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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.

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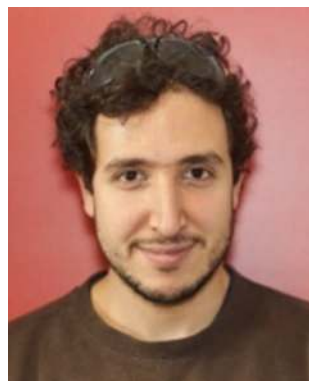
1. Introduction

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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Nicolas Chaoui

Nicolas Chaoui studied chemistry at the Technische Universität Berlin. After completing a diploma thesis in the department of organic chemistry he joined the group of Prof. Arne Thomas for his PhD studies where he is currently working on charged microporous polymers and their application in gas storage and catalysis.



Matthias Trunk

Matthias Trunk received his BSc in Chemistry and Biochemistry in 2010 and his MSc in Chemistry in 2012 from Ludwig-Maximilians-Universität München. In 2013 he joined the group of Prof. Dr Arne Thomas where he is currently working on his PhD project. He is interested in developing novel microporous polymer networks for gas storage and catalytic applications.

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

9 Within the last 10 years the field of microporous polymers
 10 has proliferated tremendously and thus the question has to be
 11 asked, what makes these materials unique and distinguishes
 12 them from other well-developed microporous materials. Chemical
 13 and thermal stability along with the possibility to introduce
 14 organic functionalities and π -conjugated backbones into high
 15 surface area materials have been frequently claimed as major
 16 advantages of microporous polymers compared to other microporous
 17 materials. However, we think it is advisable not to be too general
 18 in defining the distinct features and

19 beneficial properties of microporous polymers. Especially when
 20 named as advantages in comparison to other microporous
 21 materials such general statements might fail entirely. It is
 22 undeniable that a zeolite has a much higher thermal stability
 23 than any organic matter, that the number of chemical func-
 24 tionalities introduced into MOFs is currently outnumbering the
 25 ones in microporous polymers by far, and that no conjugated
 26 polymer will reach conductivities found in carbonaceous mate-
 27 rials. Indeed, it is rather the ability to combine different
 28 properties, which makes microporous polymers special and a
 29 highly interesting complement to conventional microporous
 30 materials. In this review we will try to carve out the very special
 31 and unique properties of microporous polymers and how they
 32 can be exploited for novel and emerging applications. To set the
 33 stage before describing the most prominent and important
 34 works published in this area, at first a critical view on structure,
 35 synthesis, properties and functionalities of microporous poly-
 36 mers will be undertaken.

37 1.1 Synthesis and structure

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

48 Synthetic protocols which can be used for the generation of
 49 microporous polymers are highly diverse and range from metal-
 50 catalyzed or -mediated (Sonogashira,^{4,5} Suzuki,⁶ Yamamoto,⁷
 51 Buchwald–Hartwig,⁸ Eglinton,⁹ Heck¹⁰) to click-type
 52 reactions,¹¹ acid or base-catalyzed polycondensation reactions
 53 (formation of polyamides,¹² -imides,^{13–15} -benzimidazoles,^{16,17}
 54 -dioxanes,¹⁸ -boroxines and boronate esters,¹⁹ -imines^{20,21}



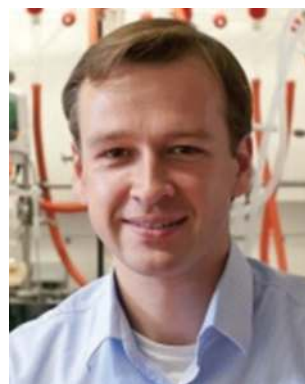
24 **Robert Dawson**

25 *Dr Robert Dawson is a Lecturer in Polymer Chemistry at the University of Sheffield. He received his MChem in Chemistry from the University of Liverpool in 2006 and completed his PhD with Prof. Andrew I. Cooper at the same institution graduating in 2010. This was followed by a further two years in the group as a post-doctoral researcher. In 2012 he moved to the Technical University of Berlin as a Marie Curie Intra-European Fellow in the group of Prof. Arne Thomas. He returned to the UK in 2014 working at the University of Bath before moving to Sheffield in 2015.*



44 **Johannes Schmidt**

45 *Dr Johannes Schmidt studied chemistry at Philipps-University of Marburg and graduated in 2007. He received his PhD at Max-Planck-Institute of Colloids and Interfaces and University of Potsdam in 2010. As a PostDoc he joined Prof. Dr Arne Thomas at TU Berlin where he holds his current position as research coordinator. His research is focused on porous materials and their potential in (photo)catalysis, gas storage/separation and energy applications.*



49 **Arne Thomas**

50 *Arne Thomas studied chemistry in Gießen, Marburg and Edinburgh and received his PhD from MPI for Colloid and Interfaces in Potsdam, Germany. After a postdoctoral stay at the University of California, Santa Barbara, as an AvH fellow, he rejoined the MPI for Colloids and Interfaces as a group leader. In 2009 he became a Professor at the Technische Universität Berlin where he is leading the department of Functional Materials. His research focuses on porous materials – from meso-porous inorganic materials to microporous organic frameworks.*

