Abstract

This doctoral dissertation, entitled “Self-Association of Supramolecular Capsules Based on Dynamic Iminium and β-Diketone Bonds”, presents comprehensive research at the interface of materials chemistry and fundamental supramolecular chemistry. The research work was carried out within two main, complementary scientific pillars. The first one focused on the design and synthesis of functional metallosupramolecular materials based on β-diketone ligands, with a focus on their catalytic potential. The second pillar was devoted to the study of fundamental principles of self-assembly and self-sorting of components in the process of creating metal-free, organic cages using the tools of Dynamic Covalent Chemistry.

Within the first research area, the work began with a detailed analysis of the coordination chemistry of a simple, unsymmetrical β-diketone ligand (bpmH). The aim was to understand and overcome potential problems, such as uncontrolled oligomerization and complex isomerism, which could complicate the design of more advanced systems. These studies showed that although the bpmH ligand does not fully prevent oligomerization (as demonstrated for the nickel(II) complex), the intermolecular interactions in its complexes are so weak that the formation of isomers in solution is mainly statistical. These observations, including the complex, temperature-dependent dynamic equilibrium in the case of the zinc(II) complex, provided a key foundation for further work. In the next step, an efficient two-step synthetic strategy was developed using a tritopic ligand (H_3L). By precisely controlling the stoichiometry, discrete, dimeric metallacycles of the $[M_2(HL)_2]$ type with Cu(II) and Pd(II) ions, possessing a free, reactive functional arm, were first obtained. Then, in the reaction with excess metal ions, their controlled polymerization was carried out. While in the case of copper(II), the process led to an insoluble product, the reaction with palladium(II) was successful, giving a fully characterized, soluble metallosupramolecular polymer $[Pd_3L_2]n$. The comparison of the catalytic activity of both palladium complexes in the Suzuki-Miyaura cross-coupling reaction was the culmination of this part of the research. It was proven that the $[Pd_3L_2]n$ polymer is a much more efficient catalyst, providing higher yields on average by 10-20% compared to its discrete, cyclic precursor. The improved catalytic properties of the polymer were attributed to the larger number of available active sites and the so-called "local concentration effect".

The second pillar of the thesis is devoted to the study of the fundamental principles governing the self-assembly process using Dynamic Covalent Chemistry (DCC). These works, conducted in metal-free organic systems, focused on the phenomenon of self-sorting during the formation of three-dimensional cages (cryptands) based on reversible imine bonds. In a series of competitive experiments, in which one triamine reacted with a complex mixture of different dialdehydes, an extremely high degree of selectivity was observed. In the vast majority of cases, the system spontaneously selected one, most privileged component to build only one, pure (homoleptic) cage product. Crucially, in none of the studied systems was the formation of mixed (heteroleptic) cages observed. Systematic studies allowed us to establish a strict hierarchy of preferences and formulate structural rules governing this process. It was shown that the outcome of sorting is determined by the molecular features of the "building blocks": the most privileged are rigid, fully conjugated components containing a heteroatom (e.g. nitrogen), while flexibility and disorders in the conjugated system significantly reduce the efficiency of a given component. Moreover, it was proven that the observed preferences result from the system reaching a true thermodynamic equilibrium. Using acid-base control over the reversibility of imine bonds, the

possibility of performing a controlled cage-in-cage transformation was demonstrated, in which a less stable structure, in the presence of more favored components, spontaneously reorganizes into the most thermodynamically stable product.

In summary, the presented doctoral thesis comprehensively combines materials chemistry with fundamental research on self-organization. As part of the completed work, not only new, functional materials with increased catalytic activity were obtained, but also the rules governing the process of selective sorting of components in dynamic combinatorial systems were thoroughly investigated and formulated, contributing to the development of both of these dynamically developing fields of chemistry.