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Trends and challenges for microporous polymers

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Microporous polymers are covalently bound, entirely organic materials which possess very high surface areas. These materials have been intensively studied within recent years and various interesting properties and possible applications have been discovered and described. This review article starts with the question, what makes microporous polymers special and are there certain features which differentiate them from other microporous materials? Indeed, there are some special structural and functional features found in microporous polymers which make them really unique and merit further exploration. We focus here on microporous polymers which are solution-processable, can be produced as thin films on electrodes by oxidative polymerizations, are π-conjugated organic semiconductors, or which provide the possibility to introduce and exploit distinct functional groups in an otherwise non-functional highly porous environment. Emerging applications for these microporous polymers which make explicit use of these unique features are further presented.

1. Introduction

Microporous polymers are a new class within the versatile family of microporous materials, *i.e.* materials with pores of diameters below 2 nm and consequently very high surface areas. However, at this point the similarities to other members of this family, *i.e.* metal–organic frameworks (MOFs), covalent organic frameworks (COFs), zeolites, and activated charcoal, end as microporous polymers exist with very different structural features, ranging from highly crosslinked networks to linear contorted polymers. In contrast to almost all other microporous materials, microporous polymers are exclusively built up from organic matter connected by covalent bonds.[1,2] The only other type of materials bearing this property are COFs, which unite crystallinity and fully covalent bonds but bring their own set of caveats to the table, which are not discussed here.[3] Whereas COFs are so far always produced *via* condensation reactions, the synthetic concepts to prepare microporous polymers are highly diverse and range from metal catalyzed couplings to metal-free condensation reactions. The generation of microporosity and sometimes astonishingly high surface areas in such polymers stems from the stable, covalent connection of rigid, contorted molecules, with at least two but most often three and more functional and polymerizable groups. Such molecules are often and also hereafter named ‘‘tectons’’.

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Polymerizations of such tectons yield polymers with highly contorted structures. Space-efficient packing of polymer chains is effectively precluded within these structures creating a large free volume seen as microporosity. When more than two functional groups can be polymerized on the tecton highly crosslinked structures are created which hinder packing of the polymer backbone even more, yielding accessible surface areas often well in excess of 1000 m^2 g^{-1}.

Within the last 10 years the field of microporous polymers has proliferated tremendously and thus the question has to be asked, what makes these materials unique and distinguishes them from other well-developed microporous materials. Chemical and thermal stability along with the possibility to introduce organic functionalities and π-conjugated backbones into high surface area materials have been frequently claimed as major advantages of microporous polymers compared to other microporous materials. However, we think it is advisable not to be too general in defining the distinct features and beneficial properties of microporous polymers. Especially when named as advantages in comparison to other microporous materials such general statements might fail entirely. It is undeniable that a zeolite has a much higher thermal stability than any organic matter, that the number of chemical functionalities introduced into MOFs is currently outnumbering the ones in microporous polymers by far, and that no conjugated polymer will reach conductivities found in carbonaceous materials. Indeed, it is rather the ability to combine different properties, which makes microporous polymers special and a highly interesting complement to conventional microporous materials. In this review we will try to carve out the very special and unique properties of microporous polymers and how they can be exploited for novel and emerging applications. To set the stage before describing the most prominent and important works published in this area, at first a critical view on structure, synthesis, properties and functionalities of microporous polymers will be undertaken.

1.1 Synthesis and structure

Synthetic methods. A first distinct advantage of microporous polymers lies in the plethora of synthesis methods available to create them. This allows a large variety of functional groups to be exploited for polymerization reactions and thus an even larger toolbox of monomers or tectons is available for creating high surface area materials. Polymerization towards microporous polymers can be carried out at low to very high temperatures, in all conceivable solvents, in reaction times from seconds to hours and days, with various reactants and catalysts or without any catalysts at all.

Synthetic protocols which can be used for the generation of microporous polymers are highly diverse and range from metal-catalyzed or -mediated (Sonogashira,[4,5] Suzuki,[6] Yamamoto,[7] Buchwald–Hartwig,[8] Eglinton,[9] Heck[10]) to click-type reactions,[11] acid or base-catalyzed polycondensation reactions (formation of polyamides,[12] -imides,[13–15] -benzimidazoles,[16,17] -dioxanes,[18] -boroxines and boronate esters,[19] -imines[20,21]

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-aminals,[22] azo-bridged compounds[23–25] and many others[26–29]), oxidative couplings,[30–33] trimerizations[34–36] or Friedel–Crafts type couplings.[37,38] Several comprehensive review articles are available in which all known polymerization methods to create microporous polymers are listed.[2,39–42]

The great variety of synthesis conditions not only allows the usage of differentially functionalized monomers, but much more importantly to find appropriate reaction conditions tolerating any given functional group which is planned to be introduced into the network, *i.e.* synthesis can be carried out with high chemical orthogonality.

A further important point for several applications is that very cheap and scalable synthetic methods exist to create high surface area, functional microporous polymers. As an example, with the scale required for a carbon capture material, many microporous materials and other polymers are not an option as they are prohibitively expensive due to their requirement for expensive group 10 metal catalysts. Catalysts-free polycondensations or Friedel–Crafts synthesis routes are therefore valuable alternative synthetic routes. Microporous polymers containing benzimidazole[16,17] or triazine linkages[43] are an example with high CO_2 uptakes which can be synthesized without the need for a catalyst. Networks synthesized from both dichloromethyl monomers[44] and those using an external crosslinker[45] by Friedel–Crafts reactions were shown to have high uptakes particularly at higher pressures used for pre-combustion capture. These materials can also be synthesized from functional tectons to increase the heats of adsorption. Alcohol groups were particularly successful in this respect as amines are more difficult to incorporate.[46,47]

The challenge of amorphicity. Microporous polymers are generated by covalent attachment of rigid and contorted organic molecules. The synthetic concept to connect these tectons by strong covalent bonds impedes reversible bond formation, which yields one inherent drawback of microporous polymers, which is their total amorphicity. Of course, several reversible covalent bond formations have been described in the literature and have been used for the generation of crystalline covalent organic frameworks (COFs).[3] Such COFs can be seen as subclass of microporous polymers or as a class of microporous materials on their own; nevertheless, here we will concentrate on the larger family of amorphous microporous polymers, even though COFs will not be entirely neglected in this review. The absence of crystallinity or ordered structures within microporous polymers is actually no drawback for most applications, except for those regarding molecular sieving or size-selective catalysis, where the exact determination of pore sizes is mandatory. Otherwise high surface areas and small pores are required for the most common applications, *e.g.* gas storage and separation, catalysis and also for newly emerging applications such as thermal insulators, in organic electronics, photocatalysis, or energy storage. For none of these applications can a plausible reason be found, as to why an amorphous material should have a lower performance than an ordered one and sometimes even the absence of crystallinity might be advantageous, for example considering anisotropic transport phenomena in some ordered porous materials.

However, it cannot be denied that the amorphous nature of microporous polymers is a significant challenge when it comes to design, characterization and prediction of properties of these materials. While the structure of zeolites, MOFs and COFs can be in principle comprehensively elucidated from XRD measurements, this is not possible for microporous polymers.

Instead, various other analytical methods have to be used to approach the structure of the materials. NMR and IR spectroscopy are important tools to analyze the chemical structure of the backbone; however, as known for solid and amorphous materials, extensive peak broadening is often observed which renders peak assignments rather difficult. Nitrogen sorption is of course an irreplaceable method for any porous material, but even for this technique some obstacles occur when analyzing amorphous microporous materials as no distinct pore sizes can be expected. Furthermore, many microporous polymers show their organic nature in these measurements as they display some amount of flexibility, which is seen in a steady increase in nitrogen adsorption even at higher relative pressures and often a very broad hysteresis is observed, which are both – sometimes wrongly – assigned to additional mesoporosity. Finally, so far no reliable models exist for a pore size distribution analysis of these rather soft materials, which show some amount of swelling during gas sorption measurements.[48]

Finally, it cannot be denied that the amorphous nature of microporous polymers is a significant challenge when thinking of design, characterization and prediction of properties of these materials. For crystalline materials it is possible, simply speaking, to design the structure, porosity and pore size of the material on the drawing board. For example the organic linker size in a MOF defines the diameter of the pores and thus the size of the unit cell, giving rise to beautiful examples of isoreticular frameworks.[49] In contrast, in microporous polymers it has been observed that the increase of linear linkers between tectons rather reduces micropore volume and overall surface area,[4] which might be due to increased flexibility and bending of the linkers to reduce the surface area or enhanced intercalation of polymer chains. Of course in MOFs and COFs interpenetration is also possible, especially when moving to longer struts, thus changing the properties of these materials as well. Moreover, polymerization degrees and defects within structures, which should all have a large impact on the observed surface area and porosity, are hard to determine by analytical tools for the reasons given above. The probably most realistic picture of the structure of microporous polymers are currently provided by Trewin and co-workers *via* simulation of the network generation process (Fig. 1).[50] Looking at such models, which are backed up by XRD measurements showing no sign of crystallinity for MPNs, it can of course be questioned if it is really supportive that novel MPNs are often presented with an "idealized", *i.e.* crystalline structure and discussed in terms of long range order and topologies. Some design rules have been suggested by considering such idealized crystalline structures, however how much such artificial unit cells have in common with the real structures is more than questionable.

Creating high surface areas. Despite this, some common principles for creating high surface area microporous polymers can be derived by screening the large amount of available literature and materials already reported.

