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Porous Materials

Functional Materials: From Hard to Soft Porous Frameworks

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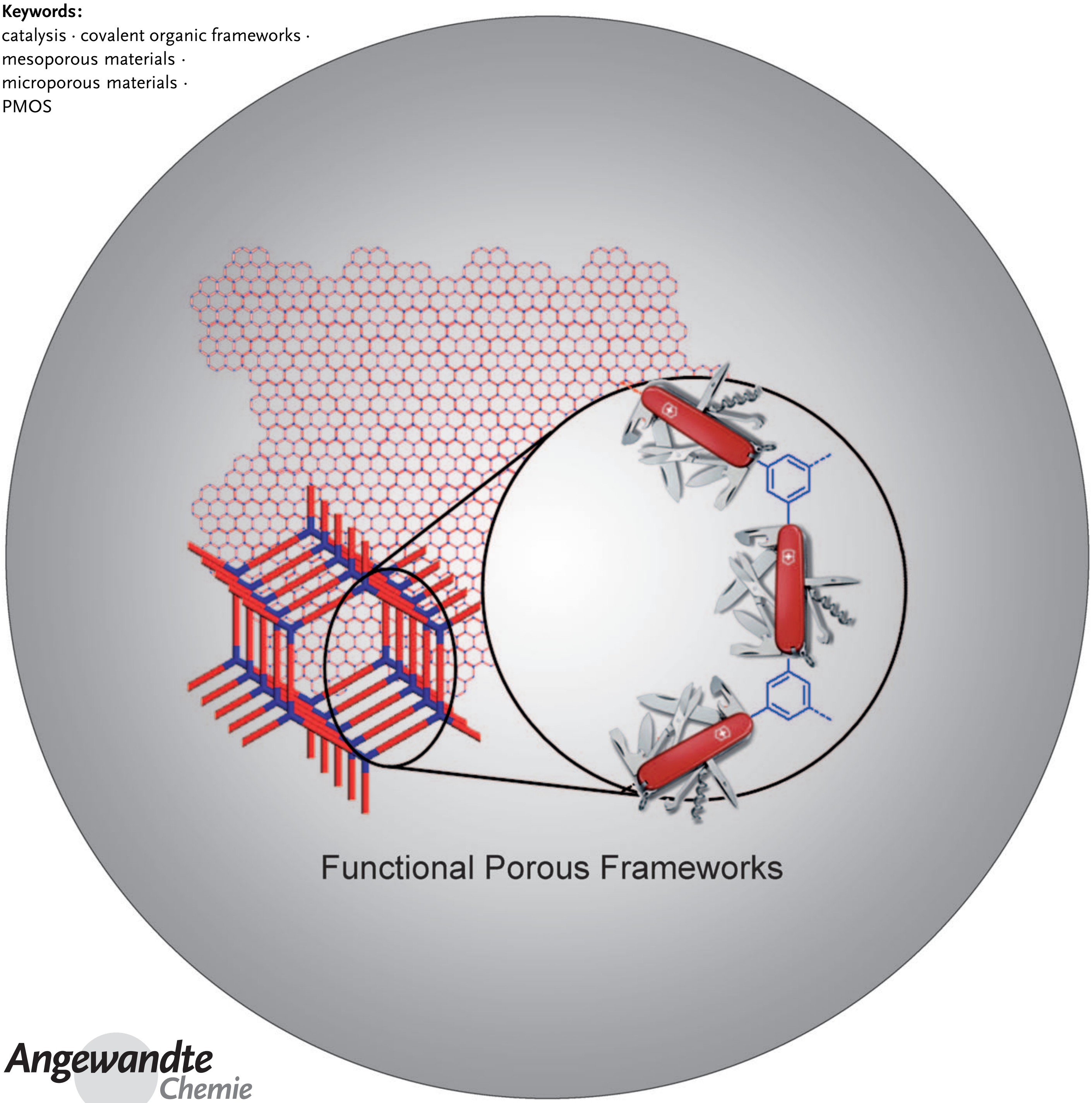

This Review aims to give an overview of recent research in the area of porous, organic–inorganic and purely organic, functional materials. Possibilities for introducing organic groups that exhibit chemical and/or physical functions into porous materials will be described, with a focus on the incorporation of such functional groups as a supporting part of the pore walls. The number of organic groups in the network can be increased such that porous, purely organic materials are obtained.

From the Contents

1. Introduction

These days, the term "functional" is often used in combination with newly prepared materials to indicate their potential for certain applications—or simply to attach some more importance to them. Indeed, the definition "functional material" has already been applied to a large number of different compounds, ranging from liquid crystals,[1] organogels,[2] biomaterials,[3,4] block copolymer nanocomposites,[5,6] and inorganic–organic hybrids[7] to silicas and zeolites,[8] metal oxides[9,10] semiconductors,[11] and metals.[12] The definition is certainly justified for all these materials, as almost every material could somehow be designated as a functional one—actually it is much harder to imagine a material which does not exhibit any kind of function or functionality. A functional material could be defined as being prepared from a "*target-motivated*" approach, that is, all its properties are adjusted and optimized to serve a specific purpose.

To exhibit function, a material has to possess chemical or physical functionality. Examples of the former are acidity/basicity or the ability to coordinate to metals. Typical examples of physical functions are electrical and optical properties. It should, furthermore, be noted that many materials display their function only when they exist or are assembled into a certain structure or morphology. Two examples are liquid crystals and semiconductor nanoparticles ("quantum dots"). The introduction of porosity into a material so as to maximize its accessible surface area is another way to enhance its function. Indeed, useful properties can arise when small pores and thus high surface areas are introduced into a material, which can lead to a number of applications. Porous materials are, for example, used as catalysts or catalyst supports,[13–15] for the sorption, purification, and storage of gases,[16,17] for electrodes,[18,19] as insulating materials for the semiconductor industry (low-k dielectrics),[20] and for optical applications.[21]

The function of porous materials relies on their high surface area and pore volume. Surface area and porosity, however, are not the only requirements for a porous material to fulfil a certain task; indeed, for all of the above-mentioned applications, the material should also possess a certain type of chemical or physical function. For catalysts, this is quite clear: a catalytically active center has to be present in the materials. Materials used for ion exchange, purification, and separation should carry functional groups which bind more strongly to a certain compound than to the others in a mixture or a solution. A porous electrode has to be made out of a conducting material, while for optoelectronic applications semiconducting functionality might be needed. At first sight, a high surface area alone appears sufficient for materials to store large amounts of gases, thus a further specific functionality does not seem to be required. This is, however, only partially true, as can be seen, for example, for the storage of hydrogen, currently one of the most intensively investigated applications of porous materials. Effective hydrogen storage is essential for future sustainable energy carriers.[22] Here, it becomes more and more apparent that the amount of hydrogen that needs to be stored for commercial applications, for example, in automobiles powered by fuel cells, can not be reached by increasing the surface area of a material alone. Therefore, there is also an increasing demand for functionalized porous materials for this application. For example, the incorporation of noble metals or heteroatoms are believed to increase the enthalpy of adsorption of hydrogen to the pore wall,[17,23–25] thus resulting in higher storage capacities. A target-motivated approach toward functional porous materials is therefore also advisable for this application.

To create a porous functional material, in general, one component that exhibits a physical or chemical functionality is combined with another, structured component. One method for the preparation of such composites is the attachment of organic molecules to the surface of porous inorganic materials. In fact, this approach is synthetically relatively simple and allows for exquisite control over the chemical nature of the accessible surface areas. Indeed, a myriad of organic groups have been attached to the pore walls of mainly mesoporous silicas.[26–29] A great number of silica phases modified with organic groups have also been synthesized by co-condensation, that is, in a one-pot synthesis where the respective organosilica is directly condensed with another silica precursor to yield mesoporous inorganic–organic hybrids.[30–32]

In contrast, this Review focuses on materials where the functional organic groups are not only attached to the pore

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wall, but mainly constitute the pore wall. In these materials, the organic compound thus represents a supporting part of the porous framework, thereby maintaining the pore structure and surface area. As the number of organic groups increases, the inorganic fraction in the materials becomes decreased, thereby creating porous frameworks which get lighter and change their mechanical properties from hard to soft.

Several approaches can be envisaged to synthesize such materials: Organosilanes can be prepared from polysilsesquioxane precursors. In these organosilianes the alkoxysilane groups are bridged by organic moities, which can indeed be a supporting part of the pore walls, provided that a small and rigid organic bridging group is used. Periodic mesoporous organosilanes (PMOs) can be produced from these precurors by using suitable structure-directing agents (SDAs), also called templates. Supramolecular aggregates of ionic surfactants or block copolymers are mainly used as the templates. Recently, some research groups even focused on covalent, purely organic, porous networks by using either templating or scaffolding approaches to generate porosity. These approaches indeed promise to greatly increase the number of valuable organic functions per material weight, volume, and surface area (Figure 1).

