Other components, like mode stirrers and turntables can be present in order to ensure homogeneity inside the cavity.

A magnetron operating at a frequency of 2450 MHz is the most common microwave source, but other sources like solid state, klystron, or gyrotron can be also found.[60] Once produced, MWs are released thanks to an antenna. The waveguide takes MWs from the antenna and drives them to the microwave cavity, in which the sample to heat is placed. The reaction mixture is placed in a container of a material transparent to microwaves at the operating frequency, most commonly made of borosilicate glass or PTFE. On the other hand, the cavity is made of metal, to reflect MWs and prevent leakages. Once in the cavity, it is important to assure a good homogeneity. Attending to the design of the microwave applicator, microwave devices can be classified into three types (Figure 5):[60]

a) Monomode reactor. Only one reactor vessel can be irradiated at a time in a monomode reactor, due to the small volume of the cavity. Microwaves are "focused" into the cavity, ensuring an extremely homogeneous inner electromagnetic field, which results in only one electromagnetic mode present in the cavity. The sample to irradiate is placed at the maximum intensity of the electromagnetic field. Small volumes, along with high-power intensities, results in fast heating rates.

b) Multimode reactor. This kind of reactors have larger cavities, can accommodate larger volumes of sample, and several vessels can be irradiated at once. However, the electromagnetic field is not as homogeneous as in monomode reactors; the field density is lower and can generate non-uniform heating profile and localized overheating (hot-spots). Moreover, these applicators present a low performance when applied to small-volume samples.

c) Traveling-wave reactor (TMR).[61] TMR avoids the drawbacks of monomode and multimode reactors and allows to accurately control the electromagnetic parameters applied to chemical reactions. This type of reactor can assure a highly uniform microwave heating because the microwave field inside the reactor just travels in one direction and thus avoids reflections and resonant conditions. Therefore, they enable the process scale-up under well-defined conditions.

3.3. Advantages of microwave heating

MWs present several advantages when applied to chemical reactions. Compared to conventional heating methods, which mainly include sand or oil baths, electric heating, and heating jackets, the first advantage of microwaves is related to energy.

Comparatively, microwaves are more energy efficient because the heat is directly generated within the desired material, and it is not necessary to consume energy heating the rest of the system (i.e., the bath), reducing the global power consumption. Furthermore, MWs can penetrate to some extent in the sample transferring heat in a much faster way than the other methods, in which heat is transferred by convection from the surface and they hugely depend on the inner thermal conductivity of the sample. In this way, MWs produce a better temperature profile than conventional heating techniques.[62] As conventional techniques transfer heat by convection from the surface, temperature is always higher there than inside the sample. This difference is more noticeable at the beginning of the reaction or when the sample to heat is thicker (or has a larger volume). Therefore, a characteristic temperature profile from the outside to the inside is produced. However, as MWs penetrate in the sample, the temperature profile is inverted, and samples are efficiently heated from the inside to the outside (in core volumetric heating). As a result, much more homogeneous temperatures are achieved in shorter times when MWs are applied, resulting in well-controlled reactions conditions.

Microwaves have been widely applied in many organic[63] and inorganic[37,64] syntheses. In particular, when applied to the synthesis of nanomaterials, the reported advantages of MWs over conventional heating are:[65--67]

-- Higher synthesis rate and shorter reaction times: heating is transferred faster and in a more homogeneous way. Moreover, the ability of microwave devices to work with closed vessels allows working with temperatures above the boiling point. Typically, there is a reduction of reaction times from hours to minutes as MWs reduce the activation barrier energy.[6,68]

-- Homogeneous products: volumetric heating results in homogeneous synthesis and well defined final products.[69]

-- Better properties: materials with smaller particle size, narrow particle size distribution, high purity, and enhanced physicochemical properties have been reported.[70]

-- Higher yields due to minimization of side products.[71--73]

-- Other advantages: selective heating, easier scale-up, lower power consumption (environmentally friendly), etc.

Considering all these outstanding features, it is not then surprising that they have been used in the synthesis of COFs.

4. Microwave assisted synthesis of 2D Covalent Organic Frameworks.

Attending to structural dimensions, COFs can be classified into two-dimensional (2D) and three dimensional (3D) frameworks. 2D COFs are the most common. In fact, more than 200 2D COFs have been reported so far.[74] 2D COFs are restrained to 2D polymeric layers of covalently linked building blocks, which can further form extended structures via non-covalent interactions.[75] In comparison with 2D COFs, 3D COFs possess building blocks extended in the three dimensions of the space. As 2D COFs are the most widely extended, this review will first summarize the most remarkable features and applications of this type of COFs obtained under MAS (Microwave Assisted Synthesis). In order to provide a more comprehensive description of the COFs reported to date, these have been further classified attending to the type of bond formed between building blocks (Figure 2). A summary of the COFs reviewed and their synthesis conditions can be found in Table 1.

4.1. Boronate ester based COFs

Boronate ester-linked COFs are synthesized through the reversible condensation reaction taking place between boronic acids and catechols. This type of bond is one of the most commonly reported in COF formation. In fact, one of the first COFs obtained (COF-5) falls into this category.[26] In general, these COFs possess high crystallinity, thermal stability, and a remarkable surface area, but the electron-deficient character of boron atom makes them sensitive to the attack of moderate nucleophiles such as water or even moist air.[76] Despite this drawback, different 2D boronate ester COFs has been developed for gas adsorption,[77] sensing,[78] and electronic applications.[79,80]

Boronate ester-based COFs are generally prepared by solvothermal methods, which imply long reaction times and high temperatures and pressures Hereafter, the most remarkable features of the microwave-assisted synthesis of boronate ester-linked COFs are summarized.

As already commented, COF-5 was the first synthesized boronate ester COF,[26] and it also became the first one obtained under microwave irradiation (Figure 6). COF-5 is nowadays a well-known mesoporous 2D COF constituted by a layered hexagonal framework formed upon condensation reaction between 1,4-benzenediboronic acid (BDBA) and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP). This framework generates an intrinsic porosity, with channels and interstitial voids between layers, which promoted its application in catalysis, gas storage, and optoelectronic devices, to cite just a few examples.[77] Attracted by its novelty and properties, Cooper and co-workers[81] developed the first microwave-assisted procedure to synthesize COF-5 and investigated how synthesis and purification method affects its formation and features. COF-5 was synthesized by solving BDBA and HHTP in a 1 : 1 (v/v) mixture of

1,4-dioxane/mesitylene in a closed vessel and irradiating the mixture in a microwave reactor for 20 min at 100 °C under stirring. The generated precipitate was further purified from starting materials or impurities that may be trapped within the porous structure by microwave-extraction with acetone at 55 °C for 20 min. As a result, a crystalline solid was obtained. They repeated the synthesis in open vessel with comparable results, deducing overpressure was not required in these syntheses. When compared with conventional solvothermal method, the microwave-assisted method provided COF-5 200 times faster (20 min vs. 72 h) and with improved porosity.[81] They realized how important extraction step was, as it increased the BET surface area from 901 to 2019 m2 g -1, considerably higher than the value of 1590 m2 g -1 reported under solvothermal heating. In order to clarify the role of microwaves in both the synthesis and purification steps, in a second article Cooper and co-workers performed a design of experiments.[82] In this way, COF-5 was synthesized 30 times either by conventional solvothermal heating (100 °C, 72 h) or by microwave heating (100 °C, 20 min), and then subjected to different purification steps. Some samples remained as made, other were washed with acetone, and the remaining ones were subjected to microwave extraction in acetone. The authors observed that conventionally prepared COFs showed more crystalline structures and higher BET surface areas, independently of the driven purification process.[82] Theoretical studies revealed that synthesis routes and purification processes gave rise to different particle sizes and morphologies, affecting the surface area of solids. In light of this, they concluded that the main advantage of microwave synthesis was the substantially reduced reaction time and developed an optimized microwave synthesis by adjusting reaction parameters. They predicted the optimized reactions conditions would consist in a

reaction temperature of 151 °C and an irradiation power of 300 W, which should yield a product with good crystallinity and with a surface area comparable to that of the solvothermally produced COF-5 in just 3 min.[82] Therefore, although microwave-assisted methods provide a way to produce COFs at a faster rate, their effects on the framework growth and, thus, on the final morphology, must be considered.

The microwave-assisted experimental conditions for the synthesis of COF-5 reported by Cooper and co-workers[81] became popular within researchers worldwide as they provided a simple and fast way to prepare this kind of materials. Consequently, different papers have used them with minor changes for the preparation of COF-5. It was even used as example of laboratory practice for undergraduate students.[83] Synthesis conditions slightly varied to 30 min irradiation at 100 °C, followed by two microwave-extraction steps in acetone for 20 min each. More recently, COF-5 has been synthesized by heating the mixture of reagents in a microwave for 3 h at 100 °C.[84] In this study, the solid was deposited by electrochemical methodology on different conducting substrates, creating films with different thicknesses with applications in catalysis. In both cases, the crystalline solid formed was indicative of the remarkable reproducibility achieved by microwave-based synthesis methods, setting a precedent for future microwave COF preparations.

Apart from electrochemical modification of electrodes, COF-5 has been also employed in the modification of ceramic supports.[85] The surface modification of an alumina support with this COF was accomplished in several reaction steps, in which the initial starting materials were synthesized or functionalized. On the one hand, the surface of an α-Al2O3 substrate was chemically modified to incorporate boronic acid groups. On the other hand, COF-5 was synthesized from a mixture of BDBA and HHTP under

continuous stirring and microwave irradiation at 300 W for 1 h (100 °C). Once the COF was thoroughly washed with acetone, both solids were placed together and further irradiated to achieve the formation of COF-5 layers on the functionalized porous α-Al2O3 ceramic support surface, forming a layer with a thickness of approximately 1 μm around alumina particles.

Other strategies have been tried in order to improve the applications of boronate ester COFs. One consists in the use of modulating agents, mono-functionalized terminating ligands that compete with the bridging ligands for the reactive positions of the net. Calik et al. employed this synthetic strategy to control COF-5 growth, looking for an increased crystallinity and porosity of the final material.[86] 4-mercaptophenylboronic acid (MPBA) and 4-carboxyphenylboronic acid (CPBA) were used as modulators as they both had only one boronic acid group, and competed with BDBA for the reaction with HHTP. Synthesis conditions were similar to those reported in absence of modulator and consisted of microwave irradiation at 300 W for 1 h (100 °C). As a result, small amounts of modulator led to an extended crystallinity and higher BET surface area, while retaining the solid structure. The capping behavior of modulating agents caused slower COF growth, thus favoring a self-healing process without affecting reaction between HHTP and BDBA. But not only structural parameters were improved. Furthermore, the inclusion of monomers such as CPBA and MPBA to the skeleton structure offers the possibility of mild functionalization of the outer surface of the COF. This can be used as a powerful tool for the easy post-synthetic modification of COFs, to improve their intrinsic physicochemical properties and their applications.