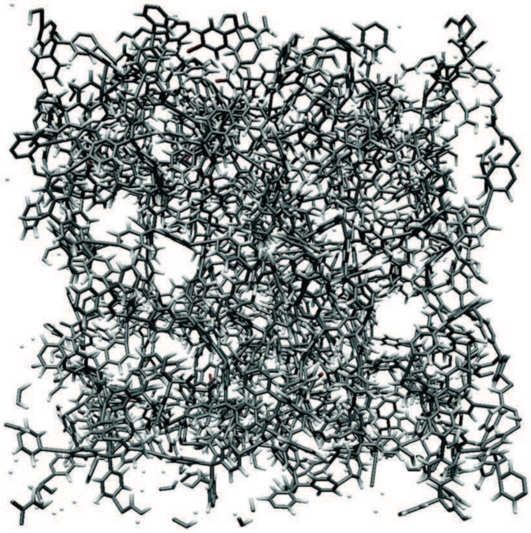

Fig. 1 Model of PAF-1 a microporous polymer network built by Yamamoto-homocoupling of tetrakis(4-bromophenyl)methane. Reproduced from ref. 48 with permission from Royal Society of Chemistry, copyright 2016.

– High polymerization degrees: polymerization methods, like Yamamoto or Sonogashira–Hagihara couplings, which yield linear polymers with high molecular weights, are also highly suitable to generate high surface area microporous polymers. Thus it is the functional groups used on the monomers which ultimately influence the obtained surface area. As example iodine *vs.* bromine functionalized monomers give different results in networks derived by metal-catalyzed couplings.

– High amount of crosslinking: when more functional, polymerizable groups are available at the tecton a higher crosslinking degree of the network is possible which rigidifies the material to maintain high surface areas.

– Reducing flexibility: as mentioned, increasing the strut length between tectons often leads to reduction of accessible surface area. Thus if the tectons cannot be connected directly, short and rigid co-monomers have to be used. Indeed the introduction of just one group with higher flexibility and rotational freedom, say a methylene –CH_2– group within the linker can yield total collapse of the surface area.

– 3D *vs.* 2D: the highest surface areas in microporous polymers have been observed when using tectons with a three-dimensional structure, *i.e.* orientation of the functional groups. Tetraphenylmethane-derived tectons are for example a very good choice when looking to increase the surface area of a network.

– Non-covalent interactions: further interactions between polymer chains, like hydrogen bonding, can yield a more space efficient packing and can reduce the available surface area.

Processing microporous polymers. Most microporous polymers share the drawback of other microporous materials when it comes to shaping, morphology control, and processing. As predominantly highly crosslinked polymers, these materials are not meltable or soluble in any solvent and the generation of thin films, membranes or molds is a formidable challenge. As for MOFs, microporous polymers have been grown from functionalized surfaces to generate thin films[51–53] or mixed with other polymers to create mixed membranes.[54,55] However, if these techniques can be converted into a feasible technology is so far questionable. Again, in this respect some microporous polymers exhibit unique features, which make their technologically relevant processing possible. At first many microporous polymer networks were prepared by oxidative polymerizations. Tectons functionalized with thiophene or carbazole moieties can be directly polymerized on electrodes to create compact but still microporous thin films.[56] As polymers of these types (*e.g.* derived from polythiophene or -carbazole) are interesting for applications in organic electronics or energy devices, their direct placement on electrodes as thin films is of great interest.

One class of microporous polymers can even be directly processed from solution: so-called polymers of intrinsic microporosity (PIMs) consist of unbranched, stiff but contorted polymer chains.[18,57] Such PIMs are therefore highly soluble in many common organic solvents. However, in the solid state, their rigid and contorted structure avoids efficient packing of the polymer chains, yielding a high free volume ultimately seen in permanent microporosity. Free-standing films and membranes of PIMs have been prepared (Fig. 2).[58] The concept of PIMs can be even further reduced to microporous cage compounds or molecular crystals.[59–64]

1.2 Properties and function

Chemical functionality. The main and most important property of microporous polymers is their high surface area and microporosity. As microporous polymers consist exclusively of light elements, gravimetric surface areas can reach extremely high values, which are so far just excelled by some MOFs and can reach values of several thousand $m^2\ g^{-1}$. So far the highest surface area of a purely organic microporous polymer has been reached by PPN-4 with a BET surface area of 6461 $m^2\ g^{-1}$ which is synthesized by connecting tetraphenylsilane tectons *via*

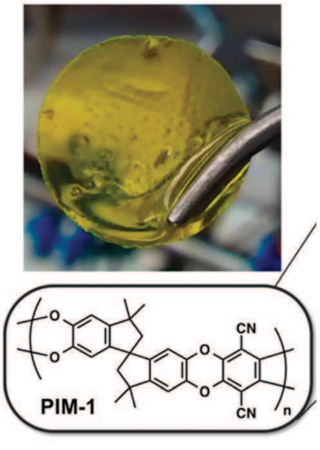

Fig. 2 Free standing membrane and chemical structure of the microporous polymer PIM-1. Reproduced from ref. 58 with permission from American Chemical Society, copyright 2015.

Yamamoto coupling.[65] However, given that some activated carbons and especially MOFs can reach ultrahigh surface areas as well,[66] so far this property is not a unique feature. High permanent surface areas are interesting for applications in gas storage, separation and catalysis, but actually useless when the surface area is not further functionalized in a certain and defined way. Here, microporous polymers provide some intriguing possibilities and this is, strangely enough, especially because it is possible to prepare microporous polymers which display no distinct functionality at all. PAF-1,[67] or the structurally identical PPN-6,[68] is a polymer featuring a backbone which is composed of biphenyls connected by a sp^3-hybridized quaternary carbon atom, thus no special functionality can be identified. However, PAF-1 can be equipped with a variety of functional groups, which can thus be seen as the only sites interacting strongly with molecules entering the porous system. This allows a highly defined tuning of for example adsorption enthalpies for different gases. Functional groups, such as amines, hydroxyls, fluoros and carboxylic acids have been found to increase the enthalpies of adsorption of CO_2 with the acid groups yielding the highest increase.[69] As an example, PPN-6 was post-synthetically modified with sulfonic acids and its lithium salt is showing an increase of over 160% for these modified networks over the parent network.[70] Further modifications using amines were also reported, again showing significant increases in the uptakes especially at 0.15 bar which corresponds to the amount of CO_2 in a typical flue gas stream.[68] Another intriguing example is that lithium doping of the otherwise non-functional PAF-1 can be carried out, which is only possible due to the high chemical stability of these networks. Binding energies of up to 9 kJ mol^{-1} in 5 wt% lithium doped PAF-1 resulting in a 22% increase in hydrogen uptake have been reported.[71]

In summary, the performance of a rather isolated functional group, bound to a permanent large surface, which itself has no special functionality can be investigated. In catalysis such a material is called an ''innocent support'' and often desired when the performance of a specific supported active site should be examined, as any further influence of the support on the reaction or interaction with the active site can be neglected. Using the right synthetic methods, such groups can be the sole functional sites within the material and *e.g.* no metal node and clusters or surface hydroxy groups have to be further considered.

Catalytic properties and stability. The synthetic schemes towards microporous polymers enable the intriguing possibility to bridge the gap between homogeneous and heterogeneous catalysis by using molecular catalysts as maintaining building block for the generation of highly microporous networks,[1,40] without the need for an additional porous support. This concept enables the introduction of the highest amount of catalytic active sites per surface area and mass of material.

Main routes to use microporous polymers in catalysis are the immobilization of molecular catalysts as supporting part of the network[72,73] or just attached to a stable network structure. A related and quite elegant approach is the immobilization of organic ligands within the network structure, which are, after formation of the network, loaded with the respective metal catalyst.[36,74,75] Such an approach can yield supported metal–organic catalysts with coordinatively unsaturated metal sites homogeneously distributed over the entire surface area. Recently, another concept has been presented, in which a molecular catalyst is not immobilized by covalent bonds within the network, but by electrostatic (Coulombic) forces. Here, novel permanently ionically charged MPNs are applied, from which the counterions are used directly or after ion exchange as the catalysts, yielding an intriguing intermediate between molecular and solid immobilized catalysts.[76] The latter approach will be described in more detail in a later chapter about the field of permanently charged MPNs. Finally, MPNs have been used as classical supports for the immobilization of metal or metal oxide nanoparticles. Here the advantage over conventional porous oxides or carbons are not too obvious, however especially regarding particle stability, functional MPNs, mainly with heteroatoms within their backbone have shown significant improvements over inorganic supports.[77,78] Furthermore, conjugated microporous polymers have come into focus of catalysis research, especially for photocatalysis.[79] This point will also be discussed in more detail later. Excellent and comprehensive reviews on the use of microporous polymers for catalytic applications were recently published by Rose[40] and Zhang and Ying.[80]

While microporous polymers certainly provide fascinating opportunities for catalytic applications some challenges remain, which are so far not or just rarely considered in the literature. It is understandable that initial works applying microporous polymers in catalysis use more or less conventional and well-studied molecular catalysts for immobilization. However, in these cases just the facile recyclability of these catalysts can be seen as the main advantage. Whether this alone will make microporous polymers interesting for realistic applications is debatable, as it is for molecular catalysts immobilized on other porous supports.[81] However, further advantages of the immobilization of molecular catalysts in MPNs can probably be identified and might become an interesting future research direction. For example catalysts immobilized in microporous polymers might be applicable at conditions where the pure molecular catalyst cannot be used. In the simplest case, a catalytic reaction can be carried out in solvents were the molecular catalyst is not soluble.[76]

Even more intriguing would be to make use of the non-functional, inert environment of the pore walls of some microporous polymers for confining and thus stabilizing highly reactive catalytic species, which as single molecules cannot easily be handled at ambient conditions and natural environment.

