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研究課題名(和文)放射性Cs-137及びSr-90の光学的検出のための蛍光化学センサーのデザイン

研究課題名(英文) Design of fluorescence chemosensors for the optical detection of radioactive Cs-137 and Sr-90 ions

研究代表者

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研究成果の概要(和文)：Cs-137の光学的検出のための新しいハイブリッド大環状分子が設計されている。マクロサイクルは、ククルビツリル(カボチャの形をした分子)とナフタレンでできている。このハイブリッドマクロサイクルは、紫外可視放射が使用されるときにCs⁺イオンの存在を感知することができる。また、ハイブリッド大環状化合物の蛍光スペクトルは、Cs⁺イオンが大環状化合物のカルボニル基に結合するときの強度の変化を示す。これらの結果は、汚染された土壌および液体中のCs-137の検出に、設計された化学センサーが使用できることを示している。

研究成果の概要(英文)：A new hybrid macrocycle for the optical detection of Cs-137 is designed. The macrocycle is made of cucurbituril (a molecule with the shape of a pumpkin) and naphthalene. This hybrid macrocycle can sense the presence of Cs⁺ ions when uv-vis radiation is used. Also, the fluorescence spectra of the hybrid macrocycle show a change in intensity when the Cs⁺ ion binds the carbonyl groups of the macrocycle. These results indicate that the designed chemosensor can be used for the detection of Cs-137 in contaminated soils and fluids.

研究分野：量子化学計算

キーワード：センサー モニタリング 量子化学計算

1. 研究開始当初の背景

In 2011 a powerful earthquake at the bottom of the Pacific Ocean triggered a giant tsunami that hit the Fukushima Daiichi Nuclear Power Plant. This event disabled both the primary and secondary cooling systems of the reactor thereby increasing the temperature of the cooling water inside the reactor. This caused the formation of gaseous hydrogen (from the oxidation of zirconium by water) and uranium metal (from the reduction of uranium dioxide by zirconium at high temperature). The subsequent explosion of the H_2/O_2 mixture released in the environment Cs-137 and Sr-90 radionuclides both of which result from the radioactive decay of U-235. Since these radioactive nuclides are characterized by half-lives of about 30 years, they represent an environmental hazard. It is therefore imperative to detect the presence of such radionuclides in the contaminated soil and fluids as well as remove them so as to reestablish a safe environment. A convenient approach for the removal of Cs-137 is using an artificial macrocycle such as cucurbit[6]uril, a pumpkin-shaped molecule that has the ability to bind Cs^+ by coordinating the ion with its carbonyl groups. As shown in Fig. 1, the cesium ion forms two strong Cs-O bonds with the carbonyl groups of the macrocycle and two Cs-O bonds with water molecules. A third water molecule is not coordinated to the metal ion but it forms three hydrogen bonds (H-bonds), one with the carbonyl group of cucurbit[6]uril and two H-bonds with the water molecules coordinated to Cs^+ . In general, metal

cations do not enter the cavity of this macrocycle since they are captured by the carbonyl groups that are present on either portal.

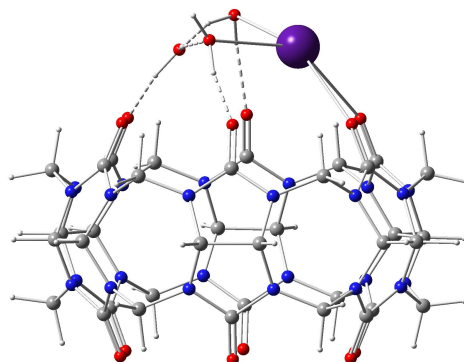


Fig. 1. Coordination of $Cs^+(H_2O)_3$ by cucurbit[6]uril (the large ball represents the Cs^+ ion).

Cucurbit[6]uril is a very stable molecule and hence it can be used in the open environment where chemical and photochemical reactions take place. A suitable structural modification of this macrocycle can be exploited in the development of a chemosensor which could be used for the optical detection of Cs^+ ions that are present in the contaminated soil.

