

博士論文の要旨

専攻名 システム創成科学専攻

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博士論文題名 Studies on Synthesis and Evaluation of Novel Ratiometric Fluorescent Chemosensors Based on Hexahomotrioxacalix[3]arenes (へ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新規蛍光性化学センサーの合成と評価に関する研究)

要旨 (2,000字程度にまとめること。)

Over the past three decades, calix[n]arenes have become one of the preeminent classes of molecular receptors, owing to their excellent abilities to act as host molecules for a wide variety of neutral or charged species. For the elaboration of the molecular receptor, the use of cavity-based calix[n]arenes is particularly attractive because, in strong relation to natural systems, it can be expected that the cavity will ensure very high selectivity. Thus, against this background, several kinds of fluorescent chemosensors for heavy metal ions, anions, ammonium ions were designed and synthesized based on calixarene in this dissertation. The sensitivity and selectivity properties of these receptors to the target analyte were carefully evaluated.

In this research, *O*-Alkylation of hexahomooxacalix[3]arene (**1H₃**) with 9-chloromethylanthracene was carried out under the different reaction conditions. The number of anthrylmethyl group introduced to the phenolic oxygen of hexahomotrioxacalix[3]arene was achieved through selective *O*-alkylation with stoichiometric amounts of 9-chloromethylanthracene in the acetone system to give mono, di, *tri-O*-alkylated product. Interestingly, by using acetone/benzene (1:1 v/v) mixed solvent system, the

cone-4An₃ was succeeded to synthesize. These results suggest that the solvent can also control the conformation of the *O*-alkylation products. The possible reaction routes of the *cone-4An₃* and *partial-cone-4An₃* were also discussed.

On the other hand, a novel type of selective and sensitive fluorescent sensor (**L**) having triazole rings as the binding sites on the lower rim of a hexahomotrioxacalix[3]arene scaffold in a *cone* conformation have been synthesized. This sensor has desirable properties for practical applications, including selectivity for detecting Zn²⁺ and Cd²⁺ in the presence of excess competing metal ions at low ion concentration or as a fluorescence enhancement type chemosensor.

Meanwhile, this compound also exhibits the high selective recognition towards alkylammonium cations, which can be also confirmed by enhancement of fluorescence spectra. The calix cavity changed from a “flattened-cone” to a more-upright form, and addition of n-BuNH₃⁺ to **L** resulted in the formation of endo-cavity inclusion complexes. Interestingly, upon addition of Zn²⁺ to this system, chemosensor **L** can be capable of binding a metal ions and alkylammonium cations simultaneously through positive allosteric effect.

In summary, homooxacalix[3]arene have two conformation isomers, and the cone results can formed when a template metal is present in the reaction system or using solvent effect. Chemosensor **L** in cone conformation were designed and synthesized based on hexahomotrioxacalix[3]arene, Click chemistry. It has been use to recognize metal cation and ammonium cations. In these research fields, there are relativity few example and will open a gate for chemical research on chemosensors based on calixarene.