Another strategy consists of the substitution of building blocks, producing different boronic-ester COFs. Only two COFs using this method and microwave irradiation have

been reported to date. Compared with COF-5, only one building block was replaced at a time, either BDBA or HHTP. In the first example, BDBA was exchanged by the boronic ester 4,7-bis[4-(4,4,5,5)-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-benzo[1,2,5]-thiadiazole (BTDBE).[87] So, as the boron atom is already forming an ester, a double-step process is mandatory to obtain the transesterification product with HHTP. First, BTDBE was hydrolyzed with concentrated HCl with stirring under MW irradiation for 10 min at 180°C. As a result, a yellow suspension was formed. In the second step, HHTP was directly added to the yellow mixture, and then irradiated again at 160°C during 30 min to yield BTD-COF. The green powder obtained exhibited high chemical and thermal stability, and a narrow pore size distribution around 4.1 nm. In the second example, HHTP was replaced by arylene-ethynylene macrocycles (AEM-1 and 2), although only the second one was synthesized under microwave irradiation.[88] The solvothermal route required an 8 days synthesis to produce COFs, whereas the microwave-assisted method provided AEM-COF-2 in just 40 min at the same reaction temperature (120°C). Once produced, the authors studied how the size of the connector affected the structure and found that the pore size increased with the size of the building block, but the BET surface area remained constant. In both cases, AEMs produced very crystalline COFs with high thermal stability and permanent porosity, thanks to the π-conjugated skeleton and strong π-π interaction between adjacent layers.

In conclusion, microwave-assisted synthesis has been successfully applied to the preparation of boronate ester-linked COFs, both using boronic acid or boronate esters. This technique provides highly crystalline materials and overcomes the drawbacks related with the solvothermal method, yielding COFs with similar properties in a much

shorter time. Although some variations regarding particle size or morphology may result from the different heating mechanism, the above examples demonstrate that microwave synthesis is an efficient and reproducible method to prepare boron-based COFs.

4.2. Imines, enamines, and azines based COFs

One of the known disadvantages of some COFs, such as boronate esters- and boroxines-linked COFs, is their easy decomposition upon contact with water. This fact has strongly limited their applications to those in which inert or at least water-free conditions are used.[1] Hopefully, imine-based COFs are superior to those other COFs, and generally possess higher chemical stability[89] (including water and acid/base solutions) and greater crystallinity, making them a better option for applications such as water treatment, catalysis, gas adsorption, and sensors.[90,91]

Imine-linked COFs are usually prepared through condensation of aryl amines and aldehydes under Brønsted acid-catalyzed solvothermal conditions.[92] Most commonly, reactions take place in a mixture of 1,4-dioxane and mesitylene, using acetic acid as a catalyst. Conventional solvothermal conditions include synthesis temperatures around 120 °C, which extend for several days in a sealed tube until the condensation reaction is concluded. For example, the first imine-based COF (COF-300), which was prepared in 2009 by Yaghi and co-workers[93] from terephthalaldehyde (PDA) and tetra-(4-anilyl)-methane, took place in 1,4-dioxane with an aqueous acetic acid 3 M solution at 120 °C for 72 h. As the solvothermal route requires high temperatures and long synthesis times, researchers have made many efforts to find faster, more reproducible, and easier synthetic routes to prepare different imine-, enamine-, and other nitrogen-linked COFs as they represent a very promising

molecular source of 2D materials.[94] Below, several examples of how microwave heating synthesis reduces the preparation time of these COFs from days to hours with equal or even improved features will be presented.

Despite the usefulness of microwave methodology for the synthesis of materials in general and COFs in particular, they were not applied to C-C-N linked COF preparation until 2015. The first example was the MAS of an enamine-COF, reported by Wei et al.[48] Enamine bonds are formed by reaction of an aldehyde with α-hydroxy groups and an amine. In an effort to understand whether microwave heating influences the synthesis of this type of COFs, the authors synthesized TpPa-1 (Figure 7) by conventional (3 days, 120^°C) and microwave methodology (1 h, 100 °C), and compared the results. In both cases the reaction combined p-phenylenediamine (PA) and 1,3,5-triformylphloroglucinol (TFP) in a mixture of mesitylene/1,4-dioxane/3 M acetic acid (3:3:1, v/v) sealed under nitrogen. Apart from providing COF in high yield with significantly less time, the MW method increased the bond formation rate and provided more crystalline materials. Moreover, TpPa-1-MW showed improved porosity, with a BET surface area much bigger ($725\ m^2g^{-1}$) than that calculated for the synthesized under conventional solvothermal heating ($152\ m^2g^{-1}$). This COF was studied for CO2 capture applications, showing a high CO2/N2 selectivity and an excellent CO2 uptake ($5.1\ mmol\ g^{-1}$ at 273 K and 1 bar). In a subsequent article, the MW-synthesized COF was also used as precursor to produce a carbonized material with outstanding electrochemical performance, able to be used as a cathode material in high-performance lithium-sulfur batteries.[95] This strategy of carbonizing imine-COFs to produce nanostructured carbon materials had been previously reported[96]

applying microwaves to the COF-composite supported on graphene oxide, a good microwave susceptor.

In another approach, PA was replaced by 2,5-dimethyl-1,4-phenylenediamine (PA-2), giving as result the COF denoted as TpPa-2. Encouraged by the improved crystallinity and porosity achieved for TpPa-1 synthesized under microwave irradiation, TpPa-2 was also prepared following the same synthesis conditions, and its result compared with a TpPa-2 COF obtained mechanochemically.[97] The reagents were irradiated at 500 W, and different temperatures and times were tested in order to reach optimal surface characteristics. In all cases, the TpPA-2-MW resulted in identical chemical composition and crystalline structure. Nevertheless, short reaction times (30 min) provided materials with lower BET surface area (SBET, about 100 m^2g^{-1}) because some unreacted monomers remained trapped within the crystal structure. Too long reaction times (90 min) also sharply decreased SBET as they promoted larger particles formation. Regarding reaction temperature, pores collapsed if 100 °C were exceeded. Consequently, 1 h and 100 °C were selected as optimal parameters, as they provided a TpPA-2 with an SBET of 535 m^2g^{-1}, much higher than the one prepared by mechanochemical synthesis (62 m^2g^{-1}), or the others reported in literature by solvothermal synthesis (350 m^2g^{-1}). The high BET surface value was related to the higher crystallinity of the microwave-prepared material, and to the smaller spherical-like morphology particles (≈500 nm). Compared to TpPa-1, the novel TpPa-2 exhibited improved hydrolytic and chemical stabilities, mainly at higher pH, which made it a good material to be applied in polymeric matrices membranes for water purification purposes. When integrated into a polysulfone (PSf) membrane, the composite exhibited double pure water permeability compared with its homologue produced

mechanochemically, and 70 % higher than a commercial PSf membrane. In fact, it was successfully applied to reverse osmosis desalination by preparing a thin-film nanocomposite membrane via interfacial polymerization.[98] Adding TpPa-2 to the membrane improved water permeability and lowered NaCl permeability compared to the undoped membrane, besides an excellent chlorine and anti-microbial resistance.

TpPa-1 and TpPa-2 structurally only differ in two methyl groups placed in the phenyl ring of the diamine. However, the stability of the second one turned out to be much higher than that of TpPa-1. Thus, placing different size or polarity substituents in such positions might result a good strategy to prepare COFs with enhanced or even new properties. Actually, several enamine-COFs with different lengths of oligo(ethylene oxide) chains were synthesized under microwave irradiation, and their improved hydrophilic character was applied for ion transport applications in aqueous solutions.[99] In particular, the selected building blocks were 1,3,5-triformylphloroglucinol (TFP) and different 4,4'-diamino-p-terphenyl units (TP-R) with different substituents in the central phenyl ring: ethoxy (OEt), ethylene glycol monomethyl ether (OMEG), diethylene glycol monomethyl ether (ODEG), and triethylene glycol monomethyl ether (OTEG). Two solvent mixtures were used, one for R =H and OEt and another one for R=OMEG, ODEG, and OTEG, but in all cases the mixture was irradiated at 170°C for 20min to obtain the five crystalline TfpTP-R COFs. All the three oligo(ethylene oxide) chains had an amphidynamic behavior that might be useful in transport applications, especially as solid-state electrolytes for Li-ion batteries, as they would allow the mobility of Li+ ions under electrochemical potentials.

The conductivity of COFs would notably increase if charged molecules were placed within the structure, due to the mobility of the surrounding counterions. A novel strategy to synthesize cationic COFs with different counterions has been recently reported.[100] Firstly, a COF containing bromide was synthesized and, consequently, a microwave-assisted anion exchange substituted bromide for chloride, acetate, or triflate anions. The initial COF was solvothermally prepared by irradiating 1,3,5-triformylphloroglucinol (TFP) with ethidium bromide (EB) for 3 h at 100°C, meanwhile anion exchange took place by placing SJTU-COF-Br in a saturated solution of the corresponding salt and applying 30 min of microwave irradiation at 80 °C. The hostage anions tailored the pore system, causing notable differences in CO_2 gas storage and separation performance. The one with acetate anion showed the highest CO_2 capacity (171.2 mg g^{-1}), which was 1.7 times than that of bromide (101.9 mg g^{-1}). This fact was justified by the charge-transfer interactions taking place between AcO- (Lewis base) and CO_2 (Lewis acid). Therefore, in addition to ion conduction applications, cationic frameworks can be further applied to CO_2 capture.

Apart from enamine-COFs, other types of C-N bonds have been also produced through a microwave-assisted procedure. In particular, imines are the most common ones. Imine bonds are formed by reaction of an aldehyde and an amine. Compared to enamines, no hydroxy groups in α-positions to the aldehydes are required, which enlarges the choice of aldehyde reagents able to be used, whereas enamine-COFs are almost entirely restricted to 1,3,5-triformylphloroglucinol (TFP). Actually, Kuehl et al. reported a synthetic procedure to prepare building blocks with different lateral chains based in a hexamine (HATN-R1) and a pyrene tetraone (TOPyr-R2), which were further combined for the preparation of four different COFs.[101] In particular, the hexamine

groups varied from neutral (R1=H) to positive [R1=N(Me)2] or negative (R1=COOH), whereas selected substituents for the pyrene tetraone were either neutral or negative (R2=H or COOH, respectively). Some of them were combined following a fast microwave synthesis, as a proof of concept to show how easily on-demand imine-COF with desired functional groups pointing the pores can be produced. As an example of the synthetic strategy developed, COF-8 (R1=CH2N(Me)2; R2=H), COF-9 (R1 =COOH; R2=H), and COF-10 (R1=H; R2=COOH) were synthesized. In all cases, the desired tetraone and hexamine reacted in a microwave oven for 2 h at 200 °C in a mixture of N-methyl-2-pyrrolidone and glacial acetic acid. As a result, three different crystalline COFs were produced, and the different position and nature of the functional groups in the final COF backbone caused the controlled reduction of pore sizes (from 2.8 nm in COF-10 to 1.9 nm in COF-8). Encouraged by these features, COF-9 was both supported on a porous anodic aluminum oxide filter and onto a track-etched polycarbonate membrane support, and it was further applied to water purification purposes. These membranes demonstrated both high water flux and high selectivity for the selective separation of cations larger than a precise size threshold. Additionally, it is important to highlight how this strategy affords the design and synthesis of nanometer sized pores to produce anion-selective membranes. They could be even used as additive for the preparation of membranes for the separation of neutral molecules, as reported in a later article for HAH-TOPyr (R1=COOH; R2=H), a COF structurally pretty close to COF-9.[102] This carboxyl-functionalized COF presented a hydrophilic pore that made it a good candidate to be incorporated as a 2D nanofiller in polyacrylonitrile polymer matrix to produce ultrafiltration membranes. Several COF concentrations (0--0.8 %) were tested, as they affected water permeability and certain mechanical properties

such as tensile strength and elongation at break. The electrostatic repulsion proved very useful for protein rejection, and the membranes containing this COF could retain almost entirely γ-globulin and bovine serum albumin.

