Preface

A wide range of fields within supramolecular chemistry are of current and great interest ranging from nanosciences, medicinal sciences, biosciences, and even organic sciences and this is a mature and extremely active area of research. In 1978, Lehn defined this chemistry as the "chemistry of molecular assemblies and of the intermolecular bond." In other words, supramolecular chemistry is noncovalent chemistry based upon covalent chemistry.

On the other hand, it is well known that replacing the carbon atom of cyclic compounds can lead to dramatic changes in chemical and physical properties and the principles of homocyclic chemistry are often of limited value and may even lead to incorrect results. This is often indeed the case in supramolecular chemistry. The modern explosion of nonochemistry is highly based upon the fundamental recognition of intermolecular interactions engendered by supramolecular scientists.

In this volume entitled *Heterocyclic Supramolecules* I, a part of the series *Topics in Heterocyclic Chemistry*, some selected topics in noncovalent chemistry from the last decade are highlighted, with attention particularly focused on heterocyclic supramolecules as well as heterocycle-based nanosciences.

The first chapter, "Molecular Recognition with designed Heterocycles and their Lanthanide Complexes" by S. Mameri, S. Shinoda, and H. Tsukube describes various synthetic receptors for specific binding of cationic anionic guests mainly in the solution states. Furthermore, special attention is directed at the heterocycle-lanthanide complexes that worked as luminescent sensory devices of biologically important anions. Thus, "rare" earth metals are making the change into "hopeful" earth metals.

The second chapter, "Syntheses and Properties of Crownophanes" by S. Inokuma, M. Ito, and J. Nishimura reviews a variety of crownophanes possessing both crown ether and cyclophane moieties, the latter ranging from benzene to condensed aromatic and heteroaromatic rings whose selective complexation in the solution states principally toward the metal cations are reviewed. The related rotaxanes and catenanes are also described in this chapter.

The third chapter, "Azacalixare: A New Class of Calixarene Family" by H. Tsue, K. Ishibashi, and Rui Tamura presents recent developments in syntheses, conformations, and inclusion properties of nitrogen-bridged calixarene derivatives possessing a $[1_n]$metacyclophane unit. Since just the replacement

of hydrogen(s) of the methylene bridge with an appropriate group(s) would offer wider functional variations as in the case of the crownophane family, further developments in this field are surely anticipated.

The fourth chapter, "Chemistry of Calixfurans" by Kei Goto presents summaries of the synthesis, reactions, structures, and host–guest chemistry of calix[n]furans and their hybrid systems containing other aromatic units like pyrrole and thiophene. Calixfurans appear to be a tactful supporting actor in the chemistry of calixarenes. Regardless of their rather modest intrinsic binding abilities, the weak coordination by the furan units of calixfurans or hybrid systems plays a crucial role in certain cases. More importantly, calixfurans can be converted into a wide variety of macrocycles including those otherwise difficult to access since the furan unit serves as a versatile functional group such as a masked 1,4-dicarbonyl equivalent and Diels–Alder diene. Further development of the synthetic strategy of calixfurans as well as the novel methods for their transformation to other functional molecules is highly anticipated. Since the conformational behavior of calixfurans has not been sufficiently clarified yet, the more sophisticated strategy for regulation of their conformational dynamics should be explored for the ready construction of the desired molecular framework.

The fifth chapter, "Supramolecules based on Porphyrins" by H. Yamada, T. Okujima, and N. Ono presents a review particularly focusing on the supramolecular architectures of porphyrins that enable their use as electronic and optical functional materials such as third-order optical susceptibilities, photoenergy conversion systems, and organic field-effect transistors. Although life as we know it would be impossible without porphyrins, they are now characterized not only as the "color of life" but also as a treasure house of material sciences. For instance, photovoltaic cells are currently of broad interest as potential low-cost approaches to solar energy conversion. Large-area electronic devices and solution-processed organic semiconductors based on porphyrins, phthalocyanines, and related molecules could have potentially a huge cost advantage over Si-based devices if conversion efficiency and durability can be improved to the level of Si-solar cells.

The final chapter, "Heterocyclic Supramolecular Chemistry of Fullerenes and Carbon Nanotubes" by N. Komatsu presents an extremely unique review that focuses on the noncovalent chemistry of fullerenes and carbon nanotubes with nitrogen- and/or oxygen-containing heterocyclic molecules such as porphyrin, DNA, protein, peptide, and carbohydrate. Not only exohedral but also endohedral functionalization is reviewed, because the above guest molecules can interact with both faces of the carbon nanotubes. The hurdles in structural separation, nanofabrication, and bioapplications of carbon nanotubes will hopefully be addressed by the supramolecular strategy.

Finally, I hope, in the near future, that heterocyclic supramolecules could figure in a practical generation of molecular machines and in highly effective production of useful materials at molecular levels, for example in a much

more efficient artificial photosynthetic process than the natural one and in an electronics revolution that will produce the carbon-heteroatom-based molecular computer—probably more than 1000-times smaller and a million-times more powerful than our present machines, via recourse to quantum mechanics rather than classical Newton mechanics that would solve environmental as well as energy problems.

Kyoto, May 2008 Kiyoshi Matsumoto

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