1 -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
5 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 tol-
erating any given functional group which is planned to be
10 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
15 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 syn-
20 thetic routes. Microporous polymers containing benzimidazole^{16,17}
or triazine linkages⁴³ are an example with high CO₂ uptakes which
can be synthesized without the need for a catalyst. Networks
synthesized from both dichloromethyl monomers⁴⁴ and those
using an external crosslinker⁴⁵ by Friedel–Crafts reactions were
25 shown to have high uptakes particularly at higher pressures used
for pre-combustion capture. These materials can also be synthe-
sized 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}

30 **The challenge of amorphicity.** Microporous polymers are gener-
ated by covalent attachment of rigid and contorted organic mole-
cules. 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
35 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
40 concentrate on the larger family of amorphous microporous poly-
mers, even though COFs will not be entirely neglected in this review.
The absence of crystallinity or ordered structures within micro-
porous polymers is actually no drawback for most applications,
except for those regarding molecular sieving or size-selective cata-
45 lysis, 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
50 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.

55 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
1 materials. While the structure of zeolites, MOFs and COFs can
be in principle comprehensively elucidated from XRD measure-
ments, this is not possible for microporous polymers.

5 Instead, various other analytical methods have to be used to
approach the structure of the materials. NMR and IR spectro-
scopy 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
10 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
15 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
20 no reliable models exist for a pore size distribution analysis of
these rather soft materials, which show some amount of swell-
ing during gas sorption measurements.⁴⁸

Finally, it cannot be denied that the amorphous nature of
microporous polymers is a significant challenge when thinking of
25 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 isorecticular frameworks.⁴⁹ In
30 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
35 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 struc-
tures, which should all have a large impact on the observed surface
area and porosity, are hard to determine by analytical tools for the
40 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
45 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 topolo-
gies. Some design rules have been suggested by considering such
idealized crystalline structures, however how much such artificial
50 unit cells have in common with the real structures is more than
questionable.

55 **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.

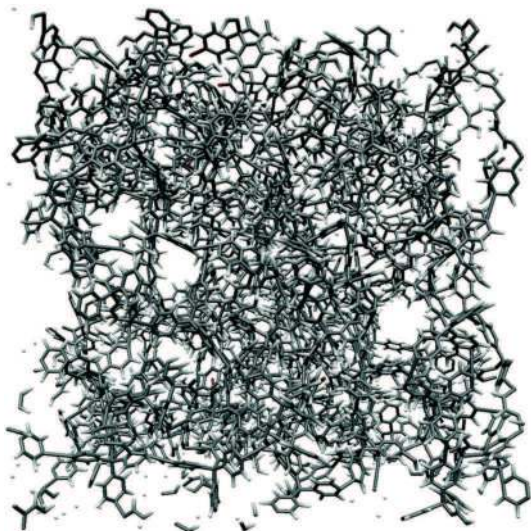


Fig. 1 Model of PAF-1 a microporous polymer network built by Yamamoto-homocoupling of tetrakis(4-bromophenyl)methane. Reproduced from ref. 48 with permission from Royal Society of Chemistry, copyright 2016.

- 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 cross-linking 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 films⁵¹⁻⁵³ 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*

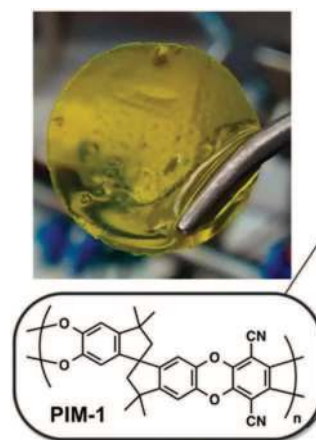


Fig. 2 Free standing membrane and chemical structure of the microporous polymer PIM-1. Reproduced from ref. 58 with permission from American Chemical Society, copyright 2015.

1 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
5 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 intri-
guing possibilities and this is, strangely enough, especially
10 because it is possible to prepare microporous polymers which
display no distinct functionality at all. PAF-1,⁶⁷ or the struc-
turally identical PPN-6,⁶⁸ is a polymer featuring a backbone which
is composed of biphenyls connected by a sp³-hybridized qua-
ternary carbon atom, thus no special functionality can be
15 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
20 amines, hydroxyls, fluoros and carboxylic acids have been
found to increase the enthalpies of adsorption of CO₂ 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
25 modified networks over the parent network.⁷⁰ Further modifi-
cations using amines were also reported, again showing sig-
nificant increases in the uptakes especially at 0.15 bar which
corresponds to the amount of CO₂ in a typical flue gas stream.⁶⁸
Another intriguing example is that lithium doping of the
30 otherwise non-functional PAF-1 can be carried out, which is
only possible due to the high chemical stability of these net-
works. 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
35 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
40 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.