Regarding procedures aimed at increasing the crystallinity of the COFs produced, in general two microwave-assisted methods have been reported, one for imines and the other one for enamines. The one for imine-COFs preparation is based on the use on mono-tert-butoxycarbonyl (BOC) diamines as reagents, rather than directly using the diamine.[103] BOC is a common protecting group of amines in organic synthesis, as it can resist many synthetic conditions and it is selectively deprotected in acid media. When used in COF synthesis, the in situ gradual deprotection with trifluoracetic acid slowed down the imine condensation reaction rate and provided a crystalline framework. In this way, the traditional synthetic route for imine-COFs based in the reversible imine condensation reaction to correct defects in amorphous polyimine precipitate firstly formed is avoided, and COFs are not produced heterogeneously. This synthetic approach served to produce several imine-COFs, both 2D and 3D, as woven structures, nanocrystals, and thin films, with synthesis times notably lower than those commonly reported in solvothermal conditions, ranging from 1.5 to 72 h depending on the solid produced. Thanks to the time-saving nature of the method, microwaves were also applied to the synthesis of nanocrystals, in order to show that it can be also applied to this technique. COF LZU-1 was synthetized by dissolving 1,3,5-triformylbenzene (TFB), 4-(tert-butoxycarbonylamino)-aniline (NBPDA), and poly(N-vinylpyrrolidone) (PVP) in an ethanol and trifluoroacetic acid medium and irradiating for 30 min at 120 °C in a microwave. The synthesis was hugely influenced by PVP concentration, as it acted as capping agent passivating the surface of the crystal

formed and regulating its growth, yielding crystal of 500, 245, or 112 nm. Analogously to LZU-1, Por-COF and TFPB-PDA were obtained from NBPDA when the aldehyde was replaced by 4,4',4'',4'''-(porphyrin-5,10,15,20-tetrayl)tetrabenzaldehyde (TBPP) and 1,3,5-tris(4-formylphenyl)benzene (TFPB), respectively. When incorporated into membranes, LZU-1 membranes were sensitive to organic vapors, producing a color change easily reverted by vapor removal.

The second microwave-assisted method for increasing the crystallinity of COFs, this time for both imine- and enamine-COFs preparation, is based on transimination technique.[92] In this case, the starting material is protected as its benzophenone-imine. This group protects amines from oxidation and increases its solubility in organic solvents, facilitating homogeneous COF formation and crystallization. In this case, Vitaku and Dichtel[92] synthesized three benzophenone-imines [N-benzidine (BND-BPh), tris-aminophenylbenzene (TAPB-BPh), and diaminobenzene-benzophenone (DAB-BPh)] and reacted them, under both conventional synthesis (120 °C, 3 days) and microwave conditions (120 °C, 5 h), with three aldehydes: TFB and PDA produced the corresponding imines, whereas TFP gave the enamine-COFs. In such a way, four different COFs where synthesized, two imine-COFs (BND-TFB, TAPB-PDA) and two enamine-COFs (DAB-TFP, BND-TFP). The powder X-ray diffraction analysis pointed out the good agreement with the modeled structures. Moreover, the authors compared the results produced by solvothermal and microwave irradiation heating between them and further with previously reported COFs obtained by direct synthesis. Regarding porosity, imine-linked COFs showed almost identical BET surface area whatever their heating method, and higher than in previous articles. β-Ketoenamine-linked COFs also provided higher values than those by direct synthesis, but

solvothermal heating yielded better results than the microwave method. In conclusion, these two methods have proven their ability to synthesize imine- and enamine-linked COFs under conventional solvothermal and microwave-assisted conditions, providing high-quality materials with enhanced crystallinity compared with those reported by the direct reaction of monomers, but with considerable time reduction.

Last but not least, other C-N linkages have been reported in the synthesis of COFs. This is the case of azine-based COFs, formed by the reaction of a polyaldehyde with hydrazine. The use of hydrazine as reagent is interesting when focused on producing narrow pore sizes, as it is the smallest diamine. This type of bond is also resistant to hydrolysis in both acidic and basic media.[78] Although azine-COFs are generally produced under conventional solvothermal heating, they have been also reported with a microwave-assisted technique. Furthermore, if azine linkage is applied to the reaction with low-symmetry aldehydes, heterogeneous-pore COFs (HP-COFs) would be synthesized.[104] As hydrazine is the smaller amine, the aldehyde is the monomer contributing the most to pore sizes, and differences in the length of the initial aldehydes should be reflected in pore sizes of final COFs. Taking this into consideration, two HP-COFs were synthesized under solvothermal (150 °C, 4 days) and microwave heating (170 °C, 6 h) conditions. The linkers used were 5-(4-formylphenyl)isophthalaldehyde (FPIP) for HP-COF-1 and 5-((4-formylphenyl)ethynyl)isophthalaldehyde (FPEIP) for HP-COF-2. No remarkable differences were observed between the solids produced under conventional or microwave heating, apart from time saving related to the second one. In both cases, two crystalline 2D COFs with high specific surface areas and dual pore structures were produced.

In summary, this section has summarized the reported microwave-assisted synthesis developed for the preparation of enamine, imine, and azine COFs. Furthermore, the strategies aimed at enhancing crystallinity during COF formation under microwave conditions have also been reviewed. Microwaves considerably reduce the required synthesis time from several days to a few hours (2-3 h) but also provide materials of equal or even superior quality, with higher BET surface and resistance to aqueous conditions.

4.2. Triazine based COFs

Covalent triazine-based frameworks (CTFs) are a subtype of COFs. They were first reported in 2008 by Kuhn et al. in an ionothermal synthesis in which nitriles were trimerized using ZnCl2 as both solvent and catalyst.[105] However, high temperatures (400-700 °C) and long reaction times (40 h) were required, producing decomposition to some extent. In any case, thanks to their outstanding properties related to a high N content, planarity, and electron delocalization, many different CTFs and applications in a wide variety of fields have been reported since then. Below, microwave-related synthesis methods of CTFs are reviewed, and a brief summary of the most remarkable applications is presented. Thanks to microwave irradiation, reaction time could be shortened, in many cases to less than 1^^h, avoiding the problems related with long synthesis times and high temperatures.

In general, CTFs can be synthesized in two different ways. On the one hand, triazines can be formed in^^situ by reaction between nitrile groups using different catalyst/solvent systems. On the other hand, these can be also previously formed in the reagents, and be further incorporated into the final CTF structure by the reaction of other functional groups, forming linkages such as imine and imide. The first method,

consisting in the direct formation of triazine rings from nitrile groups, is the most employed in the microwave-assisted synthesis of triazines. The COF named as CTF-1 (Figure 8) is formed by reaction of 1,4-dicyanobencene (DCB) in the presence of a good microwave susceptor. As the previously employed ZnCl2 is also a notable microwave absorber, it was the first solvent/catalyst system employed. In 2010, Zhang et al. reported the first method for the fast synthesis of CTF by applying microwave irradiation to a mixture of DCB and ZnCl2.[106] Different times and powers were tried to optimize the synthesis, ranging from 120 to 460 W and from 30 min to 8 h, respectively. The reactions at low power output (210 W) for 1—2 h resulted in samples with BET surface areas around 1100 m^2 g^{-1}. This porosity was applied to the study of the hydrogen adsorption capacity, which resulted to be 1.78 wt % at 77 K and 1 bar.

Once the synthesis conditions were established, they were taken as the basis for the development of different applications. Thanks to the good oxidizing properties of CTF-1, it has been used for sensing different species. By using the ZnCl2-catalyzed procedure, the solid could be produced in 30 min under microwave irradiation.[107] The microwave-prepared CTF-1 was used as catalyst in oxidation reactions and as sensor. CTF-1 forms reactive oxygen species, both with H2O2 (within 10 min) or simply with dissolved O2 (within 30 min), thus producing the oxidation of sensitive species. When the oxidation reaction is applied to the synthesis of chromophores, a deep color is generated. This mechanism was employed as a colorimetric sensor for the detection of biothiols, which acted as reducing agents fading the color.[107] Using an analogous mechanism, CTF-1 was used in the luminol chemiluminescent reaction, an oxidation reaction of luminol in alkali conditions, which was inhibited in the presence of several antioxidants (such as rutin, ferulic acid, and kaempferol), allowing its detection.[108] In

another approach, CTF-1 also served to detect species that accelerated the oxidation reaction of organic species. Copper ions enhanced the catalytic oxidation of 3,3',5,5'-tetramethylbenzidine by CTF-1, producing a blue solution.[109] The increase in absorbance values was directly related with CuII concentration and was used for its quantification even in real samples. Apart from this application, the authors further reported in the same paper an improved synthetic method, in which CTF-1 was prepared in only 6 min when the microwave power output was increased to 700 W.

Going one step forward, when an iron precursor is placed together with DCB and ZnCl2, a magnetic composite of CTF-1 is produced.[110] Synthetic conditions were optimized with regard to the conditions in absence of iron,[106] thus microwave power was raised (350 W) and synthesis time was reduced to 1 h. Despite saving time, in this case the MW-prepared material produced less uniform composites, structurally amorphous and with a broad pore size distribution. With an iron content around 10 wt %, the iron oxide (Fe_2O_3) particles generated were homogeneously distributed within the solid, and surface area was not affected by their presence and remained around 1100 m^2 g^{-1}. Thanks to the good adsorption capacity of CTF-1 and to the magnetic behavior provided by iron oxide, the composite was applied to the adsorption of organic species. First, methyl orange was used as model molecule in order to characterize its adsorption properties, showing both high adsorption capacity and fast adsorption kinetics.[110] On a subsequent article, the composite was further applied for the magnetic solid-phase extraction (MSPE) and subsequent recovery of phenols in real samples.[111]

Apart from iron oxide-containing materials, CTF-1 prepared with ZnCl2 can serve also as support material for other active species. In particular, metal nanoparticles of

rhodium, ruthenium, iridium, and platinum were directly synthesized and supported on the surface of a CTF-1 solid previously prepared under conventional conditions.[112] After stirring the mixture of CTF-1 and the different metal(0) carbonyls precursors for 24 h under argon atmosphere, a rapid microwave irradiation of just 10 min induced the formation of the corresponding nanoparticles on the solid, in all cases with an average diameter around 3 nm. Among all the metals tried, CTF-1-Rh composite was applied to the hydrogenation of benzene to cyclohexane under mild conditions, and to the electrochemical production of hydrogen, showing better properties than commercially available Pt/C electrodes.

Although $ZnCl_2$ allowed the efficient production of CTFs both with and without microwave irradiation, it has two main disadvantages. First, it remained within the CTF structure as impurity. In most of the reported papers, a considerable number of washes, even in acidic medium, were conducted in order to remove it, but this was never fully achieved. Secondly, reactions in $ZnCl_2$ were conducted at high temperatures, most probably comparable to those reported under conventional conditions (400—700 °C),[105] and thus if power/time conditions are not properly optimized, DCB might decompose, causing damage in the final structure of CTF. With this in mind, Ren et al. developed a synthetic method in which $ZnCl_2$ was substituted by trifluoromethanesulfonic acid (TFMS) as catalyst.[113] Thanks to TFMS, Zn-free CTFs could be produced in shorter times at much lower reaction temperatures. They were able to synthesize up to six different CTFs solids, including CTF-1, at room temperature using an overnight procedure, by using DCB, BPDCN, ODBN, TCPB, NTB, and MTTB, respectively, as monomers. When microwave-assisted conditions were applied, the six solids (CTF-COF 1--6 respectively) were produced at 110 °C in just 30 min in a similar

yield (≈90 %). Both techniques produced microporous solids with similar features, except for a better crystallinity observed in MW samples. Later, the synthesis of CTF-1 with TFMS as catalyst was optimized, and it was produced in a time as low as 30 s at lower power.[114] After trying several powers (from 20 up to 200 W), Xie et al. observed how high microwaves powers gave the lower defects in solids, but without exceeding a certain limit.[114] In this way, 100 W was selected as optimal power, as this one produced the most ordered structure with a high degree of polymerization between nitrile groups. Once synthesis was optimized, its behavior for water oxidation and proton reduction under visible light was characterized.