As mentioned before, the chemical robustness of microporous polymers is often mentioned, but not often exploited by applying them at indeed harsher reaction conditions.[82] Actually, in many papers thermal stabilities are stated (often >300 °C) which would make many MPNs promising materials even for catalytic gas phase reactions. These thermal stabilities are however mostly derived from TGA measurements, often

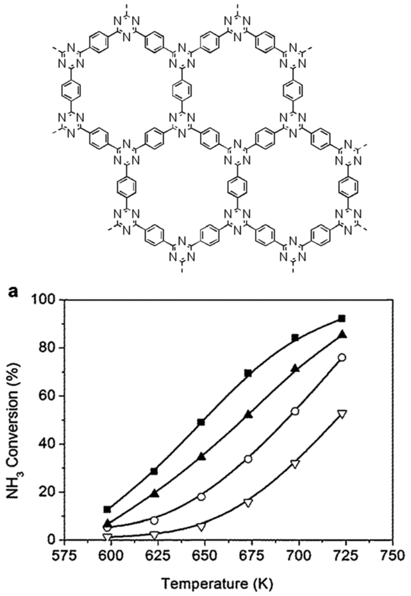

Fig. 3 Top: Chemical structure of CTF-1 and bottom: ammonia decomposition reaction using 1–2 wt% Ru-loaded CTF-1 (dark spots) and CNTs (light spots), for comparison. Reproduced from ref. 83 with permission from Royal Society of Chemistry, copyright 2015.

under inert gas, and thus have not much in common with the realistic environment and requirements on catalysts for gas phase reactions at elevated temperatures.

In this respect it is noticeable that microporous polymers are so far exclusively used for catalysis in the liquid phase. One remarkable exception is a covalent triazine framework which has been used as support for Ru nanoparticles and tested for gas phase ammonia decomposition up to 723 K by Chen and co-workers (Fig. 3).[83] In the liquid phase however, polymers which maintain a high surface area in the gas phase are not naturally the best choice. Also a polymer network with an immobilized molecular catalyst which shows no surface area at all under dry conditions might swell in solution yielding unhindered access to the catalytically active sites. More courage in using microporous polymers at really challenging catalytic conditions would therefore be desirable. In this respect it is important to note that it has been frequently reported that thermal or oxidation stabilities of microporous polymer networks can be enhanced, for example by increasing the cross-linking density[38] or introducing inorganic building blocks[84,85] or heteroatoms[15,86,87] into the frameworks. Many important catalytic gas phase reactions are carried out within temperature windows of between 250–400 °C and it should be possible to design microporous polymers to stay stable at these temperatures.

Electronic properties. A final intriguing feature of microporous polymers is the possibility to introduce electric conductivity. If microporous polymers are synthesized from entirely aromatic building blocks, such networks are distinguished by extended π-conjugation, found in so-called conjugated microporous polymers (CMPs).[4,39] The extent of the π-conjugation depends on the structure of the aromatic core segments and linkers and their connection pattern, *i.e.* the π-topology (Fig. 4).[88] The π-conjugated structure renders such aromatic networks potential organic semiconductors.

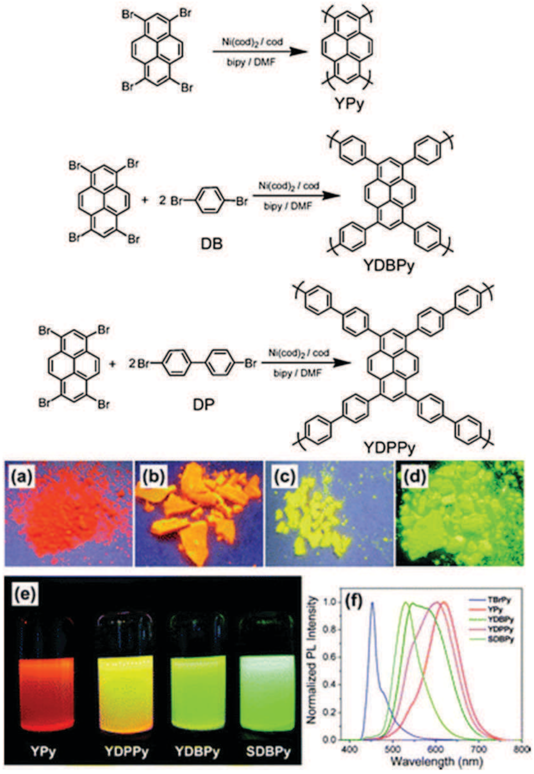

Fig. 4 Top: Synthetic routes to pyrene based CMPs. Bottom: Photographs of different CMPs under irradiation with UV light in bulk and dispersion in THF. (f) Shows the photoluminescence spectra of the pyrene monomer and the CMPs in powder form (note that SDBPy has in principle a similar structure than YDBPy but was prepared *via* Suzuki-coupling). Reproduced from ref. 88 with permission from Royal Society of Chemistry, copyright 2011.

Such an extended π-conjugation is rarely found in MOFs and then only when the integrated metal allows an electronic interaction from linker to linker. This is also documented by the fact that for linear MOF analogues (*i.e.* metal organic main chain polymers) just a few materials with semiconducting properties are found, while the field of semiconducting conjugated polymers (the linear analogues of CMPs) has been emerging for several decades. The potential semiconducting properties of CMPs certainly opens a wide field of promising applications, namely in organic electronics, energy devices or photocatalysis. This is further supported as tectons used for the generation of CMPs have been also used to form 2D and 3D architectures of π-conjugated star-shaped molecules, which were subsequently applied to organic optoelectronic devices, ranging from OLEDs to solar cells.[89,90] Furthermore, the permanent and stable porosity of CMPs enables a simple infiltration of a second phase[91] (for example a dye, or a corresponding hole or electron conductor) to yield defined interpenetrating networks as bulk heterojunctions.

Scope of this review. Given all this, within this review we will try to further highlight the unique features of microporous polymers by means of different pre-eminent examples from the recent literature. It is not the aim of this review to give a conclusive overview on the whole field of microporous polymers, as excellent reviews on these materials have been published in recent years.[1–3,39,40,42,56,57,92,93] On the contrary, we will try to identify some trends and worthwhile research directions within the field of microporous polymers. Within the following chapters we will concentrate on a special structural or functional feature of a certain class of microporous polymers and from there on develop new perspectives on emerging applications.

The first chapter will cover a highly unusual and unique property of microporous polymers, that is, that soluble and solution-processable microporous materials can be prepared. The second chapter will describe the field of π-conjugation within microporous polymers, yielding highly porous organic semiconductors, which are of high interest for organic electronics, but recently have also emerged in the field of photocatalysis. Finally, the controlled implementation of functional sites within microporous polymers will be covered. At first it will be shown how the simple introduction of elements other than carbon and hydrogen in microporous polymers can yield novel and unique properties, closing with the generation of permanently ionically charged microporous networks.

2. Soluble microporous polymers

Common for most porous materials, regardless to the reaction route, is their accruement as insoluble powders. However, for most applications it is desirable to modify the texture/shape of the porous material post-synthetically without varying material properties, which is, except for pellet production, mostly impossible for porous powders. Therefore shape control during reaction is desired to obtain materials in certain forms. However, the problem of non-processability does not occur for soluble polymers that show porosity in the dry state, *i.e.* for the so-called polymers of intrinsic microporosity (PIMs). These 2D-polymers create microporosity by inefficient packing due to kinks in the backbone structure but retain solubility in organic solvents and can thus be processed post-synthetically for example cast as films. In 2004 the first PIM (PIM-1), based on tetramethyl-1,1′-spirobiindane, was reported[18] and up till now it is, together with its modifications, one of the PIMs with the best properties in terms of film building ability, stability, and flexibility.[94–96] Beside spirobisindane other centers of contortion were integrated in the backbone of PIMs, *e.g.* triptycenes,[97] spirobifluorenes[12] or ethanoanthracenes (Fig. 5).[98]

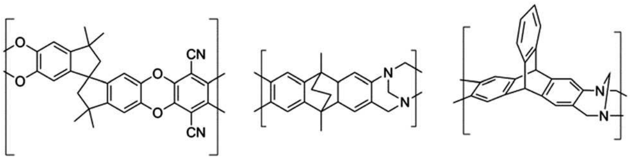

Fig. 5 Structure of spirobisindane, ethanoanthracene and triptycene based PIMs.

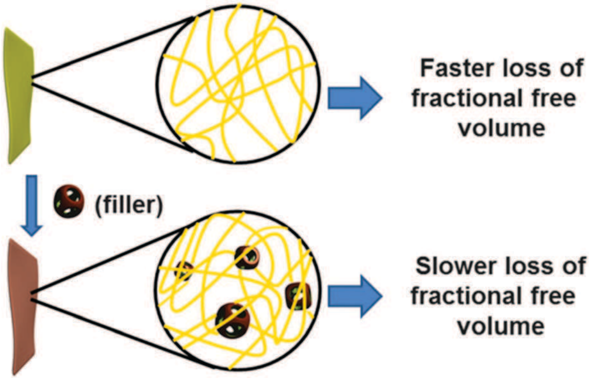

Fig. 6 Schematic illustration of effect of nanofillers on mixed matrix membranes. Reproduced from ref. 105 with permission from Royal Society of Chemistry, copyright 2016.