Differentiating these materials from others where the functionality is grafted on to the pore walls (Figure 1 a) is more than just a sophisticated distinction, since these materials have, because of their particular architecture, some distinct advantages:

1) Since the functional organic group is part of the pore wall, the material consists of large amounts of the desired compound. This approach, therefore, significantly increases the quantity of organic functional groups per material weight, volume, and surface area (Figure 1). Additionally, the homogeneous distribution of the organic group is guaranteed.
2) For the same reason it is ensured that the functional group is accessible to substances entering the pores, without the organic group blocking the pores. This concept can also be used for materials with very small pore diameters.
3) Since the functional group acts as part of the pore wall it must have a stable, rigid structure and is connected by at least two chemical bonds to the framework. Therefore, this group can be assumed to have high thermal and chemical stability. This means, however, that loss of the organic group will result in the structural collapse of the whole porous material.

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These advantages result in such materials offering solutions to different applications problems. For example, the very high number of organic functional groups which can be incorporated into such frameworks creates promising materials for one of the major tasks in the field of catalysis: bridging the gap between homogeneous and heterogeneous catalysis.[33,34] Thus, it can be envisaged that a homogeneous, organic or metal–organic, catalyst could be polymerized into a porous, heterogeneous material, in which the catalytically active center is still fully accessible. As the pore walls of this material would mainly consist of the catalyst, such systems would represent an ideal link between homogeneous and heterogeneous catalysts.

This Review will focus on covalent networks; metal–organic frameworks (MOFs) and other coordination or hydrogen-bonded networks will be excluded, even though the pathways used for the introduction of functions into such networks can be quite similar.[35–37] The Review will furthermore deal exclusively with materials with small pores and consequently very high surface areas, namely, micro- and mesoporous materials.

2. Functional PMOs

An important step towards the introduction of larger numbers of functional organic groups into porous materials was achieved by the synthesis of organic–inorganic hybrid materials through condensation reactions of bridged organosilica precursors of the type $(R'O)_3Si\text{-}R\text{-}Si(OR')_3$.[38–41] In these materials the functional organic groups are incorporated into the silica matrix through two covalent bonds and are homogeneously distributed in the pore walls. Such precursors have been used for the preparation of porous aero- and xerogels, which can reach specific surface areas of up to 1880 $m^2 g^{-1}$.[42] Xerogels have been prepared by removal of the solvent after condensation of the precursors by drying in air,[43,44] which can cause shrinkage of the materials by up to 95 %. Aerogels have been prepared by replacing the solvent with supercritical CO_2[45,46] or directly by using supercritical CO_2 as the solvent during the synthesis.[47] The resulting materials exhibit disordered pore systems with a relatively broad distribution of pore sizes. A much higher degree of control over the pore structure and pore diameters of bridged polysilsesquioxanes has been achieved by using appropriate templates during the synthesis, thereby generating periodic mesoporous organosilicas (PMOs).[48–50] Most often ionic surfactants or amphiphilic block copolymers are used as the templates, similar to the methods reported for pure mesoporous silicas.[51,52] As shown for aero- and xerogels, no co-condensation of other precursors, such as tetraethoxysilane (TEOS), is necessary to form porous materials if the bridging R group is sufficiently rigid. Therefore the organic moiety can be regarded as a supporting part of the pore wall. Indeed, calcination of the organic groups at high temperature results

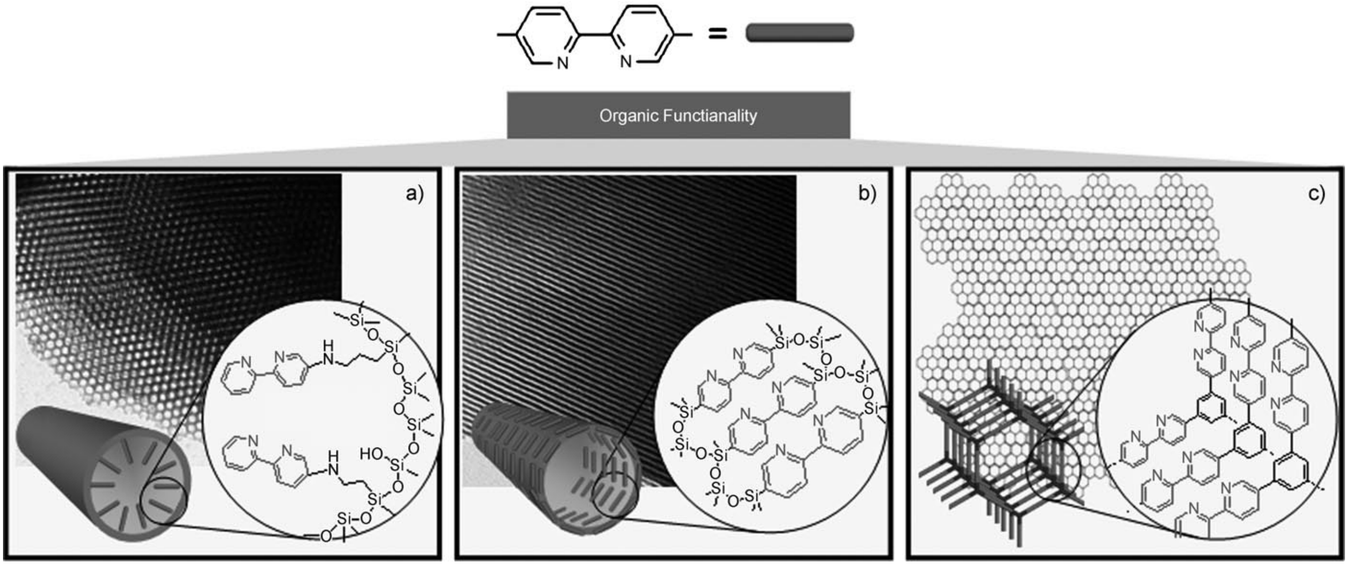


Figure 1. Schematic representation of the incorporation of an organic component (represented by a bipyridine molecule with a high ability to coordinate metals) by either a) grafting onto a mesoporous silica, b) incorporation into the pore wall by preparation of a periodic mesoporous organosilica, or c) by polymerizing it to form a covalent organic framework. The weight ratio of the bipyridine moiety in the materials increases from approximately 10 wt% (for a very high grafting density) (a) to 60 wt% (b) and 86 wt% (c).

in structural collapse of such networks.[53] Numerous organic groups have already been incorporated into PMOs,[54–56] and the resulting materials have been used for several applications, for example, catalysis.[57]

It should, however, be noted that for many of the applications described later, which make use of the functionality of the incorporated organic groups, it is sometimes questionable as to whether the more time- and labor-consuming process of surfactant templating is significantly advantageous for the preparation of porous aero- or xerogels from the same precursor. Indeed, the periodicity of the pores in the PMOs often appears as a side effect, which has more of an aesthetic than a practical benefit.[58] Nevertheless, the applications of porous, bridged, functional organosilicas has mainly concentrated on PMOs.

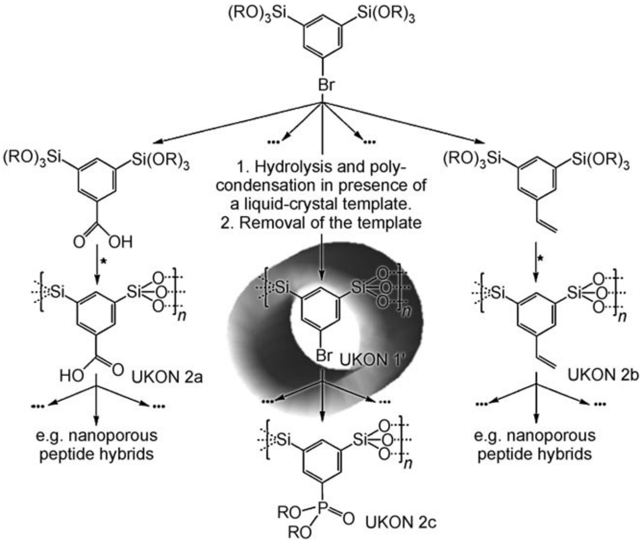
Early PMOs with relatively simple organic groups, such as methyl, ethyl, ethylene, and benzene groups[48–50,59–63] in the pore walls did not have particularly remarkable chemical properties. Still, the resulting materials are more hydrophobic and less brittle than their pure siliceous analogues.[28] Furthermore, the hydrothermal and mechanical stabilities are enhanced, and such materials have been proven to be suitable insulators because of their low dielectric constants.[64,65]

The direct use of precursors containing acidic or basic groups can cause problems as they can influence the hydrolysis and condensation of the alkoxysilane groups. Nevertheless, PMOs with bridging amine groups have been reported.[66,67] In the precursors, the amine is linked to the alkoxysilane by flexible chains (for example, propyl chains). Thus, the organic group can not act as a supporting part of the pore walls, and the precursors have to be diluted with a significant amount of another silica source, most frequently TEOS, to ensure the formation and maintenance of porosity after removal of the template. A greater number of amine groups have been incorporated into the pore walls of PMOs by a postfunctionalization method, namely the amination of phenylene-bridged PMOs with a crystalline pore structure.[68] The amine groups were introduced by nitration and reduction of the resulting nitro groups.[69] The fact that functionalization could be carried out under harsh reaction conditions (H_2SO_4/HNO_3, SnCl/HCl) showed once more the high chemical stability of PMOs. Conversions of close to 28% of the phenylene groups were reported. The resulting material was used successfully as a solid base catalyst for the Knoevenagel condensation. Another approach to achieve a dense incorporation of primary amines into the pore walls of a PMO is by hydroboration of the ethylene-bridged precursor bis(triethoxysilyl)ethylene.[70,71] Condensation of the resulting precursor generated a PMO with carbon–boron bonds in the pore walls, which could be easily transformed into primary amino groups by using hydroxylamine-*O*-sulfonic acid in a second step.

