Much ado about nothing – a decade of porous materials research

Arne Thomas

Research on porous materials has produced intriguing novel materials in terms of composition, porosity and structures recently. This perspective aims to provide a short overview on some of the highlights reported within the last decade in this field.

Porosity and surface area

Researchers working on porous materials are actually obsessed by the “nothing”, which can be introduced into a material. This value is expressed as porosity, namely the pore volume and the related created surface area. It doesn’t matter if you talk to specialists in zeolites, carbons, mesoporous oxides, metal-organic frameworks (MOFs) or porous polymers, in these terms they all speak the same language.

The specific surface area is the area of a material accessible to gas molecules in the dry state and can be largely increased when pores are introduced into a material. In 2010, MOFs with surface areas exceeding 6000 m²/g were firstly reported, 2012 the 7000 m²/g mark was surpassed and this came to a preliminary end with a MOF exhibiting the current world record of 7836 m²/g in 2018 (Fig. 1a)1. This is approximately the surface area of a football field you can hold in your hand! This came with a pore volume of 5.02 cm³/g, i.e., 90.3% of the material is free volume and a density of just 0.187 g/cm³. But these MOFs are still heavyweights compared to another material class which has gained momentum in the last decade. Indeed, more “nothing” can be introduced, when the pores are getting larger, reducing the amount of left-over material to a

1Department of Chemistry, Functional Materials, Technische Universität Berlin, Hardenbergstraße 40, 10623 Berlin, Germany. Email: arne.thomas@tu-berlin.de
minimum, as it is seen in new generations of aerogels, e.g., graphene aerogels with a porosity of ~99.9% and a density down to 0.00016 g/cm³. Aerogels are impressive also when they are made from heavy materials, thus very recently a gold aerogel was reported with a density of just 0.006 g/cm³, which is 0.03 % of the density of bulk gold.

Composition and connectivity
While the world of porous, high surface area materials was 10 years ago mainly divided up among inorganic (zeolites, ordered mesoporous oxides, porous carbons) and organic–inorganic materials (MOFs), purely organic materials, like covalent organic frameworks (COFs) and conjugated microporous polymers (CMPs) have now also entered the stage. While the first COFs and CMPs were reported already in the 2010s they have experienced tremendous interest within the last 10 years. This can be explained by their unusual properties originating from their entirely organic, often fully π-conjugated composition. The first metal-free photocatalyst for hydrogen generation from water, a polymeric carbon nitride, was reported in 2009, but it took another few years until it was realized that also COFs and CMPs could be used for this application. Since then, photocatalysis became one major application investigated for organic porous materials. Another research focus within the last 10 years was to find new reactions and linkages to connect organic molecules into high surface area materials. For highly crystalline COFs it was generally accepted that they can just be formed from chemically weak covalent bonds, as reversible covalent bond formations are required. Indeed, beginning of this decade the only known highly crystalline COFs were formed by boron–oxygen and later imine bounds, as these can be reopened easily by hydrolysis. Within the last 10 years however, the number of possible COF linkages have largely expanded and nowadays they can be as well formed from chemically stable covalent bonds, which culminated in the formation of entirely sp²-carbon connected frameworks. While this expansion of stability of COFs on the one hand is a milestone for crystalline organic porous materials, also other connectivities have been investigated to form high surface area organic materials. Thus porous materials from organic building blocks with high permanent surface areas have been built via hydrogen bonds (HOFs), supramolecular interactions (SOFs) or hypercoordinate main group elements (SiCOFs). A highly unusual bonding pattern was finally reported within a COFs showing a mechanical interlocked architecture with fabric-like woven organic threads.

Dimensions and dynamics
Ten years ago, most porous materials were 3D materials, i.e., the material and its porosity expanded into all three dimensions. Sure there were a few exceptions, like the 1D polymers of intrinsic microporosity (PIMs) and 2D layered COFs, but zeolites, porous carbons and most MOFs all felt into this category. This has changed within the last 10 years (Fig. 2). An intriguing achievement was the development of discrete molecules with permanent porosity, called organic cage compounds, which thus can be described as 0D porous materials. These porous cages are soluble, highlighted in the development of a porous liquid, thus a concentrated solution of cage compounds whose solvent molecules are too large to enter the pores and which can thus take up a high amount of gas molecules. But also the mentioned 1D PIMs have seen remarkable progress and within the last 10 years membranes composed of new PIMs have redefined the Robeson upper bound several times, a benchmark for gas pair separations (e.g., CH₄/CO₂ or CO₂/N₂) in membranes. MOFs on the other hand went 2D. While exfoliation of layered MOFs was known since some time, this field has gained further momentum by the development of π-conjugated 2D MOFs prepared by bottom-up approaches, especially due to their astonishing high electric conductivity. New dimensions were also exploited for zeolites with the generation of 2D zeolite nanosheets. Intriguingly, the layers could be used to reassemble 3D zeolite structures, which can hardly be produced by direct synthesis routes. While the latter materials have started as 3D compounds whose dimensionality were reduced over time, the original 2D COFs have been expanded to 3D COFs over the years, culminating in the formation of single crystals of these entirely covalently linked frameworks, yielding a fascinating insight into the structure of such materials. Furthermore, a reversible 2D to 3D transformation has been recently observed in COFs, triggered by a light induced [2 + 2] cycloaddition between vinylene groups in separate COF layers. But why stopping at the dimensions of our experiential reality? The timescale has been recognized as a new perspective to investigate the dynamics and spatiotemporal evolution, thus of 4D porous materials.
materials. It has been recognized that many porous materials are far from static, but can change their structure and porosity as result of an external stimuli, yielding to extraordinary properties such as selective recognition of small molecules or the quite counterintuitive negative gas adsorption, i.e., the spontaneous desorption of gas molecules occurring during pressure increase.