45 **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}
50 without the need for an additional porous support. This con-
cept 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
55 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
1 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
5 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
10 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
15 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
20 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 poly-
25 mers for catalytic applications were recently published by
Rose⁴⁰ 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
30 literature. It is understandable that initial works applying
microporous polymers in catalysis use more or less conven-
tional 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
35 applications is debatable, as it is for molecular catalysts im-
mobilized on other porous supports.⁸¹ However, further advan-
tages 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 micro-
40 porous 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 where the
molecular catalyst is not soluble.⁷⁶

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

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

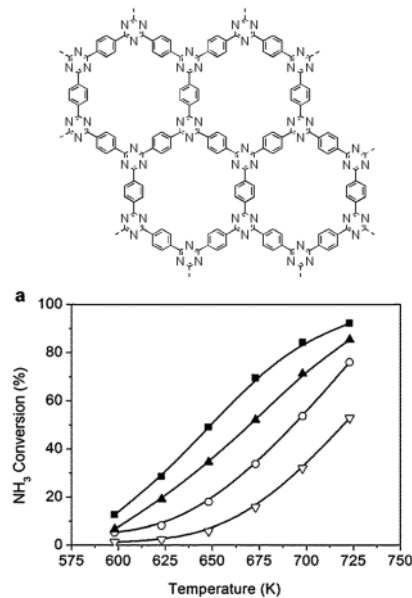


Fig. 3 Top: Chemical structure of CTF-1 and bottom: ammonia decomposition reaction using 1–2 wt% Ru-loaded CTF-1 (dark spots) and CNTs (light spots), for comparison. Reproduced from ref. 83 with permission from Royal Society of Chemistry, copyright 2015.

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 density³⁸ 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 -

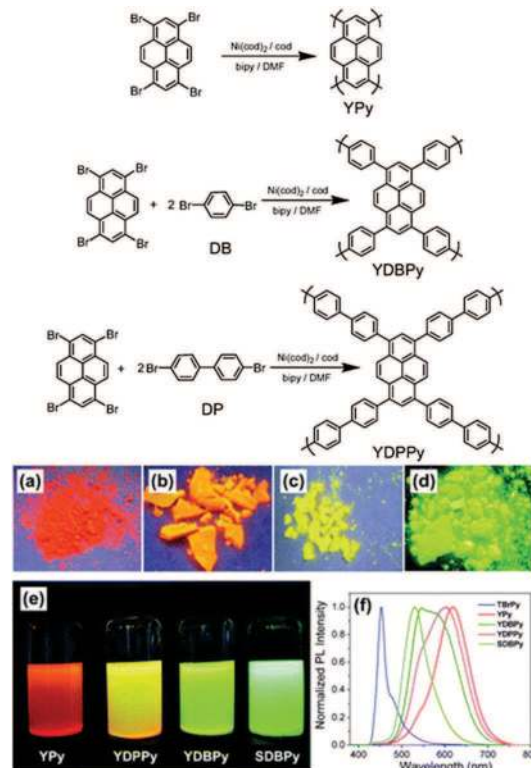


Fig. 4 Top: Synthetic routes to pyrene based CMPs. Bottom: Photographs of different CMPs under irradiation with UV light in bulk and dispersion in THF. (f) Shows the photoluminescence spectra of the pyrene monomer and the CMPs in powder form (note that SDBPy has in principle a similar structure than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

topology (Fig. 4).⁸⁸ The π -conjugated structure renders such aromatic networks potential organic semiconductors.

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 phase⁹¹ (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

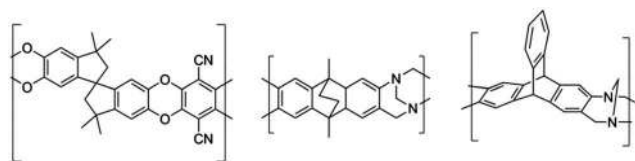
1 recent literature. It is not the aim of this review to give a
 2 conclusive overview on the whole field of microporous polymers,
 3 as excellent reviews on these materials have been published in
 4 recent years.^{1–3,39,40,42,56,57,92,93} On the contrary, we will try to
 5 identify some trends and worthwhile research directions within
 6 the field of microporous polymers. Within the following chapters
 7 we will concentrate on a special structural or functional
 8 feature of a certain class of microporous polymers and from
 9 there on develop new perspectives on emerging applications.

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

2. Soluble microporous polymers

23 Common for most porous materials, regardless to the reaction
 24 route, is their accrument as insoluble powders. However, for
 25 most applications it is desirable to modify the texture/shape of
 26 the porous material post-synthetically without varying material
 27 properties, which is, except for pellet production, mostly
 28 impossible for porous powders. Therefore shape control during
 29 reaction is desired to obtain materials in certain forms. However,
 30 the problem of non-processability does not occur for soluble
 31 polymers that show porosity in the dry state, *i.e.* for the so-called
 32 polymers of intrinsic microporosity (PIMs). These 2D-polymers
 33 create microporosity by inefficient packing due to kinks in the
 34 backbone structure but retain solubility in organic solvents and
 35 can thus be processed post-synthetically for example cast as
 36 films. In 2004 the first PIM (PIM-1), based on tetramethyl-1,1'-
 37 spirobiindane, was reported¹⁸ and up till now it is, together
 38 with its modifications, one of the PIMs with the best properties
 39 in terms of film building ability, stability, and flexibility.^{94–96}
 40 Beside spirobisindane other centers of contortion were integrated
 41 in the backbone of PIMs, *e.g.* triptycenes,⁹⁷ spirobifluorenes¹²
 42 or ethanoanthracenes (Fig. 5).⁹⁸