PIM-based films show very interesting properties in transport and separation of ions or gases. Membranes based on PIM-1 show excellent gas selectivity that lies above the Robeson upper bound of 2008, other examples of PIMs even meet the requirements of the 2015 upper bound.[99] However, one drawback of these systems is the enormous aging effect and unfortunately the performance cannot be sustained in long term experiments. Most probably a densification of chain packing occurs which leads to a decrease of free volume and gas permeability.[100]

To sustain the performance of the membranes over a longer period of time different approaches have been studied. One way to stabilize the polymer matrix is by introducing several different kinds of fillers to design mixed matrix membranes (MMMs). Main examples for fillers that are used for MMMs are porous materials like MOFs,[101–103] carbon nitrides[104] but also microporous polymer networks[105–107] and related molecular fillers like organic cages (Fig. 6).[108] By introducing these fillers the aging effect can be enormously reduced which allows super glassy polymers to be revisited for commercial application in gas separations again. It is assumed that by adding an ultraporous additive, some chains of the glassy polymers are absorbed within the pores of the additive which is holding the chains in their open position.[106] Therefore the low density and permeability of the PIM is maintained over a longer period of time. To achieve a substantial stabilization of the membrane the compatibility of glassy polymer and filler, the surface chemistry, molecular structure and size and rigidity need to be controlled.

A second way to stabilize PIM membranes is by cross-linking of the polymer chains. This can be done *via* thermal processing,[109,110] UV treatment,[111] molecular or polymeric azides[112,113] or complexation with multivalent metal ions.[114] The resulting crosslinked polymers also show enhanced stability over a longer period of time.

Additionally PIMs can be strengthened by stiffening their backbone. One example reported is the incorporation of porous bowl structures like beta-cyclodextrin. The interactions between beta-cyclodextrin and PIM can also restrict chain movement and make ultrafine micropores difficult to collapse. Thus a greater resistance to physical aging than PIM membrane can be achieved.[115] In 2013 McKeown *et al.* introduced a bridged bicyclic amine 2,8-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine, commonly called

Tröger's base, as bridge between the contortion centers, which showed excellent permeation and selectivity in gas separation, while the long term stability could also be enhanced.[98] Since then several studies on PIMs based on Tröger bases have been published, showing the potential of this system.[116–118] With the development and innovations in the field of soluble PIMs in the last couple of years these polymers are being reconsidered for commercial application again. Recently one PIM was even commercialized as sensor in the visual lifetime indication of organic vapor filters.[119]

3. π-Conjugation in microporous polymers

3.1 Conjugated microporous polymers (CMPs) for organic electronic devices

One unique feature of microporous polymers is that their backbone can be fully π-conjugated, so that they resemble porous organic semiconductors.[4,39,88] Indeed, one of the prerequisites for polymer networks to achieve high surface areas is a rigid backbone, direct coupling of aromatic moieties is a common method for generation of microporous polymers. Without counting exactly it can be estimated that the number of conjugated microporous polymers (CMPs) far exceeds the ones which are not conjugated. Thus the here presented materials are rather the rule than the exception. The conjugated nature and semiconducting properties of CMPs together with their high surface area and porosity makes them interesting for a number of applications. As most of these CMPs show strong photoluminescence, optical sensing of molecules or metal ions entering the porous framework have been frequently exploited.[120–126] Another obvious idea would be to use CMPs in organic electronic applications, drawing on the large work done on conjugated, semiconducting polymers for *e.g.* organic light-emitting diodes, solar cells or field effect transistors. Indeed, three-dimensional, branched or star-shaped conjugated molecules have been intensively investigated for such applications[89] and these molecules are literally just one further covalent bond away from creating a CMP. Many tectons used for such molecules have later been applied to create CMPs, such as 1,3,5-substituted benzene, spirobifluorene, carbazole or triphenylamine moieties. However, it must be stated that CMPs have so far not made a breakthrough in organic electronics. The main reason here is the problem regarding processing of microporous polymer networks in general. Thin homogeneous films of the conjugated material are required for application in electronic devices but with some exceptions this cannot be achieved by the highly crosslinked and entirely insoluble polymer networks. The main challenge so far is therefore not the performance testing of CMPs but the generation of thin films on electrodes of these materials.

Thiophene- and carbazole-based building blocks are therefore interesting choices as these tectons can be electropolymerized to create thin films on electrodes.[56,126] For the first reliable measurements of the surface areas of such films, which is hard to achieve as very low sample masses are naturally obtained, krypton sorption was used to determine a surface area of up to 1300 $m^2\ g^{-1}$ in a carbazole based CMP film, which compares nicely to the surface area found in a related bulk material.[126,127] These values could be even increased applying thiophene based monomers ($>2000\ m^2\ g^{-1}$).[31] Notably, the surface area of such films depends strongly on the solvents in which the electropolymerization is carried out. Addition of boron trifluoride diethyl etherate (BFEE) to dichloromethane (DCM) yields the formation of films with optimized porosity. A review on the generation of thiophene and carbazole-based CMP films prepared by electropolymerization has been published by the Scherf group recently and thus just some highlights in applications of these films are repeated here.[56] Both carbazole and thiophene-based thin films of CMPs have been applied for sensing applications, for example as electrochemical detectors or luminescent sensors for explosive nitroaromatic compounds (*e.g.* nitrobenzene, dinitrotoluene and trinitrotoluene), showing a significantly increased current response or a quenched luminescence compared to a reference electrode without film deposition.[31,126–128] Furthermore CMP thin films derived from dithiothiophene by electropolymerization could be reversibly oxidized and reduced, yielding a pronounced electrochromic effect.[129]

CMP films from thiophene-based tectons have been further applied as hole conducting materials to create bulk heterojunctions with fullerenes incorporated into the pores and applied in a photovoltaic device (Fig. 7).[130] CMP-fullerene blends, thus not as thin films, have also been prepared from low band-gap CMPs based on benzothiadiazole (BTZ) and thiophenebenzothiadiazole (TBT) functional groups. The polymers exhibit broad light absorption covering the whole visible light region and fluorescence quenching can be observed by incorporation of fullerenes exemplified for a donor–acceptor polymer with alternating BTZ and triphenylamine moieties.[131] Ma and co-workers polymerized carbazole-based tectons for the generation of microporous films, which were subsequently used as anode interlayers in organic light emitting diodes (OLEDs) and solar cells (OSCs).[132] An OLED with the CMP interlayer showed a maximum luminous efficiency, which was 37% higher than in a comparable OLED without an interlayer. In OSCs power-conversion

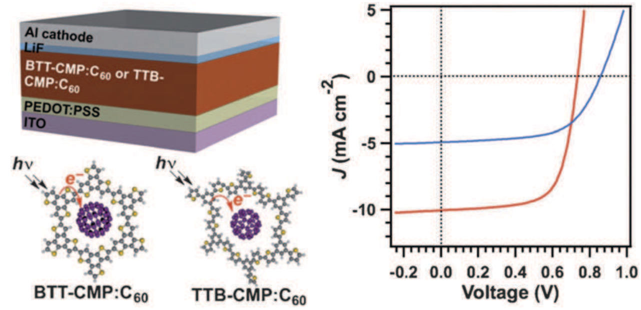

Fig. 7 Left: Device configuration of solar cells and charge separation process using thiophene based CMP with incorporated C60 as photoactive layers. Right: *J–V* curves of the solar cells. Reproduced from ref. 130 with permission from Wiley-VCH, copyright 2015.

efficiencies of 8.42% have been reached *vs.* 5.68% for the OSC without an interlayer.[133] Jiang *et al.* later built CMPs from carbazole-functionalized tris(2,3,5,6-tetramethylphenyl)borane (TPB) by electropolymerization, which acted as hole- and electron-selective electrode interlayers between the active layers and conducting electrodes that control the transport of charge carriers in and out of devices. The work function of these polymers could be tuned by ionic ligation on the central boron atom and further by electrooxidation, switching the networks from electron to hole conductors.[134]

3.2 CMPs for photocatalytic hydrogen evolution

Within the last few years the interest in the use of CMPs for photocatalytic applications has risen tremendously.[79] First, the research on metal-free photocatalysts for water splitting has gained momentum with the discovery in 2009 that polymeric carbon nitride can act as a photocatalyst for hydrogen and oxygen generation from water.[135] In the following years more than one thousand papers have appeared on the usage of polymeric carbon nitride for photocatalytic applications. It is thus more than understandable that researchers also started to consider other purely organic semiconductors for use in this application; and CMPs seem to be a particular good choice in this respect. Another reason for the interest in applying CMPs for this application is even simpler – testing photocatalytic performance can be done with powders, *i.e.* the morphology in which CMPs are normally observed after synthesis. Thus no further special preparations were required, the main challenge for application in electronic devices as seen above, and the powders prepared during bulk synthesis can be directly tested as dispersion in a photocatalytic reactor.

