行政院國家科學委員會專題研究計畫期中報告

含螢光及發色團 Calix[4]arenes 的合成與主客化學(1/2)
The Synthesis of Fluorophore or Chromophore Containing Calix[4]arenes and its Host-Guest Chemistry (1/2).

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一、中文摘要

本研究計畫為期兩年，我們期望陸續合成多種含螢光基團或含發色團的 Calixarenes 分子，並利用它們進行主客化學的研究，探討這類分子成為螢光或紫外可見光感測器的可行性。預計合成的分子有兩大類： (1) 含偶氮類 Calixarenes 分子，內又包含上緣具有單取代、1,2-、及 1,3-雙取代的體系，而其下緣可以另外再接枝；(2) 含 Aryl-isoxazolinomethyl 類 Calixarenes 分子。同樣的，此類分子又包含上緣具有單取代、1,2-、及 1,3-雙 isoxazoline 取代的體系，其芳基可有多種選擇，且其下緣也可以另外接枝。

對於上緣含偶氮的 Calixarenes 分子體系（包含上緣具有單取代、1,2-、及 1,3-雙偶氮取代的分子），我們也將多方嘗試下緣的修飾合成。除此之外，我們將進行其光誘導反式轉換為順式的反應，而順式偶氮在熱平衡狀況下會逐漸回復到熱力學上較安定的反式，經由變溫反應將可獲得此順反異構化反應之活化能，而經由各種不同下緣與上緣取代的活化能大小之量測與比較，將對其反應機制的探討甚具意義。

對於上緣含 Aryl isoxazolinomethylcalixarenes 分子體系（包含上緣具有單取代; 1,2-及 1,3-雙取代），我們將進行三類型的工作：(1)合成的芳基將做多種嘗試，例如合成含奈基(nathalene)、恩基(anthracene)、派基 (pyrene) 或雜環芳基的 Arylisoxazolinomethyl 類 Calixarenes 分子，(2) 進行此類分子中 isoxazoline 環的開環反應探討，期望能由開環而獲得多種雙官能基的 Calixarenes 宿主，(3) 進行主客化學之探討，例如對金屬離子與胺類陽離子的錯合反應研究。此類宿主因為具有多種芳基之選擇，因此其螢光光譜與錯合之研究將是個重點。

關鍵詞: 螢光感測、紫外/可見光感測、偶氮類芳杯化合物、主客化學、1,3-偶極環化加成反應、Isoxazolinomethyl-calix[4]arenes.

Abstract:

In this two-year's project, we plan to synthesize several fluorophores and/or chromophores containing calix[4]arenes, and study their host-guest chemistry to find out their applicability in fluorescent or chromogenic sensors. Two types of compounds are planned to be synthesized: (1) Upper-rim azo-containing calix[4]arenes, which include mono-substituted, 1,2- and 1,3-disubstituted calix[4]arenes. These azo-compounds can be further

modified through its lower-rim substitutions such as etherification or esterification. (2) Upper-rim aryl-isoxazolinomethylcalix[4]arenes, which also include mono-substituted, 1,2- and 1,3-disubstituted calix[4]arenes. The aryl groups of these aryl-isoxazolinomethylcalix[4]arenes have many choices and their lower-rims can be further modified too.

For the upper-rim azo-containing calix[4]arenes, we shall also modify its lower-rims. Beside this modification, we plan to study their photo-induced *trans*-to-*cis* isomerization. The *cis*-azo calixarenes will transform back to its *trans*-isomers under thermal condition. From the temperature dependent measurement of this *cis*-to-*trans* isomerization, we are able to determine the activation energy Ea_{ct} of this process. The activation energies obtained from the series of upper-rim and lower-rim modified azo compounds will allow us to evaluate the structure and function relationship.

About the modification of Calix[4]arenes we shall synthesize mono-, 5,11- and 5,17-diisoxazolino-methylcalix[4]arenes. Three types of work are planned: (1) To vary their aryl groups, e.g. synthesize naphtho, anthraceno and pyreno substituted isoxazolines, (2) To explore ring-opening reactions of these isoxazolines for the synthesis of multi-bifunctional-calix[4]arenes, (3) To explore their host-guest chemistry, e.g. Study their complexation with metal and cationic ions. Due to the aryl group substitution of these calixarenes, their fluorescence and complexation spectroscopy will be very important and valuable.

Key words: Fluorescent Sensors, Uv/vis Sensors, Azo compounds, Host-Guest Chemistry, Calix[4]arenes.

二、緣由與目的

本研究方向是主持人持續進行的一個領域，而主客化學及化學偵測器的研究在國內外也仍是個非常熱門的主題。化學偵測器在醫療、環境分析、食品檢驗、廢水處理上極具應用價值，因此仍有許多基礎研究待進行，而其用途也仍待開發。從基礎研究的觀點而言，偶氮的順反異構化之機制，也仍然有許多爭議待釐清。

三、結果與討論

第一年我們已成功進行了一些合成，包括上緣與下緣分別有不同取代的 Calixarenes：例如上緣含單取代、1,2-、及 1,3-雙偶氮取代的 Calixarenes 分子，這些偶氮的下緣也進行了酯基的修飾反應。

我們也已經針對上述這些偶氮化合物，進行光誘導反式轉換為順式的反應。順式的偶氮在熱平衡狀況下會逐漸回復到熱力學上較安定的反式，經由變溫反應，可獲得此順反異構化反應之活化能 Ea_{ct}，而經由各種不同下緣與上緣取代的活化能大小之量測與比較，將對其反應機制的探討甚具意義。