Among all the commercially available reagents containing a triazine ring, melamine (Mel) is the most widely employed for the synthesis of CTFs. Thanks to its high nitrogen content, the CTFs synthesized possess an electron-rich structure that strongly influences its applications. Melamine can react with cyanuric chloride (CNCl), another molecule containing a triazine ring, in a condensation reaction to produce NENP-1. Under microwave-assisted synthesis, they can react in DMSO to produce the COF in 30 min.[115] The solid was formed by nearly spherical nanoparticles with and average size of 220^^nm. The very high N content, combined with its microporous properties consisting of a high specific surface area (850 $m^2 g^{-1}$) and narrow pore size distribution, made it a good candidate to be applied as heterogenous catalyst in Knoevenagel condensation,[116] a base-catalyzed reaction between carbonyl compounds and derivatives containing acidic methylene groups for the formation of C-C bonds, and as an electrode material in supercapacitors.[115]

Another CTF, called SNW-1, was produced by the reaction between Mel and terephtalaldehyde (PDA). This COF, along with others produced with three different di-

and tri-aldehydes, were first reported in 2009 by Müllen and coworkers.[117] Under these conventional synthetic conditions, COF was obtained in a 60 % yield after a reaction time of 3 days at 180 °C.[117] When synthesized under microwave irradiation, the reaction time was reduced to 6 h.[118] The solid was formed by nanoparticles with a size ranging from 20—50 nm, and a double pore system: a micropore system produced by packing of COF layers and a mesopore one formed by textural holes between particles. However, the BET surface area (476 $m^2 g^{-1}$) by MAS is less than half that obtained under conventional heating (1377 $m^2 g^{-1}$). Despite this fact, several applications have been reported for SNW-1 solids synthesized under MW heating. This CTF was found to be fluorescent both in suspension and in solid state, and thanks to its electron-rich structure, it was successfully applied to the detection of nitroaromatic compounds, both in solution and in vapor phase.[118] If SNW-1 was synthetized in presence of a NH2-functionalized magnetite (Fe3O4), a layer of CTF with a thickness slightly lower than 40^^nm was homogenously formed on the magnetite surface [SNW-1 (Fe3O4)] after a reaction time of 4 h.[119] The produced composite showed high selectivity for the coordination of HgII over many others metal ions and a high adsorption capacity of almost 100 mg Hg g^{-1}. Apart from magnetite, SNW-1 can be synthesized separately under microwave irradiation following a complex process at different temperatures, and then deposited over a Si-OH-activated silica forming a variable thickness layer.[120] This layer showed good chemical stability and microporous properties, with a narrow pore size distribution from 1.2 to 1.6 nm and a specific surface area of 231 $m^2 g^{-1}$. The composite was applied to selective adsorption and separation of both polycyclic aromatic hydrocarbons (PAHs) and volatile fatty acids (VFAs) and used for the determination of trace VFAs in tea and tobacco shred samples

if combined with a GC-MS device. Finally, if SNW-1 is driven to high temperatures at high heating rates and subsequent fast cooling, like those produced under microwave irradiation, it can partially decompose, producing a carbonaceous cyanide-functionalized COF in which the initial bulk morphology and porosity is retained.[121] As a result, a carbonaceous covalent organic framework (CCOF) with outstanding chemical, irradiation, and thermal stability was prepared and applied to the adsorption of U(VI).

The reaction of Mel with pyromellitic dianhydride (PMDA) gave a CTF with imide bonds (CTF-PI). As the imide bond is easily formed, a crystalline polyimide was synthesized in only 3^^min under a microwave-assisted method.[122] The polyimide has a multilayered structure with large π--π delocalization, responsible for its fluorescent properties. This fluorescence was selectively quenched in the presence of CrIII, because of its coordination to imide groups, allowing its quantification.

Finally, CTFs can be prepared by the reaction of other less conventional reagents. TTA-DFP COF was synthesized under 30 min of microwave irradiation by condensation of 2,6-diformylpyridine (DFP) with 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline (TTA).[123] When ultrasonicated in water, the CTF was separated in highly monodisperse and stable nanosheets. These covalent organic nanosheets (CONs) had an average size of 22 nm and a six-fold fluorescent intensity enhancement compared to bulk material. These good physical properties were used for cellular bioimaging of HeLa nucleus cell, showing no cytotoxic effect within 48 h.

Another triazine-based solid can be formed by the Ni-catalyzed homocoupling of 2,4,6-tris-(4-bromophenyl)-[1,3,5] triazine (TBT) under MAS, to produce COP-4.[124] Although two irradiation times were tried, 2 and 4 h, similar COFs were produced. Both

solids showed complete reaction of bromine groups, forming a homogeneous porous structure with high surface areas around 1400 m^2 g^{-1} which may be applied for CO2 capture.

Lastly, CTFs can be prepared from the MOF HKUST-1 in presence of urea.[125] When the mixture was irradiated for 6 min, urea produced covalent oxygen-rich networks (CNO) nanosheets and removed Cu from the initial structure. After characterizing the properties of the layered structure, it was dispersed in polylactic acid matrix, producing composites with improved mechanical properties and flame retardancy that might be applied as additive to certain polymeric materials.

In summary, microwaves have been demonstrated as a viable alternative for the rapid synthesis of high-quality CTFs. This can be directly formed by reaction between nitrile groups in monomers, in which a catalyst such as ZnCl2 or trifluoromethanesulfonic acid is required, or being part of the structure of the reagents, most commonly as melamine and cyanuric chloride. Thanks to the easiness of their preparation, stability and high nitrogen content, they have been widely applied in many applications, from sensors to catalyst and capture of gases. Therefore, microwaves have shown as a very interesting approach to become the main route for the synthesis of large amounts of CTFs, as they allow reaching the required synthesis temperatures quickly and in a reproducible way.

4.3. Other

In addition to the most common functional groups mentioned above, other groups such as esters, imides, amides, or direct C-C coupling have been used in the microwave-assisted synthesis of bidimensional COFs (Figure 9). Although they occur in bibliography much less frequently than those bonds collected in previous sections,

these linkages are very useful in the way they offer the opportunity to synthesize a wide variety of materials with different applications and with properties even superior to those discussed so far.

Regarding amides, they have been applied for the preparation of carbonaceous COFs.[121] By using the "segregated" microwave irradiation method, which has been previously described in the triazine section, the presence of C and N atoms in COF-amides was also applied to obtain this kind of COFs. The starting amide solid was prepared by reaction of trimesoyl chloride (TMC) and p-phenylenediamine (PA) under conventional synthesis. Once COF-SCU-1 was formed and purified, the solid was irradiated for 3 min at 800 W to form carbonaceous COFs from the partial decomposition of the initial framework. As in the case of triazine derivatives, the carbonaceous amide COF was applied to the adsorption and recovery of U(VI).

Imides are another N-containing functional group formed by the reaction of an amine with an anhydride. Lee et al. prepared polyimides with different composition under a microwave irradiation method.[126] In particular, the authors reacted pyromellitic dianhydride (PMDA) with tris(4-aminophenyl)amine (TAPA) to produce a highly crystalline COF (PI-COF) with remarkable thermal stability. The reaction time was hugely reduced thanks to microwave irradiation, from 5 days, necessary under conventional solvothermal conditions at 200 °C, to just 2 h at the same temperature under MAS, resulting in solids with comparable physicochemical parameters. The polar imide backbone was applied to SO2 capture, a harmful air contaminant emitted from burning fossil fuels in different industries and processes. PI-COF showed enough BET surface area (1003 m^2 g^{-1}) and imide groups to provide a good SO2 sorption capacity (41 wt %), but desorption was not good enough and SO2 sorption decreased to 80 %

after five cycles. This issue was solved by adding a third building block to the synthesis: 4-((dimethylamino)methyl)aniline (DMMA). Tertiary amine groups improved the SO2 sorption capacity and reversibility, based in the strong charge-transfer complexes formed between basic dimethylamine and acidic SO2. However, if the DMMA percentage added to the synthesis exceeded 20 %, the resulting structure framework and porosity were dramatically reduced. Several percentages were tried, and the best results were produced with a 10 % tertiary amine functionalization.

On the other hand, alcohols react with activated carboxylic acids to produce ester bonds. The esters can be conjugated with triple bonds forming the TCD family of COF. These can be prepared under MAS by reaction of TMC and 2,4-hexadiyne-1,6-diol (HD) for 16 min.[127] The TCD formed can be also successfully modified with different functional groups (cyano, amidoxime, and hydroxy group) in post-synthesis procedures. TCD was obtained as uniform sized spherical nanoparticles with good thermal stability up to 280 °C, when it began to decompose. TCD and its functional derivatives were tried as adsorbents versus a broad selection of cations, showing in all cases a preferred adsorption for U(VI).

Other COFs having triple bonds in their structure were prepared by catalyzed C-C coupling of 2,3,5,6-tetrakis(4-bromophenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (t-BrDPP) with up to three different alkynes ([1,4-diethynylbenzene (DEB), 4,4'-diethynyl-1,1'-biphenyl (DEBP), 1,3,5-triethynylbenzene (TEB)].[128] Under slightly different catalyzed synthesis conditions (with Ni or Pd complex), 1 h irradiation at 100 °C produced the homocoupling of this building block (N1) or the formation of 3 different polyynes, named as N2-4 depending on the alkyne employed (DEB, DEBP, and TEB, respectively). All the derivatives were formed by a large π-conjugated system, which

promoted broad fluorescence bands around 650^^nm. Moreover, the BET surface areas of up to 500 m^2 g^{-1} could be useful in gas storage and sensing of gases such as NOx, which might quench their intrinsic luminescence.

Charged building blocks have been also used in the development of COFs. In this case, properties do not only depend on the framework, that is topology, types of bonds formed between building blocks, and host-guest interactions, but also on the counterions present within the structure. In such a way, two different covalent organic networks containing a bipyridinium ion moiety were prepared following the Zincke reaction under MAS. In the first one, Trabolsi and co-workers performed the reaction between 1,3,5-tris(4-aminophenyl)benzene (TAPB) and 1,1'-bis(2,4-dinitrophenyl)-[4,4'-bipyridin]-1,1'-diium dichloride (TNV) under either solvothermal (3^^days, 120^°C) or microwave conditions (2 h, 100 °C) to yield COGF (Covalent Organic Gel Framework).[129] By controlling solvent polarity and heating method, the polymeric network could be prepared in three different forms: hollow spheres, hollow tubes, or as covalent organic gel frameworks. MW irradiation not only accelerated reaction rates but also enhanced the crystallinity of the products, which in the case of organic gel was formed by crystalline nanosheets with honeycomb lattices. All three materials were stable in acidic, neutral, and basic aqueous solutions. Although chloride counterions hugely reduced the network surface area to values lower than 40 m^2 g^{-1}, all three materials exhibited high iodine adsorption by electrostatic interactions. However, Trabolsi and co-workers did not stop at this point as they though that introducing a building block able to produce hydrogen bonding in the structure would reinforce interactions and might improve selectivity for certain analytes. This was exactly what they did in their second article: they prepared a COF formed by porphyrins [5,10,15,20-

tetrakis(4-aminophenyl)porphyrin, TPAPP] connected by the same bipyridinium ion linker.[130] The cationic porphyrin COF with viologen units (PV-COF) was formed by stacked square layers, which were grouped together forming uniform spherical particles with an average diameter of 1.4 µm. As in the previous solid, COF had very good chemical stability but low surface area (38.2 m^2 g^{-1}). Despite the limited value, PV-COF was successfully applied to the selective removal of bromate ions from contaminated water, thanks to double electrostatic and H-bonding interactions. The process was very efficient and fast, and the COF could be easily regenerated by washing with basic and acidic media.