2. 研究の目的

The purpose of the study is to design a chemosensor with the ability to selectively bind Cs^+ ions while producing an optical signal. This task is achieved with the aid of quantum chemical calculations and using structural data obtained from a database of crystal structures.

3. 研究の方法

In this project I employed different computational methods. The Cambridge

Structural Database (CSD), distributed by the Cambridge Crystallographic Data Centre, contains the crystal structures of a very large number of organic and organometallic molecules characterized by single-crystal x-ray diffraction analyses. The CSD is a useful tool when searching for specific chemical moieties which could be used to modify the scaffold of macrocycles. The advantage in using such chemical moieties is that having been characterized, the designed molecule that incorporates them could in principle be synthesized. Also, the crystal structures of existing macrocycles (cucurbiturils, calixarenes, crown ethers, etc.) can be modified and used as the starting geometries for density functional theory (DFT) calculations. DFT is a popular computational method in which the energy of the molecular system under investigation is a functional of the electronic charge density. This approach is suitable for modeling large molecules such as macrocycles containing metal atoms or ions. When using suitable basis sets, it is possible to obtain molecular geometries that are often in excellent agreement with the crystal structures. The effect of the solvent was modeled in two ways, namely explicitly or implicitly. In the first approach I used explicit water molecules bonded to the Cs⁺ ion. In the second approach, I employed the polarizable continuum model (PCM) of Tomasi and coworkers which simulates the physical effect of the solvent with a continuum electrostatic field placed around the solute (macrocycle). The inclusion of the solvent either explicitly

or implicitly is important for obtaining realistic results. Finally, both absorption and emission (fluorescence) spectra were calculated with the time-dependent DFT (TD-DFT) method.

4 . 研究成果

As the starting point of the chemosensor design process I selected the complex between cucurbit[6]uril and one Cs⁺ ion bearing three water molecules (see Fig. 1). This complex has been characterized by the group of Kim (Whang et al., *Angew. Chem. Int. Ed.* 1998, 37, 78-80) using single-crystal x-ray diffraction analysis and the corresponding atomic coordinates are available in the CSD. Also, this complex was investigated by this author in a past project using DFT methods (Pichierri, *Dalton Trans.* 2013, 42, 6083-6091). In the crystal structure of the complex there are two Cs⁺ ions bonded to the macrocycle, one on each carbonyl-laced portal. Each Cs⁺ ion is partially hydrated with three water molecules while forming two strong Cs-O bonds with cucurbituril (other two weak Cs-O interactions are also present). To simplify the calculations, only one hydrated Cs⁺ ion is considered here. In order to obtain a fluorescent chemosensor, it is necessary to introduce suitable aromatic moieties into the macrocycle. This was done by considering the hybrid macrocycles obtained by fusing three different acenes (benzene, naphthalene, and anthracene) with cucurbituril. The resulting cucurbituril-acene hybrids and their fluorinated analogues were geometry optimized with the aid of DFT calculations. Among these hybrid macrocycles, the

cucurbit[6]uril-naphthalene macrocycle containing four fluorine substituents (F) was selected for its large dipole moment (4.26 Debye) and for the fact that the naphthalene moiety is often employed as a fluorophore. Next, using this macrocycle I did optimize the geometry of the corresponding complex with the hydrated cesium ion, $\text{Cs}^+(\text{H}_2\text{O})_3$. The DFT optimized geometry of this complex shown in Fig. 2 is similar to the geometry of the metal complex with unmodified cucurbituril investigated earlier (see Fig. 1).

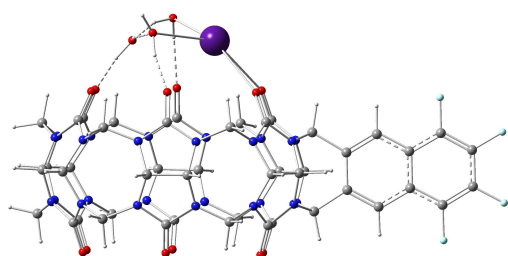


Fig. 2. Coordination of $\text{Cs}^+(\text{H}_2\text{O})_3$ by the cucurbit[6]uril-naphthalene macrocycle (the large ball represents the Cs^+ ion).

