

行政院國家科學委員會專題研究計畫 成果報告

自由基對化學與雜環偶氮芳杯之溶膠化學(2/2)

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行政院國家科學委員會專題研究計畫進度報告

自由基對化學與雜環偶氮芳杯之溶膠化學 (2/2)

Radical Pair Chemistry and Sol-Gel Chemistry of Heterocyclic Azo-Calix[4]arenes (2/2).

計劃編號：NSC 93-2113-M-009-008

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一、中文摘要

本研究計畫包含兩個主題為期兩年，第一個主題為自由基對化學：我們完成了 alpha 芳基-咯之衍生物以及其 sultines 類化合物的合成，這些化合物可以是雙自由基（熱化學反應）、自由基對或四自由基對的前驅物（光化學反應），其構造如計畫書之摘要所示。針對這些化合物我們進行其光化學反應，並以自由基捕捉試劑（各式烯類及 MNP, DMPO 等），希望能確認反應中間體是自由基對或雙自由基。除了產物的分析與鑑定，此類化合物的電子順磁共振光譜(EPR)以及低溫介質質氏紅外光譜的量測，提供了自由基極為寶貴的資訊。過去這一年我們與台大王瑜教授以及同步輻射的李之釗博士合作，進行氮-苯磺基取代之比咯固態晶體的低溫 (30 K)光解。以 X-Ray 單晶解析以及固態樣品的 EPR，在光解產物的自由基對之鑑定與確認上獲得直接且最有力之證據。

主題二為雜環偶氮芳杯之溶膠化學：我們合成了多種含螢光基團或含偶氮發色團的芳杯 (Calix[4]arenes)，並利用它們進行主客化學的研究以及溶膠化學的嘗試，探討這類分子成為金屬離子螢光或紫外可見光感測器的可行性。利用核磁共振以及紫外可見光譜法，成功的完成這些芳杯對鹼金屬、鹼土族、以及過渡金屬(含重金屬)離子的篩選

工作。意外發現這些含偶氮的芳杯分子對過渡重金屬離子有非常好的結合能力，特別是金屬汞(II)以及 Cu(II)離子，因此可應用於重金屬離子的環保篩檢與除污工作上。此外，我們也研究以環糊精當作分子反應器，用於控制 1,3-偶極環化加成反應的方位與面向選擇性。

關鍵詞： 自由基對、雙自由基、電子順磁共振光譜、X-ray 單晶解析、螢光感測、紫外/可見光感測、偶氮類芳杯化合物、環糊精、主客化學、1,3-偶極環化加成反應、

Abstract:

There are two main themes in this project which is a two-year's project. The first subject is radical pair chemistry: We have completed the syntheses of several alpha-substituted-pyrroles and their sultine derivatives. These molecules are precursors for diradicals (from thermolysis), radical pair or a pair of radical pairs (from photolysis) and the structures are shown in the abstract of my proposed project. Photolysis of these molecules in the presence of radical trapping reagents (such as olefins, MNP, and DMPO etc) would allow us to establish biradical or radical pairs. Besides

product analysis, the EPR and matrix isolated FTIR are very informative to the identification of the reactive intermediates. Collaborated with Prof. Yu Wang (NTU) and Dr. J. J. Lee (Synchrotron Radiation Center), we have successfully carried out low temperature photolysis experiments on single crystals of *N*-tosylpyrrole derivatives. Based on X-ray analysis and low temperature EPR, we have provided a direct and very convincing evidence for the radical pairs formation from these precursors.

Subject 2 is azo-containing calix[4]arenes and their sol-gel chemistry: We have synthesized several fluorogenic and chromogenic calix[4]arenes, and have studied their application in molecular recognition and sol-gel chemistry. We have also explored their metal ion selectivity through NMR and UV/Vis titration spectroscopy. Interestingly, these azo containing calix[4]arenes are selective toward heavy metal ions especially for Hg^{+2} and Cu^{+2} and are therefore useful as metal ion sensors. Furthermore, we continued our research of using cyclodextrins as molecular reactors to control the regio and face selectivity of 1,3-dipolar cycloaddition reactions.

