



A. Müller

The author presented on this page has recently published his **25th article** since 2000 in *Angewandte Chemie*: "Picking up 30 CO₂ Molecules by a Porous Metal Oxide Capsule Based on the Same Number of Receptors": S. Garai, E. T. K. Haupt, H. Bögge, A. Merca, A. Müller, *Angew. Chem.* **2012**, 124, 10680–10683; *Angew. Chem. Int. Ed.* **2012**, 51, 10528–10531.

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Current research interests:	Processes under confined conditions, especially in capsules with stepwise closable pores and tunable internal functionalities; coordination chemistry in the cavity and pores of nanocontainers; sphere surface supramolecular chemistry; tuning the hydrophobicity of nanocontainer interiors to influence, for example, encapsulated water structures; cation transport/separation under confined conditions; molecular porosity; designed synthesis of nanosized clusters based on constitutional dynamic libraries; chemical adaptability
Hobbies:	Classical music, mountain hiking, swimming

I like refereeing because ... I can help to improve the quality of science.

My favorite place on earth is ... somewhere in the mountains.

My best investment was ... the purchase of many books from very different academic disciplines.

If I were not a scientist, I would be ... perhaps a musician.

My most exciting discovery to date has been ... the synthesis of nanocapsules with stepwise closable pores and tunable internal functionalities.

My worst nightmare is ... to publish false results.

Will the synthesis of polyoxometalates ever become as predictable as organic synthesis?

The question can be answered positively but with limitations. For example, most complex giant nanocontainers with different skeletons and internal functionalities can be predictably synthesized on the basis of accumulated knowledge of a dynamic library containing "molybdates". The addition of one type of building block to a related library results in the spontaneous(!) self-assembly of a giant spherical metal oxide porous capsule, while the required complementary pentagonal building blocks, needed for producing spherical systems, are "immediately" formed as expected. Important: The nanocontainers with different internal functionalities influence events taking place inside.

Could polyoxometalate assemblies be the basis of noncarbon life forms?

It is definitely not possible that polyoxometalates could lead to a "noncarbon life form" comparable to the present one: the extreme variety of organisms with their complex biochemical pathways was the result of a long evolution process based on adaptation and selection. For instance, analogues of the complex important organelles such as mito-

chondria and ribosomes with the required functions can not be obtained on a different basis. But polyoxometalate chemistry based on a huge variety of building blocks can be formally compared with organic chemistry with its huge number of molecules containing a variety of functional groups (I remember having read an equivalent question: "Oxo-Metalate Building Blocks: Conceptual Competitors for Tetravalent Carbon?"). Polyoxometalate chemistry facilitates the synthesis of materials such as artificial functionalized inorganic cells, which enable one to investigate basic processes in confined spaces.

Is the time over for "playing around with supramolecules"?

No, the "game" has just started! There is probably no "collection" of discrete inorganic compounds besides the well-known giant wheel- and sphere-shaped polyoxometalates that offers such a versatile chemistry and the opportunity to investigate new phenomena of interdisciplinary interest, especially under confined conditions. Because the giant spherical metal oxide based capsules are rather rigid, they can be appropriately manipulated in various ways, thereby increasing the probability of discovering new and different reactions and phe-

nomena, especially in their cavities. Porous capsules can be designed with tailor-made hydrophobic and hydrophilic interiors. There is probably no (pure) organic species known thus far that allows this design. Furthermore, new results of relevance for materials science are continuously being published.

Will supramolecular approaches ever be as powerful as classical homogeneous catalysis?

We should first realize that most industrial processes are based on heterogeneous catalysis though homogeneous catalytic processes are easier to rationalize. Papers based on “supramolecular approaches” have been published, for example by Makoto Fujita and Julius Rebek, Jr. (the related POM-based approaches are only in an early stage). But these give primarily significant information about the difference between the reaction pathways in confined spaces and in bulk systems. Whether such reactions can ultimately play an important role in industry remains to be seen.

The internet has changed the way we publish and read. What will be its future impact on science?

There is no doubt that the internet has the advantage to provide updated and often attractive information on important scientific works. On the other hand, too much interaction with the internet can have a negative influence and lead to a real addiction to “being permanently connected” at the expense of the necessary recoil required to analyze scientific data. In short, too much connection with the internet favors actionism at the expense of thinking and creativity.

How do you come up with new ideas?

Apart from the basic condition to have a peaceful and secluded setting so I am not disturbed by trivial problems, the condition to “come up with new ideas” for me is to be able to “connect” intellectually my own discoveries with those from other disciplines because this could, in principle, lead to performing experiments with far-reaching results. Important discoveries are often found in domains lying between disciplines.

