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From Molecules to Molecular Systems

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Abstract: The assembly, integration and functioning of various molecular components in complex systems is illustrated.

Keywords: Molecular motors · Molecular switches · Molecular systems

Ben L. Feringa obtained his PhD degree in 1978 at the University of Groningen and named the distinguished Jacobus H. van ‘t Hoff Professor of Molecular Sciences in 2004. He was elected foreign honorary member of the American Academy of Arts and Sciences and member of the Royal Netherlands Academy of Sciences. In 2008 he was appointed Academy Professor and was knighted by Her Majesty the Queen of the Netherlands.

Feringa’s research has been recognized with a number of awards including the Koerber European science award, the Spinoza Award (2004), the Prelog gold medal (2005), the Norrish award of the ACS (2007), the Paracelsus medal (2008) and the Chirality medal (2009). He is President of the 2009 Burgenstock Stereochemistry Conference.

The research interests include stereochemistry, organic synthesis, asymmetric catalysis, molecular switches and motors, self-assembly and molecular nano-systems.

The fascinating structures and complex functions present in biological systems offer a great source of inspiration to develop synthetic systems with functions controllable at the molecular and supramolecular level.[1] However, building on the remarkable achievements in the synthesis of complex molecules, one immediately realizes that structural complexity of individual molecules is often insufficient in the design of new complex functions.[2] In our body molecules do not act in isolation but typically a large collection of ingenious multi-component systems operate under kinetic control, usually in a mutually dependent way. Multiple integrated catalytic cycles, molecular information storage and retrieval, triggering and signal transduction, repair mechanisms and molecular motors and machines are among the many features of biomolecular systems.[3] Chemical systems ultimately also require control over structure, organisation and function of multi-component molecular assemblies at different hierarchical levels. It appears to be the right time to take up the challenge and enter the largely uncharted territory of molecular systems.

The design of chemical systems that allow the exploration of new functions or properties can be based on a combination of entirely synthetic molecules operating in concert. Alternatively, a bio-hybrid system can be designed, taking advantage of a structure from Nature by incorporating or co-assembling synthetic functional units. An illustrative example of the latter approach is a DNA-based asymmetric catalyst as presented in Fig. 1.[4] The supramolecular catalytic system comprises Cu (ii) bound to an achiral bipyridine-type ligand which upon intercalation to DNA accelerates C–C bond forming reactions, like the Diels Alder and Michael addition reactions.

Fig. 1. DNA-based asymmetric catalysis.
In a different approach, control of dynamics and organisation at different hierarchical levels is achieved (Fig. 3).[7] The system is based on a single enantiomer of a second-generation molecular motor that is used as an initiator for the polymerisation of hexylisocyanate. In this case the helical switching function of a single motor unit[8] is used to control, in a reversible manner, the preferred chirality of the dynamic helical polymer. This polymer forms a liquid crystalline (LC) film and by transmitting the change in chirality from the molecular via the macromolecular to the mesoscopic level, the chirality and organization of the LC film can be controlled by light. Again the cooperative effect of several components in the molecular system allows the control of a set of specific functions and materials properties.

The control of dynamic properties by the concerted action of a number of components is perhaps most elegantly seen in an autonomous propulsion system based on the molecular design shown in Fig. 4.[9] The key element is a dinuclear manganese complex that was designed as a functional mimic of the active site of the catalase enzyme. Via anchoring groups several catalyst moieties can be bound to a variety of objects including polymer rods and silica micro- and nano-particles. The addition of hydrogen peroxide to the system triggers a fast catalase-like decomposition of this fuel, generating water and molecular oxygen. Oxygen bubble formation is accompanied by autonomous translational movement of the object as long as hydrogen peroxide is supplied as fuel.

The molecular systems briefly discussed here are still extremely primitive compared to any of the dynamic systems Nature uses. However, in moving from molecules to molecular systems we will have to learn how to integrate structure and function in a dynamic multi-component ensemble. Far beyond this challenge are, among others, the inclusion of kinetically driven processes, autonomous processes, feedback loops and adaptive behaviour. Systems chemistry ultimately demands for a symphony of chemistries.

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[1] D. S. Goodsell, ‘Our Molecular Nature: The Body’s Motors, Machines and Messages’, Springer-Verlag, New York, 1996.
Fig. 4. Autonomous propulsion system based on a dinuclear manganese catalase mimic.