Polymeric carbon nitrides are prepared by thermal condensation of nitrogen-rich molecules such as cyanamide, dicyandiamide, melamine or urea at 550 °C. It is an organic semiconductor with an intense yellow color and a band gap of 2.7 eV allowing the use of parts of the visible spectrum for the generation of charge carriers.[135,136] Soon after the first activity of photocatalytic hydrogen production was presented from bulk polymeric carbon nitride, a variety of optimizations were carried out to enhance its performance. Porous polymeric carbon nitrides have been prepared, which indeed showed largely enhanced photocatalytic activity.[137–139] Porosity in these materials mainly by hard templating, *i.e.* replication of nanostructures of silica for example.[140] It should be noted however, that the explanation for the increased activity is not as simple as just being caused by the increased amount of active sites at an increased surface area, but also the higher amount of amine functionalities, increased charge carrier stability and an optimized packing of the polymer layers have been identified as playing a crucial role.[141,142]

In addition, very often co-monomers, *e.g.* with other heteroatoms than nitrogen have been added to the carbon nitride synthesis to tailor the band gap by the formation of copolymers or heteroatom-doped carbon nitrides.[143–146] However, here the high temperatures needed for carbon nitride synthesis are a serious disadvantage as the chemical structure of organic substances can be difficult to control when heating to 550 °C for several hours. Indeed some of the suggested structures for heteroatom-doped carbon nitrides seem rather questionable and hard to be proven by analytical methods. In this respect CMPs are indeed an interesting opportunity, as they are prepared in solvents and at ambient temperature, so that in most cases it can be fully predicted which organic moieties are present in the conjugated backbone. Tailoring of band gaps and enhancing charge carrier mobility and lifetime seem indeed to be much more feasible in these materials.

The first report on microporous polymer networks used for photocatalytic hydrogen generation from water under visible light was motivated by the performance of polymeric carbon nitrides as the same organic moiety, namely a heptazine (C_6N_7) unit was applied as structure directing tecton. While in the polymeric carbon nitride these heptazines units are formed during a thermal reaction and are connected by secondary amines, in the heptazine based microporous polymers (HMPs) a trichloroheptazine was connected *via* diaminobenzene.[147] The yellow precipitate showed a low surface area (185 $m^2\ g^{-1}$) compared to other CMPs probably due to the flexibility of the secondary amines in the backbone which can interact with each other. Photocatalytic hydrogen production was achieved with HMP-1, however with relatively low values. The activity of HMPs could be largely increased by connecting the heptazine moieties with a donor–acceptor type structure using benzothiadiazole moieties within the linkers.[148] This approach thus shows that the controlled synthesis of CMPs can indeed be used to tailor their electronic properties and thus photocatalytic performance.

In the meantime, Sprick *et al.* reported the application of other CMPs for photocatalytic hydrogen production and thus opened the field to the conventional CMPs prepared by metal-catalyzed coupling reactions. In this work conjugated microporous co-polymers were prepared by a Suzuki–Miyaura coupling, yielding variable amounts of benzene and pyrene moieties within the backbone. Thus it was possible to tailor the optical band gap of the microporous polymers continuously from 1.94–2.95 eV, shifting the absorption over the whole visible spectrum (Fig. 8). It was furthermore shown that this band gap tailoring had a crucial effect on the catalytic performance, going through a maximum at 2.3 eV.[149] Following this work, several more CMPs have been suggested as interesting photocatalysts for hydrogen production, *e.g.* conjugated benzene and spirobifluorene,[150] benzodiazole[151] and triazine[152]-based networks.

An illustrative example to which level the tailoring of organic photocatalysts can possibly proceed was recently shown in the preparation of CMPs in which certain tectons as chromophores were connected with metal coordinating linkers, namely bipyridine (Fig. 9).[153] The latter was thought to coordinate and stabilize the used palladium co-catalysts and indeed increasing its amount in the network has a beneficial effect on the photocatalytic performance. This work thus picks up an idea, developed in recent years in the field of homogeneous photocatalysis, *i.e.* covalent attachment of a photosensitizer to a hydrogen evolving catalyst, just that this concept is now transferred to highly porous solids.[153]

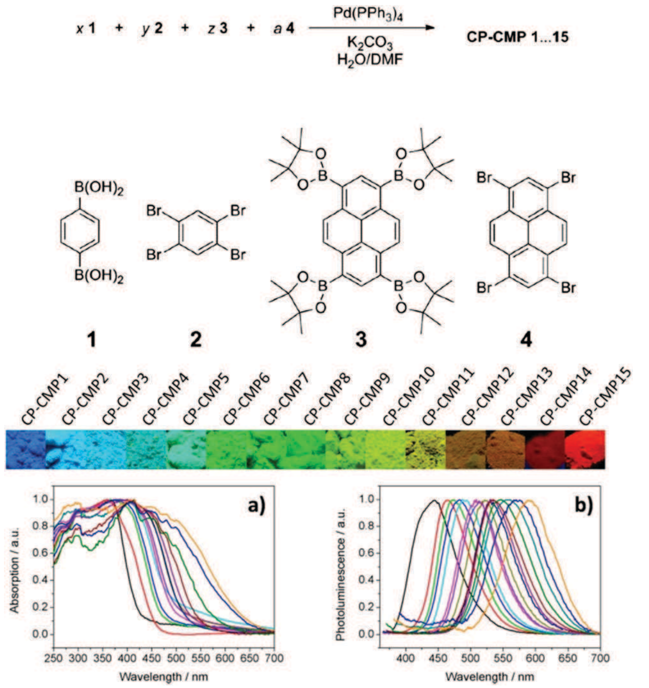

Fig. 8 Top: Continuous tuning of the photophysical properties of organic CMP based photocatalysts by statistical copolymerization *via* Suzuki–Miyaura polycondensation. Bottom: Photographs on top of CMPs imaged under irradiation with UV light and the UV-visible absorption and photoluminescence spectra at the bottom prove the fine tuning of band gap energy of the CMPs. Reproduced from ref. 149 with permission from American Chemical Society, copyright 2015.

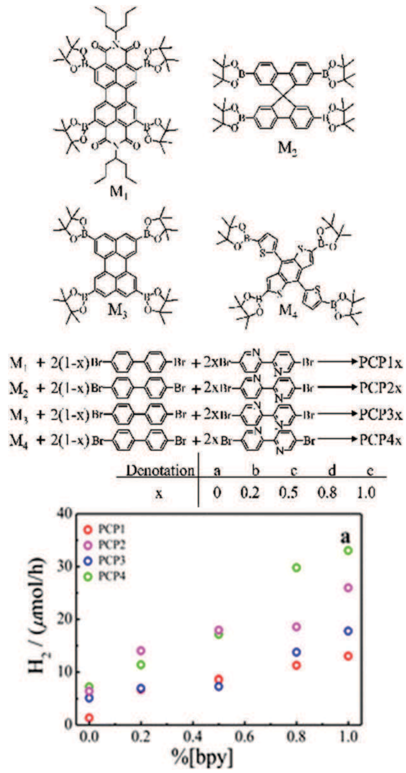

Fig. 9 Top: Structures of monomers of PCP photocatalysts prepared by Suzuki polycondensation. Bottom: Photocatalytic hydrogen production rates of PCPs with different bpy contents. Reproduced from ref. 153 with permission from American Chemical Society, copyright 2016.

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Given all these promising examples what is still missing is a judgement on the photocatalytic performance. Hydrogen evolution values up to 164 μmol h^{-1} have been reported,[153] but most published values are much lower and it seems there is still much room for improvement when applying CMPs as photocatalysts. Nevertheless given that the famous polymeric carbon nitride started from 8 μmol H_2 per h,[135] a value which is already outperformed by several CMPs, and can now (a suitable up-scaled setup provided) produce approx. 100 ml (∼4500 μmol) h^{-1} of H_2,[154] the investigation of photocatalytic hydrogen evolution on CMPs is still a highly promising field and further improvements are to be expected before long.

A much bigger problem seems to be how to judge and compare the different reported activity values. The final value of interest is of course the overall amount of hydrogen which can be produced per time. However, especially this value is highly dependent on sample mass, reactor setup, light source and applied filters and many other parameters and it can be assumed that one and the same material would produce different values when tested in different labs, a problem which CMPs share with the entire field of photocatalysis.[155] The often given amount of hydrogen per time and mass catalyst (mol h^{-1} g^{-1}) just helps on the first glance, as hydrogen production and catalyst mass do not follow a linear relation. Apparent quantum yields as another possible value to compare catalytic performance bears the same problems and is often not measured with a reliable protocol.[155]

For further progress it is of course also essential to think about the properties a CMP should exhibit to be a good photocatalyst and which could be further optimized. At first, a suitable band gap is indispensable and also a considerable accessible surface area seems to be beneficial for CMP-based photocatalysts. But some additional points should be considered. At first, most CMPs are rather hydrophobic and even float on water. How should then protons reach and be reduced on the CMP surface? It is noticeable that in some reports not pure water, but mixtures of water and an organic solvent are used or that relatively large amounts of the sacrificial electron donor, as well an organic molecule, is added to observe hydrogen production. Whether such mixtures could also be applied in real applications is questionable. Surface polarity of CMPs might therefore be another important point to be considered. It should also be noted that beside the semiconductor very often a co-catalyst for the hydrogen evolution reaction (HER) is needed, which usually consists of a noble metal. For some CMPs it was reported that they even work without any metal co-catalyst. In these cases the role of noble metal catalysts used in CMP synthesis, thus almost always present in the final CMP in small amounts,[153] has to be better understood.