Next, in order to compare the electronic transitions of the complexes without and with the hydrated Cs^+ ion, I performed a series of TD-DFT calculations on their optimized geometries. The interesting result is that in the hybrid complex the lowest-unoccupied molecular orbitals LUMO and LUMO+1 are localized on the naphthalene moiety whereas in the unmodified cucurbituril macrocycle these frontier orbitals are localized on the carbonyl groups of the portals (Pichierri, *Chem. Phys. Lett.* 2004, 390, 214-219). When the Cs^+ ion is bonded by the macrocycle, the absorption band at 223 nm is quenched both in the gas-phase and in PCM water, as

shown in Fig. 3. The presence in cucurbit[6]uril of two carbonyl-lined portals suggests that a second Cs^+ ion can be captured by this macrocycle. This issue, however, was not investigated given the large number of possible binding sites that can be occupied by the second cation with respect to the first one (see Fig. 2). On the other hand, I investigated the optical response of M^+ -cucurbit[6]uril complexes with other alkali cations, $\text{M}^+=\text{Li}^+-\text{Rb}^+$. The TD-DFT calculations indicated that the absorption spectra of the Na^+ and Rb^+ complexes are the most similar to that of the Cs^+ complex. Hence, to optimize the optical response of the macrocycle toward the Cs^+ ion, the selectivity for this ion could be enhanced by a further chemical modification.

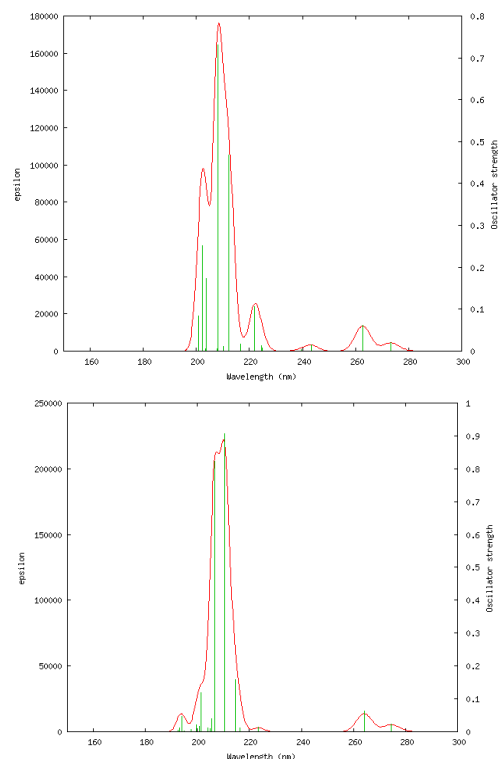


Fig. 3. UV-vis absorption spectra of the free (top) and Cs^+ -complexed (bottom) hybrid macrocycles.

As far as the fluorescence (emission) spectra are concerned, we investigated a simplified (reduced) model of the cucurbit[6]uril-naphthalene macrocycle containing only two (instead of six) glycoluril units. The results of the TD-DFT calculations indicate that although the emission bands do not change their position, there is a significant increase in the intensity once the Cs⁺ ion is coordinated by the macrocycle. These results thus indicate that the hybrid macrocycle designed in this project is able to sense the presence of Cs⁺ ions by changing its optical response.

Finally, using the CSD, we have found that besides cucurbituril other macrocycles such as calixarenes also have the ability to bind Cs⁺ ions. Particularly interesting are those macrocycles where multiple Cs⁺- π interactions are formed. This result suggests the possibility of designing novel macrocycles equipped with two or more aromatic moieties which could be useful in the capture of radioactive Cs-137 by exploiting the formation of Cs⁺- π interactions.

5. 主な発表論文等

(研究代表者、研究分担者及び連携研究者には下線)

[雑誌論文](計 2件)

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[その他]

ホームページ等

6. 研究組織

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