

摘 要

Calixarenes，為一種甲醛和酚的環狀聚合物，由於這類分子具有分子中空，故可以嵌合一些小型的有機分子或金屬離子，而形成 " 主-客化合物 "，而此種特性應可應用於微量金屬檢測，離子分離及酵素模擬的研究；本論文主要研究目的首先為將 calix[4]arene 鍵結於矽膠上，以製備出 calix[4]arene grafted silica gel，再進一步的研究其對金屬離子的選擇性，期望能發展出能進行金屬分離的矽膠產物。

三級丁基酚和甲醛在鹼性的催化下，可聚合成黃綠色的聚合物，我們稱此種化合物為前驅物。此前驅物可在二苯醚的迴流下，被轉換為 *p*-*tert*-butylcalix[4]arene；此環狀聚合物的對位三級丁基可利用三氧化鋁進行反向的 Friedel-Crafts 反應，進行減除而得到對位無取代之 calix[4]arene。

Calix[4]arene 能利用標準的四步驟製程，鍵結至矽膠上。利用 3-aminopropyl triethoxy silane 可將 3-aminopropyl 的官能基團鍵結至矽膠上，進而得到化合物 aminopropyl silica gel；aminopropyl silica gel 可和 *p*-nitrobenzoyl chloride 作用而引進硝基苯官能團；接著使用 sodium dithionite 來還原硝基苯官能團而生成苯胺官能團；最後再利用偶氮偶

合反應和 calix[4]arene 作用，便得到紅色的 calix[4]arene grafted silica gel 化合物。此一 calix[4]arene grafted silica gel 再經過熱重分析儀 (TGA) 分析後可推算出在每一單位重量下之 silica gel 可鍵結約 17.91% 重量百分比的 calix[4]arene 有機分子團。

此一數據可以讓我們在利用 calix[4]arene grafted silica gel 進行檢測金屬離子時，與矽膠對照組作比較，進而判定出所能吸附金屬離子量的多寡。化合物之合成製備的條件、熱重分析儀分析的結果以及原子光譜分析的鑑定結果，在論文中均有詳細之敘述及說明。



Abstract

Calixarenes, which are cyclic oligomers of *p*-substituted phenols and formaldehyde, are able to include small organic molecules or metal ions within molecular cavities to form the “host-guest complexes”. This phenomenon has been proposed in the research area of micro-analysis detection devices, ion separation, and enzyme-mimic studies. The main purpose of this thesis is to develop a standard procedure for grafting the calix[4]arene onto silica gel. The grafted product was then subjected to serve as a stationary phase for the ion separation.

In the presence of a base, *p-tert*-butylphenol and formaldehyde was polymerized to form a yellowish precursor. Refluxing of this precursor in diphenyl ether for two hours yielded the *p-tert*-butylcalix[4]arene. The *p-tert*-butyl groups were then removed by AlCl₃-catalyzed reverse Friedel-Crafts reaction to give parent calix[4]arene.

The calix[4]arene grafted silica gel was prepared in a four-step procedure. An 3-aminopropyl groups was introduced by reacting triethoxy silane with silica gel, and the resulting aminopropyl

silica gel (APSG) was further treated with *p*-nitrobenzoyl chloride to supply a *p*-nitrobenzoate moiety. The nitro group was then reduced by sodium dithionite, and the diazotization of the resulting aniline followed with diazo-coupling reaction with calix[4]arene gave the red calix[4]arene grafted silica gel.

The thermal gravimetric analysis (TGA) was applied to the products to determine the composition of the organic portion on grafted silica gel. The amount of the organic portion was in the range of 17.91% for the calix[4]arene grafted silica gel, which is equivalent to 0.2925 mmole of calix[4]arene per gram of calix[4]arene grafted silica gel. The preliminary ionic extraction resulted for Cu^{+2} indicated that calix[4]arene grafted silica gel composed a better extraction that each gram of calix[4]arene grafted silica gel was able to extract 1.53×10^{-4} gram of Copper(II) ion from 4 ppm of Cu^{+2} solution in basic conditions.