It must also be asked, if a permanent surface area is actually needed for observing high photocatalytic performance. So far there seems to be no relationship between BET surface area and hydrogen evolution. Indeed, also networks with low or even no apparent surface area can swell in solution, thus there is no reason why a network whose surface area was measured in vacuum should give a reliable conclusion on the accessible sites in the liquid-swollen state. Indeed, several linear or planarized, thus non-crosslinked and non-porous conjugated polymers have been recently shown to exhibit comparable or even better photocatalytic activities than their microporous network counterparts.[151,156,157]

It is thus slightly surprising that so far no single paper on gas phase photocatalysis, *e.g.* CO_2 reduction has appeared as CMPs seem to be ideal candidates for such reactions. We anyhow predict that such a work on a photocatalytic gas phase reaction with will appear very soon.

3.3 CMPs for other photocatalytic reactions

While water splitting and selective CO_2 reduction can be seen as the Holy Grail in photocatalysis, it should not be forgotten that there are various other chemical reactions for which a photocatalytic process would be highly beneficial. Consequently, CMPs have been also tested for other photocatalytic applications.[158] Especially the ease of incorporation of photo-/electroactive organic moieties into the π-conjugated structures of CMPs allows tailoring the properties of these organic photocatalysts. In one of the first works regarding this application, thiadiazole-based CMPs have been used as heterogeneous photosensitizers for the generation on singlet oxygen within a continuous flow photoreactor.[159] Phthalocyanine based CMPs are as well active in singlet oxygen generation.[160] A CMP with benzodifuran moieties, formed *via* intramolecular cyclization after network formation, was as well used for the generation of singlet oxygen with subsequent oxidative conversion of amines in symmetrical imines. CMPs with BODIPY moieties have been applied for the selective oxidation of sulfides[161] and thioxanthone based CMPs were used as photoinitiators to initiate free radical and cationic polymerizations of vinyl monomers and cyclic ethers.[162] Even typical dyes such as rose bengal[163] or photosensitizers such as Ru-[164] or Ir-complexes[165] have been immobilized in CMPs to generate efficient heterogeneous photocatalysts (Fig. 10).

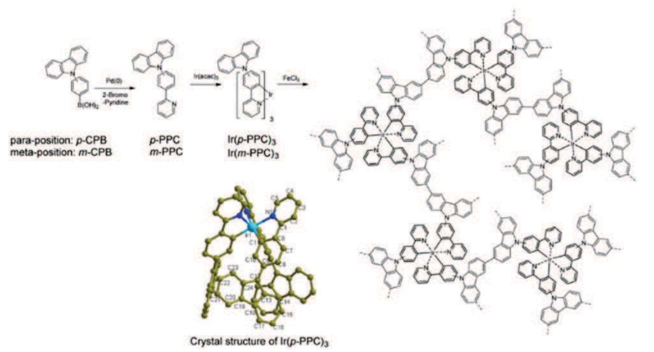

Fig. 10 Immobilization of an Ir-photosensitizer into a microporous conjugated polycarbazole polymer *via* $FeCl_3$-promoted oxidative coupling. The polymers proved to be active and recyclable as heterogeneous photocatalysts in the aza-Henry reaction. Reproduced from ref. 165 with permission from Royal Society of Chemistry, copyright 2016.

Furthermore, Zhang and co-workers have applied different CMPs for a range of organic reactions, for example the oxidation of amines and sulfides,[166] photooxidative cyclizations,[167] reduction of metal ions (Cr(VI)–Cr(III))[168] as well as Suzuki type couplings.[169,170] Another recent work showed the versatility of carbazole based CMPs in photocatalytic applications, as one single carbazole-based CMP was able to photocatalyze a range of reactions, including dehalogenation of phenacyl bromide, oxidative hydroxylation of arylboronic acids, alpha-alkylation of aldehydes, oxidative coupling of primary amines, aerobic dehydrogenation of nitrogen heterocycles, and selective oxidation of sulfide using molecular oxygen and visible light.[171,172]

4. Functional networks through incorporating main group elements in microporous polymers

As mentioned in the introduction, compared to other microporous organic chemistry-based materials, microporous polymers are unique in that they can exist as pure hydrocarbon materials and completely forgo the use of metals or heteroatoms. Therefore, the material surfaces are covered by π-electrons and highly aprotic hydrogen atoms. The overall absence of disruptive effects gives rise to a relatively even distribution of electron density throughout the polymer skeletons and largely unpolar surfaces, which only display weak interactions with guest molecules. Correspondingly, even the highest surface area porous polymers[65,67] display relatively small uptake capacities regarding most gases compared to functionalized networks.[173] As mentioned above, starting from these high surface area polymers, many postsynthetic modifications were explored to increase their affinity towards guest molecules,[70,174] which consequently allows a precise evaluation of the effect of the respective functional groups towards gas molecules.

Poly(aryleneethynylene) networks, a subclass of CMPs, are somewhat special in that they contain triple bonds which have localized high π-electron densities, which offers relatively strong interactions with guest molecules such as H_2 and CO_2 compared to polymers solely comprising benzene rings, but the strength of the interaction still lies in the realm of physisorption. Their eligibility for H_2 sorption has been shown experimentally as well as computationally.[5,9,175]

Selective incorporation of heteroatoms can provide disruptions in the otherwise homogeneous electron density and have beneficial effects on gas sorption, depending on the nature of the adsorbate. Donor moieties with lone electron pairs such as phosphines or amines provide nucleophilic sites capable of strong interactions with electron-deficient moieties, *e.g.* CO_2.[68,176]

Early attempts to create main group element-centered polymers were effected *via* nucleophilic substitution of main group element chlorides, affording the so-called element-organic frameworks (EOFs) with BET surface areas between 260 and 1050 $m^2\ g^{-1}$.[177–179] The step-wise nature of the polymerization reaction eventually leads to steric congestion around a significant part of the partially substituted main group element nodes upon which further reaction is precluded. Following this direct incorporation approach, Uptmoor *et al.* synthesized a tetrahedral tin-based monomer to generate a homocoupled CMP network following a reported procedure for the direct coupling of alkynes.[180] This material was not studied for its gas uptake properties but was readily digested by acid treatment and, by analysis of the fragments, gave very detailed insights into the polymerization mechanism of PAE networks.[181]

In 2013 Zhang *et al.* polymerized tris(4-chlorophenyl)-phosphine to obtain polymeric triphenylphosphine, which could be oxidized to polymeric triphenylphosphine oxide.[176] The networks exhibited BET surface areas of 1284 (PP-P) and 1353 $m^2\ g^{-1}$ (PP-PO). Interestingly, the oxidized polymer displayed stronger affinity towards the adsorption of CO_2 than the reduced form (3.83 *vs.* 2.46 mmol g^{-1}). Furthermore, the incorporation of phosphorus atoms enabled efficient formation and deposition of Pd nanoparticles in the polymeric triphenylphosphine which yielded a functional Suzuki cross-coupling catalyst and showed the ability of these materials to serve as a support for catalytically active nanoparticles. Fritsch *et al.* used a conceptually similar material, which was synthesized based on the EOF approach, to obtain a microporous polymer network with a BET surface area of 458 $m^2\ g^{-1}$.[179] This material was used as a support for Pd and Rh to obtain a solid catalyst for transfer hydrogenation of cyclohexanone.

Recently, Trunk *et al.* synthesized a series of microporous polymer networks based on sterically demanding triphenylphosphine derivatives to lessen the nucleophilicity of the phosphorus lone pair and facilitate the use of the networks as basic components in semi-immobilized frustrated Lewis pairs (FLP), for the first time making the transition from this novel class of molecular catalysts to solid organic materials (Fig. 11).[182] The ability of solid FLPs to cleave dihydrogen at ambient temperature and low pressure was demonstrated *via* isotope scrambling experiments.

Nitrogen containing porous polymers for the capture of CO_2 are great in number and the subject of reviews of their own.[183,184] The majority of materials incorporates amine functions either as aromatic (aniline-like) amino groups or triarylamine linkages. The binding affinity of amines to CO_2 is greatly enhanced when the amine is not directly attached to an aromatic system but separated by short, aliphatic spacer. Such systems are best accessed by postsynthetic modification since amines are strong ligands and tend to affect the polymerization when present in the monomer itself.[68,174]

Far less is known about the incorporation of electron acceptor moieties. Main group elements such as boron in their neutral form have empty orbitals and can accept lone pairs of donating adsorbates. This feature is especially interesting for optical or electronic properties as it allows for the transfer of electron density from neighbouring aromates or donor moieties. The group of Mu prepared a tris(tetramethylphenyl)borane containing polymer *via* alkyne homocoupling. Despite the incorporation of boron sites, the uptake capacity for CO_2 was comparable with reported boron-containing COFs at the time.[185] Suresh *et al.* coupled tris(tetramethylphenyl)borane *via* Sonogashira coupling with a biphenyl unit to obtain a microporous polymer network with a surface area of 390 $m^2\ g^{-1}$ which could be used as a Lewis acidic sensor for the detection of fluoride ions.[186] Moreover, combining donor and acceptor moieties within one material can yield interesting electronic properties for optical applications or sensing. The separate functionalities can be combined in one monomer to create an intrinsic function, which is then polymerized, or an alternating copolymerization of building blocks with contrasting functionality can polymerized to synergistically

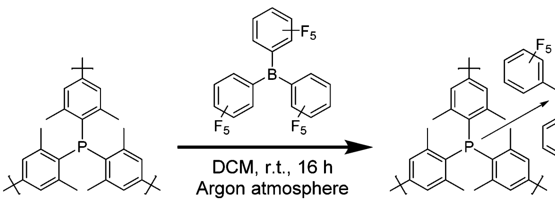

Fig. 11 Synthesis of a semi-immobilized frustrated Lewis pairs (FLP) by impregnation of a triphenylphosphine based microporous polymer with tris(pentafluorophenyl)borane. Reproduced from ref. 182 with permission from American Chemical Society, copyright 2017.