43 PIM-based films show very interesting properties in transport
 44 and separation of ions or gases. Membranes based on PIM-



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

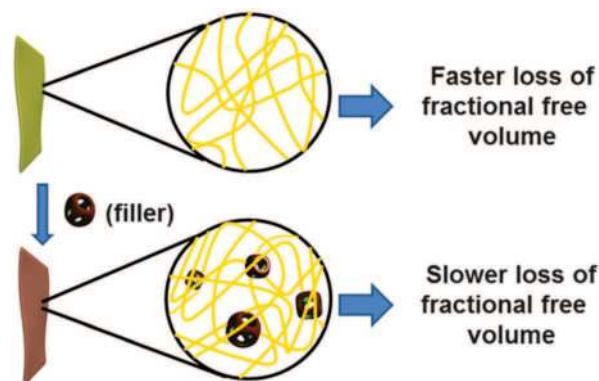


Fig. 6 Schematic illustration of effect of nanofillers on mixed matrix membranes. Reproduced from ref. 105 with permission from Royal Society of Chemistry, copyright 2016.

1 show excellent gas selectivity that lies above the Robeson
 2 upper bound of 2008, other examples of PIMs even meet the
 3 requirements of the 2015 upper bound.⁹⁹ However, one drawback
 4 of these systems is the enormous aging effect and unfortunately
 5 the performance cannot be sustained in long term experiments.
 6 Most probably a densification of chain packing occurs which
 7 leads to a decrease of free volume and gas permeability.¹⁰⁰

8 To sustain the performance of the membranes over a longer
 9 period of time different approaches have been studied. One way
 10 to stabilize the polymer matrix is by introducing several different
 11 kinds of fillers to design mixed matrix membranes (MMMs).
 12 Main examples for fillers that are used for MMMs are porous
 13 materials like MOFs,^{101–103} carbon nitrides¹⁰⁴ but also micro-
 14 porous polymer networks^{105–107} and related molecular fillers
 15 like organic cages (Fig. 6).¹⁰⁸ By introducing these fillers the
 16 aging effect can be enormously reduced which allows super
 17 glassy polymers to be revisited for commercial application in
 18 gas separations again. It is assumed that by adding an ultra-
 19 porous additive, some chains of the glassy polymers are absorbed
 20 within the pores of the additive which is holding the chains in
 21 their open position.¹⁰⁶ Therefore the low density and permeability
 22 of the PIM is maintained over a longer period of time. To achieve
 23 a substantial stabilization of the membrane the compatibility of
 24 glassy polymer and filler, the surface chemistry, molecular
 25 structure and size and rigidity need to be controlled.

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

32 Additionally PIMs can be strengthened by stiffening their
 33 backbone. One example reported is the incorporation of porous
 34 bowl structures like beta-cyclodextrin. The interactions between
 35 beta-cyclodextrin and PIM can also restrict chain movement and
 36 make ultrafine micropores difficult to collapse. Thus a greater
 37 resistance to physical aging than PIM membrane can be achieved.¹¹⁵
 38 In 2013 McKeown *et al.* introduced a bridged bicyclic amine
 39 2,8-dimethyl-6H,12H-5,11-methanodibenzo[*b,f*][1,5]diazocine,
 40 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 applications⁸⁹ 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 m² 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 m² 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 dithiophene 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

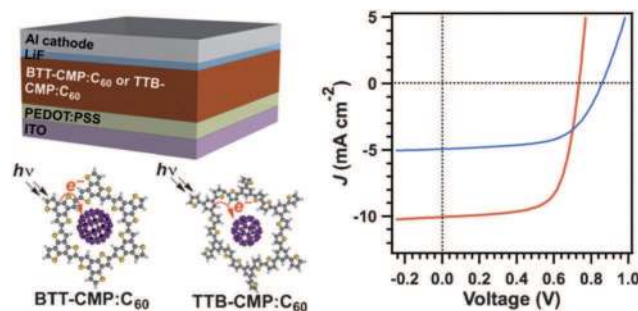


Fig. 7 Left: Device configuration of solar cells and charge separation process using thiophene based CMP with incorporated C60 as photo-active layers. Right: J - V curves of the solar cells. Reproduced from ref. 130 with permission from Wiley-VCH, copyright 2015.

1 efficiencies of 8.42% have been reached vs. 5.68% for the OSC
without an interlayer.¹³³ Jiang *et al.* later built CMPs from
5 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
10 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

15 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
20 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
25 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
30 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,
35 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
40 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,
45 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
50 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
55 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
5 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
10 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 (C₆N₇)
unit was applied as structure directing tecton. While in the
15 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 m² g⁻¹)
20 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
25 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
30 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 micro-
porous co-polymers were prepared by a Suzuki–Miyaura coupling,
yielding variable amounts of benzene and pyrene moieties
35 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
40 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
benzodiazole¹⁵¹ and triazine¹⁵²-based networks.