Phthalocyanines are another class of N-containing aromatic macrocycles with two-dimensional geometry that have been incorporated into COF structure by microwave-assisted reactions. A fully aromatic conjugated 2D COF containing nickelphthalocyanine and pyrene-4,5,9,10-tetraone (TOPyr) as building blocks showed an intrinsic bulk conductivity, which was applied for the detection in ppb levels of oxidizing (NO, NO2) or reducing (NH3, H2S) gases.[131] As in the case of triazine rings, which were explained in the previous section, planar COFs containing N-rich structures are generally characterized by good conductive properties. If these structures comprise conjugated phthalocyanines, conductivity of the whole COF is enhanced, as phthalocyanines promote out-of-plane charge transfer. In the cited article,[131] COF-DC8 was prepared by reaction between 2,3,9,10,16,17,23,24-octa-aminophthalocyanine nickel(II) (NiOAPc) and pyrene-4,5,9,10-tetraone (TOPyr) through both conventional solvothermal synthesis and microwave-assisted synthesis. In this case, microwaves were not preferred as they provided the resulting material with slightly lower crystallinity, an extremely important factor for the desired

application, although synthesis time was hugely reduced from 10^^days to only 10^^h.

In another approach, two closely related phthalocyanines-COFs, in which the coordinated metals were rather Fe or Mn, were obtained starting from benzene-1,2,4,5-tetracarbonitrile (BTC). Firstly, a COF based in a quasi-phthalocyanine iron structure (COF-BTC-Fe) was prepared by reaction of BTC with ferric chloride at 180 °C for 10 min in a microwave synthesizer.[74] Although this material showed a long-range ordered two-dimensional rigid structure in which Fe atoms were regularly coordinated, the most characteristic behavior of this COF was the possibility of being exfoliated in basic media. Hydroxy groups inserted into the COF structure and were absorbed onto the positively charged centers, promoting the exfoliation of single COF flakes that were very stable in solution. This solution showed great performance in oxygen reduction catalysis and was applied in a flow battery with improved results when compared with conventional cells. When the metal was changed to a Mn salt, Mn-phtalocyanines (COF-BTC-Mn) were obtained after 20 min microwave irradiation at 150 °C.[132] Again, the structure was easily exfoliated, this time in DMF with no basic media. Once separated into flakes, the positively charged metal centers were absorbed through electrostatic interactions onto carbon fibers. As COFs were homogenously distributed on the carbon surface, these were applied as flexible electrodes in supercapacitors, producing an outstanding capacitive performance and retaining its capacitance for more than 3000 cycles.

Also, a COF containing a germanate knot has been synthetized from germanium dioxide, 9,10-dimethyl-2,3,6,7-tetrahydroxy-anthracene (DMTHA), and lithium methoxide at 180 °C during 6 h.[133] In this case, the Ge-COF-1 produced was highly crystalline, with a hexacoordinated germanate surrounded by the counterion Li+. Ge-

COF-1 showed a CO2 adsorption of 88.5 cm^3 g^{-1} at 273 K and relatively low conductivity (0.25 mS cm^{-1}), most probably due to the constrained Li-channels.

In summary, microwaves have efficiently provided COFs with many different types of bonds supposing a time saving with regard to conventional solvothermal methodology. Furthermore, they have been applied not only to neutral COFs, but also to COFs containing charged moieties and counterions, which interestingly affect final structure and properties

5.   3D covalent organic frameworks

As the examples reviewed have shown, 2D COFs are most common ones. Although 3D COFs possess promising properties derived from the linkages extended in the three dimensions of the space, such as high porosity and low density, the limited choice of tetrahedral building blocks and other related synthetic difficulties have hampered their development,[75] and only a relatively low number of examples have been reported to date. Moreover, when focused on 3D COFs produced under microwave irradiation, the number of publications is drastically reduced.

In general, 3D COFs contain a tetrahedral building block in the knot, most typically a sp3-hybrized carbon or silicon element. Actually, the first example of this kind of materials can be found in the synthesis of COF-102 (shown in Figure 10), COF-103, COF-105, and COF-108.[134] All these materials are 3D boronate ester or boroxine-linked COFs with carbon nitride or boracite topology formed from the self-condensation of tetra(4-dihydroxyborylphenyl)methane (TBPM) and its silane analogue (TBPS), or by the co-condensation with triangular 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP). In particular, COF-102 was the first 3D COF synthesized in a microwave oven.[81] This was accomplished by irradiating TBPM at

100 °C for 20 min, a time considerably shorter than that reported under conventional solvothermal method, which took 4 days at 85 °C. A large BET surface area of 2926 m^2 g^{-1} was obtained, a little below the value of 3472 m^2 g^{-1} exhibited by the conventionally prepared material. In any case, this article demonstrated how microwaves could be successfully applied in the synthesis of both 2D and 3D COFs.

Despite these outstanding results, no other 3D COFs were prepared in a microwave oven until 7 years later, when a tetraphenylmethane served as the central sp3 knot. The Cu-catalyzed homo-coupling of tetrakis(4-bromo-3-nitrophenyl)methane (TBNPM) produced a porous aromatic framework (NO2-PAF-1).[135] Once again, the main advantage of the microwave irradiation method was that the solid was obtained much faster (30 min) than under traditional synthesis (48 h at 175 °C). The solid was formed by a wide range of micropores and mesopores, from 1 up to 40 nm. Although the BET specific surface area was relatively low (610 cm^2 g^{-1}), the strong interaction between nitro groups and CO2 molecules made it a good candidate for the selective removal and storage of CO2.

More 3D porous aromatic frameworks (PAFs) were reported in the same year, but this time for catalysis applications. Three different PAFs were synthesized,[136] based on the same chemical reactions but with a different central unit: a sp3 carbon atom (PAFc), an adamantine (PAFad), or a spirobisfluorene (PAFsbf). All them were prepared by the C-C coupling between the corresponding aromatic tetra-iodide [tetrakis(4-iodophenyl) methane (TIPM), 1,3,5,7-tetrakis(4-iodophenyl)adamantane (TIPA), or 2,2',7,7'-tetraiodo-9,9'-spirobisfluorene (TISBF)] with 1,4-benzenediboronic acid (BDBA) under MW heating at 145 °C for 10 or 5 min. Once prepared, the mesoporous solids produced were post-functionalized in several steps and used as supports for N-

heterocyclic carbine complexes with Ir and Ru. Their catalytic activity was applied to the catalytic transfer hydrogenation of ketones and N-alkylation of amines with alcohols. Later on, the same research group used microwave synthesis to prepare new PAFs containing chiral units, able to be used in asymmetric catalysis synthesis.[137] Monterde et al.[137] prepared different adamantil-BINOL based chiral porous aromatic polymers (Ad-BINOL-PAFs) starting from enantiomerically pure (R)-BINOL [(R)-2,2'-diethoxy-6,6'-adamantyl-BINOL]. This was first brominated in 4-positions, giving the DBDEA monomer, and further subjected to the microwave-assisted Suzuki coupling with 1,3,5-triphenylbenzene-4',4'',4'''-triboronic acid (TBAPB) to provide the ethoxy-protected PAF in only 15^^min. After deprotection with BBr3, Ad-BINOL-OH-PAF was afforded. With a BET surface area of 365 m^2 g^{-1}, this PAF contains chiral groups that were further modified to obtain efficient chiral catalyst in different organic reactions. Reaction with an excess of Ti(OiPr)4 provided an efficient catalytic system for the addition of diethylzinc to benzaldehyde, in which (R)-1-phenylpropan-1-ol was synthesized with an enantiomeric excess of 88 %, superior to other cross-linked polymers based on the 1,10-binaphthyl building block. Other BINOL phosphoric acid derivatives and rhodium-based catalysts were prepared and applied to some organic reactions, producing good yields, enantioselectivity, and diastereoselectivity. Moreover, these heterogeneous catalysts can be easily recovered by centrifugation and reused for several cycles without loss of conversion efficiency.

Similarly to COFs and PAFs, and based in rigid aromatic moieties, an amorphous porous organic polymer (POP), named as 1E, was synthesized under microwave irradiation of a mixture of 1,3,5-trihydroxyphenol (THB) and 4,4'-biphenyldicarboxaldehyde (BPDC).[138] The resulting solid was obtained after 2 h at 220 °C, a time notably

shorter than that typically required for conventional solvothermal reactions (1—3 days). As a result, strong C-C covalent bonds were formed. These created a stable framework, which was retained after a post-synthetic modification in which sulfonic acid groups were introduced into the structure. Sulfonic groups were mainly incorporated into the biphenyl units of the framework, reducing the porosity of the POP but hugely improving its conductivity. The increased conductivity (1.59×10^{-1} S cm^{-1}), even slightly superior to that of the well know Nafion, was successfully applied to proton exchange membrane fuel cells, a promising technology that might transform the future of transportation.

Finally, apart from those based in rigid aromatic rings, 3D COFs containing flexible building units have also been synthesized with the aid of microwaves. The reaction of γ-cyclodextrin (γ-CD) with trimethyl borate (BO) at 120 °C for 4 h led to the formation of a periodic 3D extended network with tetrahedral tetrakis(spiroborate) units (CD-COF).[75] These are anionic and require counterions in order to balance their negative charges. By selecting the most suitable counterions, the interactions and some characteristics of the solid could be modulated. In this way, lithium, dimethylamine, or piperazine were selected as counterions. In all cases highly crystalline isostructural COFs, were obtained; thus, the cation did not affect the topology of the backbone. However, the porosity and the interactions with guest species were affected to some extent. Porous properties were predominantly due to spiroborate linkages and counterions modulated it, whereas γ-cyclodextrin showed no intrinsic porosity despite its inner cavity. All three COFs were studied for the same applications, but the COF with Li showed the highest uptake and selectivity for CO_2 capture and a good behavior

to be applied as Li-ion solid-state conductor in batteries, with a Li-ion conductivity of up to 2.7 mS cm^{-1} at 30 °C.

6.   Summary and expectations

Covalent organic frameworks (COFs) are relatively recent materials that have emerged in the last decades. Their great relevance is driven by the interesting opportunities derived from their chemical characteristics, structure, and properties. They combine the properties of mesoporous materials, widely studied in other materials such as mesoporous silicas or metal-organic frameworks (MOFs), along with the characteristics of two-dimensional materials, as in many cases COFs present laminar structures.

Some of the benefits of using microwaves as source of energy in COFs are

- faster reactions

- higher yield

- improved porosity

- higher crystallinity

- higher reproducibility

- more homogeneous materials

- the possibility to obtain different materials than those we can find by conventional methods

We have summarized the reported examples of COF materials prepared using microwaves as source of energy. As can be seen above, this strategy of synthesis has been applied in some of the most representative COFs, such as boronate ester-, imine-, and triazine-containing COFs. It suggests that it could be widely applied as a general strategy for the synthesis of this kind of nanomaterials.

