紫質在溶液中、氧化鋁奈米管內以及與脫輔基肌紅蛋白結合後之光譜與緩解動力學研究

學生：陳鈺菁　　指導教授：刁維光博士

國立交通大學應用化學所碩士班

摘　　要

本論文利用時間相關單光子技術系統（Time-Correlated Single Photon Counting; TCSPC）來研究紫質衍生物 Protoporphyrin (IX) Zinc (II) (ZnPP) 在 THF 溶液、不同 pH 值之水溶液、氧化鋁奈米管 (Anodized Aluminum Oxcide Nanotube, AAO) 內以及與脫輔基肌紅蛋白 (Apo-myoglobin, Apo-Mb) 結合後的動態學。在 THF 溶液中，我們發現 ZnPP 分子產生聚集後，在螢光光譜上除了紫質原有的放光頻帶 Q(0,0)及 Q(0,1)以外，在此兩頻帶的中間隱含了一個新的頻帶。在生命期的測量方面，我們發現其螢光衰減曲線包含了兩個指數函數衰減：短時間的衰減生命期為 0.4 ns 而長時間的衰減生命期為 2.2 ns。經由變化溶液的濃度，我們得知前者隨濃度愈高所佔的比例亦愈大，故推測 0.4 ns 為 ZnPP 的聚集體 (aggregates) 進行分子間能量轉移 (intermolecular energy transfer) 之時間常數，而 2.2 ns 則為 ZnPP 的單體進行系統間轉換過程（$S_1 \rightarrow T_1$ intersystem crossing）之時間常數。

我們觀測 ZnPP 在氧化鋁奈米管內因為聚集所產生的螢光淬熄現象 (fluorescence quenching)，遠比其在 THF 溶液中更為嚴重。藉由改變實驗的條件，例如溶液的濃度、浸泡樣品的時間及氧化鋁奈米管之孔徑大小，可以變化分子產生聚集的形式，造成其在吸收、螢光光譜及激發態生命期上的變化。另外，我們嘗試將 ZnPP 和脫輔基肌紅蛋白結合在緩衝溶液 (buffer) 中，以改善 ZnPP 容易聚集的特性。我們並改變緩衝溶液之 pH

值，探討 pH 值對於 ZnPP 聚集在靜態及瞬態光譜上的影響。藉由比較此兩者的光譜及動力學結果的差異，可推測 ZnPP 與 Apo-Mb 結合的形式，同時我們也利用時間—解析螢光非等向性光譜 (time-resolved fluorescence anisotropy) 的技術來探討其動力行為。

Spectroscopy and Relaxation Dynamics of Protoporphyrin (IX) Zinc (II) in Solutions, inside AAO Nanotubes and in Combination with Apomyoglobin

Student：Yu-Chying Chen Advisor：Dr. Eric Wei-Guang Diau

Institute of Applied Chemistry

National Chiao Tung University

ABSTRACT

The aggregation behaviors of Protoporphyrin (IX) Zinc (II) (ZnPP) in solutions, inside anodized aluminum oxide (AAO) nanoporous environments, and in combination with apomyoglobin (Apo-Mb) have been observed by using time-correlated single photon counting (TCSPC) technique. In ZnPP / THF solution, we observed a new band in addition to the Q (0,0) and Q (0,1) bands in the emission spectrum, and the fluorescence decays can be well described by a bi-exponential decay function with time coefficients of ~0.4 ns and ~2 ns. By observation of the change of the transients as a function of the concentration of the ZnPP / THF solution, we assign the fast and slow decay times being due to the intermolecular energy transfer of the aggregated molecules, and the $S_1 \rightarrow T_1$ intersystem crossing (ISC), respectively. Inside AAO, the fluorescence of ZnPP was significantly quenched. Changing the different experimental conditions such as the initial ZnPP / THF concentration, the sample immersion time, and the radial size of the AAO nanotubes, we discussed the observed relaxation dynamics. On the other hand, ZnPP molecules bound to Apo-myoglobin in buffer solution have shown sharp and red-shifted spectral feature in comparison with that of ZnPP in free buffer solutions. We studied the dynamics of the ZnPP • Apo-Mb complex using the technique of time-resolved fluorescence anisotropy.