Acid functions, mainly in the form of sulfonic acid groups, have been introduced in PMOs by postfunctionalization methods, for example, by sulfonation of phenylene-bridged PMOs.[68,72] An alternative approach is based on a Diels–Alder reaction with an ethylene-bridged PMO to introduce a phenyl group into the pore wall, and this group was subsequently sulfonated with sulfonic acid.[73] Such materials have mainly been used as solid acid catalysts.

2.1. Acidic and Basic PMOs

Another approach that increases the scope of possible surface functional groups was recently reported. In this approach, a bromophenyl-bridged PMO precursor allowed subsequent functionalization with different functional groups by bromine substitution, either directly in the precursor or after surfactant-mediated condensation at the pore walls. Thus, the incorporation of carboxylic, vinyl, or posphonic ester groups yielded mesoporous organosilicas denoted as UKONs (Scheme 1).[74,75] The carboxylic acid groups could be



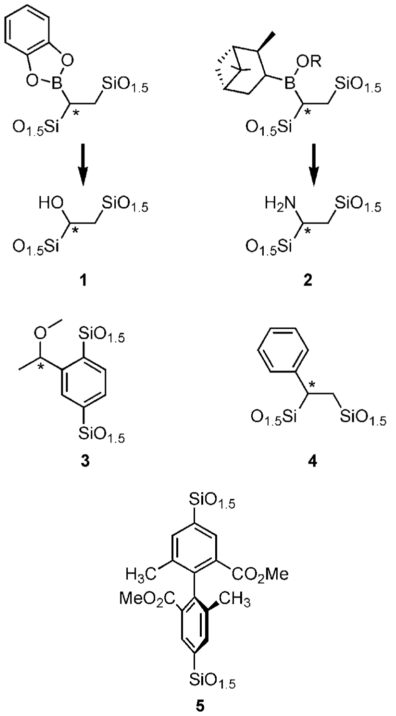
Scheme 1. Synthesis of carboxy, vinyl, and phosphonic acid functionalized PMOs (UKON 2a–c).[74]

transformed into carboxylic acid chlorides and then treated with amino acids to generate PMOs with chiral surfaces. The chirality of the surface was probed by the adsorption of chiral gases onto the surface of the materials.

Besides the preparation of acid- or base-functionalized PMOs, even more advanced functional groups, such as whole organometallic complexes,[76–80] have been introduced into PMOs.[57] In these cases, however, the complexes were connected to the trialkoxysilane groups through long flexible linkers, thus necessitating the admixing of a larger amount of the pure silica source. In contrast, the introduction of an N-heterocyclic carbene (NHC) ligand in the pore wall could be achieved without the use of flexible linkers.[81] However, the use of a pure disilylated diarylimidazolium (Si-IMes-) precursor and a block copolymer (Pluoronic P123) as a template led to a material with a specific surface area of about 100 $m^2 g^{-1}$ and without a defined pore structure. Nevertheless, the addition of small amounts of a pure silica source enables the formation of a PMO, which after loading with metals could be a highly promising heterogeneous catalyst.

2.2. Chiral PMOs

The introduction of chiral groups has also gained increasing interest in recent years. This approach has led to the formation of materials with potential applications in enantioselective catalysis and chiral separations. As mentioned above, chiral surfaces have been prepared by bonding amino acids to PMOs functionalized with carboxylic acids.[75] Chiral organometallic complexes[76] and chiral diaminocyclohexane, binaphthyl, and other moieties have been introduced as bridges in PMOs;[77,82,83] however, the use of long and flexible linkers was again necessary. Several research groups recently demonstrated that chiral centers could be incorporated directly into the organic bridges of PMOs through the use of chiral, but rigid precursors (Scheme 2).



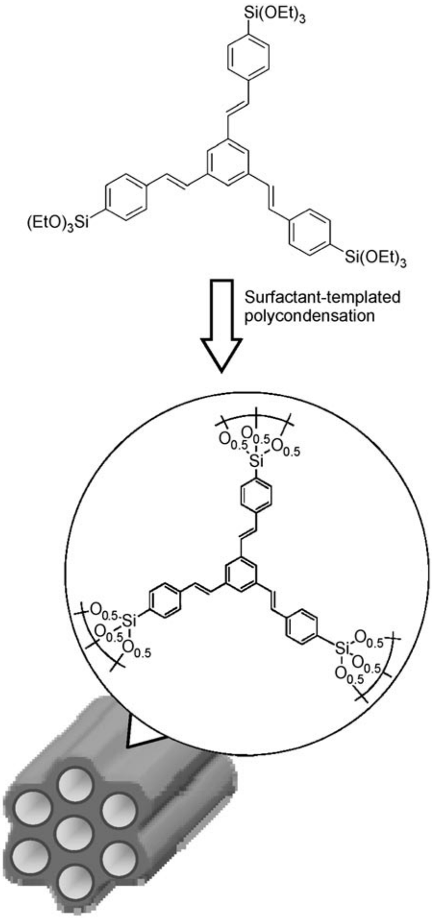
Scheme 2. Chiral organic functional groups that form the pore walls of PMOs. Mesoporous PMOs could be prepared solely from these precursors without admixing any other silica precursor.

Such precursors were synthesized by the asymmetric hydroboration of ethylene-bridged precursors, which allowed further transformation into hydroxy-[84] (**1**) and amine-functionalized (**2**) organosilicas.[85] Further chiral PMOs were obtained by asymmetric hydrogenation of a keto group linked to a phenylene-bridged precursor (**3**),[86] asymmetric hydrosilylation of a phenylsilylethene (**4**),[87] and chiral resolution of axially chiral, biphenyl-bridged precursors (**5**).[88] Porous organosilicas could be prepared using only these chiral precursors. The enantiomeric purity of the organosilanes could be determined by several methods, such as eluting the organic groups from the solids by HF treatment and analyzing the resulting organic groups by HPLC on a chiral stationary phase.[87] Circular dichromism (CD) spectroscopy could also be used to measure the optical activity of the compounds dispersed in an isorefractive solvent[85,86] or pressed into KBr pellets.[88] The addition of a nonchiral acid chromophore (benzoic acid) to the chiral amine-functionalized PMO **2** and subsequent CD measurements even showed a chiral induction, and thus demonstrated that the chiral functional groups in these networks are accessible to materials entering the pores.[85] Interestingly, it was shown that chirality transfer can even occur between chiral and nonchiral organic groups within one PMO. It was demonstrated that a single PMO prepared from a combination of 4,4′-bis(triethoxysilyl)biphenyl and axially chiral, enantiomerically pure biphenyl derivatives **5** of similar structure contains regions in which the chiral bridging groups appear to influence the structure of the nonchiral biphenyl unit, thereby resulting in new chiral aggregates within the material.[88]

2.3. PMOs with Conjugated Bridging Groups

Besides the exploitation of the chemical properties of organic groups incorporated in the pore walls of PMOs, other studies considered the physical properties of the groups. Larger aromatic groups have been incorporated into PMOs and their optical properties have been investigated. The use of chromophores as bridges in PMOs is indeed an attractive goal, since the architecture of the PMO ensures a high loading of the compound exclusively in the pore wall, while the pore channels are open for other optical compounds; thus materials can be created with two spatially separated regions that have different optical properties.[89] The synthesis and optical properties of PMOs prepared from 100 % of the PMO precursors with a bridging chromophore have been reported.[90–92] Cornelius et al. showed that increasing the length of the π systems of the organic moiety or by integration of heteroatoms in the π system led to the optical absorption properties of the materials being tuneable.[93] An interesting effect of the structural environment of the chromophore was observed for a 2,6-naphthylene-bridged PMO, which was prepared with both amorphous and crystalline pore walls.[94] While the amorphous form showed a broad emission band ascribed to excimer fluorescence, the crystalline form showed a sharp emission band attributed to the fluorescence of an isolated naphthalene unit. This measurement suggests that, against expectation, the naphthalene moieties in the crystalline material are isolated, despite their dense packing in the pore wall. This was explained by the three-dimensional rigid siloxane networks fixing the naphthalene rings in their lateral directions, at intervals larger than needed for interaction between the rings and thus the formation of excimers.