Key words: Radical Pair, Biradical, EPR, Fluorescent Sensors, X-ray single crystal analysis, Uv/vis Sensors, Azo-calix[4]arenes, Cyclodextrins, Host-Guest Chemistry, 1,3-Dipolar addition.

二、緣由與目的

本計畫的兩個主題是主持人長期進行中的研究領域。自由基對化學屬於基礎研究，探討電子自旋如何受分子構造及空間排列影響，目的在於建構分子磁鐵及光學導引之磁性材料。這些新的光電材料在資料儲存資料上，將可以進一步縮小儲存空間及應答時間。主客化學及化學偵測器的研究在國內外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

三、結果與討論

我們初步完成了 alpha 芳基? 咯衍生物 (化合物 10 及 11) 的合成，正在針對這些化合物進行光化學反應，並加入自由基捕捉試劑 (各式烯類及 MNP, DMPO 等)，希望能確認反應中間體是自由基對或雙自由基。我們也成功進行 thienosultines 化合物 8a-d 與碳六十的加成反應，並完成產物之分析與各種光譜鑑定。除了產物的分析與鑑定，此類化合物的電子順磁共振光譜(EPR)以及其變溫實驗 (Curie Plot)，提供了活性中間體自由基的基態之資訊。與李遠鵬教授合作，針對上述分子我們也進行低溫介質霍氏紅外光譜的量測，加上理論計算之推論，對於瞭解自由基中間體獲得較明確之驗證。與台大王瑜教授及同步輻射中心的李之釗博士合作，進行氮-苯磺基取代之比咯固態晶體的低溫 (30 K)光解。經由 X-Ray 單晶解析光解產物，我們對於活性中間體是自由基對而不是雙自由基首次獲得直接且最有力之證據。這將與某個重要的文獻有重大衝突，也因此將會在化學界造成相當大的衝擊。

有關主客化學方面，我們完成了上緣或下緣含有 Arylisoxazolinomethylcalixarenes 的分子體系之合成，包含上緣具有單取代，5,11-及 5,17-雙取代的芳杯。所合成的芳香基團包含奈基、? 基、派基 (pyrene) 或雜環芳基。我們也利用偶極反應進行芳杯分子間架橋的反應，分別獲得上緣以及下緣 1:1 以及 1:2 的分子間架橋之芳杯分子。這些特殊分子的結構，經由有機光譜資料所確認：包括氫與碳的核磁共振光、質譜、高解析質譜等的鑑定，最後再經由 X 光單晶繞射實驗證實(感謝台大貴儀中心李錦祥先生在 X-ray 單晶繞射實驗上的協助)。此類含有 isoxazoline 取代的芳杯雖具有掌性，初步的篩選結果並不理想，可能是因為分子之剛性較強不

易整合，因此我們正在進行上述 isoxazolines 芳杯分子之開環反應，期望能增強其錯合能力並運用於分子辨識之工作。過去這一年我們對於上源修飾偶氮的化合物進行了詳細的金屬篩選工作，發現它們對於金屬過濾酸鹽類中的二價汞與銅離子具有良好的辨識性，以肉眼就可以觀測其錯和與否，文章發表在今年的 *J. Org. Chem.* **2005**, *70*, 2912.

