PREFACE

I think that the most important appoint task of the organic chemistry including biochemistry is to solve the mechanism of the biological functions, and then to endeavor to design, or mimic such functions with a synthetic molecule.

Very recently, -maybe in latest three years, the progress in the field of biochemistry is dreadful enough to depict the mechanism of functions, which is standing upon not only the DNA sequences but also the structural analyses of the complex by the X-ray diffraction, NMR, and mass spectrometry. For instance, how the integrin family recognizes and adhesive collagen or RGD-containing proteins, which is realized by the multivalent hydrogen bonds, coordination bonds, and hydrophobic interactions with approximately equilibrium constant 10 nM^{-1} has been almost completely demonstrated. After the mechanism has been solved by the biochemists, the organic chemists, in turn, should try to design the molecules to mimic such functions, although in general, the molecular recognition is realized by the multi-strand interactions, utilizing the very accurate, complicated structure of the biomacromolecules.

In the previous century, the “art” of organic syntheses reached to the apex in a sense. Probably almost all of the molecules can be synthesized unless the much efforts and troublesome works are avoided. The functions of protein, however, cannot reproduce by the conventional synthetic molecule completely. Since the functions of the protein are controllable in selectivity, or reactivity, and rely on the high-ordered structural changes or rearrangements, which the flexible non-covalent interactions allow. For example, in hemoglobin (Hb), dynamic conformational changes of the subunit, which is induced and amplified from the small movement of the central ion from the porphyrin plane in the first dioxygen binding, reduces the activation energy of the continuous dioxygen-bindings to the hemes embedded inside the neighboring globins. We call these multi-step coordination profiles as allosteric phenomena, which is typical example, that will be never mimicked by the synthesized molecule. Therefore, supramolecules which are the potent candidate to inhibit such high-ordered functions, are recently widely studied. The supramolecule is defined as polymeric arrays of monomeric units that are brought together by reversible and highly directional secondary interactions to be constructed highly ordered (not only two- but three-dimensionally) structure, and possess unique functions that the building blocks never indicate. In this thesis, the construction and analyses of multivalent hydrogen bonded porphyrin-calix[4]arene duplexes as a brand-new hemoglobin model using strategy of supramolecular architecture, were described. Author wishes these results would be useful and become a firm scaffold to realize allosteric functions of the supramolecules like elegant biomacromolecules.

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