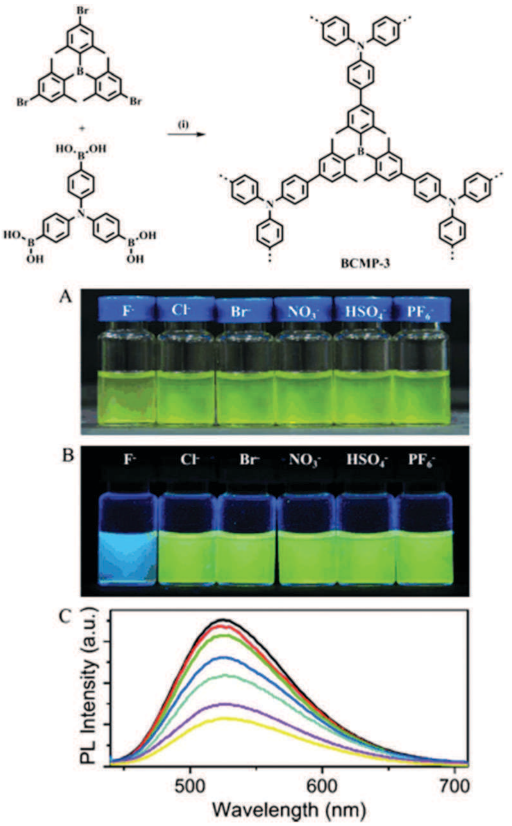

Fig. 12 Top: Synthesis of a boron and nitrogen-containing microporous network and bottom: photographs and photoluminescence spectra of THF suspensions of the polymer framework, showing the size-selective fluorescence quenching by fluoride anions. Reproduced from ref. 189 with permission from Wiley-VCH, copyright 2015.

enhance each other, with an ''emerging function''.[187] In 2013, Feng *et al.*[188] and Mu *et al.*[185] were the first to couple tritopic, sterically demanding tris(tetramethylphenyl)borane and nitrogen containing monomers to form porous π-conjugated donor–acceptor polymers *via* Suzuki coupling and Sonogashira coupling, respectively. The resulting materials featured BET surface areas between 600 and 1300 m^2 g^{-1} and displayed strong fluorescence properties as well as capability of fluoride collection.

Two years later, Mu *et al.* also coupled a less sterically encumbered tris(dimethylphenyl)borane building block to a triarylamine-based unit *via* Suzuki coupling.[189] The resulting polymer exhibited a surface area of 950 m^2 g^{-1}. It was found to act as a highly selective sensor towards fluoride over other common anions yet easily recyclable by stirring in THF solutions of $BF_3 \cdot OEt_2$ as fluoride scavenger (Fig. 12).

5. Microporous polymers with permanent ionic charges

Beside the introduction of heteroatoms, the presence of permanent ionic charges represents a versatile method to further introduce functionality into microporous polymers. Ionic metal organic frameworks (iMOFs) represent a crystalline class of charged microporous networks with many interesting applications and have been intensely investigated in recent years.[190] These studies greatly motivate to design covalently bound microporous materials with permanent ionic charges.[92] The incorporation of a positive or negative charge into the polymer backbone making the structure ionic can happen in several ways: (i) starting from already charged monomers or tectons which can be linked together to afford a charged scaffold, (ii) using neutral monomers which upon building further covalent bonds will lead to charged functional groups and generate an ionic backbone or (iii) synthesize a neutral porous network where a (permanent) charge is then introduced post-synthetically.

5.1 Cationic microporous polymers

One option to create permanently charged cationic networks is the introduction of phosphonium moieties as building blocks. By synthesizing tetrakis-(4-chlorophenyl)phosphonium Zhang *et al.* were able to generate a cationic microporous phosphonium network by the Yamamoto homo-coupling reaction.[191] The polymer exhibited a S_{BET} of 650 m^2 g^{-1}, however, magic angle spinning ^{31}P solid state NMR revealed that many of the phosphonium linkages were cleaved during the reaction affording a phosphonium to phosphine ratio of approximately 3 : 2. The Br$^-$ containing cationic network was successfully employed as a catalyst for the conversion of 2-(phenoxymethyl)oxirane to the cyclic carbonate in the presence of CO_2. By ''diluting'' the cationic charges within a MPN the first two cationic microporous networks were synthesized, in which the phosphorus moiety is entirely present as phosphonium cation. Tetrakis-(4-bromophenyl)phosphonium was polymerized in a Yamamoto copolymerization with tetrakis-(4-bromophenyl)methane and in a Sonogashira–Hagihara cross coupling with 1,3,5-triethynylbenzene to afford the cationic microporous polymers CPN-1-Br and CPN-2-Br with S_{BET} of 1455 m^2 g^{-1} and 540 m^2 g^{-1}.[192] Here too, a simple anion exchange was performed to introduce chlorine counter anions resulting in a rise in S_{BET} for CPN-1-Cl to 1540 m^2 g^{-1}. The investigated CO_2 uptakes for the charged networks proved to increase by 40% compared to the uncharged microporous analog PAF-1[67] even though the S_{BET} of the latter is by far the higher. In a different approach Zhang *et al.* were able to generate a series of cationic microporous polymers *via* Friedel–Crafts reactions of asymmetric phosphonium molecules with benzene,[193] and Ma *et al.* used a tetrahedral phosphonium building block in a radical polymerization procedure with AIBN (azobisisobutyronitrile) to generate a polymer with a S_{BET} of 758 m^2 g^{-1} and with pores in the microporous as well as mesoporous range.[194] Anion exchange was performed with this polymer introducing a highly active peroxotungstate anion $[W_2O_{11}]^{2-}$ into the cationic network as the balancing charge. The resulting material was proven to be a very active phase transfer catalyst for the catalytic epoxidation of olefins as well as for the oxidation dibenzothiophene with equivalent H_2O_2.

Cationic phosphonium networks can also be generated by post functionalization. Recently Zhuang *et al.* have synthesized a porous non-ionic phosphine network through radical polymerization with AIBN.[195] The network was then charged by generating phosphonium species through protonation of the phosphine moieties. Solid state ^{31}P-NMR spectroscopy confirmed the completion of conversion and total lack of residual phosphine species.

A large number of cationic microporous polymers are composed of iminium linkages and in some cases can be of crystalline structure due to a reversible condensation bond-forming process. By condensation of a charged ethidium bromide building block Zhu *et al.* synthesized a cationic covalent organic framework EB-COF-X (X: counter anion),[196] which after anion exchange with poyloxometallate (POM) anions $PW_{12}O_{40}{}^{3-}$ exhibited high proton conductivities of 3.32×10^{-3} S cm^{-1} with a relative humidity of 97% making it comparable if not better than many of the proton conducting MOFs (Fig. 13). The generation of a positive charge into 2D sheets will lead to an exfoliation of the sheets due to electrostatic repulsion. Based on this strategy Banerjee *et al.* synthesized ionic covalent organic nanosheets (iCONs) by reacting a planar C_3 symmetric cationic triaminoguanidinium halide TG_X with 1,3,5-triformylphloroglucinol.[197] The obtained materials exhibited low crystallinity with a major broad peak at $2\theta = 27.3°$ indicating poor π–π stacking between the layers due to the loosely bound halogen anions and positive charge of the guanidinium units.

Imidazolium ions are a class of organic cations very often found in ionic liquids, thus a rich chemistry is already reported on their chemical modification and functionalization. Not surprisingly, imidazolium ions have been also frequently introduced into microporous polymers. For example, in 2009 Dai *et al.* showed that cationic microporous networks can be formed by performing a salt melt catalyzed trimerization of

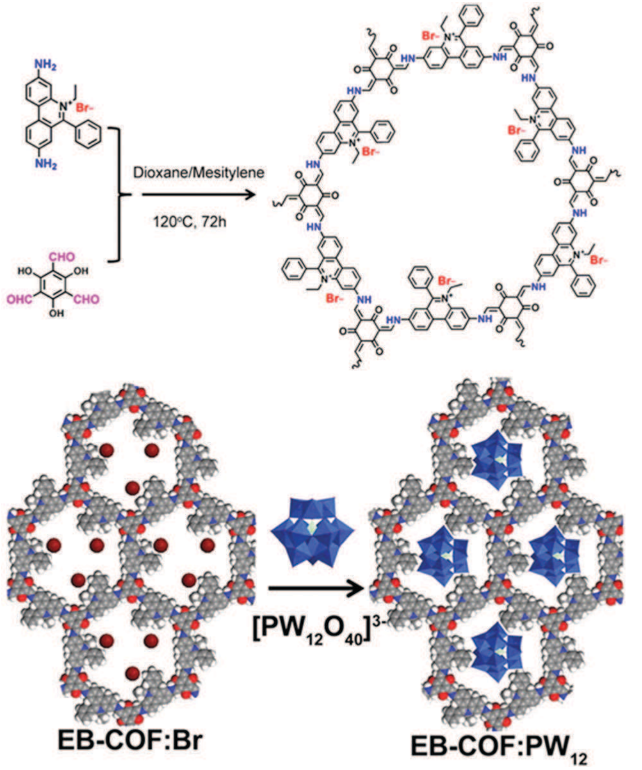

Fig. 13 Synthesis of cationic ethidium bromide covalent organic frameworks (EB-COF) where polyoxometallates were introduced by anion exchange post-synthetically. Reproduced from ref. 196 with permission from American Chemical Society, copyright 2016.