Probably the main advantage of applying microwaves in the synthesis of COFs is a great reduction of the synthesis times. COFs are crystalline materials that require a long synthesis time at high temperatures, since to reach the structure it is necessary to break and form covalent bonds. Many of the materials included in this article require synthesis times ranging from days to a week or even more. This makes synthesis and optimization processes time consuming, limiting their practical application. In contrast, microwaves allow these syntheses to be carried out in a matter of minutes to hours in many cases, facilitating both laboratory research and practical applications.

In addition to the main advantage, related to the reduction in time, microwaves are particularly interesting for the preparation of some materials such as nanomagnetite containing COFs,[110,119] COFs loaded with metallic nanoparticles,[112] or carbonaceous materials that maintain partially the COF structure.[121] Also, some materials can be obtained under MAS (Microwave Assisted Synthesis) conditions only. For example, COF 8-9-10[101] or LZU-1[103] cannot be obtained in their crystalline form under conventional heating. The authors hypothesize that growth is driven by the increasing conductivity of the developing extended π system resulting in increased microwave absorption, thus favoring the activation of larger grains for polymer growth over additional nucleation. This could be an example of a "microwave effect" mentioned in section 3. Neither COGF (Covalent Organic Gel Framework) is obtained crystalline by the Zincke reaction in absence of microwaves.[129]

Regarding the applications, in some cases MAS materials offer excellent properties. For example TpPa-1 has a 21.8 wt % CO_2 uptake under ambient conditions, the highest among the COFs under the same conditions at the time, even though other materials have larger surface areas.[48] Also, SJTU-COF offers high CO_2 loading capacities (171

m^2g^{-1}) comparable to the most active materials,[100] and the values for COP-4 are better for the MAS material.[124] H2 adsorption by CTF-1 was determined to be as high as 1.78 wt % at low pressure, the highest reported value for a COF,[106] and PV-COF offers one of the fastest absorption rates of bromate in water and a loading capacity of a 20 % (w/w).[130] Studies of the peroxidase activity of CTF-1 place this material in the range of Horseradish Peroxidase as one of the best peroxidase mimetics.[107] Furthermore, this kind of materials can be applied for proton reduction and water oxidation with an activity 50 and 20 times higher than the reference polymer.[114] CD-COFLi shows one of the highest conductivities for all reported crystalline porous materials and conventional polymer electrolytes with/without fillers. The conductivity even rivals those of gel polymer electrolytes with the advantage of a well-defined structure and better thermal stability.[75] NENP-1 presents a maximum specific capacitance that is very high for a nonmetallic system. Tests with an asymmetric supercapacitor device has shown an energy density higher than the best reported supercapacitors and also close to the commercial batteries.[115] Among the 3D materials, a sulfonated 1E derivative offers high proton conductivity (0.159 S cm^{-1}) exceeding any other porous organic polymer reported to date. Finally, microwaves can improve the compatibility with other materials. TpPa-2 was blended with polysulfone material for the preparation of water purification membranes. In comparison with the COF prepared by mechanochemical approaches, the membrane loaded with the material prepared with microwaves showed smoother membrane surface, higher porosity, higher water transport property, and better separation performance.[97] COF 9 was also supported on a porous anodic aluminum oxide for water filtering applications and compared with graphene oxide-containing membranes. The COF-9-

containing membrane offered higher filtration rates and stability due to its more rigid structure.[101] In other applications such as catalysis[116] or sensing of nitroaromatic explosives,[118] interesting results are also reported.

For a wide application of microwaves it is necessary to improve the control capacity over the synthesis systems. The examples included, particularly those using home microwaves, may be using too high powers or too short times with the corresponding impact on the quality of the materials obtained. In this sense, the microwave oven is a key aspect in this class of synthesis. Using specially designed equipment for chemical synthesis is very important if reproducible synthesis procedures over time and between laboratories are intended to be obtained. Another aspect of special relevance is having sufficiently detailed synthesis procedures. In microwave synthesis, it is quite common that the procedures do not include all the necessary information to be able to carry them out. Apart from temperature and power, we can cite as important examples the characteristics of the device, the volumes of the reactors, the volume of dissolution, whether there is stirring or not, how the cooling of the reactor is carried out, and others. All these aspects are crucial in the synthesis of the materials.

The need for expensive specific equipment to carry out the synthesis together with an insufficient description of the procedures are likely the two most important factors why microwaves are still a minority option. In recent years, microwave technology based on solid-state generators has emerged and offers interesting opportunities when developing low-cost, long-lasting reactors that allow precise power control and that, due to its digital characteristics, can be programmed to obtain greater precision in the synthesis. We believe that this technology is going to be crucial in the application of microwaves in laboratories and its extension to many other fields. We

will start to see such benefits as these kinds of generators are included in the commercial reactors and their possibilities are available to materials scientists.

Another fundamental aspect that needs to be addressed is a greater understanding of the interaction of electromagnetic radiation with the reaction mixture. It is to be expected that the choice of the solvent and its dielectric properties is of the greatest relevance. Also, the properties of the reaction mixture will vary according to the hydrolysis and condensation processes necessary to obtain the crystalline structure of COFs. The analysis and modeling of such behavior require basic research and the interaction of multidisciplinary groups specialized in the chemical, materials, and physics areas.

Apart from the advantages mentioned above, in particular the testing of faster reaction conditions, and despite the youth of the COF research field, microwaves may offer other opportunities. The future perspectives of microwave application in the synthesis of COFs are aligned with the discipline's own trends. Among them we can mention the development of stable materials with a relatively large size and custom design. We can already find some examples of double-pore systems and others in which the pore size varies with the counterion or the presence of functional groups. Another trend is the incorporation of COFs as components of composites with advanced properties or as part of membranes. Microwaves can also offer interesting opportunities for monomer preparation or subsequent functionalization, in line with their extensive use for decades in organic synthesis.

Currently, the application of microwaves for the synthesis of 3D COFs is almost testimonial. There are very few examples, although the prepared compounds have very good characteristics. They are very crystalline materials with well-defined

structures, high porosity, and low density. However, the limited availability of monomers and the difficulties of synthesis have limited their development. Microwaves, thanks to their accelerated material preparation capacity, as well as the possibility of applying them in the preparation of monomers, can be an interesting alternative.

Lastly, a higher synthesis speed and lower energy consumption may also be relevant in industrial scale-up and application processes, both bottlenecks when transferring advances in nanomaterials from the laboratory to a real plant application. In these cases, it is essential to have reproducible syntheses with the lowest possible energy and reagent costs. Microwaves, by reducing the reaction time, allow a substantial reduction in the time in which the entire system needs to be kept at a high temperature and therefore in the total energy cost.

In conclusion, microwaves are a very interesting tool for preparing COFs, which we hope will gain ground in the coming years. We hope that this article will be useful for all those groups that work in the field of COF synthesis to illustrate and to identify new synthesis pathways.

Acknowledgments

Conflict of Interest

The authors declare no conflict of interest

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Figure captions

Figure 1: Monomers used in COFs reviewed in the manuscript with their acronyms.

Figure 2: Typical linkage bonds in COF materials

Figure 3: General topologies of COFs

Figure 4: Schematic diagram of (a) dipolar polarization and (b) ionic conduction mechanisms under microwave irradiation.

Figure 5. Scheme of multimode (a), monomode (b), and travelling-wave (c) microwave reactors.

Figure 6: Structure of the boroester containing COFs reviewed in the manuscript with their acronyms

Figure 7: Structure of the imines-, enamines-, and azines-based COF reviewed in the manuscript with their acronyms

Figure 8: Structure of the triazine-based COFs reviewed in the manuscript with their acronyms.
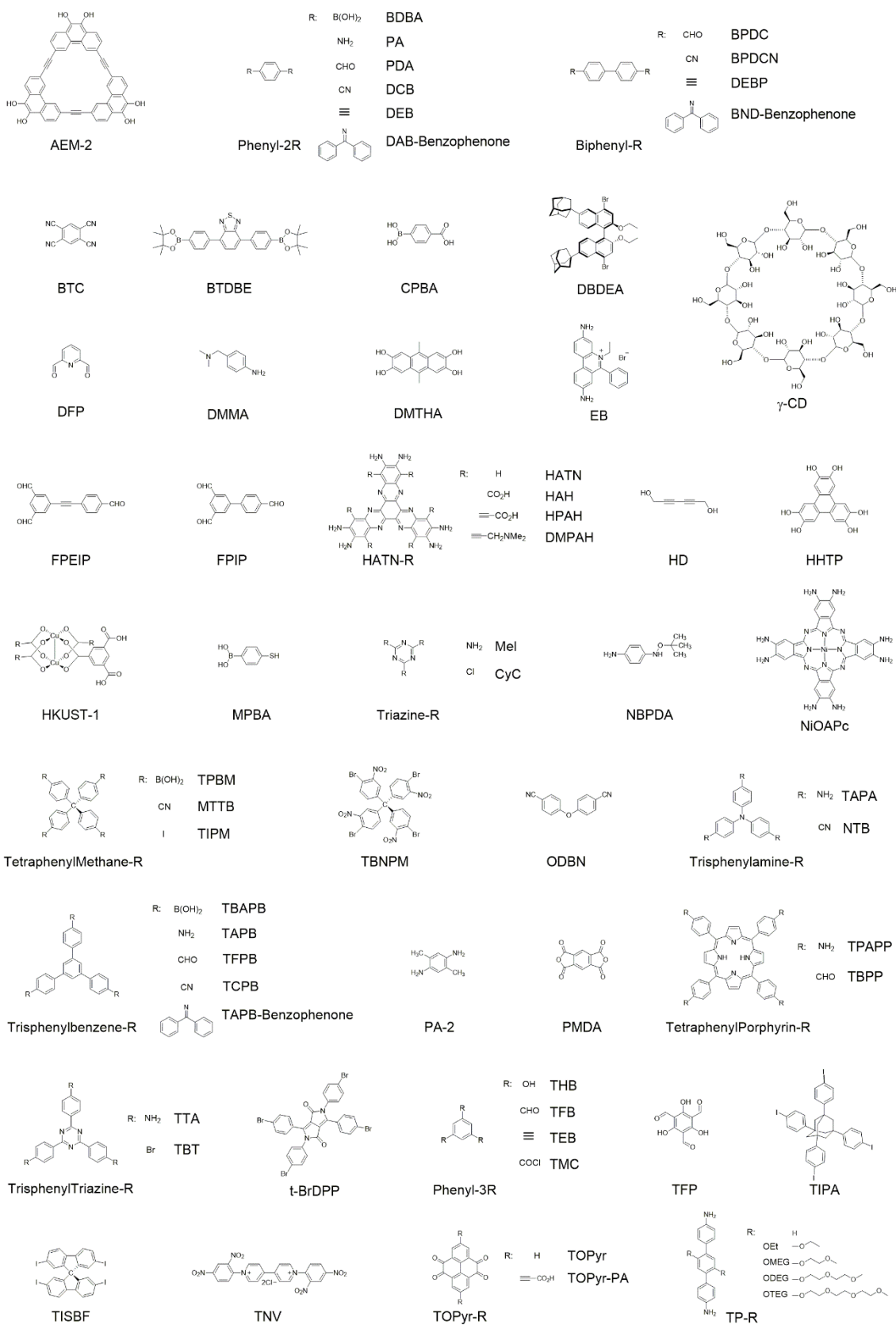
Figure 9: Structure of other COFs reviewed in the manuscript with their acronyms.

