Foreword

Supramolecular chemistry has been defined as "chemistry beyond the molecule". It aims at constructing highly complex, functional chemical systems from components held together by intermolecular noncovalent forces. It has relied on the development of preorganized molecular receptors for effecting molecular recognition, on the basis of the molecular information stored in the covalent framework of the components and read out at the supramolecular level through specific interactional algorithms. Suitably functionalized receptors may display supramolecular reactivity and catalysis and selective transport processes.

A most basic and far-reaching contribution of supramolecular chemistry to chemical sciences has been the implementation of the concept of molecular information. It involved the storage of information at the molecular level; in the structural features; and its retrieval, transfer, and processing at the supramolecular level, through molecular recognition processes operating via specific spatial relationships and interaction patterns. Supramolecular chemistry has thus paved the way toward apprehending chemistry also as an information science.

The control provided by recognition processes allowed the development of functional molecular and supramolecular devices, defined as structurally organized and functionally integrated systems built from suitably designed molecular components performing a given action (e.g., photoactive, electroactive, and ionoactive) and endowed with the structural features required for assembly into an organized supramolecular architecture. Thus emerged the areas of supramolecular photonics, electronics, and ionics.

Beyond mastering preorganization and taking advantage of it, supramolecular chemistry has been actively exploring the design of systems undergoing self-organization, that is systems capable of spontaneously generating well-defined, organized supramolecular architectures by self-assembly from their components, under the control of molecular information processes. They operate as programed chemical systems and are of major interest for supramolecular science and engineering. They give access to advanced functional supramolecular materials, such as supramolecular polymers, liquid crystals and lipid vesicles as well as solid-state assemblies.

The implementation of ‘programed’ self-organizing systems amounts to performing self-organization by design. It also provides an original approach to nanoscience and nanotechnology. In particular, the generation of well-defined, functional supramolecular architectures of nanometric size through self-organization represents a means of performing programed engineering and processing of nanomaterials. Technologies resorting to self-organization processes are, in principle, able to provide a powerful complement and/or alternative to nanofabrication and nanomanipulation procedures by making use of the spontaneous but controlled generation of the desired superstructures and devices from suitably instructed and functional building blocks. The long-range goal is to shift from entities that need to be made to entities that make themselves, that is, from fabrication to self-fabrication.

From another point of view, self-organization is, in principle, able to select the correct molecular components for the generation of a given supramolecular entity from a diverse collection of building blocks. It may thus take place with selection, by virtue of a basic feature inherent in supramolecular chemistry, that is, its dynamic character.

Indeed, supramolecular chemistry is intrinsically a dynamic chemistry in view of the lability of the interactions connecting the molecular components of a supramolecular entity and the resulting ability of supramolecular species to exchange their constituents. Such a dynamic character is also conferred to molecular chemistry when the molecular entity contains covalent bonds that may form and break reversibility, so as to allow a continuous change in constitution by reorganization and exchange of building blocks. Thus, supramolecular chemistry has also fertilized molecular chemistry, leading to the definition of a Constitutional Dynamic Chemistry on both the molecular and supramolecular levels. It takes advantage of dynamic diversity to allow variation and selection. It operates on dynamic constitutional diversity in response to either internal or external factors to achieve adaptation.

Supramolecular chemistry has progressed over the years along three overlapping phases. The first is that of molecular recognition and its corollaries, supramolecular reactivity, catalysis, and transport; it relies on design and preorganization and implements information storage and processing.
The second concerns self-assembly and self-organization, that is self-processes in general; it relies on design and implements programing and programed systems for controlling the generation of specific entities in complex mixtures.

The third concerns constitutional dynamics of both molecular and supramolecular entities, defining a constitutional dynamic chemistry as a unifying concept. It relies on self-organization with selection in addition to design, and leads to the emergence of adaptive and evolutive chemistry.

Since it has been named in 1978 by the undersigned, about 10 years after the seed had been planted, the field of supramolecular chemistry has experienced a spectacular growth at the triple meeting point of chemistry with biology and physics. Its concepts and the perspectives it opens have been delineated, attracting scientists with a wide range of expertise. It has given rise to numerous review articles and special issues of journals and books. The present monumental work comes very timely. It provides thorough reviews and discussions, covering a broad range of topics, authored by many of the major players in the field. It takes stake and opens perspectives to the creative imagination of all participants in our common adventure.

I would like to very warmly congratulate and thank the editors and the contributors alike for this precious gift to the science of chemistry.

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