Multivariate Catalytic Materials

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Learning from nature to create catalytic materials and the present state of research on reticular chemistry

Nature has created fascinating materials whose structures are precisely controlled over several scales of length. Furthermore, nature has developed catalysts that dwarf all human-made catalysts, not only in terms of activity and selectivity, but also function under ambient conditions and without harmful or toxic substances, solvents or reagents. For chemists that want to develop materials for catalysis, nature has thus created a blueprint that can be used in terms of design, structural control, precision and sustainability.

However, despite the great advances that chemistry has made in recent decades, our synthetic capabilities are far from sufficient to even come close to the perfection of nature's synthetic toolbox –in fact, nature’s advantage of having several billion years of time to optimize materials and catalysts can discourage anyone who tries to approach such systems synthetically.

However, that doesn't mean we can't draw inspiration from natural materials and catalysts, especially when it comes to the chemistry of different components within them. Be it the interplay of nano- and microstructured inorganic crystallites with a soft polymer matrix in biomaterials, or of metal cofactors and protein shells in enzymes – the optimized mutual interaction of different functional units in such materials and molecular assemblies ultimately leads to their outstanding properties.

Reticular chemistry is a promise to create novel materials with unprecedented structural control.[1] By linking molecular building blocks via strong covalent bonds to crystalline open scaffold materials, our synthetic toolbox has expanded significantly to create materials with an unprecedented level of control over chemistry, structure and porosity at the molecular level, thus bringing us one step closer to the functionality of natural materials.

While simple molecular building blocks were initially used, primarily to build new structures and topologies without decisive functions, recent years of progress in reticular chemistry has increasingly focused on incorporating molecular building blocks with a wide variety of functions into open framework structures and thus creating novel materials that could be used in a number of applications.[2] This includes materials for energy storage or conversion, for the purification of drinking water, the separation of gas mixtures or for catalysis, i.e. for all areas that are of the highest relevance for the sustainable development of our society.

Materials produced via reticular chemistry will therefore play an important role in solving the Chemistry Challenges of the 21st Century.

Our research contributions to reticular chemistry and new materials

Our group deals with the synthesis and application of nanostructured materials, with a special focus on the production of porous functional materials for catalytic applications. We try to push the boundaries of the traditional disciplines of chemistry and materials science by working on inorganic and organic materials, as well as hybrid materials and developing unconventional approaches for their production, e.g. by synthesizing organic materials in inorganic molten salts [3] or incorporating main group elements as structure-building units in organic framework materials.[4] A turning point in our research was the development of metal-free semiconductors that can be used, among other things, as photocatalysts to produce hydrogen from water.[5] The generation of storable chemical energy from the energy of sunlight is one of the great chemistry challenges of the 21st century. Photocatalytic water splitting for the synthesis of hydrogen or the reduction of CO_2 into useful basic chemicals are two important reactions, which would yield independence from fossil raw materials and the reduction of greenhouse gases. The development of photocatalysts based exclusively on abundant elements would enable a new, decentralized production of chemical energy sources and products. After initially investigating polymeric carbon nitrides as photocatalysts, we also succeeded in the first synthesis of a porous organic network at room temperature as a photocatalyst.[6] In recent years, we have increasingly focused on the use of the principles of reticular chemistry to build covalent organic framework materials (COFs) as new organic photocatalysts.[7]

As described above, reticular chemistry, inspired by natural catalytic systems, allows various functional units to be incorporated into an open scaffold material with high precision. With such multifunctional or multivariate COFs structure and properties of a photocatalyst can be tailored, e.g. by controlling its band gap and band positions, improving charge carrier separation and mobility in the polymer backbone, varying the polarity of the material or introducing molecular co-catalysts. (Figure 1)

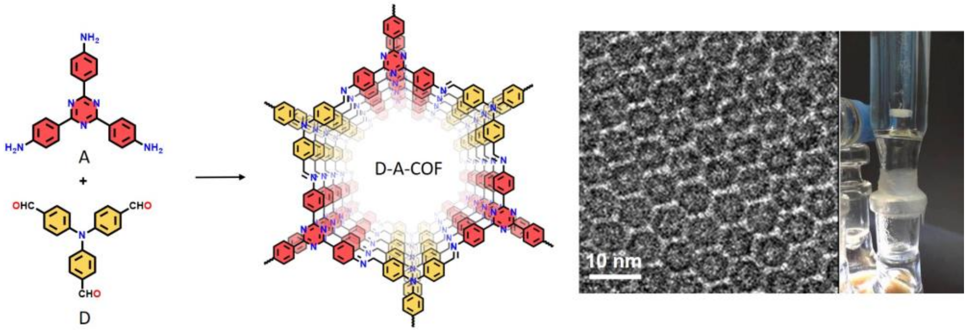

Figure 1: Synthesis of a COF including electron donor (D) and acceptor (A) moieties, HRTEM micrograph of the D-A-COF and experiment for photocatalytic hydrogen generation

We can also learn from nature that the structures of a functional material must be controlled not only at the molecular level, but in the best case over several length scales. Therefore, we have tried to create COFs that have defined structures even on micrometer and even larger length scales by adding additional templates or building composites with other materials such as graphene[8,9].

Outlook to future developments of research on reticular chemistry and new materials

The field of materials chemistry has expanded significantly with the development of reticular chemistry. For the first time, we have the opportunity to introduce a large number of different functional units into a single material with high precision in terms of distance, orientation and electronic coupling to each other. How can this help to create advanced materials of the future that are urgently needed for the sustainable development of our society? As an example, let's consider again materials for catalysis. As described in the opening statement, nature has created perfect catalysts, namely enzymes consisting of a complex protein shell and several cofactors whose functions have so far only been partially revealed. However, it can be safely assumed that nature would not have developed such complex assemblies if a much simpler solution would have offered similar catalytic performances and functions. The idea that just because certain metal ions are found in the active center of an enzyme, the same metals could exert similar reactivity on the surface of a simple support material or an organic ligand is tempting, but certainly too short-sighted. Perhaps we should rather consider a systemic approach to material development, i.e. dealing with complexity rather than simplifying things too much. The protein shell of enzymes fulfills a wide variety of functions in the catalytic process and is not only a complex ligand for metal ions. Inspired by this, we should strive for catalytic materials that not only immobilize a catalytic center, but whose multivariate structure can control the entire catalytic process, including the control of chemical and electrical potentials and the transport of mass and energy to and from the actual active center. Furthermore, why should we limit ourselves to materials that are only suitable for one single chemical reaction as a catalyst, when we can also consider a cascade of successive or simultaneous chemical or catalytic processes coupled by the transfer of reactants, products, and energy in the material, as we can eventually observe in our cells? Such an approach would require the construction of one or more multivariate materials, which are nevertheless spatially coupled with each other, so that different catalytic reactions can take place in separate compartments – which suggests a structural complexity of the materials, which we can potentially achieve through the promises of reticular chemistry. Such approaches will not preemptively create a synthetic enzyme or an artificial cell, but at least materials that come a significant step closer to this goal.

In Berlin, we are currently investigating such concepts in an interdisciplinary research network entitled "Unifying Systems in Catalysis – UniSysCat", in which more than 60 research groups from 9 institutions with expertise from bio- to inorganic solid-state chemistry, from theory to engineering sciences are involved.[10]

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