Figure 10: Structure of 3D COFs reviewed in the manuscript with their acronyms.

Table captions

Table 1: COFs summarized in the review with their main synthesis parameters and applications.
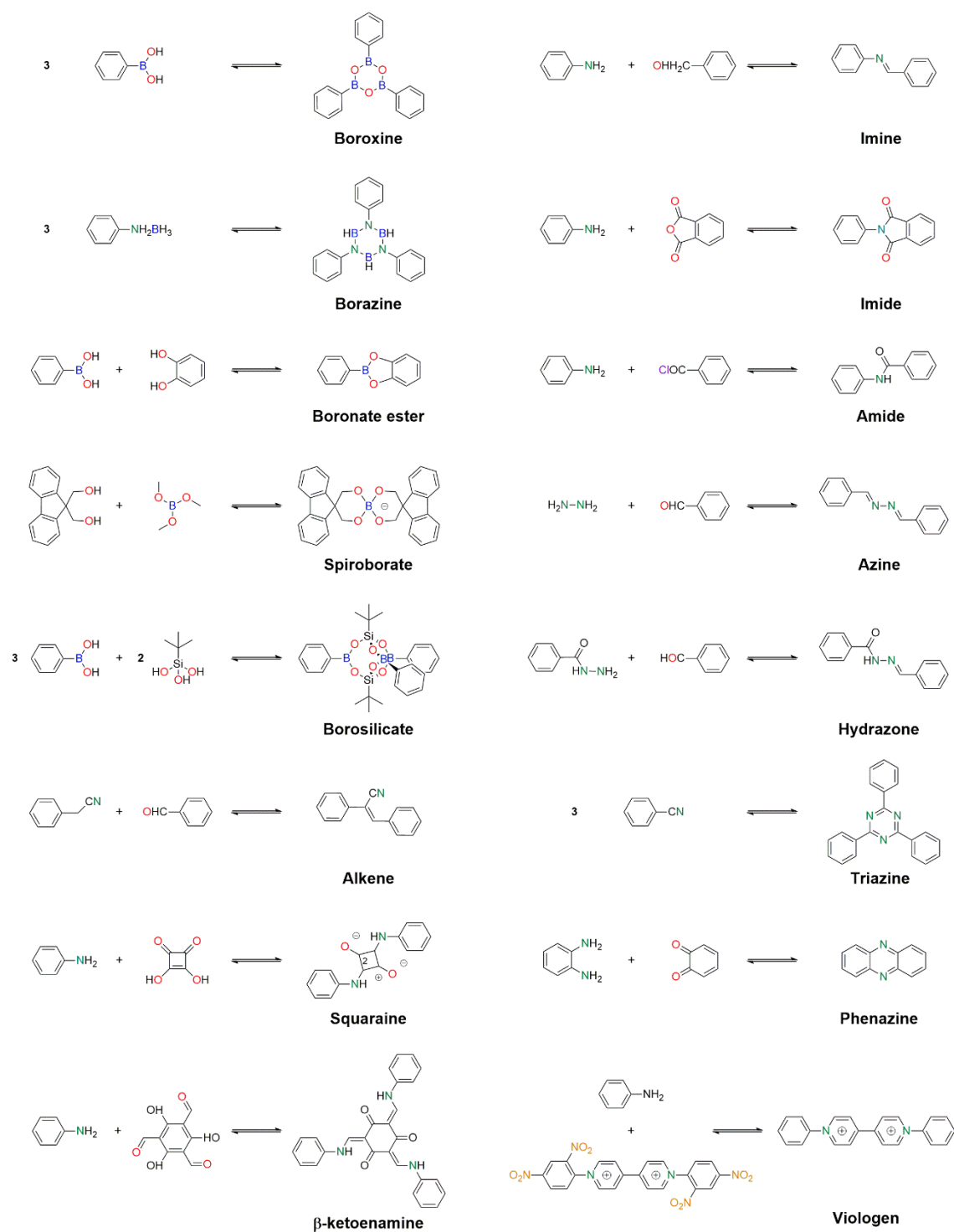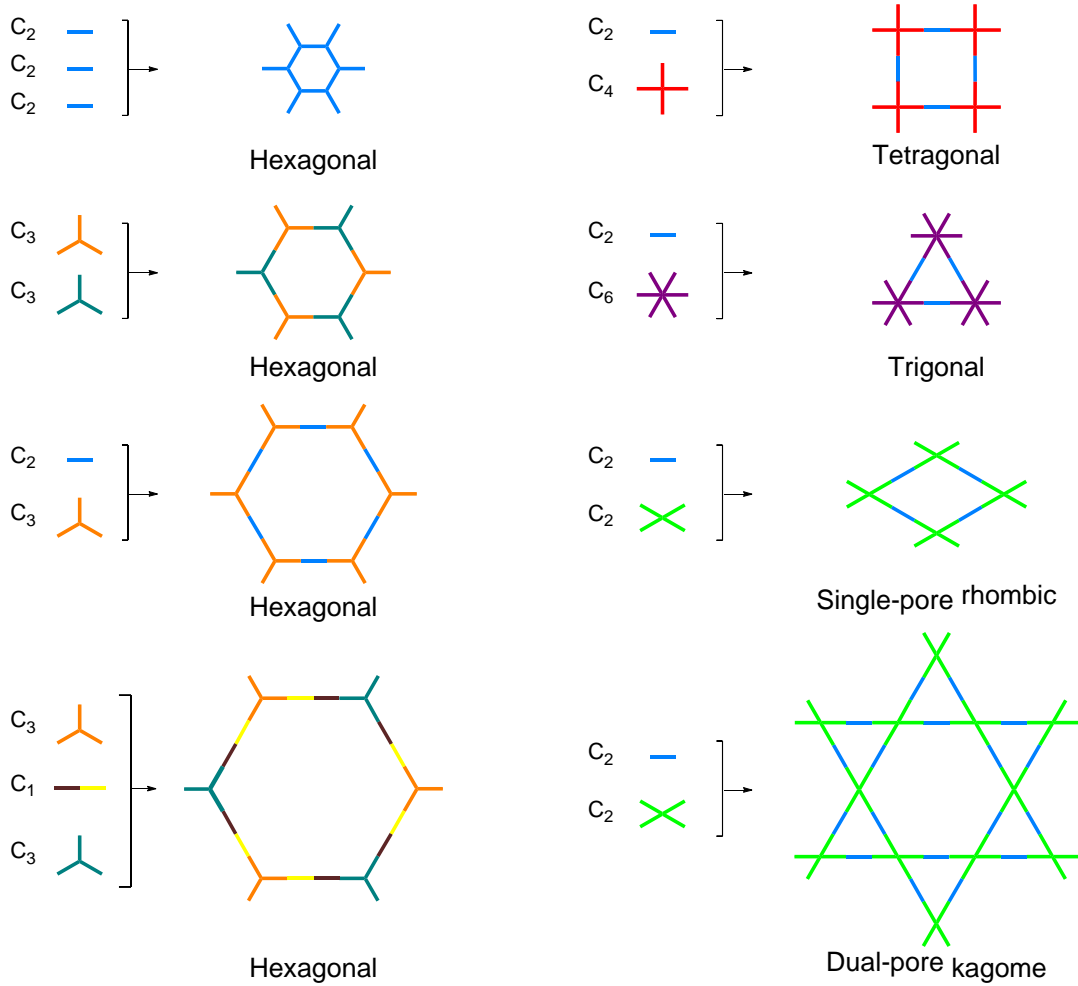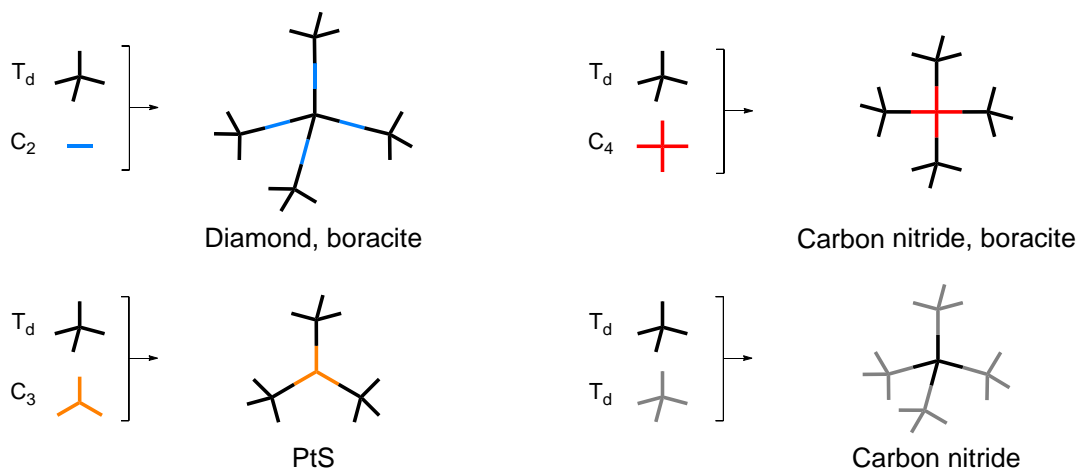
Figure 1

Figure 2

Boroxine

Borazine

Boronate ester

Spiroborate

Borosilicate

Alkene

Squaraine

β-ketoenamine

Imine

Imide

Amide

Azine

Hydrazone

Triazine

Phenazine

Viologen

Figure 3

2D Topologies

Hexagonal

Tetragonal

Hexagonal

Trigonal

Hexagonal

Single-pore rhombic

Hexagonal

Dual-pore kagome

3D Topologies

Diamond, boracite

Carbon nitride, boracite

PtS

Carbon nitride

Figure 4

	No Electric Field	Electric field	
Polar Molecules			Dipolar polarization
Ions			Ionic conduction

