Anal Bioanal Chem (2017) 409:1–2
DOI 10.1007/s00216-016-9971-4

EDITORIAL

ABC Spotlight on metal-organic frameworks (MOFs)

Günter Gauglitz[1]

Published online: 11 November 2016

Functionalization of surfaces or interfaces, coatings, or thin layers has been in the focus of research for decades and given rise to completely new applications. For approximately 15 years, metal–organic frameworks (MOFs) have developed into a new class of porous materials with hierarchic structures, combining materials of organic and inorganic nature with interesting properties. In principle, these are coordination polymers, formed by connecting metal ions with polytopic organic linkers. Methods of fabrication (a large number of applications are reviewed in [1]) by colloidal deposition, microwave-induced thermal deposition, even direct-oriented growth layer-by-layer, or liquid-phase epitaxy (LPE) allow one to tailor the properties of the frameworks. Crystalline porous thin films called SURMOFs (surface-grown crystalline metal–organic framework multi-layers layer by layer) are produced which are anchored to the surface. Advantages of these materials in comparison to classical layers such as zeolites induced the German Research Foundation to form a new priority program which pushed research in this area in Germany to the front.

This new material is considered to offer possibilities for storing energy through high specific surface areas and pore volumes, allowing new approaches in catalysis as carriers for drug synthesis, photocatalysis, and enantioselective catalysis by forming microreactors for the synthesis of new chemicals. Furthermore, they allow separation procedures, are capable of purifying gasses and air, and offer the chance of optimal sorption interactions by selected organic linkers and metallic atoms. Quality and perfect orientation of SURMOF thin films can be achieved through heteroepitaxial growth. The quality of such layer-by-layer fabricated thin films has been examined by X-ray photoelectron spectroscopy to characterize structural and electronic properties of molecular nanostructures in comparison to other molecular films [2].

The separation properties of such materials opened up new applications in analytics. Their permanent nanoscale pore structure, uniform pore size, large specific surface areas, and good thermostability make MOFs an interesting alternative to adsorption and/or separation of analytes. Thus, MOFs have found many applications in chromatographic stationary phases and are applied for trace elemental analysis [3]. Sample preparation can be optimized by magnetic solid-phase extraction techniques. The unusual properties of MOFs, especially their uniform, structured nanoscale cavities and their potential in-pore functionality and outer-surface modification, make them an interesting tool for rapid sampling of polycyclic aromatic hydrocarbons from water samples. Their capabilities are compared with a large variety of other nanostructured magnetic particles in a survey on the quality for separation and preconcentration of analytes from a wide variety of matrices [4].

In principle, sensors not only depend on a highly advanced detection principle but also on recognition elements which can allow the selective and sensitive detection of analytes. Thus, the development of new recognition elements is currently considered a highly interesting field of research. In another spotlight article, carbon nanotubes were introduced as possible recognition elements combining selectivity and stability [5]. Now, MOFs turn out to be another interesting approach,

✉ Günter Gauglitz
guenter.gauglitz@uni-tuebingen.de

1 Institute of Physical and Theoretical Chemistry, Eberhard Karls Universität, Auf der Morgenstelle 18, 72076 Tübingen, Germany

especially in the case of SURMOFs which combine a sieve effect and selectivity by the functional groups. Even enantiomeric separation of chiral molecules is discussed, using the properties of heterostructured SURMOFs, investigated by circular dichroism [6].

MOFs show aggregation-induced emission mechanisms, demonstrating a turn-on fluorescence upon interaction with volatile organic compounds (VOCs) [7]. This is interesting in the case of exhaled breath VOC biomarkers, offering new possibilities in cancer diagnostics and non-invasive breath control methods. MOFs are also promising luminescent materials; they are able to enhance the chemiluminescent emission of a luminol–H_2O_2 system; modifications can be used to determine dopamine in biological samples, sensitively measuring L-cysteine in human cell samples, and even forming a glucose biosensor [8].