In many cases, a highly decorated pore wall might even be unfavorable in terms of the optical properties of the introduced chromophores, as a high concentration can lead to fluorescence quenching. Therefore, PMOs with chromophores as bridging groups have often been prepared by diluting the chromophore precursor with another silica or PMO precursor not bearing an organic functional group.[95–97] While a high concentration of chromophores can have a detrimental effect on the optical properties, the opposite is true for charge-transport applications. In this case, a high and homogeneous concentration of the functional groups is essential for good transport throughout the whole material. Very recently, Mizoshita et al. were able to synthesize mesostructured phenylenevinylene–silica hybrids from 100 % of the π-conjugated organosilica precursor (Scheme 3). The material showed hole transport within the pore walls, with hole mobilities on the order of $10^{-5}\,cm^2\,V^{-1}\,s^{-1}$, a value comparable to those of organic π-conjugated amorphous polymers.[98]



Scheme 3. Preparation of a mesostructured organosilicas with electroactive phenylenevinylene bridges to generate hole-transport properties in the pore walls.[98]

2.4. From Porous Organosilicas to Porous Polymers

As shown in these examples, when silsesquioxanes with bridging organic groups are used exclusively for the preparation of PMOs, the organic content can be increased greatly compared to an organosilica with the same groups grafted on the pore wall. As the organic groups are the origins of function, researchers searched for methods to further increase the ratio of the organic group to the inorganic part in the porous network. This has been achieved by the development of PMOs where each Si atom is bound to two or more bridging organic groups. For example, a three-ring precursor $[\{SiCH_2(OEt)_2\}_3]$[99] or even dendrimer building blocks with hydrolizable alkoxysilyl groups at the outer edge could be used.[100] The use of such precursors in template-assisted synthetic pathways gave highly ordered periodic mesoporous dendrisilicas (PMDs). The combination of high porosity and the high number of organic groups in the pore walls led to materials with low dielectric constants that are interesting for low-k dielectrics. Interestingly, such precursors could also be chemically modified by replacing a proton from the bridging CH_2 groups with a halogen atom.

A further increase in the number of organic groups would finally afford building units of the type SiR_4 (where R is a bridging group). Since no alkoxysilane group is present in such precursors, such a material could not be produced by sol–gel approaches, as used for the synthesis of PMOs. Furthermore, such a precursor could, depending on the bridging organic group, be so hydrophobic that no favorable surfactant–precursor interaction could be assumed. Thus, new pathways towards porous materials with SiR_4 motifs in the pore walls had to be developed, and were achieved by the synthesis of so-called "elemental organic frameworks" (EOFs).[101,102] In these materials, the silane groups are linked by four organic groups. The porosity in these materials is, however, generated by the rigid and open structure of the organosilane network. The silicon atoms in such frameworks can in principal be replaced by carbon atoms[102] to yield fully organic materials, namely porous polymers and organic frameworks.

3. Functional Meso- and Microporous Polymers

3.1. Functional Mesoporous Polymers

Meso- and microporous polymers have gained increasing interest in recent years because they might complement their inorganic counterparts, such as mesoporous silicas or zeolites, in a number of applications. This is particularly true for applications where properties such as low weight and high flexibility are advantageous. Since the entire porous framework is composed of organic matter, any porous polymer or organic framework naturally exhibits some kind of organic functional group in the pore wall. However, in terms of defining such materials as functional organic frameworks, only compositions will be described which were chosen to exhibit certain properties for a special purpose. Mesoporous polybenzimidazole (mp-PBI) serves as an example (Figure 2).[103] This polymer is prepared by polycondensation of an aromatic tricarboxylic acid ester with diaminobenzidine in the presence of silica nanoparticles as templates. After formation of the network and removal of the silica template, mp-PBI is formed with pores of 12 nm and a surface area of around 200 $m^2 g^{-1}$. The formation of the benzimidazole group does not only yield a stiff aromatic network, but basic functional groups are also introduced into the polymer. These materials were treated with phosphoric acid to form proton-conducting membranes. Thus, mp-PBI satisfies the prerequisites of a functional porous material, that is, it contains a defined functional organic group (the benzimidazole) in the pore wall, and leads to the creation of a designed property (basicity) for a specified application (binding of phosphoric acid to form proton-conductive membranes).

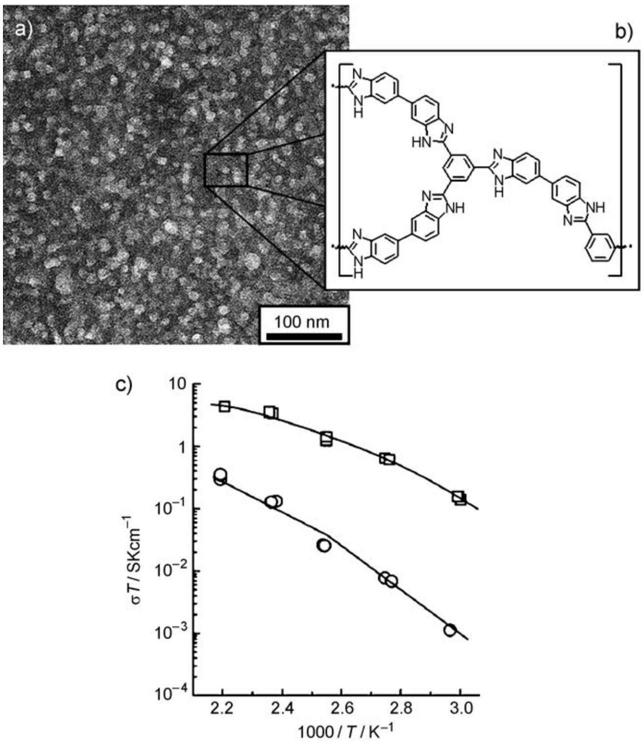


Figure 2. a) TEM micrograph and b) chemical structure of mesoporous, cross-linked PBI; c) proton conductivities of phosphoric acid doped mesoporous (○) and nonporous PBI (□).[103,104]

It was shown that the introduction of a defined nanosized biphasic structure into the PBI/H_3PO_4 system leads to a considerable enhancement in the proton conductivity compared to nonporous PBI loaded with the same amount of phosphoric acid (Figure 2c). The conductivity values could, furthermore, be tuned by varying the porosity and cross-linker content of the preformed network. Thus, materials exhibiting high proton conductivities at high temperatures (ca. 180 °C) and zero humidity have been prepared.[104] The functional, basic imidazolium groups in mesoporous PBI have also been employed effectively for catalytic applications, more precisely for the Knoevenagel condensation of various aldehydes with malonic acid derivatives.[105]

The versatility of such a "hard-templating" procedure in which silica nanoparticles or other inorganic nanostructures have been used as templates, has been demonstrated by the preparation of a variety of mesoporous polymers.[106] However, it is still a quite time- and labor-intensive process that involves several preparation steps. An improvement in the synthesis of mesoporous polymers was reported by Zhao and co-workers, who used Pluronic surfactants as soft templates in the synthesis of highly ordered mesoporous phenolic resins called "FDUs".[107–109] Parallel to this work, Ikkala and co-workers showed that the self-assembly of functional block copolymers, that is, poly(styrene)-*block*-poly(4-vinylpyridine), could also be used for the synthesis of mesoporous phenolic resins.[110] Phenolic resins with high specific surface areas ($S_{BET} \approx 550–650\ m^2 g^{-1}$) could be produced by using this approach. Heat treatment of these resins led to their conversion into mesoporous carbons.[107–109] Phenolic resins contain mainly hydroxy and benzene groups as the functional groups, thus little improvement is expected in their functional properties for applications (for example, as a catalyst support) compared to mesoporous silica. Nevertheless, metals and metal oxides were incorporated into the phenolic resins[111,112] and the supports showed good chemical and mechanical stability as well as reduced leaching of the metal species. The hydroxy or phenolic groups in the resin could, of course, be further functionalized, although only the aromatic parts have so far been used for this purpose. The self-assembly of surfactants and functionalized phenolic monomers with formaldehyde yielded mesoporous polymers functionalized with carboxylic acid, sulfonic acid, and amino groups.[113] The obtained materials possess a high density of functional groups in their pore walls which can be used for several purposes. As an example, silver ions were adsorbed on the pore walls of a mesoporous polymer functionalized with carboxylic acid groups and on a nonfunctionalized mesoporous resin as a reference. After reduction of the metal, much smaller silver nanoparticles were formed in the functionalized polymer and were also better distributed throughout the material.[113] Mesoporous phenolic resins functionalized with sulfonic acid were produced by sulfonation of phenolic resins with different pore structures (FDU-15 ($P6mmm$) and FDU-14 ($Ia\bar{3}d$)). Considerable amounts of sulfonic acid groups ($2\,\text{mmol}\,\text{g}^{-1}$) could be introduced into the materials without a significant change in the mesoporous structure (Figure 3).