How do you challenge a good student in your lab?

One way is by discussing fascinating and important discoveries of past creative scientists. While doing his/her experiments, the (good) student should not only be sensible enough to avoid overlooking unexpected or unusual observations, but also be able to interpret them. By referring to the history of science, it is possible in principle to recognize the conditions for optimal research and learn how difficult problems have often finally been solved. Some important advice for the student: never give up and always look at related results from neigh-

boring fields to succeed optimally, in order to become a recognized chemist.

Which are the hottest topics you would currently suggest to a young chemist to build their research career on?

We should distinguish hot topics related to society needs, to which chemists can contribute (e.g., discoveries of new renewable energy resources), from those not directly related to applications, namely discoveries of new phenomena or reactions that improve our understanding of the basic aspects of chemistry. A hot topic for me personally is to understand the important role played by water in self-assembly processes as well as in prebiotic chemistry. (This knowledge could be of value for the improved planning of such types of experiments.) Independent from that, if we can persuade young scientists to plan complicated experiments, the results of which could have an impact on different disciplines, they should be strongly motivated and realize the positive effect on their career.

You have a passion for Greek philosophy. What can modern scientists learn from the ancient Greeks?

The Greek philosophers had the advantage to be able to “think” without much disturbance and distraction by, say, bureaucracy! They thought like Thales about the first principles of existence of things expressed in terms such as *arche* (origin). Today chemists can be stimulated by Aristotle’s very important correlated regulative “potentiality” (*dynamis*) and “actuality” (*energeia*). “Potentiality” refers to the dispositional properties of systems (like those in chemistry) and “actuality” to a change/fulfillment of possibility. There are many examples in modern chemistry related to the Aristotelian concept pair; an important one refers to dynamic libraries, which need a stimulant for change/development leading to the actuality, that is, the intended reaction product.

Which discovery are you most proud of?

The isolation of quite a large number of differently shaped molybdenum and tungsten oxide based nanoobjects that have become well-known in the meantime. What is important is that I could design experiments based on specific manipulations, for example of our rather rigid porous spherical capsules, which lead to results of importance for other disciplines, such as nanoscience, physics, biophysics, and discrete mathematics. Furthermore, I was happy that we were able, based on related dynamic libraries, to design and synthesize spherical giant porous clusters with different internal hydrophilic and hydrophobic functionalities.

The interview questions were provided by Guido Clever (University of Göttingen).



The work of A. Müller has been featured on the cover of Angewandte Chemie: “A Nanosized Molybdenum Oxide Wheel with a Unique Electronic-Necklace Structure: STM Study with Submolecular Resolution”: D. Zhong, F. L. Sousa, A. Müller, L. Chi, H. Fuchs, Angew. Chem. 2011, 123, 7156–7159; Angew. Chem. Int. Ed. 2011, 50, 7018–7021.

My 5 top papers:

1. "Changeable Pore Sizes Allowing Effective and Specific Recognition by a Molybdenum-Oxide Based Nanosponge": En Route to Sphere-Surface and Nanoporous-Cluster Chemistry": A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, S. Roy, A. Berkle, *Angew. Chem.* **2002**, *114*, 3756–3761; *Angew. Chem. Int. Ed.* **2002**, *41*, 3604–3609.

The discovery of the unique spherical $\{Mo_{132}\}$ -type nanocapsule exhibiting 20 pores with properties similar to the classical crown-ether-type macrocycles opened up new techniques in supramolecular nanotechnology, while pore closing can influence the structures of encapsulated molecules. This can be formally compared with biological signal transduction where an extracellular signaling molecule activates a cell surface receptor that creates a response by altering intracellular molecules. The pore sizes can be varied since the fixed basic pentagonal $\{(M)M_5\}$ -type ($M = Mo, W$) building blocks of the $\{(pentagon)_{12}(linker)_{30}\}$ -type nanocapsules can be connected with larger and smaller linkers. Whereas monotopic receptors can only accept one guest, the present spherical system exhibiting polytopic receptors can bind 20 guests simultaneously, and even different ones, thus facilitating the study of cooperative, allosteric, and regulatory effects.

2. "Trapping Cations in Specific Positions in Tuneable "Artificial Cell" Channels: New Nanochemistry Perspectives": A. Müller, S. K. Das, S. Talismanov, S. Roy, E. Beckmann, H. Bögge, M. Schmidtman, A. Merca, A. Berkle, L. Allouche, Y. Zhou, L. Zhang, *Angew. Chem.* **2003**, *115*, 5193–5198; *Angew. Chem. Int. Ed.* **2003**, *42*, 5039–5044.