carbonitriles tethered on cationic imidazolium ionic liquid (IL) precursors.[198] The obtained materials exhibit typical microporous behavior with a sharp increase at low relative pressures and S_{BET} differing from 2 m^2 g^{-1} to 814 m^2 g^{-1} varying on the counteranion of the IL precursor later located inside the charged framework. The cationic structure exhibited very good capacity for adsorption of perrhenate anions ReO_4^- which can be directly related to the adsorption of the harmful Tc^{99} isotope. Starting from Imidazolium cations Son *et al.* reported a cationic microporous polymer synthesized by a Sonogashira–Hagihara cross-coupling reaction of the tetrahedral building block tetrakis(4-ethynylphenyl)methane with the cationic 1,3-bis(2,6-diisopropyl-4-iodophenyl)imidazolium chloride.[199] The network showed a good activity for the conversion of CO_2 into cyclic carbonates with turn-over frequencies (TOF) ranging from 92–142 h. Similar imidazolium containing polymers were reported by Wang *et al.* where the imidazolium building blocks were incorporated inside the microporous backbone by either a palladium catalyzed Suzuki cross-coupling reaction or by a Yamamoto reaction with $Ni(COD)_2$ as a reagent.[200,201] The cationic networks proved to be effective for the adsorption and removal of $Cr_2O_7^{2-}$ from water surpassing most other materials such as cationic MOFs or macroporous anion exchange resins.

Imidazolium ions were also incorporated in microporous polymers as intermediate structure to generate N-heterocyclic carbenes within the polymer backbone.[199,202,203]

Recently Coskun *et al.* reported a series of cationic microporous networks based on bipyridinium salts as monomers which were reacted into a porous polymer by a Sonogashira–Hagihara cross-coupling reaction with tetrakis(4-ethynylphenyl)methane.[204] The porous cationic polymers exhibited a high affinity towards CO_2 with isosteric heats of adsorption between 28.5 and 31.6 kJ mol^{-1} and good CO_2/N_2 selectivity. Additionally, the networks proved to be active as organocatalysts for the conversion of CO_2 into cyclic carbonates. By using a similar cationic viologen monomer D'Alessandro *et al.* synthesized two charged microporous networks by Sonogashira–Hagihara cross coupling of 1,1′-bis(4-bromophenyl)-4,4′-bipyridinium chloride with either tris(*p*-ethynylphenyl)amine or 1,3,5-tris(4-ethynyl)benzene.[205] By combining the electron accepting viologen with the electron donating triarylamine the obtained materials were donor–acceptor-polymers with differential electronic and physical properties in their distinct redox states. Depending on the redox state and therefore charge of the network the host guest properties can be altered having a visible impact on S_{BET}, pore size and more interestingly on gas uptake properties of CO_2 and H_2 as well as CO_2/N_2 selectivity and isosteric heats of adsorption of CO_2.

Porous organic polymers from triazatriangulenium salts (TAPOPs) were developed *via* oxidative polymerizations and showed interesting properties for optical sensing of gases.[206] Recently Chen *et al.* reported a series of porous cationic frameworks (PCF) by crosslinking inorganic polyhedral oligomeric silsesquioxane (POSS) units with different ratios of the non-ionic N-heterocycle 4,4′-bipyridine.[207] The N_2 sorption properties of the obtained materials indicated the presence of micro- as well as mesopores with S_{BET} ranging between 448 and 942 m^2 g^{-1}. The materials were tested for anion exchange in which the Cl^- anions present after synthesis were exchanged with the catalytically active polyoxometallate anions $PMo_{10}V_2O_{40}^{5-}$ (PMoV) resulting in a drop of S_{BET} as well as of pore size and volume. The PMoV immobilized materials PMoV@PCIF were then successfully tested as efficient heterogeneous catalysts for the aerobic oxidation of benzene to phenol and the H_2O_2-mediated oxidation of cyclohexane to cyclohexanol and cyclohexanone (KA oil).

5.2 Anionic microporous polymers

In contrast to the cationic networks, anionic microporous polymers are much less frequent due to the lack of negatively charged building blocks available for a porous structure formation. Negatively charged porous networks can be considered as organic zeolites and therefore bear great potential for many applications such as catalysis, sensing as solid electrolytes for modern battery applications. Weakly coordinating anions (WCAs) protrude as versatile molecules for the introduction of a negative charge into a porous network as they consist of organic anions where the negative charge is delocalized over non-nucleophilic, chemically robust moieties that lack an accessible basic site.[208] Unlike tetraphenylmethane, tetraarylborates consist of an anionic borate core while maintaining a three dimensional and rigid structure perfectly suited as a tecton for the formation of a microporous polymer. Based on

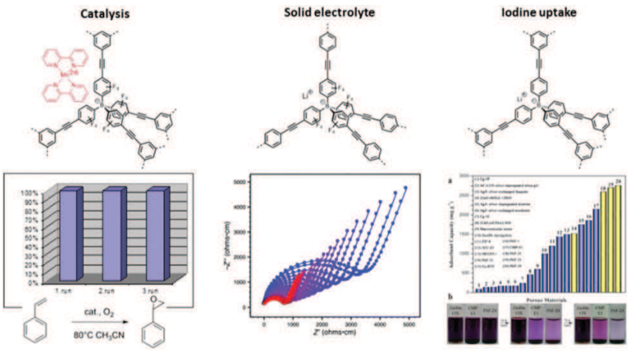

Fig. 14 Examples of anionic tetraarylborate based microporous polymers and their applications in catalysis (a), as single ion conducting solid electrolytes (b) and for iodine capture (c). Reproduced and adapted from ref. 76, 209 and 210 with permission from Wiley-VCH, copyright 2013 and 2015; Royal Society of Chemistry, copyright 2015.

this strategy Fischer *et al.* reported the synthesis of an anionic microporous polymer by reacting the WCA salt lithium tetrakis-(4-bromotetrafluorophenyl)borate with triethynylbenzene through a Sonogashira–Hagihara cross-coupling reaction (Fig. 14).[76] The network exhibited a S_{BET} of 890 $\mathrm{m}^2\ \mathrm{g}^{-1}$ and it was possible to exchange metal cations inside the network post-synthetically by cation exchange where Li was exchanged with Na and effects on S_{BET} could be observed. By introducing a catalytically active, cationic Mn–bipy complex the network could be applied for a catalytic epoxidation of styrene proving the viability of such a network for immobilizing molecular catalysts, this time not by covalent attachment of the catalyst to the polymer backbone but by Coulombic interaction with the anionically charged network. Similar microporous borate networks were investigated by Long *et al.* Here too, lithium cations were introduced inside the anionic polymers post-synthetically and the structures were tested for lithium conductivity showing promising potential for an application as solid electrolytes in lithium ion batteries.[209]

In an analogous approach Zhu *et al.* reported the synthesis of anionic microporous borate based networks based on unfluorinated tetraphenylborate WCAs (Fig. 14).[210] The negatively charged polymers exhibited moderate S_{BET} ranging between 82 and 262 $\mathrm{m}^2\ \mathrm{g}^{-1}$ and proved to be applicable for the capture of volatile iodine.

Apart from the Sonogashira–Hagihara coupling reaction other transformations are possible to generate anionic microporous structures. Dai *et al.* were able to generate an anionic PIM like structure based on tetrakis(pentafluorophenyl)borate by reacting it with a highly contorted tetrahydroxy spirobisindane moiety in a mechanochemical procedure.[211]

WCAs such as the above mentioned tetraphenylborates represent a practical way to prepare anionic microporous systems from rigid anionic precursors. By using the Lewis acidic borane a negative charge is precluded but the possibility to build rigid and porous scaffolds still persists due to geometry of triphenylborane moieties. Lewis acidic boron centers appear very suitable for many applications such as chemical sensing or organic electronics. Furthermore, a borane inside the polymer backbone can be transformed into a negatively charged borate post-synthetically. Jiang *et al.* developed microporous polyborane carbazol films through electropolymerization.[134] By ligating the borane centers with F^- post-synthetically an anionic FPBC film was obtained and further functionalized through electro-oxidation. A similar strategy was very recently applied by Feng *et al.* generating a non-ionic borane network and afterwards ligating the boron centers with F^- to obtain a permanently anionic microporous polymer. After loading the network with cobalt cations the network proved to be very active for homo-coupling reactions of Grignard magnesium aryl compounds.[212]

6. Conclusion

This review article presents some of the recent trends and challenges for the emerging materials class of microporous polymers. The topics described in this article are certainly chosen in a highly subjective manner; however we tried to mainly focus on identifying and describing the unique properties and advantages of microporous polymers. While high surface areas and chemical and thermal stabilities, based on the entirely covalent bonds, are probably the first features which come to mind when listing the advantages of microporous polymers, these properties can be also found in other microporous materials such as MOFs, activated charcoals or zeolites. However, the possibility to produce solvent processable microporous polymers or to generate thin films on electrodes by oxidative polymerizations, to make use of extended π-conjugated backbones in organic electronics or photocatalysis, to introduce distinct functional groups in an otherwise non-functional environment and finally to create weakly coordinating, *i.e.* permanently charged networks in which the counterions can be exchanged altering the overall properties of these materials – all this makes microporous polymers an exciting field for further research.

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