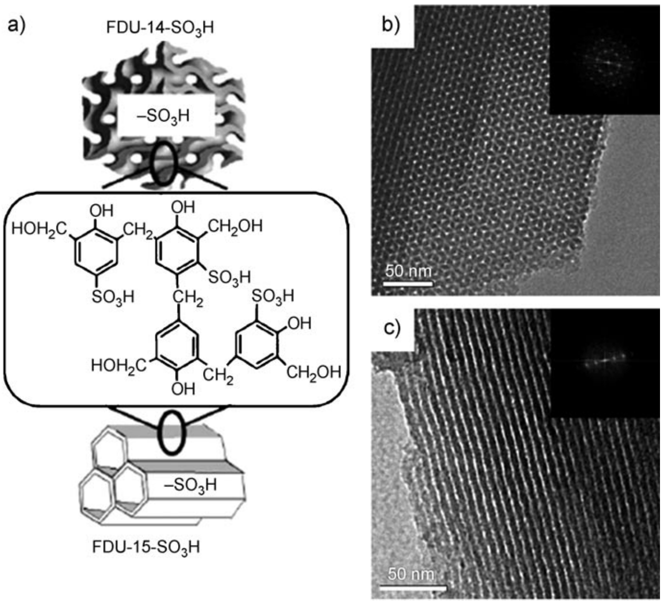


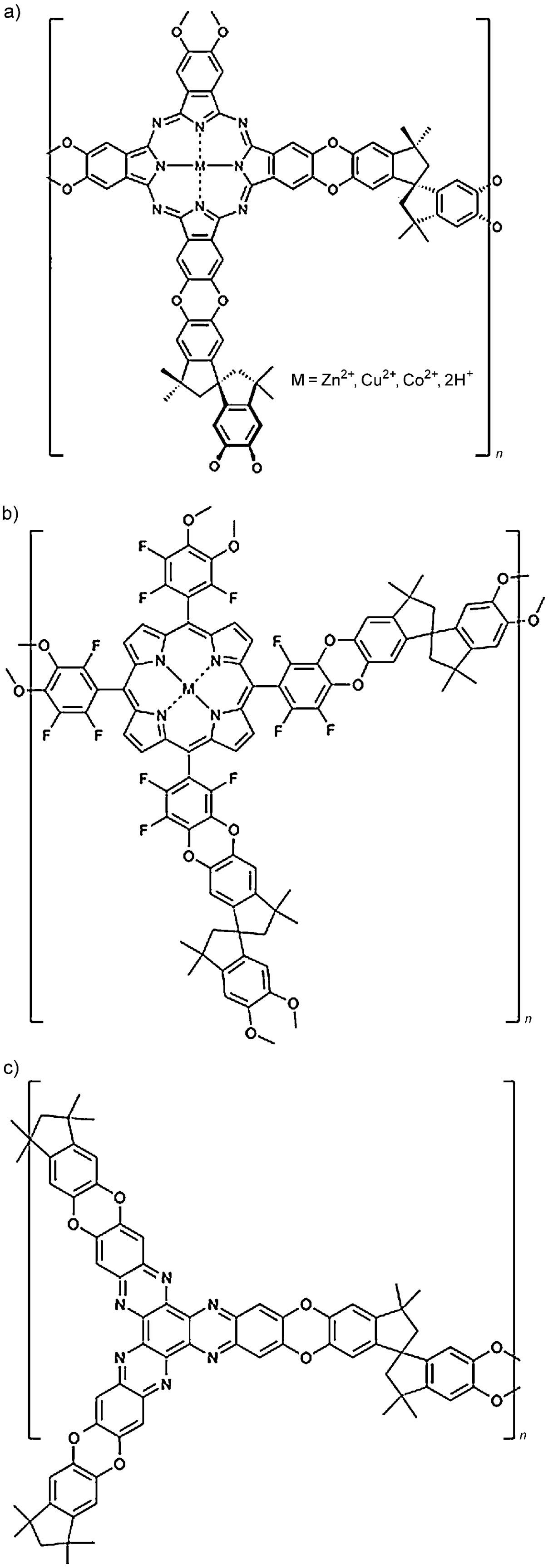
Figure 3. a) Mesostructure and chemical structure of sulfonic acid functionalized mesoporous phenolic resins as well as TEM images of sulfonic acid functionalized mesoporous phenolic resins b) FDU-14 and c) FDU-15; inset: selected-area electron diffraction (SAED) pattern of the mesoporous resins.

Such mesopolymers functionalized with sulfonic acid groups were tested as heterogeneous catalysts in acid-catalyzed reactions, such as the Beckmann rearrangement, and showed superior activities compared to commercial acidic resins and zeolites.[114] A series of amino-functionalized mesoporous phenolic polymers with different mesostructures has been synthesized by a two-step chloromethylation/amination sequence. As could be expected, such materials showed high activity in amine-catalyzed reactions, such as the Knoevenagel condensation.[115] Soft templating has recently also been used to prepare mesoporous resins with novel chemical compositions. An ordered mesoporous melamine resin was prepared by using the precursor hexamethoxymethylmelamine (HMMM) and amphiphilic block copolymers as templates. The resulting mesoporous melamine resins inherently contain a large number of basic functional groups.[116]

3.2. Functional Microporous Polymers

In recent years another, template-free approach towards porous polymers was developed which has certain similarities to the methods used for the formation of MOFs. Here, structure-directing monomers (called knots or tectons), mostly rigid molecules with multiple functional groups extending into two or three dimensions, are covalently bound together directly or through linear linkers to generate two- or three-dimensional frameworks.[117] These polymers were named polymers of intrinsic microporosity (PIMs) or, in the case where fully aromatic compositions were used, conjugated microporous polymers (CMPs). As entirely covalently connected structures, such polymers are chemically stable. Therefore, a variety of post-functionalization processes could in principle be carried out on these networks, although no such attempt has so far been reported. Tectons and linkers of different chemical structures can be connected by using different chemical reactions; thus, the functional properties can also be incorporated directly during the synthesis by choosing suitable monomers. For PIMs, this was even shown in one of the first examples: The polymerization of porphyrin and phthalocyanine complexes with a spirobisindane led to porous polymer networks (Scheme 4a,b). Nitrogen adsoption/desorption isotherms for the porphyrin network determined a BET surface area of $980\,\text{m}^2\,\text{g}^{-1}$.[118] The phthalocyanine network had BET surface areas of $895\,\text{m}^2\,\text{g}^{-1}$, $750\,\text{m}^2\,\text{g}^{-1}$, $489\,\text{m}^2\,\text{g}^{-1}$, and $535\,\text{m}^2\,\text{g}^{-1}$ for the Zn^{2+}-, Cu^{2+}-, and Co^{2+}-loaded samples and an unloaded sample, respectively.[119] The same principle for building porous organic networks was used to incorporate hexaazatrinaphthylene (Hatn) groups (Scheme 4c).[120] The nitrogen substituents in the Hatn motif can strongly bind to metals. Stirring the polymer in chloroform containing an excess of bis(benzonitrile)dichloropalladium(II) yielded a polymer which had adsorbed over three (3.3 equiv) palladium dichloride moieties per Hatn unit. These first examples of network PIMs nicely show that it is possible to create covalent organic networks with high porosities and surface areas, where functional groups—in these examples a ligand or even a complete metal–organic complex—are a supporting part of the pore wall. The high number of such functional groups (better described as with the pore wall consisting almost entirely of the functional group) makes these materials promising heterogeneous catalysts. A cobalt-loaded phthalocyanine network was shown to be an active catalyst for the degradation of hydrogen peroxide and for the oxidation of cyclohexene to 2-cyclohexene-1-one.[121] The Hatn network loaded with Pd^{2+} ions catalyzed a model Suzuki aryl–aryl coupling reaction efficiently. Even though leaching of the Pd was observed in the first run, the amount of Pd was stabilized in the following runs.[122]

Thiophene-based conjugated microporous polymers prepared by oxidative polymerization of 1,3,5-tris(thienyl)benzene have also been used as catalyst supports.[123] These microporous networks with specific surface areas of $1060\,\text{m}^2\,\text{g}^{-1}$ contain large amounts of thio substituents (S content: 26.4 wt%). Since the thiophene units are part of the organic bridges it was assumed that they are accessible to



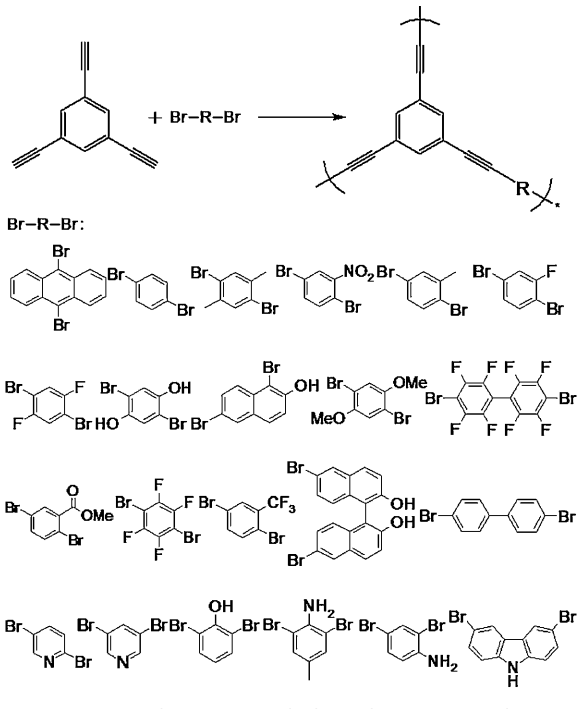
Scheme 4. Polymers with intrinsic microporosity based on a) phthalocyanine, b) porphyrin, and c) hexaazatrinapthylene.[118–120]

molecules or ions entering the porous system. Metal loadings of up to 15 wt% have been achieved by impregnation of the polythiophene network with a palladium salt solution. Reduction of the palladium ions yielded very small, monodisperse palladium clusters with an average diameter of 1.5 nm that were homogeneously dispersed in the polymer matrix. The first catalytic test showed the so-prepared catalyst had promising activity in the hydrogenation of diphenylacetylene to 1,2-diphenylethane.

