國 立 清 華 大 學

碩 士 論 文

含二茂鐵與噻吩寡聚物的 Pseudorotaxane 所構成之固態分子開關的合成及特性探討

Synthesis and characterization of pseudorotaxanes: solid state molecular switches comprising ferrocene and oligothiophenes

系所別：化學工程學系碩士班

學號姓名：102032541 楊厚怡 (Hou-Yi Yang)

指導教授：堀江正樹 博士 (Prof. Masaki Horie)

中華民國 104 年 8 月

Abstract

In this thesis, novel supermolecular pseudorotaxane switches, comprising ferrocenyl group and oligothiophene conjugated group in an axle molecule and dibenzo[24]crown-8 as a ring molecule, have been synthesized to analyze their photo-responsive behaviors in crystal states. The obtained pseudorotaxanes were characterized using ^{1}H NMR spectroscopy, fast atom bombardment mass spectroscopy, and elemental analysis. Crystallographic structure of the pseudorotaxane with bithienyl group was analyzed by single crystal X-ray crystallography. We found that the pseudorotaxane crystals contain chloroform molecule when the crystallization was performed in a chloroform/ether solvent system resulting in the crystals with smoother surface, whereas the crystals do not have any solvent molecules when the crystallization was done in a dichloromethane/ether solvent system. Thermal properties of the single crystals of the pseudorotaxanes were analyzed using polarizing optical microscopy with a hot stage, differential scanning calorimetry, and thermogravimetric analysis. The crystals have a melting point at 178 ℃ for the bithiophene pseudorotaxane and 188 ℃ for the terthiophene pseudorotaxane. However, these crystals do not show solid-to-solid phase transition, which can be observed for a pseudorotaxane comprising tolyl group instead of oligothiophenes. In addition, photo irradiation test on the pseudorotaxane crystals were performed using 405-nm and 445-nm continuous wave diode lasers incorporating with an optical microscope. The crystals showed dimension change by 405 nm and 445 nm laser irradiation. The crystal length increased with increase in the laser power and maximum change was observed to be 1.229% with the 405-nm laser irradiation with laser power at 25.05 mW. However, area change of a crystal top

surface did not follow same tendency. The crystal area reached to the largest area (+0.767%) by 445-nm laser irradiation at 14.99 mW, then this was gradually decreased to +0.483% with increase of the laser power to 24.97 mW.

中文摘要

在這篇論文中，我們合成了一種新穎的超分子，其軸分子由二茂鐵(Ferrocene)和含噻吩寡聚物(Oligo thiophene)的共軛結構所組成；而環分子使用二苯并-24-冠醚-8(Dibenzo-24-crown-8 ether)，並且進一步觀察這種結構的 Pseudorotaxane 在結晶態下的光致變行為。我們使用了核磁共振光譜儀(^{1}H-NMR)、快速原子衝擊游離質譜儀(FAB mass)與元素分析儀(Elemental Analysis)來定性合成的分子。Pseudorotaxane 的單晶結構則是使用 X-ray 單晶繞射儀來進行分析。我們發現，使用氯仿/乙醚系統所產生的單晶，氯仿分子也會出現在晶格中，使得單晶有更平整的表面；然而，使用二氯甲烷/乙醚系統所製備的單晶晶格中，並不會有溶劑分子，因此單晶表面不像使用氯仿/乙醚系統那樣的平滑。我們另外使用附有加熱板的偏振光顯微鏡(POM)、差示掃描量熱法(DSC)以及熱重分析儀(TGA)來進行熱性質的量測。含有雙噻吩(bithiophene)和三噻吩(terthiophene)的 pseudorotaxane 單晶的熔點分別是 178 和 188℃。然而我們發現含噻吩寡聚物的 pseudorotaxane 並不像我們先前論文所研究的含甲苯基的 pseudorotaxane 一般，在加熱時呈現固態-固態的相變化。在光學性質的量測方面，我們使用了 405-nm 和 445-nm 兩種連續波二極管雷射，透過光學顯微鏡裡的光學路徑來照射單晶。在雷射照射下，單晶產生了維度變化，晶體的長度隨著雷射能量提昇而變長，在使用 25.05mW 能量的 405-nm 波長雷射照射下，晶體的長度增加了 1.229%，是我們所觀測到的最大值。然而晶體的上表面積並不完全呈現相同的變化趨勢，當使用 445-nm 波長雷射，晶體的上表面積隨著能量提昇而增加，到 14.99mW 時達到最大值(+0.767%)，然後隨著雷射能量繼續增加，上表面積開始縮小，在雷射能量提升到 24.97mW 時面積下降到+0.483%。