An illustrative example to which level the tailoring of organic
45 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
50 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
55 to highly porous solids.¹⁵³

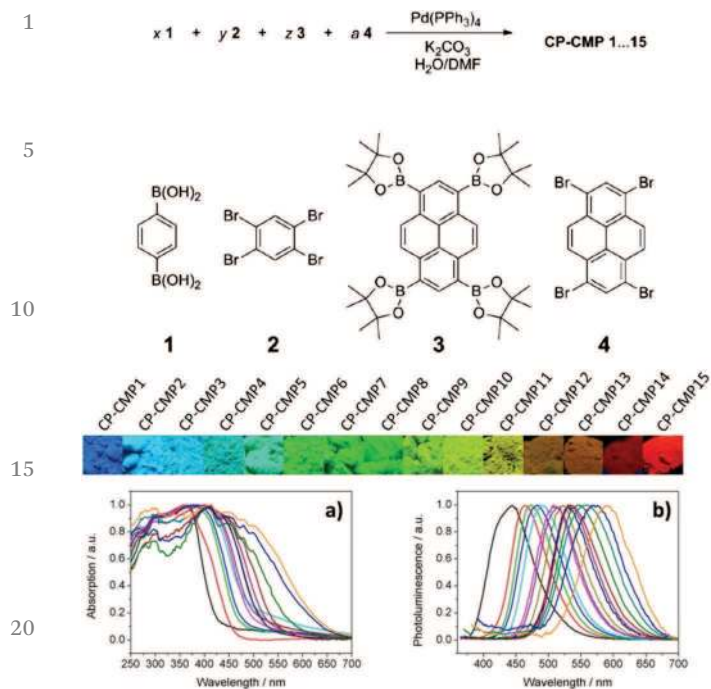


Fig. 8 Top: Continuous tuning of the photophysical properties of organic CMP based photocatalysts by statistical copolymerization via Suzuki–Miyaura polycondensation. Bottom: Photographs on top of CMPs imaged under irradiation with UV light and the UV-visible absorption and photoluminescence spectra 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.

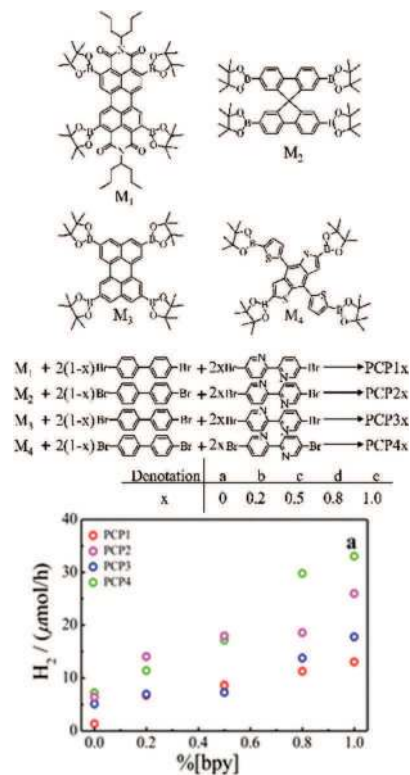


Fig. 9 Top: Structures of monomers of PCP photocatalysts prepared by Suzuki polycondensation. Bottom: Photocatalytic hydrogen production rates of PCPs with different bpy contents. Reproduced from ref. 153 with permission from American Chemical Society, copyright 2016.

Given all these promising examples what is still missing is a judgement on the photocatalytic performance. Hydrogen evolution values up to $164 \mu\text{mol h}^{-1}$ 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 $8 \mu\text{mol H}_2$ 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 ($\sim 4500 \mu\text{mol}$) 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 ($\text{mol h}^{-1} \text{g}^{-1}$) 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.

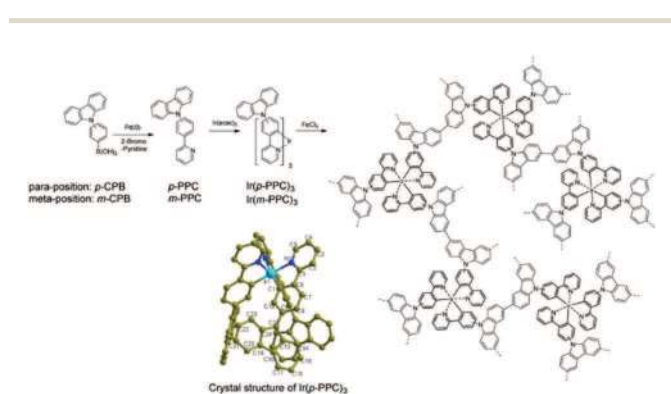
It must also be asked, if a permanent surface area is actually needed for observing high photocatalytic performance. So far there seems to be no relationship between BET surface area and hydrogen evolution. Indeed, also networks with low or even no

1 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-
 5 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.* CO₂ reduction has appeared as
 10 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.

15 3.3 CMPs for other photocatalytic reactions

While water splitting and selective CO₂ 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. Conse-
 20 quently, 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 photo-
 catalysts. In one of the first works regarding this application,
 25 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
 30 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 sulfides¹⁶¹ and thiox-
 anthone based CMPs were used as photoinitiators to initiate
 35 free radical and cationic polymerizations of vinyl monomers
 and cyclic ethers.¹⁶² Even typical dyes such as rose bengal¹⁶³ or
 photosensitizers such as Ru-¹⁶⁴ or Ir-complexes¹⁶⁵ have been
 immobilized in CMPs to generate efficient heterogeneous
 photocatalysts (Fig. 10).