When aromatic monomers are polymerized by C–C coupling reactions, such as the Sonogashira,[124–126] Suzuki,[127] or Yamamoto[128] coupling, conjugated microporous polymer (CMP) networks can be prepared.[129] Even though most of these networks possess no decisive chemical functional groups, their conjugated structure could result in them exhibiting valuable physical functions, for example, for organic electronic devices. Porous networks derived from the coupling of spirobifluorenes have shown an intensive blue emission.[127,128] Tectons, as used for the generation of CMPs, have also been used to form 2D and 3D architectures of π-conjugated polymers in the form of large, fully conjugated, star-shaped molecules, which were subsequently applied to organic optoelectronic devices, from OLEDS to solar cells.[130–133] The special architecture of these molecules results in them having the advantage of being more soluble than their linear counterparts and have a lower tendency to crystallize. No such application has so far been described for CMP networks. However, as both approaches—the synthesis of branched, conjugated molecules and the synthesis of conjugated porous networks—use the same synthetic principles, it would not be surprising if they were to merge together soon. The porosity of CMPs could further enable the introduction of a second phase (for example a dye, or a corresponding hole or electron conductor) by simple infiltration into the networks to yield defined interpenetrating networks. However, porous conjugated polymer networks first have to be produced as thin films on electrodes for these applications, which is quite a synthetic challenge. A possible way to achieve this task would be to use soluble PIMs[134–138] with conjugated backbones and coat these polymers on the electrode or by the direct deposition of CMPs on electrodes by electropolymerization of suitable conjugated tectons.

The Yamamoto coupling reaction, previously applied for the preparation of CMPs with spirobifluorene monomers,[128] has also been used recently for the preparation of another microporous polymer by coupling of the tetrahedral monomer, tetrakis(4-bromophenyl)methane. The result was both stunning and impressive: Ben et al. reported the synthesis of a microporous polyphenylene network (PAF-1) with an unprecedented BET surface area of 5640 $m^2 g^{-1}$ (Langmuir surface area: 7100 $m^2 g^{-1}$).[139] This value exceeds any specific surface areas measured so far for other materials, for example, for crystalline MOFs[140] and covalent organic frameworks[141] (COFs, see Section 3.3). As can be expected, this material also showed high uptakes of other gases, such as H_2 (10.7 wt% at 77 K, 48 bar) and CO_2 (1.3 $g g^{-1}$ at 298 K, 40 bar). The high surface area and porosities of PAF-1 was partially ascribed to a diamond-like ordering of the polymer network; however, the XRD analysis of the material supports the formation of a predominantly amorphous polymer network with little long-range order. Indeed, Trewin and Cooper showed shortly after that such high surface areas could also be explained using an amorphous “expanded silica analogue” model, thus challenging the notion that exceptionally high surface areas are the preserve of molecular networks with high degrees of long-range crystalline order.[142] Thus, the development of PAF-1 by Ben et al. certainly open up new avenues towards the preparation of functional microporous polymers with exceptionally high surface areas.

The synthesis of CMPs based on the use of polyaryleneethynylenes and the Sonogashira Hagihara coupling reaction[124] has been used for the first systematic study on the introduction of functional groups into porous organic networks. Dawson et al. prepared a variety of CMPs by the Sonogashira–Hagihara cross-coupling of 1,3,5-triethynylbenzene with a number of functionalized dibromo compounds (Scheme 5).[143] The properties of the networks could be controlled by the choice of the monomer. For example, the dye sorption behavior of the networks was shown to be controlled by varying the hydrophobicity of the pore walls (by using different functional dibromo compounds). This approach greatly expanded the range of microporous polymers that could be prepared, as it allows the preparation of networks with high surface areas and properties that can be tailored for specific applications such as catalysis and separations. One recent study by Wang and co-workers has shown this nicely: a Troegers base was introduced as a functional moiety into a microporous framework.[144] The resulting network displayed a surface area of 750 $m^2 g^{-1}$ and a porosity of 0.74 $cm^3 g^{-1}$. The polymer was subsequently used as a catalyst for the addition of diethylzinc (Et_2Zn) to 4-chlorobenzaldehyde. The polymer showed a catalytic activity that was quite comparable to that of a free Troegers base in a homogeneous catalysis. This study is a nice example of the merging of homogeneous and heterogeneous catalysis, as mentioned before.



Scheme 5. Functional monomers which can be incorporated into conjugated microporous networks through Sonogashira–Hagihara coupling.[143]

Microporous polymer networks that are highly functionalized with amine groups have been produced by treating melamine with various di- and trialdehydes, thereby forming a series of highly cross-linked microporous aminal networks with BET surface areas as high as 1377 $m^2 g^{-1}$. The materials contain up to 40 wt % of nitrogen.[145] A comparable Schiff base approach, however, yielded imine instead of aminal networks, which have been used to prepare crystalline organic networks. Condensation of the tetrahedral building block tetra-(4-anilyl)methane with the linear linking unit terephthaldehyde was used to produce a material with an extended 3D framework structure (COF-300).[146]

3.3. Functional Covalent Organic Frameworks

In general, for the formation of covalent organic frameworks (COFs), that is, microporous polymers with crystalline structures, it is necessary that the condensation reaction occurs in a reversible or dynamic fashion. The chemical bonds of the forming polymer network have to close and open to yield the thermodynamically (meta)stable, yet crystalline structure. This was possible, for example, through the reversible Schiff base reaction that led to COF-300.

To create covalently bound organic frameworks either covalent bonding schemes have to be identified which are rather weak and thus can reopen under mild conditions, or harsher reaction conditions have to be applied which, however, have to selectively and reversibly open and close certain bonds in the network. The first approach was applied by Yaghi and co-workers to generate the first periodic COFs by the formation of boron oxide (B_3O_3) rings or boronate esters. These materials were formed by either trimerization reactions of diboronic acids or condensation of diboronic acids with alcohols.[147,148] In analogy to the synthesis of MOFs, it has been shown that reticular chemistry can be used to control the pore sizes in the resulting materials.[149] While the first COFs exhibited a layered 2D architecture it was later shown that the formation of 3D periodic frameworks is also possible by this approach.[141] Such 3D COFs exhibit surface areas exceeding 4000 $m^2 g^{-1}$, and possess high capacities for hydrogen, methane, and carbon dioxide.[150,151] Calculations on 3D COFs furthermore suggested that COFs decorated with Li and Mg ions would give hydrogen adsorption energies suitable for practical applications.[152–154] Such an incorporation of metal ions in the pore walls would generate adsorption sites that are highly accessible; in contrast, the metal centers in most MOFs are shielded by the linkers. The synthesis of metal-incorporated COFs should not be too demanding and could probably use existing strategies such as wet impregnation; however, no such approaches have so far been reported. Nevertheless, metal@COF composite materials could exhibit interesting properties and, besides the enhanced storage of gases, could also find other applications, especially in catalysis. Furthermore, it would certainly be interesting to prepare COFs with functional groups in the pore walls. So far, only the incorporation of alkyl chains of various lengths on the aromatic rings of the COFs has been reported; this enabled the pore size of such frameworks to be tailored.[155] Besides alkyl groups, other organic groups could also be incorporated provided they do not affect the formation of the boroxine bridges.

Jiang and co-workers introduced large π-conjugated units into a COF for optoelectronic applications. Pyrene groups were introduced into COFs by either a condensation reaction of 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and pyrene-2,7-diboronic acid (TP-COF)[156] or by self-condensation of pyrenediboronic acid (PPy-COF) under solvothermal conditions.[157] Both networks align in a perfectly eclipsed fashion to yield porous COFs with specific surface areas of 868 $m^2 g^{-1}$ and 932 $m^2 g^{-1}$, respectively (Figure 4a). The channels formed in TP-COF were so large that a mesoporous material with a pore size of 3.2 nm was formed. The eclipsed alignment of the sheets results in PPy-COF showing a fluorescence shift because of the formation of excimers. Furthermore, it was proven that the materials show p-type semiconductor characteristics and PPy-COF shows effective photoconduction accompanied by a quick response to light irradiation (Figure 4b,c). These studies thus are certainly an important step up from the synthesis of new covalent frameworks towards applications, in this case for organic optoelectronic and photovoltaic materials.

