

# Supramolecular structure and dynamics

Highlighting this issue of PNAS is a special feature comprised of two Perspectives and four research articles dealing with aspects of supramolecular chemistry and dynamics. The term “supramolecular” invokes a chemistry beyond the molecule. Although the term supramolecular assembly or supermolecule is now widely used in the chemical, biological, and materials literature, a precise definition is difficult to pin down. One way to obtain some insight to the term is to define a molecule as an assembly of atoms that is held together by relatively *strong* intramolecular bonds, and to define a supermolecule as an assembly of molecules that is held together by relatively *weak* intramolecular bonds. This definition of supramolecular chemistry implies that the successful ideas of structure that have been so successful in describing molecules will also be successful in describing supermolecules.

With this analogy in mind, in the same way that atoms are telescoped to a mathematical point to describe molecular structure, molecules are telescoped to points in supramolecular structures. We now can understand the properties of supermolecules that will describe them with the same clarity as those of molecules: the structural concepts of composition (numbers and kinds of molecules), constitution (the way the molecules are connected), and configuration (the way the molecules are oriented relative to one another in space). Supramolecular dynamics is the study of the change of one or more of these structural features with time. A distinct feature of the structure of many important supramolecular structures is that they are held together by a large number of weak intramolecular bonds, but that at any instant a large number of these weak bonds are in place and contribute to the overall stability of the supermolecule. Because of this feature, the local dynamics of supramolecular bond breaking and bond making is an important aspect that allows for the rich diversity and complexity of many supramolecular systems.

The special feature articles in this collection can be viewed in the framework of the above introduction to supramolecular structure.

My Perspective in this special feature (1) provides an overview of how molecular structure can serve as a blueprint for supramolecular structure and, in confined spaces, introduces the enzyme-inspired concept of guest@host, which can be used as exemplar for describing the structure of supramolecular systems. The term host can be used to describe any confining space, such as cage or cavity. Chemists now seek to obtain a mastery of the intermolecular bond and apply this knowledge to understanding systems as complex as the cell and living systems.

An example of the use of guest@host complex is provided by Purse and Rebek (2), who describe functionalized cavities based on a resorcinarene platform. The latter allows a systematic exploration of chemical reactivity as a function of supramolecular environment. These authors show how and why structures such as guest@cavity control the properties and reactivity of guest molecules.

Garcia-Garibay (3) provides an example of a modified version of the guest@host system in which the guest, embedded in a crystalline matrix, is a guest@crystal complex that serves as the basis for the design of molecular machines. In this case, supramolecular ideas and crystal engineering are wedded to uncover the relationship of supramolecular structure and supramolecular dynamics for the construction of a molecular gyroscope.

Liu, Hammond, and Mirzadegan (4) provide an example of a guest@host system in which they propose a subtle difference in the intermolecular binding of rhodopsin in a protein that can be viewed in terms of supramolecular isomers of rhodopsin@protein. One of these supramolecular isomers is competent to undergo the photoinduced cis-trans isomerization that triggers the visual response, but the other supramolecular isomer undergoes efficient

return to its ground state and does not isomerize.

DeRosa, Sancar, and Barton (5) provide an example of one of nature's most magnificent supramolecular systems, double-helix DNA. They show how a combination of supramolecular chemical biology coupled with electrochemistry can be used to monitor the repair of thymine dimers in DNA at an electrode surface.

Buchachenko, Kouznetsov, Orlova, and Markarian (6) report an investigation of the supramolecular chemical biology of phosphoglycerate kinase (PGK) through a remarkable magnetic isotope effect, the latter often a signature of the involvement of supramolecular systems. These authors show that the rate of phosphorylation in  $^{24,26}\text{Mg}$ -PGK (non-magnetic Mg isotopes) is suppressed by reversible back electron transfer, whereas in  $^{25}\text{Mg}$ -PGK (magnetic Mg isotope), a fast singlet-triplet conversion induced by the nuclear spin of  $^{25}\text{Mg}$  competes successfully with the back electron transfer and creates an efficient channel for ATP production.

For several years, PNAS has published special feature issues on many cutting edge research topics. Some of the themes of past special features have included: Gene Regulatory Networks, Social and Behavioral Sciences, Asymmetric Catalysis, Science and Technology for Sustainable Development, Long-Range Electron Transfer, and, most recently, Molecular Electronics. Scheduled for future issues of the journal are special features on Cluster Dynamics and Chemistry, Demography, and Tissue Engineering. One objective of these special features is to advance the journal's ongoing initiative to expand its coverage of the physical and social sciences and mathematics. PNAS continues to encourage and welcome research articles in all areas of the natural and social sciences and mathematics.

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3. Garcia-Garibay, M. A. (2005) *Proc. Natl. Acad. Sci. USA* **102**, 10771–10776.

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6. Buchachenko, A. L., Kouznetsov, D. A., Orlova, M. A. & Markarian, A. A. (2005) *Proc. Natl. Acad. Sci. USA* **102**, 10793–10796.