40
 45
 50
 55 **Fig. 10** Immobilization of an Ir-photosensitizer into a microporous con-
 jugated polycarbazole polymer *via* FeCl₃-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 oxida-
 tion of amines and sulfides,¹⁶⁶ photooxidative cyclizations,¹⁶⁷
 reduction of metal ions (Cr(vi)–Cr(III))¹⁶⁸ as well as Suzuki type
 5 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
 10 aldehydes, oxidative coupling of primary amines, aerobic dehy-
 drogenation of nitrogen heterocycles, and selective oxidation of
 sulfide using molecular oxygen and visible light.^{171,172}

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

As mentioned in the introduction, compared to other micro-
 porous organic chemistry-based materials, microporous poly-
 20 mers are unique in that they can exist as pure hydrocarbon
 materials and completely forgo the use of metals or heteroa-
 toms. 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
 25 distribution of electron density throughout the polymer skele-
 tons 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
 30 functionalized networks.¹⁷³ As mentioned above, starting from
 these high surface area polymers, many postsynthetic modifi-
 cations 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
 35 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 H₂ and CO₂
 40 compared to polymers solely comprising benzene rings, but the
 strength of the interaction still lies in the realm of physisorp-
 tion. Their eligibility for H₂ sorption has been shown experi-
 mentally as well as computationally.^{5,9,175}

Selective incorporation of heteroatoms can provide disrupt-
 45 tions 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.*
 50 CO₂.^{68,176}

Early attempts to create main group element-centered poly-
 55 mers 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 m² g⁻¹.^{177–179} The step-wise nature of the polymerization

1 reaction eventually leads to steric congestion around a signifi- 1
 cant part of the partially substituted main group element nodes 2
 upon which further reaction is precluded. Following this direct 3
 incorporation approach, Uptmoor *et al.* synthesized a tetrahe- 4
 5 dral tin-based monomer to generate a homocoupled CMP net- 5
 work following a reported procedure for the direct coupling of 6
 alkynes.¹⁸⁰ This material was not studied for its gas uptake 7
 properties but was readily digested by acid treatment and, by 8
 analysis of the fragments, gave very detailed insights into the 9
 10 polymerization mechanism of PAE networks.¹⁸¹

In 2013 Zhang *et al.* polymerized tris(4-chlorophenyl)- 11
 phosphine to obtain polymeric triphenylphosphine, which 12
 could be oxidized to polymeric triphenylphosphine oxide.¹⁷⁶ 13
 The networks exhibited BET surface areas of 1284 (PP-P) and 14
 1353 m² g⁻¹ (PP-PO). Interestingly, the oxidized polymer dis- 15
 played stronger affinity towards the adsorption of CO₂ than the 16
 reduced form (3.83 vs. 2.46 mmol g⁻¹). Furthermore, the 17
 incorporation of phosphorus atoms enabled efficient formation 18
 and deposition of Pd nanoparticles in the polymeric triphenyl- 19
 phosphine which yielded a functional Suzuki cross-coupling 20
 catalyst and showed the ability of these materials to serve as a 21
 support for catalytically active nanoparticles. Fritsch *et al.* used 22
 a conceptually similar material, which was synthesized based 23
 on the EOF approach, to obtain a microporous polymer net- 24
 work with a BET surface area of 458 m² g⁻¹.¹⁷⁹ This material 25
 was used as a support for Pd and Rh to obtain a solid catalyst 26
 for transfer hydrogenation of cyclohexanone.

Recently, Trunk *et al.* synthesized a series of microporous 27
 polymer networks based on sterically demanding triphenylphos- 28
 phine derivatives to lessen the nucleophilicity of the phos- 29
 phorus lone pair and facilitate the use of the networks as basic 30
 components in semi-immobilized frustrated Lewis pairs (FLP), 31
 for the first time making the transition from this novel class of 32
 molecular catalysts to solid organic materials (Fig. 11).¹⁸² The 33
 ability of solid FLPs to cleave dihydrogen at ambient tempera- 34
 ture and low pressure was demonstrated *via* isotope scrambling 35
 experiments.

Nitrogen containing porous polymers for the capture of CO₂ 36
 are great in number and the subject of reviews of their 37
 own.^{183,184} The majority of materials incorporates amine func- 38
 tions either as aromatic (aniline-like) amino groups or triaryla- 39
 mine linkages. The binding affinity of amines to CO₂ is greatly 40
 enhanced when the amine is not directly attached to an 41
 aromatic system but separated by short, aliphatic spacer. Such 42
 43

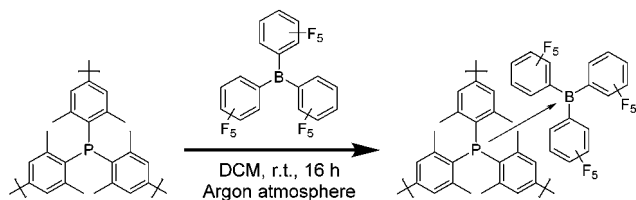


Fig. 11 Synthesis of a semi-immobilized frustrated Lewis pairs (FLP) by impregnation of a triphenylphosphine based microporous polymer with tris(pentafluorophenyl)borane. Reproduced from ref. 182 with permission from American Chemical Society, copyright 2017.