Another class of COFs have been synthesized by the trimerization of dicyano compounds.[158] However, to enable reversibility, the reaction had to be carried out under much harsher reaction conditions. The trimerization of 1,4-dicyanobenzene in molten zinc chloride at 400 °C affords covalent triazine-based frameworks (CTFs) with high chemical and thermal robustness. As the reaction conditions are harsh, control over the crystallinity of the frameworks is more difficult than for boroxine-based COFs. However, new CTF structures were recently synthesized by trimerization of 2,6-dicyanonaphthaline, but unfortunately they were not porous, probably because of a partial staggered arrangement of the layers.[159] The application of salt melts also allows the preparation of networks at even higher temperatures. However, the reaction no longer occurs in a reversible fashion at higher temperatures, as more and more side reactions take place, and thus no crystalline products were observed. On the other hand, CTFs prepared at, for example, 600 °C exhibit hierarchical pore structures and high specific surface areas of up to 3000 $m^2 g^{-1}$,[160–162] and show a remarkable performance as sorbents.[163]

The formation of the triazine rings inherently results in a high number of heteroatoms in the networks which can be used, for example, for the coordination and thus stabilization of metal particles. Palladium particles have been supported onto a CTF network (Pd@CTF) and the catalytic performance was compared to the same metal particles supported

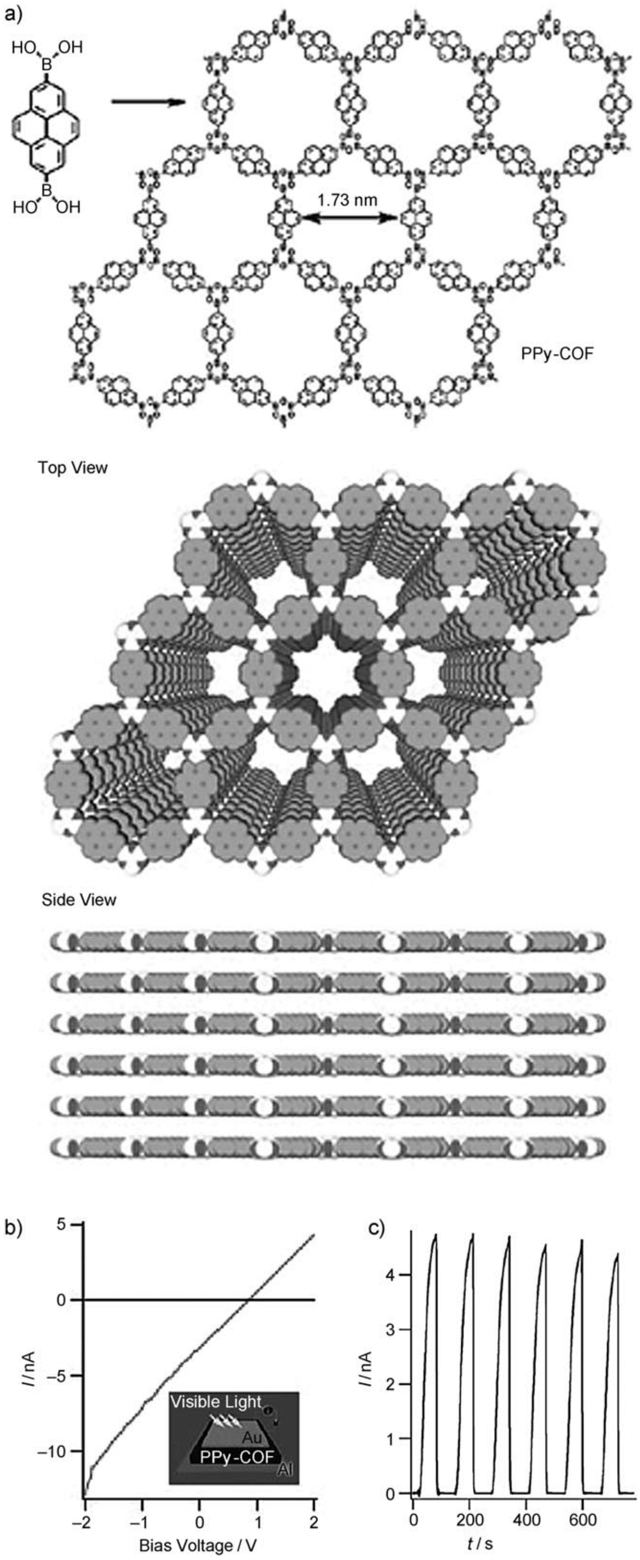
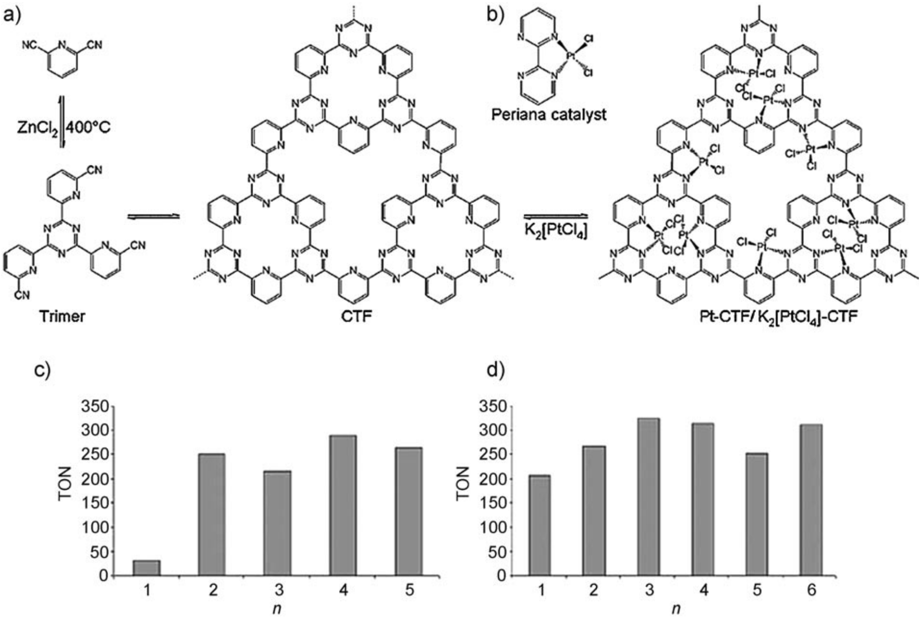


Figure 4. a) Chemical and space-filling structure of PPy-COF. b) *I–V* profile of PPy-COF sandwiched between two Al-Au electrodes (black curve: without light irradiation, gray curve: with light irradiation); inset: schematic representation of the PPy-COF sandwich type Al/Au electrodes. c) Photocurrent during switching the light on and off.[157]

on activated carbon (Pd@AC).[164] The Pd@CTF catalyst showed a much higher stability than the Pd@AC catalyst for the oxidation of glycerol. This observation was ascribed to the better coordination ability of the CTF surface, thereby preventing agglomeration and leaching of the metal nanoparticles.

The use of dicyano compounds with heterocyclic arenes enabled the introduction of further functional groups, that is, heteroatoms into such networks.[162] Such heteroatoms could be used for enhanced metal binding. In a recent example, platinum salts were introduced into a CTF network formed by trimerization of 2,5-dicyanopyridine.[165] The resulting framework resembles a polymerized form of a platinum-bipyridinium catalyst (Periana's catalyst),[166] which was used for the selective catalysis of methane to methanol. The platinum-loaded network was, therefore, tested in the same reaction. Two catalysts were prepared, one by impregnation of Pt into the network before the catalytic reaction (Pt-CTF) and the second by simply adding $K_2[PtCl_4]$ and the triazine network into the reaction vessel ($K_2[PtCl_4]$-CTF; Scheme 6)



Scheme 6. a) Trimerization of 2,5-dicyanopyridine in molten $ZnCl_2$, conversion into a covalent triazine-based framework (CTF), and subsequent coordination to platinum (Pt-CTF). b) Periana's platinum bipyrimidine complex. Catalytic activity of c) Pt-CTF and d) $K_2[PtCl_4]$-CTF in the direct oxidation of methane to methanol over several recycling steps. TON = turnover number.[165]

The catalytic reaction was carried out at 200 °C in oleum (30 % SO_3), and both solid catalysts were stable over at least six reaction cycles, thus showing the stability of CTF networks even under harsh conditions. No leaching of the platinum species was detected and the heterogeneous catalyst showed activities and selectivities comparable to the homogeneous one.[165] Therefore, this approach can be seen as a first step towards the concept of bridging the gap between heterogeneous and homogeneous catalysis, by polymerizing homogeneous catalysts into porous frameworks.

