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## Beyond the Molecule

The Nobel prize awarded in 1987 to Cram, Lehn, and Pedersen honored achievements in molecular recognition and the ability to design molecules that assemble through non-covalent interactions. The complexity of the final molecular structures obtained through self-assembly has evolved considerably since this pioneering work, as have the designed functions. The 2016 Nobel Prize in Chemistry to Feringa, Sauvage, and Stoddart represents one such example, which recognized contributions to the development of artificial molecular machines. Supramolecular chemistry, or “chemistry beyond the molecule,” continues to be widely explored and impactful in many different areas owing to advances in the preparation of novel supramolecular structures, the development of improved methods of preparation of supramolecular structures, and the design of new functional supramolecular assemblies.

This Special Issue of *Accounts of Chemical Research* highlights the numerous and varied advances in supramolecular chemistry in confined space and organized assemblies. The field of supramolecular chemistry draws on these advances to construct large, intricate, and highly ordered functioning chemical species of higher complexity. This is wonderfully demonstrated by Anderson and Bols’ oligopyridine-derived molecular nanorings, Jin’s template-free self-assembly of molecular Borromean rings, Chiu’s alkali metal ion templated interlocked molecular structures and in Chen and Han’s account describing the synthesis of chiral macrocyclic arenes they call helicarenes. Moreover, the ability to control the size, shape and topology of supramolecular interactions has enabled a myriad of applications. This feature is beautifully highlighted by Severin and Jansze’s description of modular supramolecular synthesis with transition metal clathrochelate as metalloligands, Stang’s hierarchical self-assemblies with well-defined shapes, sizes, and internal cavities, and Yam and Chan’s structural modification of alkynylplatinum(II) terpyridine complexes to engender diverse functions. Yang and Chen describe how these hierarchical self-assemblies are involved in the preparation of stimuli-responsive functional materials.

The interior cavities of supramolecular assemblies, generally protected from bulk solution, provide a unique environment for encapsulated guest molecules and can stabilize otherwise unstable species or lead to enhanced reactivity and selectivity. This paradigm is articulated in Reek’s account describing the templated synthesis of homogeneous catalysts in molecular cages and their application to reactions in which the selectivity and stability can be controlled by the cage as second coordination sphere. Supramolecular catalysts can also activate otherwise unreactive substrates

without the use of distinct covalent interactions between the catalyst and substrate. This principle is described by Yu and Rebek's account of guest binding by cavitands and the chemical reactions that occur in the space defined by these molecular containers and Tiefenbacher's report describing that the different chemical environment inside supramolecular resorcinarene capsules leads to altered product selectivity. Supramolecular assemblies based on transition metal coordination complexes also offer defined environments for selective catalysis, sometimes with remarkable rate accelerations, as described by Ward and Toste in their accounts of catalytic transformation performed by  $M_8L_{12}$  and  $M_4L_6$  assemblies, respectively.

These synthetic host molecules can promote complex reactions within their cavities despite the fact that they lack the type of specifically tailored functional groups normally located in the analogous active sites of enzymes. They can also mimic other features of their biological counterparts. For example, Barboiu describes efforts aimed at employing supramolecular interactions to design artificial ion channels, Nitschke reports on the development of stimuli-responsive capsules with various applications, including to multi-cage networks that might allow biomimetic transfer of signals and information, and Sessler and Park describe chemically-driven supramolecular switches using tetrathiafulvalene-annulated calix[4]pyrroles. Additionally, Duan details their approach to constructing photoactive supramolecular assemblies that might mimic photosynthesis and Kim describes the use of their porphyrin boxes in light harvesting and beyond.

Supramolecular structures can be described as chemical species of higher complexity that are held together and organized by means of intermolecular binding interactions. This definition also encompasses networks derived from supramolecular interactions to form new materials. The seminal contribution of Hosono and Kitagawa to this concept describes their efforts to build porous soft materials derived from supramolecular metal-organic cages. These types of materials have found numerous applications in adsorption and separations as demonstrated by the pillarene-based nanoporous adaptive crystals and the imine-based shape persistent porous cage materials of Huang and Mastalerz, respectively. Clever and Pullen provide an important overview of and comparison between molecular systems (metal organic cages) and infinite porous networks (metal organic frameworks). Additionally, Lin shows that these metal organic frameworks can be leveraged to design single-site metal organic framework catalysts that shut down deactivation pathways experienced by molecular catalysts. Finally, Wang describes the multi-component assembly of platinum(II) terpyridine complexes into well-ordered nanostructures and their application as functional supramolecular materials.

While great advances have been made in the 30 years that have passed since Cram, Lehn, and Pedersen were honored with the Nobel Prize, the field

of supramolecular chemistry still offers numerous opportunities for preparation of new structures, advancement of new methods for synthesis of known structures, and designing new functions. We hope this account, which details many of these advances, will serve to inspire the next generation of discoveries in this remarkable field.

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