systems are best accessed by postsynthetic modification since 44
 amines are strong ligands and tend to affect the polymerization 45
 when present in the monomer itself.^{68,174}

Far less is known about the incorporation of electron 46
 acceptor moieties. Main group elements such as boron in their 47
 neutral form have empty orbitals and can accept lone pairs of 48
 donating adsorbates. This feature is especially interesting for 49
 optical or electronic properties as it allows for the transfer of 50
 electron density from neighbouring aromates or donor moieties. 51
 The group of Mu prepared a tris(tetramethylphenyl)borane con- 52
 taining polymer *via* alkyne homocoupling. Despite the incor- 53
 poration of boron sites, the uptake capacity for CO₂ was 54
 comparable with reported boron-containing COFs at the time.¹⁸⁵ 55
 Suresh *et al.* coupled tris(tetramethylphenyl)borane *via* Sonogashira 56
 coupling with a biphenyl unit to obtain a microporous polymer 57
 network with a surface area of 390 m² g⁻¹ which could be used as a 58
 Lewis acidic sensor for the detection of fluoride ions.¹⁸⁶ Moreover, 59
 combining donor and acceptor moieties within one material can 60
 yield interesting electronic properties for optical applications or 61
 sensing. The separate functionalities can be combined in one 62
 monomer to create an intrinsic function, which is then polymer- 63
 ized, or an alternating copolymerization of building blocks with 64
 contrasting functionality can be polymerized to synergistically 65

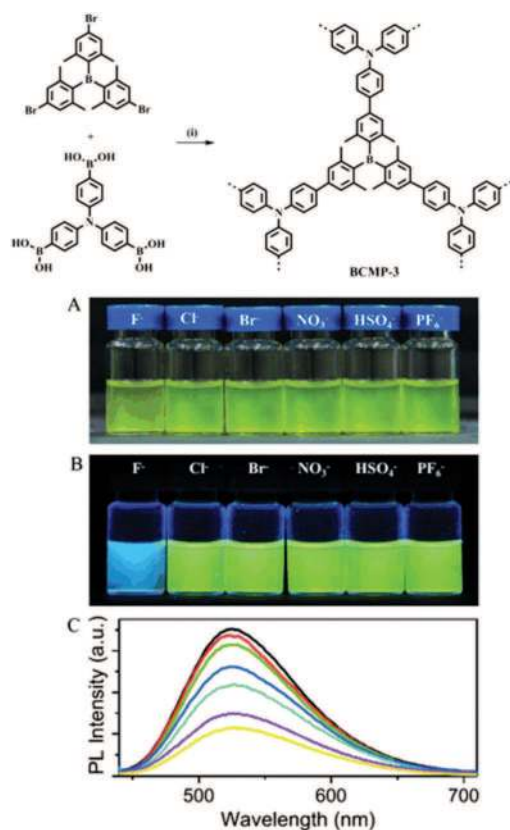


Fig. 12 Top: Synthesis of a boron and nitrogen-containing microporous network and bottom: photographs and photoluminescence spectra of THF suspensions of the polymer framework, showing the size-selective fluorescence quenching by fluoride anions. Reproduced from ref. 189 with permission from Wiley-VCH,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

1 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
5 containing monomers to form porous π -conjugated donor–acceptor
polymers *via* Suzuki coupling and Sonogashira coupling, respec-
tively. The resulting materials featured BET surface areas between
600 and 1300 m² g⁻¹ and displayed strong fluorescence properties as
well as capability of fluoride collection.

10 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 m² g⁻¹. It was found to
act as a highly selective sensor towards fluoride over other
15 common anions yet easily recyclable by stirring in THF solu-
tions of BF₃·OEt₂ as fluoride scavenger (Fig. 12).

5. Microporous polymers with permanent ionic charges

20 Beside the introduction of heteroatoms, the presence of per-
manent 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 applica-
25 tions 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
30 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
35 where a (permanent) charge is then introduced post-
synthetically.

5.1 Cationic microporous polymers

40 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 phospho-
nium network by the Yamamoto homo-coupling reaction.¹⁹¹
45 The polymer exhibited a S_{BET} of 650 m² g⁻¹, however, magic
angle spinning ³¹P solid state NMR revealed that many of the
phosphonium linkages were cleaved during the reaction afford-
ing a phosphonium to phosphine ratio of approximately 3 : 2.
The Br⁻ containing cationic network was successfully employed
50 as a catalyst for the conversion of 2-(phenoxyethyl)oxirane to
the cyclic carbonate in the presence of CO₂. By “diluting” the
cationic charges within a MPN the first two cationic micro-
porous networks were synthesized, in which the phosphorus
moiety is entirely present as phosphonium cation. Tetrakis-(4-
55 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 m² g⁻¹ and 540 m²
g⁻¹.¹⁹² Here too, a simple anion exchange was performed to
introduce chlorine counter anions resulting in a rise in S_{BET} for
5 CPN-1-Cl to 1540 m² g⁻¹. The investigated CO₂ uptakes for the
charged networks proved to increase by 40% compared to the
uncharged microporous analog PAF-1⁶⁷ 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
10 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 m² g⁻¹ and with pores in the microporous as well as
15 mesoporous range.¹⁹⁴ Anion exchange was performed with this
polymer introducing a highly active peroxotungstate anion
[W₂O₁₁]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
20 oxidation dibenzothiophene with equivalent H₂O₂.