4. Conclusion

In the first few years after the discovery of a novel class of porous materials, for example, ordered mesoporous oxides, metal–organic frameworks, periodic mesoporous organosilicas, or covalent organic networks, it was often observed that the number of publications regarding the synthesis of new structures increases out of proportion to those having applications, processing, or up-scaling as the topic. This is certainly justified, as the value of a new material class also rests on the scope and versatility of the chemical compositions, structures, and morphologies that can be assembled. Moreover, new or optimized synthetic methods are mostly developed during this period. However, besides the preparation of more and more novel structures and compositions, another target should be to implement a certain function into the porous material, so as to use it for a specific application. The synthesis of porous functional materials is therefore an important and attractive research topic. Besides the incorporation of functional groups into porous materials by grafting procedures, porous materials have been produced where the functions are substantial and supporting parts of the pore walls. This approach has certain advantages, especially regarding the amount, accessibility, and stability of the functional groups. Examples of different classes of porous materials where this has been achieved have been described in this Review, where the amount of the (here organic) functional group increases from porous organosilicas to porous polymers and organic frameworks.

Porous, bridged organosilicas make use of silsesquioxane monomers where two or more alkoxysilane groups are bonded to organic moities. These precursors are condensed into porous materials by using sol–gel and templating approaches, finally affording periodic mesoporous organosilicas, the PMOs. Several functional groups have been introduced into the pore walls of PMOs to generate materials that have been used for several applications—from adsorption to catalytic to optoelectronic applications. It is certainly advisable to use a target- and function-oriented approach to tailor the materials properties for a specific application. The synthetic methods for synthesizing the precursor so as to control the pore structure are at least available to fulfil this task. However, there are still some challenges to be met: While some smaller functional groups (for example, acidic or basic) have been successfully introduced into PMOs as a supporting part of the pore walls, this was mostly only achieved for larger, more advanced functional groups, such as ligands or metal–organic complexes), by connection through long and flexible linkers. However, such materials do not have significant advantages in terms of the number and stability of the functional groups compared to organosilicas, where the organic groups are grafted on to the pore wall. A better, that is, denser, incorporation of, for example, catalytically active groups into the pore walls of the PMOs would certainly enhance their stability, but might also significantly influence their activity and selectively in a catalytic reaction. The sol–gel synthesis of such materials also allows the preparation of a mixture of different functional groups in one material by using two or more organosilica precursors.[167–169] In this way, certain properties of the network can be adjusted. The incorporation of different catalytically active centers in the pore walls of one material could yield, for example, interesting materials for consecutive catalytic reactions.[170]

For some applications, the concept of "periodicity" might at least be revisited. Even though such an arrangement is easy on the eyes, for most applications a highly ordered pore system does not lead to more advantages. On the contrary, an ordered but anisotropic pore structure can even have detrimental effects, since the diffusion and transport of substances is hindered in one or more dimensions. Templating with structure-directing agents is often time consuming and costly. In many cases, therefore, the approach for generating porous aero- and xerogels from the same organosilica precursors is the more logical alternative so as to develop applications. To finally enable an industrial application of such materials, up-scaling has to be possible, thus the costs and complexity of the synthesis have to be acceptable. It should also be noted that for most applications the structure of a material not only has to be controlled on the molecular and nanometer scale, but also over a much wider size range. The fine powders formed most often during PMO synthesis are not ideal for applications as materials in chromatography or in catalysis. Instead, a controlled adjustment of the morphology of PMOs, for example, in the form of μm-sized spherical particles,[168,169,171–173] membranes,[174] or monoliths[175,176] would be an attractive research target.

Mesoporous, purely organic materials have also been produced by using hard and soft templates. The discovery of mesoporous phenolic resins, in particular, showed that synthetic approaches for the generation of mesoporous polymers can in principle be applied, as demonstrated for the preparation of mesoporous inorganic and inorganic–organic hybdrid materials. It will be rather interesting to see if these principles can also be applied to other polymer networks with different chemical compositions. Quite attractive would be the formation of such materials with chemical compositions known, for example, from ionic-exchange resins, or to π-conjugated systems, which would introduce interesting chemical or physical properties to the networks.

Self-assembled, porous, organic materials (PIMs, CMPs, and COFs) are probably the newest members in the family of porous materials. As they are also solely composed of organic components, it is in principle possible to incorporate the maximum number of organic functional groups into the network. As the prospects of such materials are indeed huge, porous polymers and organic frameworks have been claimed to be the new all-rounder, with applications in separation, gas storage, catalysis, and organic electronics. These claims are still waiting to be realized, but the first reports on the storage of gases (from hydrogen to methane), the optoelectronic properties, and the catalytic performance of several of the networks described herein are at least a promising start for this new class of materials. In particular, the polymerization of highly active and selective homogeneous organic or metal–organic catalysts into porous frameworks seems to be an interesting pathway towards bridging the gap between homogeneous and heterogeneous catalysis. Such a framework would combine the advantages of both worlds: the tuneable activity and selectivity of the homogeneous catalyst with the recyclability of the heterogeneous one. The open network structure should allow, in the ideal case, that all the active centers of the corresponding homogeneous catalyst are accessible to the substrate. Of course, in terms of commercial applicability, the same prerequisites are valid for these materials as described for the PMOs. Adjusting the morphology, processing, and up-scaling are thus topics which have to receive greater focus.

The next generation of porous materials, however, already seems to be underway, as represented by "porous molecules". Indeed, the recently reported microporous organic cages illustrate that the research on porous materials is still open to novel discoveries.[177]

Finally, it should be noted that the preparation of functional porous materials is generally not at all trivial. For any targeted functionality, it might be necessary to develop new synthetic pathways to reach the target. Thus, there are still enough challenges in the synthesis of functional porous materials, but it can be predicted that further progress in this field will result in exciting new structures, properties, and applications.

5. Addendum (September 23 2010)

During the production of this Review, several papers were published that underline the great interest and progress in the field of functional porous materials. Furthermore, some of the urgent needs to further improve the applicability of such materials described in the conclusion of this Review have been addressed by these works.

Novel pathways for the introduction of basic functional groups into PMOs have been described by Hesemann et al.,[178] and Sozzani, Froeba, et al.[179] In the first case, novel silylated amine or ammonium precursors were applied in combination with anionic surfactants by using the electrostatic interactions between the cationic centers of ammonium precursors and the anionic head group of the sulfate surfactant to create periodic mesoporous organosilicas.[178] In the second case, a divinylaniline-bridged precursor was used to prepare the PMO. The resulting amine group was accessible for further chemical modification and a chiral amino acid could be attached by peptide bond formation, thus creating a PMO with a chiral surface.[179] A chiral norbornanebridged PMO with a 2D hexagonal mesostructure has been synthesized from a chiral precursor prepared by a asymmetric hydrosilylation from norbornadiene.[180] A PMO with a chiral secondary alcohol on the pore walls was modified with Al^{III} to produce a catalyst, which was used in an asymmetric ene reaction. The observed enantioselectivity was much higher than for an analogous homogeneous catalyst.[181] The synthesis of PMOs containing benzoic acid, dithiobenzoic acid, acetylacetonate, and aniline groups was also described.[182] Bifunctional PMOs that contain both aniline and benzoic acid have been prepared and the cooperativity of the two groups in a two-step catalytic process was demonstrated.[183] A PMO with interesting optical properties was synthesized from a tetraphenylpyrene-containing organosilane precursor. Doping of the mesostructured films with a fluorescent dye enabled color-tunable photoluminescence over a wide range of the visible spectrum, including white-light emission.[184] Materials that bridge porous organosilicas and porous polymers, such as new EOFs, have been described.[185] In another approach, bromophenylethenyl-terminated cubic siloxane cages have been used to prepare poly(organosiloxane) networks (PSNs).[186] In this case, the organic and not the silica groups of the precursor were used to assemble the network. This strategy is an intriguing reversal of the common synthetic concept for the generation of PMOs.

The field of polymers with intrinsic microporosity has been outlined in a recent Review.[187] Novel microporous polymers have been prepared by the cyclotrimerization reaction of bifunctional diketo-*s*-indacene-type monomers under acidic conditions in order to incorporate carbonyl groups into the network.[188] The light-harvesting properties of a conjugated microporous polyphenylene network (PP-CMP) were described. Donor–acceptor compounds were prepared by introducing Coumarin 6 into the pores; excitation of the PP-CMP skeleton led to intensive green emission from Coumarin 6 only, thus showing the effective energy transfer from the light-harvesting PP-CMP framework to the guest molecule.[189]

CMPs have been further shown to act as supports for noble-metal nanoparticles.[190] Some novel materials that bridge the gap between homogeneous and heterogeneous catalysis have been described: a platinum-modified mesoporous poly(benzimidazole) material was used as a solid catalyst for the selective oxidation of methane to methanol, and showed superior activity compared to the homogeneous Periana system.[191] A porous framework with metalloporphyrin building blocks (FeP-CMP) has been developed as a heterogeneous catalyst for the activation of molecular oxygen for the efficient conversion of sulfides to sulfoxides.[192] A similar architecture was produced by introducing phthalocyanines as tectons for the preparation of boronate ester based COFs.[193] To finish, the preparation of COFs and CTFs has been simplified and accelerated by using microwaves.[194,195] The preparation times for CTFs could be reduced from 40 hours to tens of minutes.[195] Further novel triazine-[196] and heptazine-based[197] networks and frameworks have also been described.

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