別紙第１号様式　　No.1

博　士　論　文　の　要　旨

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博士論文題名 Synthesis and Evaluation of Hexahomotrioxacalix[3]arene-based Fluorescent Chemosensors via Click Chemistry

(クリック反応を用いるヘキサホモトリオキサカリックス[3]アレーンを基盤とする蛍光性化学センサーに関する研究)

要旨（２，０００字程度にまとめること。）

Hexahomotrioxacalix[3]arene as the new generation of supramolecular host molecules, it can provide a suitable binding environment for species that require trigonal-planar, tetrahedral or octahedral coordination. Based on this excellent structure characteristic, homooxacalix[3]arenes have been used as ideal molecular platforms for the development of chemo-sensors in the molecular recognition of chemical and biological targets. In this dissertation, we explored the application of hexahomotrioxacalix[3]arene to develop novel fluorescent chemosensors.

In chapter 1, a brief introduction of fluorescent chemosensor is presented at the beginning. And then, we have summarized the application of calixarene derivatives in the field of chemosensors.

In chapter 2, a novel quinoline-functionalized homooxacalix[3]arene was synthesized via Click chemistry and its chemosensing properties with various metal ions were investigated. The designed chemosensor exhibited a high selectivity and antidisturbance for Fe^{3+} among environmentally and biologically relevant metal ions, leading to a prominent off-on-type fluorescent signaling behavior. Further study demonstrates the detection limit on fluorescence response of the sensor to Fe^{3+} is down to 10^{-7} M range.

Chapter 3 introduced a upper rim pyrene-functionalized hexahomotrioxacalix[3]arene, which can be utilized as a highly selective and sensitive fluorescent chemosensor to Hg^{2+} with a detection limit in nM level. Interestingly, the quenched fluorescence emission can be successfully revived upon the addition of water. In this process, the heavy atom effect and blocking thereof were demonstrated within the same system by the use of a C_3-symmetric homooxacalix[3]arene scaffold.

Chapter 4 described a new type of chemo-sensor-based approach to the detection of 2,4,6-trinitro-phenol (TNP). Two hexahomotrioxacalix[3]arene based chemosensors were synthesized through click chemistry, which exhibited high binding affinity and selectivity toward TNP as evidenced by UV-vis and fluorescence spectroscopy studies. ^{1}H NMR titration analysis verified that CH···O hydrogen bonding is demonstrated as the mode of interaction, which possibly facilitates effective charge-transfer.

In summary, several kinds of fluorescent chemosensors for heavy metal ions and neutral molecule were designed and synthesized based on homooxacalix-[3]arene. The sensitivity and selectivity properties of these receptors to the target analyte were carefully evaluated. This work can expand the application of the homooxacalix[3]arene skeleton in the design and synthesis of novel fluorescent chemosensors.