四、計劃成果自評

我們在此研究相關領域三年來發表論文如下：

(1) *J. Org. Chem.* **2002**, *67*, 9267, (2) *Chem. Eur. J.* **2003**, *9*, 951, (3) *Chemistry* (Taipei), **2003**, *61*, 553 ; (4) *Chemistry* (Taipei), **2004**, *62*, 13 , (5) *Tetrahedron*, **2004**, *60*, 9493, (6) *Tetrahedron*, **2004**, *60*, 10869, 以及 (7) *J. Org. Chem.* **2005**, *70*, 2912。

另外有兩篇文章送審之中：(1) J.-H. Chu, W.-S. Li, I. Chao, and W.-S. Chung, “Regio Selectivity in the 1,3-Dipolar Cycloaddition of Adamantylidene fulvene and Its Modification by Inclusion in Cyclodextrin Solutions”, submitted. (2) A. Senthilvelan, M.-T. Tsai, G.-H. Lee, and W.-S. Chung, “New Mo(CO)₆-Mediated Ring Opening Reactions of Adamantane-2-spiroisoxazolines and Calix[4]arene-Isloxazolines/Isloxazoles”, Submitted

2. Purposes and Objectives

The two themes in this project have been the long term interests of the current investigator. Radical pair chemistry is a fundamental research which studies the effects of molecular structure and relative orientation on spins. The ultimate goal is to construct high spin molecules and optomagnetic materials for high speed data storage. Host guest chemistry and chemical sensor research continues to draw a lot of attention of all chemists. Chemical sensing is useful in medicinal diagnostic,

environmental and food analysis and deserves to have continuous efforts.

3. Results and Discussion

We have synthesized alpha-arylpyrrole derivatives (**10** and **11**) and studied their photochemistry in the presence of radical trapping reagents (olefins, MNP, and DMPO etc.). We hope to clarify the character (biradical or radical pair) of the reactive intermediates formed. Furthermore, compounds **8a-d** have been prepared and their reactions products with C₆₀ have been isolated and characterized with organic spectroscopy. EPR and Curie plot of the radical species provide information about of the ground state of them. In collaboration with Prof. Y.-P. Lee of Tsing-Hua University, we also used matrix isolated FTIR and theoretical calculation to confirm the radical species involved. Through detailed studies from EPR and X-ray analysis, we can now fully confirm the reactive intermediates observed from the photolysis of *N*-tosylpyrrole derivatives are radical pairs instead of biradicals. The results will cause a severe conflict with the existing literature and will have a strong impact in the society.

In host-guest chemistry project, we have synthesized several upper-rim or lower-rim modified arylisoxazolinomethyl-calixarenes; which include 5-, 5,11-, and 5,17-disubstituted calix[4]arenes. The aryl groups include: naphthaleno, anthraceno, pyreno and other heterocyclics. We also studied the inter- and intramolecular bridges between calix[4]arenes using bis-1,3-dipolar cycloaddition reactions with dipolarophiles. Several 1:1 and 1:2 isoxazoline bridged calix[4]arenes in their upper of lower rims were obtained. The unique structures of these calix[4]arenes were fully characterized by organic spectroscopy include: ¹H, and ¹³C NMR spectroscopy,

mass spectrometry, HRMS, and finally by X-ray single crystal analysis (We thank Mr. Li, G.-S. of the Instrument Center of NTU for X-ray analysis). Although these calix[4]arenes are chiral molecules, their application in chiral recognition have been so far unsuccessful. One possible reason for their lack of recognition ability is the rigidity of the hosts, therefore, we are aiming to explore the ring-opening reaction of these isoxazoline modified calix[4]arenes. Upper-rim azo substituted calix[4]arenes have been used to do screening tests with metal perchlorates, among them Hg^{+2} and Cu^{+2} have been shown to show good binding ability which can be detected with naked eye. The results have been summarized and part of them have been published in *J. Org. Chem.* **2005**, *70*, 2912.

4. Self-Evaluation

We have published **seven** papers in the past three years in the research area, and two more manuscripts have been submitted: (1) *J. Org. Chem.* **2002**, *67*, 9267; (2) *Chem. Eur. J.* **2003**, *9*, 951; (3) *Chemistry (Taipei)*, **2003**, *61*, 553; (4) *Chemistry (Taipei)*, **2004**, *62*, 13 (5) *Tetrahedron*, **2004**, *60*, 9493, (6) *Tetrahedron*, **2004**, *60*, 10869, and (7) *J. Org. Chem.* **2005**, *70*, 2912.

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