Holes with molecular dimensions are responsible for important properties of natural as well as synthetic materials as they can, for example, lead to substrate separations on the nanoscale. Although it has been known for a long time that a large number of extended materials containing pores, such as zeolites, can entrap guests, analogous processes in aqueous solutions within structurally well-defined discrete porous, rigid(!) inorganic capsules became known only quite recently. These processes allow investigation of the entrance and transport of different substrate types through the pores into the capsule cavities while the affinity of *different* substrates for *different* internal sites/(modifiable) functionalities can be logically understood. Small cations such as Li^+ , Na^+ , Ce^{3+} , and Pr^{3+} can easily pass through the pores and get fixed/trapped at well-defined positions, that is, separated on the nanoscale ("nano-ion-chromatograph" principle) while specialized NMR spectroscopic studies show that the Li^+ uptake–release process is in equilibrium.

3. "Molecular growth from a Mo_{176} to a Mo_{248} cluster": A. Müller, S. Q. N. Shah, H. Bögge, M. Schmidtman, *Nature* **1999**, *397*, 48–50.

A unique nucleation process can occur in the cavity of the wheel-shaped $\{Mo_{176}\}$ -type cluster, while the two $\{Mo_{36}O_{96}(H_2O)_{24}\}$ fragments—formed under the influence of the internal wheel functionalities—close the cavity-like hub caps and result in the formation of an $\{Mo_{248}\}$ -type cluster. Such types of processes can be

compared with those occurring in metal-storage proteins, especially in the case of the nucleations leading to *different*(!) well-defined polyoxomolybdates and tungstates in the molybdenum/tungsten-storage protein of the nitrogen-fixation bacteria *Azotobacter vinelandii*. As these processes, investigated by us, leading to the different polyoxometalates are template-directed by *different* protein-pocket functionalities, this work may lead to a better understanding of assembly processes under confined conditions.

4. "Hydrophobic Interactions and Clustering in a Porous Capsule: Option to Remove Hydrophobic Materials from Water": C. Schäffer, A. M. Todea, H. Bögge, O. A. Petina, D. Rehder, E. T. K. Haupt, A. Müller, *Chem. Eur. J.* **2011**, *17*, 9634–9639.

Hydrophobic effects that are not optimally understood play a major role in a variety of important phenomena, for example in protein folding and formation of lipid bilayers, as well as the insertion of proteins into biological membranes. In this context, studies were performed within the porous capsules of the type $\{(pentagon)_{12}(linker)_{30}\} \equiv \{(M)M_5\}_{12}\{Mo_2(ligand)\}_{30}$ ($M = Mo, W$), which can be constructed with varying hydrophobic interiors and therefore with *different* amounts and structures of encapsulated water. In the present case, it could be shown that a capsule containing 30 hydrophobic propionate ligands allows the removal of (toxic) hydrophobic species such as *n*-hexanol from water solutions based on their uptake and internal interactions, namely hydrophobic clustering studied by NMR spectroscopy. (This effect leads—in the presence of butyrate ligands—to the formation of an encapsulated unique $\{butyrate\}_{24}$ micelle-like aggregate containing a hydrophobic cavity.) The title process was considered as a paradigm shift with respect to recognition and clustering based on hydrophobic materials in water.

5. "Softening of Pore and Interior Properties of a Metal-Oxide-Based Capsule: Substituting 60 Oxide by 60 Sulfide Ligands": C. Schäffer, A. M. Todea, H. Bögge, E. Cadot, P. Gouzerh, S. Kopilevich, I. A. Weinstock, A. Müller, *Angew. Chem.* **2011**, *123*, 12534–12537; *Angew. Chem. Int. Ed.* **2011**, *50*, 12326–12329.

The $\{(W)W_5\}_{12}\{Mo_2\}$ -type capsule containing 60 sulfide functions can be prepared by adding dinuclear building blocks containing sulfide ligands to a dynamic library based on "tungstates" while the new "soft" skeleton influences reactions in the capsule interior differently than those in purely molybdenum oxide based capsule. One important result refers to the unprecedented segregation (comparable formally with the repelling characteristics of the Lotus effect) between the mostly hydrophobic internal capsule wall—spanned by the acetate/water ligand arrangement—and the encapsulated "water molecule collection", which has unique properties and forms an unprecedented shell with strongly interacting water molecules. Importantly, one can influence the "water assembly" by changing the ratio of acetate and water ligands, that is, the hydrophobicity.

DOI: 10.1002/anie.201209135