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

A large number of cationic microporous polymers are
30 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
35 which after anion exchange with polyoxometallate (POM)
anions PW₁₂O₄₀³⁻ 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
40 sheets will lead to an exfoliation of the sheets due to electro-
static repulsion. Based on this strategy Banerjee *et al.* synthe-
sized ionic covalent organic nanosheets (iCONs) by reacting a
planar C₃ symmetric cationic triaminoguanidinium halide TG_X
with 1,3,5-triformylphloroglucinol.¹⁹⁷ The obtained materials
45 exhibited low crystallinity with a major broad peak at $2\theta = 27.3^\circ$
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
50 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 intro-
duced into microporous polymers. For example, in 2009 Dai
et al. showed that cationic microporous networks can be
55 formed by performing a salt melt catalyzed trimerization of

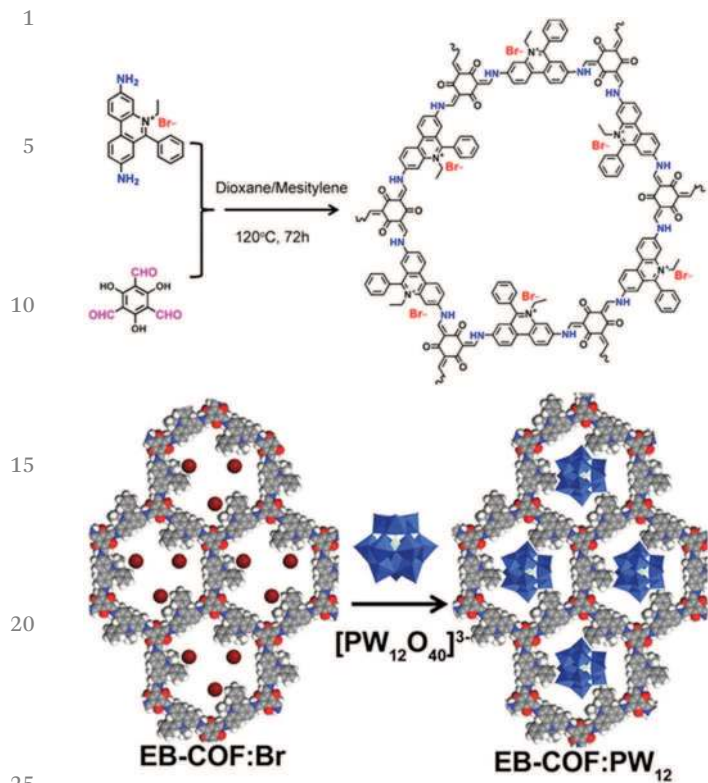


Fig. 13 Synthesis of cationic ethidium bromide covalent organic frameworks (EB-COF) where polyoxometallates were introduced by anion exchange post-synthetically. Reproduced from ref. 196 with permission from American Chemical Society, copyright 2016.

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 $2 \text{ m}^2 \text{ g}^{-1}$ to $814 \text{ m}^2 \text{ g}^{-1}$ 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 $\text{Ni}(\text{COD})_2$ as a reagent.^{200,201} The cationic networks proved to be effective for the adsorption and removal of $\text{Cr}_2\text{O}_7^{2-}$ 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 $942 \text{ m}^2 \text{ g}^{-1}$. The materials were tested for anion exchange in which the Cl^- anions present after synthesis were exchanged with the catalytically active polyoxometallate anions $\text{PMo}_{10}\text{V}_2\text{O}_{40}^{5-}$ (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

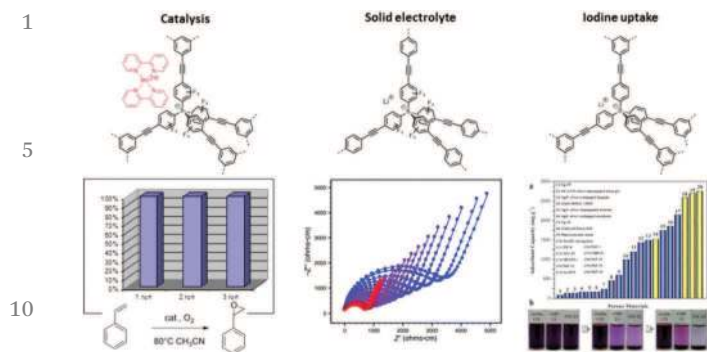


Fig. 14 Examples of anionic tetraarylborate based microporous polymers and their applications in catalysis (a), as single ion conducting solid electrolytes (b) and for iodine capture (c). Reproduced and adapted from ref. 76, 209 and 210 with permission from Wiley-VCH, copyright 2013 and 2015; Royal Society 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 $890 \text{ m}^2 \text{ g}^{-1}$ 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 $262 \text{ m}^2 \text{ g}^{-1}$ 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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