**Beyond synthesis**

It’s a common phrase nowadays that a material has been created by design. Even though many porous materials have indeed gained a structural precision and predictable function, that they seemed to be (and probably are) designed on a drawing board, every one of us know that real life in the laboratory still means to carry out countless reactions until a new material can be presented. Thus what’s ending up with a few lines in the experimental part of a publication is often the labor of weeks, months or even years. But there is hope—indeed the synthesis of porous materials (and synthesis in general) will probably look very different end of the next decade. Machine learning, big data and robotics have entered the field of porous material development and have already shown to yield materials, optimized in terms of structure, porosity and/or applications. It is conceivable that this trend will revolutionize the way we do (porous) materials synthesis in the future. Thus the next ten years of porous materials research promise to be even more exaggerating as the last ones—fingers crossed.

Received: 31 August 2020; Accepted: 9 September 2020; Published online: 02 October 2020

**Acknowledgements**

I would like to thank my entire group for their continuous efforts in the exploration of porous materials within the last 10 years.

**Competing interests**

The author declares no competing interest.

**Additional information**

Correspondence and requests for materials should be addressed to A.T.

**Reprints and permission information** is available at [http://www.nature.com/reprints](http://www.nature.com/reprints)

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

**References**

1. Hönicke, I. M. et al. Balancing mechanical stability and ultrahigh porosity in crystalline framework. *Mater. Angew. Chem. Int. Ed.* 57, 13780–13783 (2018).
2. Sun, L., Campbell, M. G. & Dinca, M. Electrically conductive porous metal-organic frameworks. *Science* 351, 365–369 (2016).
3. Giri, N. et al. Liquids with permanent porosity. *Nature* 527, 216–220 (2015).
4. Comesana-Gandara, B. et al. Redefining the Robeson upper bounds for CO2/CH4 and CO2/N2 separations using a series of ultra-permeable benzotriptycene-based polymers of intrinsic microporosity. *Energy Environ. Sci.* 12, 2733–2740 (2019).
5. Roth, W. J. et al. A family of zeolites with controlled pore size prepared using a top-down method. *Nat. Chem.* 5, 628–633 (2013).
6. Achariya, A., Pachfuhe, P., Roesser, J., Schmitt, F. J. & Thomas, A. Vinylene-linked covalent organic frameworks by base-catalyzed aldol condensation. *Angew. Chem. Int. Ed.* 58, 14865–14870 (2019).
7. Jadhav, T. et al. Transformation between 2D and 3D covalent organic frameworks via reversible [2+2] cycloaddition. *J. Am. Chem. Soc.* 142, 8862–8870 (2020).
8. Sato, H. et al. Self-accelerating CO sorption in a soft nanoporous crystal. *Science* 343, 167–170 (2014).
9. Krause, S. et al. A pressure-amplifying framework material with negative gas adsorption transitions. *Nature* 532, 348–352 (2016).
10. Liu, Y. et al. Weaving of organic threads into a crystalline covalent organic framework. *Science* 351, 365–369 (2016).
11. Stegbauer, L., Schwinghammer, K. & Lotsch, B. V. A hydrazone-based covalent organic frameworks. *Science* 351, 365–369 (2016).
12. Roth, W. J. et al. A family of zeolites with controlled pore size prepared using a top-down method. *Nat. Chem.* 5, 628–633 (2013).
13. Lyu, H., Diercks, C. S., Zhu, C. & Yaghi, O. M. Porous crystalline olefin-linked covalent organic frameworks. *J. Am. Chem. Soc.* 141, 6848–6852 (2019).
14. He, Y., Xiang, S. & Chen, B. A microporous hydrogen-bonded organic framework for highly selective C3H6/C2H4 separation at ambient temperature. *J. Am. Chem. Soc.* 133, 14570–14573 (2011).
15. Krause, S. et al. A pressure-amplifying framework material with negative gas adsorption transitions. *Nature* 532, 348–352 (2016).
16. He, Y., Xiang, S. & Chen, B. A microporous hydrogen-bonded organic framework for highly selective C3H6/C2H4 separation at ambient temperature. *J. Am. Chem. Soc.* 133, 14570–14573 (2011).
17. Jadhav, T. et al. Transformation between 2D and 3D covalent organic frameworks via reversible [2+2] cycloaddition. *J. Am. Chem. Soc.* 142, 8862–8870 (2020).
18. Sato, H. et al. Self-accelerating CO sorption in a soft nanoporous crystal. *Science* 343, 167–170 (2014).
19. Krause, S. et al. A pressure-amplifying framework material with negative gas adsorption transitions. *Nature* 532, 348–352 (2016).
20. Burger, B. et al. A mobile robotic chemist. *Nature* 583, 237–241 (2020).
21. Moosavi, S. M. et al. Capturing chemical intuition in synthesis of metal-organic frameworks. *Nat. Commun.* 10, 559 (2019).