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FINDINGS

The thesis entitled **"Design, synthesis and properties of calix[4]pyrrole derivatives"** is composed of six chapters and focuses on the development, synthesis, and properties of calix[4]pyrrole (C4P) derivatives, which are gaining prominence as advanced supramolecular functional materials.

Chapter I: This chapter presents an overview of recent advances in supramolecular chemistry, particularly emphasizing the concepts of molecular recognition and self-assembly in the development of functional molecular systems. It highlights the significance of the non-aromatic tetrapyrrolic macrocyclic framework calix[4]pyrrole (C4P) as a versatile supramolecular platform. Due to its unique structural features and ability to participate in multiple non-covalent interactions, C4P has shown wide applicability in ion and ion-pair recognition, neutral molecule sensing, polymer development, catalysis, drug delivery, pharmacology, ion transport, molecular devices, and adsorption processes. The chapter also discusses different synthetic strategies employed for the preparation of C4P derivatives and how structural modifications influence their properties. Particular attention is given to the anion-binding and sensing abilities of C4P-based host systems. These interactions are mainly governed by NH-hydrogen bonding along with additional stabilization through anion-π interactions. Furthermore, the chapter emphasizes the importance of various spectroscopic techniques in understanding the binding and sensing behaviour of C4P receptors toward different anionic guests. Overall, the chapter establishes the theoretical background of the study and outlines the objectives and organization of the thesis.

Chapter II: This chapter demonstrate the successful synthesis of a one-walled pyrene-extended calix[4]pyrrole receptor, which was fully characterized using ^{1}H-NMR, ^{13}C-NMR, and HRMS techniques. The receptor was investigated for anion recognition toward various anions with different geometries in acetonitrile using UV-Vis spectrophotometric titrations. Binding studies analyzed through BindFit v0.5 indicated a clear 1:1 host-guest binding stoichiometry, which was further confirmed by Job's plot analysis. Among the tested anions, the receptor showed the strongest binding affinity toward fluoride ion due to its small size and strong hydrogen bonding ability. Spectroscopic studies also revealed the presence of anion-π interactions in addition to the conventional NH hydrogen bonding interactions. These interactions were supported by noticeable upfield shifts in the ^{1}H NMR spectra. To further validate the role of π-systems in anion binding, a phenyl-extended one-walled C4P receptor was also synthesized and examined. The similar upfield shifts observed in the phenyl ring protons upon fluoride addition confirmed the involvement of anion-π interactions in the receptor system.

Chapter III: This chapter highlight the successful synthesis of two new one-walled superpyrrolyl-extended calix[4]pyrrole receptors using the Clauson-Kaas and Paal-Knorr protocols as key synthetic steps. The synthesized receptors were comprehensively characterized through standard spectroscopic techniques including ^{1}H-NMR, ^{13}C-NMR, and mass spectrometry. After structural confirmation, both receptors were evaluated for their anion recognition abilities toward various anions of different geometries using UV–Vis spectrophotometric titrations in solution. The binding data analyzed through non-linear curve fitting with BindFit v0.5 indicated a clear 1:1 host-guest binding stoichiometry, which was further supported by Job's plot analysis. Among all the investigated anions, both receptors exhibited the highest binding affinity toward fluoride ion. This enhanced affinity was attributed to the small size of fluoride and its strong hydrogen-bonding capability with the receptor framework.

Chapter IV: This chapter demonstrate the application of indicator displacement assay (IDA) as an effective strategy for optical sensing using calix[4]pyrrole-based receptors. In this study, two novel aryl-extended one-walled C4P receptors were successfully synthesized and utilized for IDA-based sensing with *p*-nitrophenolate anion as an indicator. Initially, the anion binding affinities of both receptors toward various anions were evaluated using UV-Vis spectrophotometric titrations to determine their association constants. Based on the obtained

K_a values, IDA sensing experiments were carried out only with anions such as F^-, Cl^-, and CH_3COO^- that exhibited stronger binding than the indicator. The sensing studies revealed a significant response toward fluoride ion, indicating selective detection capability. The calculated limit of detection (LOD) and limit of quantification (LOQ) for the *meso*-bis-(trifluoromethyl)-aryl-extended C4P were found to be 5.78 mg/L and 6.21 mg/L, respectively. For the *meso*-2,4,6-trifluoro-aryl-extended C4P receptor, the LOD and LOQ values were determined to be 17.53 mg/L and 18.83 mg/L. Furthermore, the anion complexation mechanism was confirmed through ^{1}H-NMR spectroscopy, which indicated strong NH-hydrogen bonding interactions. These interactions were further supported by secondary anion–π interactions within the receptor framework.

Chapter V: This chapter highlights the successful design and synthesis of a new pyrene-strapped calix[4]pyrrole receptor. The synthesized receptor was thoroughly characterized using standard spectroscopic techniques including ^{1}H-NMR, ^{13}C-NMR, mass spectrometry, and X-ray crystallography. After structural confirmation, the anion binding behaviour of the receptor was investigated using UV-Vis spectrophotometric titrations in acetonitrile with a variety of anions of different geometries. The binding studies revealed a clear 1:1 host-guest binding stoichiometry, which was determined through non-linear curve fitting using BindFit v0.5 and further validated by Job's plot and X-ray diffraction analysis. Among all the tested anions, the receptor showed the highest binding affinity toward fluoride ion due to its small ionic radius and strong hydrogen bonding ability. Additionally, fluorescence titration studies were performed to examine the interaction of the receptor with halide anions. Significant fluorescence quenching was observed only in the presence of fluoride ion, while other halide anions showed negligible changes. These observations highlight the selective recognition ability of the pyrene-strapped C4P receptor toward fluoride anion. Overall, this receptor provides a valuable contribution to supramolecular chemistry and the development of functionalized calix[4]pyrrole-based sensing systems.

Chapter VI: This chapter presents the successful synthesis of a novel calix[2]pyreno[4]pyrrole receptor, which was fully characterized using standard spectroscopic techniques such as ^{1}H-NMR, ^{13}C-NMR, and HRMS. Following structural confirmation, the anion binding affinity of the receptor was investigated through ^{1}H-NMR and fluorescence titration studies. The binding analysis indicated the formation of a 1:1 host-guest complex, which was further confirmed by Job's plot analysis. Among the tested anions, fluoride ion exhibited the highest binding affinity

toward the receptor compared to iodide ion, mainly due to its stronger NH-hydrogen bonding interactions and higher charge density. Fluorescence titration experiments with F^-, I^-, and CH_3COO^- showed a significant fluorescence enhancement in the monomer emission band at 390 nm along with simultaneous quenching of the excimer band at 504 nm. These observations demonstrate the receptor's potential for selective anion recognition. Overall, this study provides valuable insights into the development of expanded variants of calix[4]pyrrole systems and their applications in supramolecular chemistry.