Cataluminescence is generated from a catalytic reaction on the surface of solid catalytic materials. Regarding this, doped MOFs exhibit interesting new activities, forming cataluminescence-based sensors. Their working principle, instrumentation, and sensing material are under discussion, but MOFs demonstrate new qualities [9]. The cataluminescence of MOFs is becoming increasingly interesting as an explosives detector. Interesting aspects of such luminescence sensors in comparison to Raman spectroscopy, cavity ringdown spectroscopy, laser-induced breakdown spectroscopy, and photoacoustic spectroscopy are discussed in ref. [10]. The sensor applications have been reviewed recently [11].

SURMOFs can be converted into surface-bound gels (SURGELs, covalently connected to the surface, absence of metal atoms, pronounced stability under biological conditions) which combine the advantages of MOFs with the possibility of loading bioactive material [12]. These can be used as drug-release platforms, in biotransformations, and for manipulation of adherent cells.

Following their initial use in catalysis and energy applications, the possibilities of storing gasses, separating CO_2, and purifying gasses have started to interest analytical chemists for applications in chromatography. The possibility of tailoring the structure of the layer, varying the nuclear centers, allowing even gradients of properties horizontally or vertically, combining sieve effects with selectivity by functionalization, have prompted new interest in research and applications for sensors. The specific properties of MOFs, SURMOFs, and SURGELs will open up new opportunities for interesting applications of such thin layers and nanostructured particles for analytical chemistry in the future. The analytical community should take full advantage of these new layers.

References

1. Shekhah O, Liu J, Fischer RA, Wöll C. MOF thin films: existing and future applications. Chem Soc Rev. 2011;40:1081–106.
2. Gulino A. Structural and electronic characterization of self-assembled molecular nanoarchitectures by X-ray photoelectron spectroscopy. Anal Bioanal Chem. 2013;405:1479–95.
3. Hu B, He M, Chen BB. Nanometer-sized materials for solid-phase extraction of trace elements. Anal Bioanal Chem. 2015;407:2685–710.
4. Xie LJ, Jiang RF, Zhu F, Liu H, Ouyang GF. Application of functionalized magnetic nanoparticles in sample preparation. Anal Bioanal Chem. 2014;406:377–99.
5. Gauglitz G. ABC Spotlight on carbon nanotubes (CNTs). Anal Bioanal Chem. 2014;406:6077–9.
6. Heinke L, Tu M, Wannapaiboon S, Fischer RA, Wöll C. Surface-mounted metal-organic frameworks for applications in sensing and separation. Microporous Mesoporous Mater. 2015;216:200–15.
7. Sun XH, Shao K, Wang T. Detection of volatile organic compounds (VOCs) from exhaled breath as noninvasive methods for cancer diagnosis. Anal Bioanal Chem. 2016;408:2759–80.
8. Yi XL, Dong WF, Zhang XD, Xie JX, Huang YM. MIL-53(Fe) MOF-mediated catalytic chemiluminescence for sensitive detection of glucose. Anal Bioanal Chem. 2016. doi:10.1007/s00216-016-9681-y.
9. Long Z, Ren H, Yang YH, Ouyang J, Na N. Recent development and application of cataluminescence-based sensors. Anal Bioanal Chem. 2016;408:2839–59.
10. Brown KE, Greenfield MT, McGrane SH, Moore DS. Advances in explosives analysis – part II: photon and neutron methods. Anal Bioanal Chem. 2016;408:49–65.
11. Kumar P, Deep A, Kim K-H. Metal organics frameworks for sensing applications. Trends Anal Chem. 2015;73:39–53.
12. Tsotsalas M et al. Fabrication of highly uniform gel coatings by the conversion of surface-anchored metal-organic frameworks. J Am Chem Soc. 2014;136:8–11.

Günter Gauglitz is Senior Professor at the Eberhard Karls University of Tübingen working in analytical and physical chemistry. He was chairman of the GDCh Division of Analytical Chemistry and chaired the Europt(r)ode VIII meeting. For more than 15 years, his main scientific interests have centered on research and development in chemical and biochemical sensors with special focus on the characterization of interfaces of polymers and biomembrane surfaces, spectroscopic techniques, use of spectral interferometry to monitor changes in optical thickness of thin layers, and effects of Fresnel reflectivity at interfaces. He has been editor of *Analytical and Bioanalytical Chemistry* (ABC) since 2002.