Figure 5

Figure 6

COF-5   BTD-HHTP   AEM

Figure 7

TpPa

TfpTP-R

TfpTP-H   R=H
TfpTP-OEt   R=OEt
TfpTP-OMEG   R=OMEG
TfpTP-ODEG   R=ODEG
TfpTP-OTEG   R=OTEG

SJTU-COF-Br

COFs 8-10

LZU-1

Por-COF

TFPB-PDA

BND-TFB

TAPB-PDA

DAB-TFP

BND-TFP

HP-COF-1

HP-COF-2

69

igure 8

CTF-1

CTF-2

CTF-3

CTF-4

CTF-5

CTF-6

NENP-1

SNW-1

CTF-PI

TTA-DPF-COF

COP-4

CNO

Figure 9

COF-SCU-1 CCOF-SCU-1   PI-COF   TCD

N1 N2 N3 N4

COGF   PV-COF

COF-DC-8   COF-BTC-Fe   COF-BTC-Mn

Figure 10

COF-102

NO$_2$-PAF-1

PAFad

PAFc

PAFsbf

Ad-Binol-OH-PAF

1E

CD-COF

Ge-COF-1

Table 1

COF	Knot/Vertice	Linker/Edge	Microw. oven	Power (W)	Time	Pressure	T(°C)	Solvent	Pore size (nm)	S_{BET} (m² g⁻¹)	Application	Ref.
COF-5	HHTP	BDBA	CEM-S	200	20 min	n.a.	100	Dx/Ms	n.a.	2019	n.a.	[81]
COF-5	HHTP	BDBA	CEM-S	200	20 min	n.a.	100	Dx/Ms	n.a.	2335	n.a.	[83]
COF-5	HHTP	BDBA	CEM-D	n.a.	30 min.	n.a.	100	Dx/Ms	n.a.	n.a.	n.a.	[84]
COF-5	HHTP	BDBA	Biotage	n.a.	3 h	n.a.	100	Dx/Ms	n.a.	n.a.	Electrodes	[85]
COF-5 (α-Al2O3)	HHTP	BDBA	Milestone	300	1 h	n.a.	100	Dx/Ms	n.a.	n.a.	n.a.	[86]
COF-5	HHTP	BDBA MPBA CPBA	n.a.	300	60 min	n.a.	100	Dx/Ms	2.7	1200-2100	n.a.	[87]
BTD-COF	HHTP	BTDBE	n.a.	n.a.	30 min	n.a.	160	Dx/Ms	4.1	1000	n.a.	[88]
AEM-COF-2	AEM-2	BDBA	n.a.	200	40 min	n.a.	120	DMAC/DCB	3.8	1487	n.a.	[89]
TpPa-1	TFP	PA	CEM-S	n.a.	1 h	n.a.	100	Dx/Ms/HAc	1.3	725	CO₂ capture	[48]
TpPa-2	TFP	PA-2	XH-MC-1	500	1 h	n.a.	100	Dx/Ms/HAc	1.4	535	Additive in membranes for water purification	[98]
TfpTP-H	TFP	TP-H	CEM-D	250	10 min	3.4 atm	175	DCE/Dx/HAc	n.a.	n.a.	Molecular transport	[100]
TfpTP-OEt	TFP	TP-OEt	CEM-D	250	15 min	3.4 atm	175	DCE/Dx/HAc	n.a.	n.a.	Molecular transport	[100]
TfpTP-OMEG	TFP	TP-OMEG	CEM-D	250	20 min	3.4 atm	175	Prop/DCB/HAc	n.a.	n.a.	Molecular transport	[100]
TfpTP-ODEG	TFP	TP-ODEG	CEM-D	250	20 min	3.4 atm	175	Prop/DCB/HAc	n.a.	n.a.	Molecular transport	[100]
Tfp-TP-OTEG	TFP	TP-OTEG	CEM-D	250	20 min	3.4 atm	175	Prop/DCB/HAc	n.a.	n.a.	Molecular transport	[100]
SJTU-COF-Br	TFP	EB	CEM-S	n.a.	3 h	n.a.	100	Dx/Ms/HAc	1.6	944	CO₂ capture	[101]

COF 8-9-10	HATN-R	TOPyr-R	AP-Mon	n.a.	2 h	n.a.	200	NMP/HAc	1.9-2.8	n.a.	Additive in membranes for water purification	[102]
HAH-TOPyr	HAH	TOPyr	AP-Mon	n.a.	2 h	n.a.	200	NMP/HAc	2.8	n.a.	Additive in membranes for protein separation	[103]
LZU-1	TFB	NBPDA	n.a.	n.a.	30 min	n.a.	120	Et/TFMS	2.2	729	n.a.	[104]
TFPB-PDA	TFPB	NBPDA	n.a.	n.a.	30 min	n.a.	120	Et/TFMS	n.a.	n.a.	n.a.	[104]
Por-COF	TBPP	NBPDA	n.a.	n.a.	30 min	n.a.	120	Et/TFMS	n.a.	n.a.	n.a.	[104]
BND-TFB	TFB	BND-BPh	CEM-D	n.a.	5 h	n.a.	120	Dx/Ms/HAc	2.4	2100	n.a.	[93]
TAPB-PDA	PDA	TAPB-BPh	CEM-D	n.a.	5h	n.a.	120	Dx/Ms/HAc	3.3	1310	n.a.	[93]
DAB-TFP	TFP	DAB-BPh	CEM-D	n.a.	5h	n.a.	120	Dx/Ms/HAc	1.6	1470	n.a.	[93]
BND-TFP	TFP	BND-BPh	CEM-D	n.a.	5 h	n.a.	120	Dx/Ms/HAc	1.8	694	n.a.	[93]
HP-COF 1	FPIP	Hydrazine	n.a.	n.a.	6 h	n.a.	170	Dx/DCB/HAc	1.1 and 1.9	1197	n.a.	[105]
HP-COF 2	FPEIP	Hydrazine	n.a.	n.a.	6 h	n.a.	170	Dx/DCB/HAc	1.3 and 1.9	804	n.a.	[105]
CTF-1	DCB		Glanz-DF	120	1.5 h	n.a.	n.a.	ZnCl$_2$	2-30	1049	H$_2$ adsorption	[107]
CTF-1	DCB		Glanz-G5	n.a.	30 min	n.a.	n.a.	ZnCl$_2$	n.a.	n.a.	Sensor for biothiols	[108]
CTF-1	DCB		n.a.	n.a.	n.a.	n.a.	n.a.	ZnCl$_2$	n.a.	n.a.	Sensor for radical-scavengers	[109]
CTF-1	DCB		Glanz-B8	700	6 min	n.a.	n.a.	ZnCl$_2$	n.a.	1188	Sensor of Cu	[110]
CTF-1 (Fe$_2$O$_3$)	DCB		Glanz-DF	350	1 h	n.a.	n.a.	ZnCl$_2$	2-140	Aprox. 1100	Dye adsorption	[111]
CTF-1 (Fe$_2$O$_3$)	DCB		Glanz-DF	350	1 h	n.a.	n.a.	ZnCl$_2$	n.a.	n.a.	SPME: Phenols adsorption	[112]
CTF-1-Rh	DCB		CEM-D	70	10 min	n.a.	260	IL	n.a.	n.a.	Catalysis: a) Conversion of benzene to cyclohexane; b) H$_2$ evolution reaction	[113]
CTF-COF-1-6	DCB, BPDCN, ODBN, TCPB, NTB,		CEM-D	300	30	< 4 bar	110	TFMS	1.5-3.0	464-1152	Optoelectronic devices or supercapacitors	[114]

CTF-1	DCB		CEM-D	100	30 sec	n.a.	n.a.	TFMS	n.a.	n.a.	Water splitting	[115]
NENP-1	Mel + CNCl		n.a.	400	30 min	n.a.	140	DMSO	1.6 and 3.8	838	Supercapacitator	[116]
NENP-1	Mel + CNCl		n.a.	400	30 min	n.a.	140	DMSO	1.3 and 4.1-6.9	850	Catalysis (Knoevenagel reaction)	[117]
SNW-1	Mel	PDA	Glanz-D3	280	6 h	1 atm	Reflux	DMSO	1 and 40	476	Sensor of explosives	[119]
SNW-1 (Fe$_3$O$_4$)	Mel	PDA	Glanz-D3	280	4 h	n.a.	n.a.	DMSO	n.a.	480	Hg(II) adsorption	[120]
SNW-1	Mel	PDA	MAS-I	n.a.	24 h	n.a.	90	DMSO	1.4	231	Adsorption of aromatic hydrocarbons (PAHs) and volatile fatty acids (VFAs)	[121]
CTF-PI	Mel	PMDA	n.a.	600	3 min	n.a.	n.a.	ZnCl$_2$	n.a.	n.a.	Sensor of Cr	[123]
TTA-DPF	TTA	DFP	n.a.	n.a.	30 min	n.a.	110	Dx	1.7	900	Bioimaging	[124]
COP-4	TBT	n.a.	AP-Syn	n.a.	4 h	n.a.	105	DMF	n.a.	1461	CO$_2$ capture	[125]
CNO	HKUST-1	Urea	n.a.	700	6 min	n.a.	n.a.	H$_2$O	n.a.	n.a.	Polymer additive	[126]
CCOF-SCU-1	TMC	PA	Dom	800	3 min	n.a.	n.a.	None	0.4	507	U(VI) adsorption	[122]
CCOF-SCU-2	Mel	PDA	Dom	800	3 min	1 atm	-	None	0.6	244	U(VI) Adsorption	[122]
PI-COF	TAPA	PMDA	AP-Mon	300	2 h	n.a.	200	Ms/NMP/IQ	2.9	1003	SO$_2$ capture	[127]
TCD	TMC	HD	Dom	600	12 min	n.a.	-	Ms/EA	1.1	316	U(VI) adsorption	[128]
N1	t-BrDPP		Biotage	n.a.	1 h	n.a.	100	DMF	6.5	216	Detection of NO$_x$	[129]
N2	t-BrDPP	DEB	Biotage	n.a.	1 h	n.a.	100	DMF	3.5	477	Detection of NO$_x$	[129]
N3	t-BrDPP	DEBP	Biotage	n.a.	1 h	n.a.	100	DMF	8.7	384	Detection of NO$_x$	[129]
N4	t-BrDPP	TEB	Biotage	n.a.	1 h	n.a.	100	DMF	5.0	290	Detection of NO$_x$	[129]
COGF	TAPB	TNV	n.a.	n.a.	2 h	n.a.	100	Et/ H$_2$O	n.a.	n.a.	I$_2$ adsorption	[130]
PV-COF	TPAPP	TNV	n.a.	n.a.	2	n.a.	90	Et/ H$_2$O	2.3	38	Bromate adsorption	[131]
COF-DC8	NIOAPc	TOPyr	CEM-D	n.a.	10 h	n.a.	240	TCB/DMAC/H$_2$SO$_2$	n.a.	n.a.	n.a.	[132]
COF-		BTC	CEM-D	n.a.	10 min	n.a.	180	EtGly	n.a.	n.a.	Flow batteries	[74]

BTC-Fe

COF-BTC-Mn		BTC	CEM-D	n.a.	20 min	n.a.	150	EtGly	n.a.	n.a.	Flexible electrodes in supercapacitors	[133]
COF-102	TPMB		CEM-S	200	20 min	n.a.	100	n.a.	n.a.	2926	n.a.	[81]
NO$_2$-PAF-1	TBNPM		n.a.	150	30 min	n.a.	n.a.	DMF	1 – 40	610	CO_2 capture	[136]
PAFc	TIPM	BDBA	CEM-D	75	10 min	12 bar	145	DMF/ H$_2$O	8.5	393	Catalyst: (a) N-alkylation of amines with alcohols, transfer hydrogenation of ketones	[137]
PAFad	TIPA	BDBA	CEM-D	75	10 min	12 bar	145	DMF/ H$_2$O	5.5	515	Catalyst: (a) N-alkylation of amines with alcohols, (b) transfer hydrogenation of ketones	[137]
PAFsbf	TISBF	BDBA	CEM-D	75	5 min	10 bar	145	DMF/ H$_2$O	3.0	580	Catalyst: (a) N-alkylation of amines with alcohols, (b) transfer hydrogenation of ketones	[137]
Ad-BINOL-OH-PAF	TBAPB	DBDEA	CEM-D	75	15 min	n.a.	145	THF	3.0	366	Catalyst in asymmetric reactions	[138]
1E	THB	BPDC	n.a.	n.a.	2 h	n.a.	220	Dx	0.7 and 1-2	604	Fuel Cells	[139]
CD-COF-Li	BO	γ-CD	n.a.	n.a.	4 h	n.a.	120	DMF/Ms	0.6	760	Li ion solid-state conductor and CO_2 capture	[75]
CD-COF-DMA	BO	γ-CD	n.a.	n.a.	4 h	n.a.	120	DMF/Ms	n.a.	934	CO_2 capture	[75]
CD-COF-PPZ	BO	γ-CD	n.a.	n.a.	4 h	n.a.	120	DMF/Ms	n.a.	494	CO_2 capture	[75]
Ge-COF-1	Ge	DMTHA	n.a.	n.a.	6 h	n.a.	180	Me	1.5	808	CO_2 adsorption and batteries	[134]