SUMMARY OF THE DOCTORAL DISSERTATION

Influence of the structural factors of amino acid-decorated benzene-1,3,5-tricarboxylic acid derivatives on supramolecular aggregate formation

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This doctoral dissertation, entitled *"Influence of the structural factors of amino acid-decorated benzene-1,3,5-tricarboxylic acid derivatives on supramolecular aggregate formation"*, describes the synthesis and characterization of a series of new benzene-1,3,5-tricarboxylic acid derivatives functionalized with amino acids. The work analyzes how structural variations within different molecular positions, such as the ester group, amino acid side chain, chirality, and α-position substitution, affect the type and properties of the resulting supramolecular structures. The dissertation is divided into four chapters, covering both theoretical foundations and experimental results.

Chapter I, serving as an introduction, presents a review of the key aspects relevant to the research topic. It begins with the structure and role of amino acids as building blocks in supramolecular chemistry and continues with the characteristics of benzene-1,3,5-tricarboxamide (BTA) derivatives, with particular emphasis on amino acid-decorated systems. This chapter includes an overview of the literature concerning the relationship between structure and self-assembly behavior in tripodal BTA-based systems. The section concludes with a discussion of hydrogen-bonded capsule formation, the role of BTA derivatives in such architectures, identification of the research gap, and the rationale for the undertaken studies.

Chapter II describes the design and synthesis of four tripodal (C_3-symmetric) derivatives based on the benzene-1,3,5-tricarboxamide core decorated with amino acid esters, aimed at examining the influence of steric hindrance of amino acid side chains and ester groups on aggregation behavior in both the solid state and in solution. The target compounds were functionalized with glycine or L-valine esters (–OMe, –OiPr). Two types of structures were identified: a dimeric capsule stabilized by –NH···O=C(ester) hydrogen bonds and a columnar supramolecular arrangement based on –NH···O=C(amide) interactions. Solid-state analyses revealed that steric hindrance of the ester group at the C-terminus strongly influences aggregation type, bulkier substituents suppress columnar organization in favor of simpler dimeric motifs. In chloroform solution, this effect was not observed; instead, the character of aggregation was primarily determined by the nature of the α-substituent. The results emphasize the key role of steric factors at both the α-carbon and ester positions.

Chapter III focuses on the formation of hydrogen-bonded octameric capsules based on the benzene-1,3,5-tricarboxamide (BTA) core functionalized with amino acids bearing unblocked carboxylic termini. The study investigated the influence of structural factors (amino acid side chains) on self-assembly and their impact on the ability to encapsulate fullerene guest molecules (C_{60} and C_{70}). Complementary analytical techniques, including NMR, FT-IR, and UV-Vis spectroscopy, were employed to systematically compare the behavior of structurally related BTA derivatives. Additionally, a preliminary attempt to utilize the resulting supramolecular structure as a hydrogen-bonded catalytic capsule was presented. The results demonstrated that while the type of amino acid substituent affects encapsulation efficiency, it does not alter the overall capsule architecture.

Chapter IV examines the impact of structural factors on the formation and physicochemical properties of the supramolecular assemblies. Eleven compounds representing different structural classes were synthesized, enabling a comprehensive analysis of their aggregation behavior. Three key factors: chirality, amino acid side chain, and α-hydrogen atom, were identified as determinants of aggregate formation in both solid state and solution. Achiral derivatives were found to be completely insoluble in nonpolar media, preventing their characterization in solution. Chiral derivatives containing an α-hydrogen atom exhibited good solubility and formed hydrogen-bonded octameric capsules. In contrast, chiral α-methyl-substituted analogues showed decreased solubility, similar to achiral compounds; however, the issue was resolved by introducing long aliphatic chains, which improved solubility. These α-methyl derivatives also formed hydrogen-bonded octameric capsules, though less stable than their α-H-containing analogues. Furthermore, the studies revealed that both chirality and α-substitution significantly influence self-recognition phenomena and modify host–guest properties.

In addition to extensive literature references, the dissertation includes detailed experimental procedures, synthetic protocols, and supplementary spectroscopic data supporting all presented results.