初步的成果顯示，當含有單偶氮及三個丙烯基修飾的 Calixarene 時，偶氮基團之順反異構化的活化能 (Ea_{ct}) 約在 5.3~7.2 kcal/mol 之間 （四個例子）。含有雙偶氮及雙丙烯基修飾的 Calixarenes 時（兩個例子），其順反異構化的活化能 (Ea_{ct}) 約在 2.9~5.1 kcal/mol 之間。 這些上緣含有雙偶氮及雙丙烯基修飾的 Calixarenes 之下緣若有酯基修飾時（三個例子），其順反異構化的活化能 (Ea_{ct}) 約在 1.9~10.1 kcal/mol 之間。總體而言，這些含杯狀物偶氮的活化能 Ea_{ct} 約在 2~10 kcal/mol 之間，而一般類似的偶氮高分子之活化能 Ea_{ct} 約在 16~22 kcal/mol 之間，有一些明顯的差異。其詳細原因仍有待利用雷射光譜技術來研究，這也將是未來與本系刁維光教授、王念夏教授及清華陳益佳教授合作的工作重點。

未來一年，我們將合成上緣含 Arylisoxazolino-methylcalixarenes 的分子體系（包含上緣具有單取代;

1,2-及 1,3-雙取代的 Calixarenes）。此類工作將分兩個方向進行： (1) 所合成的芳基將做多種嘗試，例如合成含奈基(naphthalene)、恩基 (anthracene)、派基 (pyrene) 或雜環芳基的 Arylisoxazolinomethyl 類 Calixarenes 分子，(2) 進行此類分子中 isoxazoline 環的開環反應探討，期望能由開環而獲得多種雙官能基的 Calixarenes 宿主。

最後也將針對上述所有含各種上下緣修飾的 Calixarenes 分子進行主客化學之探討，例如對金屬離子與胺類陽離子的錯合反應研究。此類宿主因為具有多種芳基之選擇，因此其螢光光譜與錯合之研究將是個重點。

四、計劃成果自評

我們在此研究相關領域三年來已發表論文六篇，分別是: (1) *J. Org. Chem.* **1999**, *64*, 1099-1107, (2) *J. Org. Chem.* **1999**, *64*, 2673-2679, (3) *J. Org. Chem.* **1999**, *64*, 6710-6716, (4) *Chem. Review* **1999**, *99*, 1387-1413, (5) *J. Chinese Chem. Soc.* **2000**, *47*, 173-182 , (6) *Int. J. Quantum Chem.* **2001**, *83*, 318-323。另外有兩篇文章正在整理之中。

2. Purposes and Objectives

Host guest chemistry and chemical sensor research continues to draw a lot of attention of all chemists. This area has been a continuous effort by the current investigator. It is very promising in medicinal, environmental, food, and water analysis and deserves to have continuous efforts.

3. Results and Discussion

In the first year, we have already synthesized several upper-rim azo modified calixarenes, and they are further modified with ester groups in the lower rim. These include mono-azo-, 5,11- and 5,17-diazosubstituted calix[4]arenes.

We have studied the photo-induced trans-to-cis isomerization of these azo-containing calix[4]arenes. The *cis*-azo group of these calixarenes will undergo cis-to-trans isomerization under thermal equilibrium. Through the measurements of temperature dependent cis-to-trans isomerization rates, one would be able to obtain the activation energy of Ea_{ct}. The activation energy (Ea_{ct}) of these azo- and allyl-substituted calix[4]arenes will provide us important information about the structure and function relationship.

Preliminary results show that the activation energy (Ea_{ct}) falls in the range of 5.3~7.2 kcal/mol for several 5,11,17-triallyl-23-(*X*-phenyl)azo-calixarenes (with four examples). The activation energy (Ea_{ct}) falls in the range of 2.9~5.1 kcal/mol for 5,17-diallyl- 11, 23-diazo-calixarenes (with two examples). The activation energy (Ea_{ct}) falls in the range of 1.9~10.1 kcal/mol for 5,17-diallyl-11,23-diazo-25,26,27,28-tetrakis-((ethoxycarbonyl)methoxy)calix[4]arenes (with three examples). As a whole, these azo-containing calix[4]arenes have much lower cis-to-trans activation energies (Ea_{ct} in the range of 2~10 kcal/mol) when compared to those of azo benzenes or other azo-containing polymers (Ea_{ct} are in the range of 16~22 kcal/mol). The exact nature of the lowering in cis-to-trans isomerization energy remains to be explored, and it will be our focus in next few years as a collaboration project with Professors Wang and Diau (of our Department at NCTU), and Professor I.-C. Chen (of Tsing-Hua University).

Next year we shall carry out the synthesis of upper-rim aryl-isoxazolinomethy-substituted calixarenes which includes: mono-, 5,11- and

5,17-diisoxazolinomethyl-substitued calix[4]arenes. This work will be divided into two parts: (1) The synthesis of aryl groups that includes: naphthaleno, anthraceno, pyreno and other heterocyclics. (2) Ring-opening reaction of these aryl-isoxazolino-methyl calix[4]arenes.

Besides, we shall also explore the application of these upper and lower rim modified calix[4]arenes in metal ion complexation studies. The complexation research can be studied by NMR, uv/vis and fluorescence spectroscopy methods.

4. Self-Evaluation

We have published **six** papers in the past three years in the research area, and two further work will be submitted soon: (1) *J. Org. Chem.* **1999**, *64*, 1099-1107**,** (2) *J. Org. Chem.* **1999**, *64*, 2673-2679**,** (3) *J. Org. Chem.* **1999**, *64*, 6710-6716**,** (4) *Chem. Review* **1999**, *99*, 1387-1413**,** (5) *J. Chinese Chem. Soc*. **2000**, *47*, 173-182**,** (6) *Int. J. Quantum Chem.* **2001**, *83*, 318-323。