行政院國家科學委員會專題研究計畫　期中進度報告

氫鍵辨識，轉移分子之設計、合成、光譜動力學及應用(2/3)

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計畫主持人：周必泰

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氫鍵辨識，轉移分子之設計、合成、光譜動力學及應用(2/3)

NSC-92-2113-M-002-030

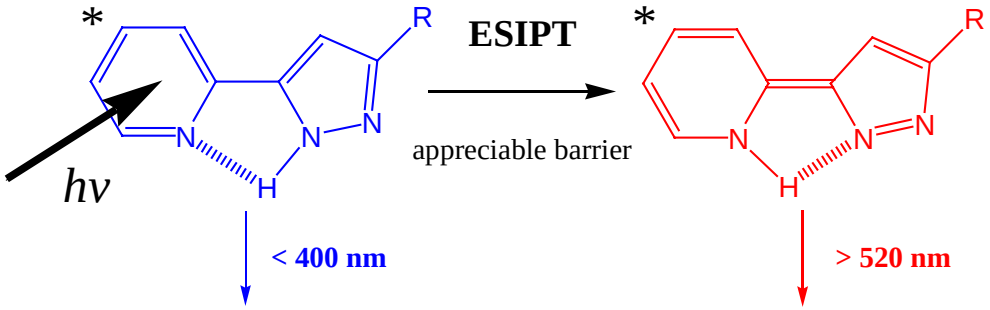
周必泰

成果報告

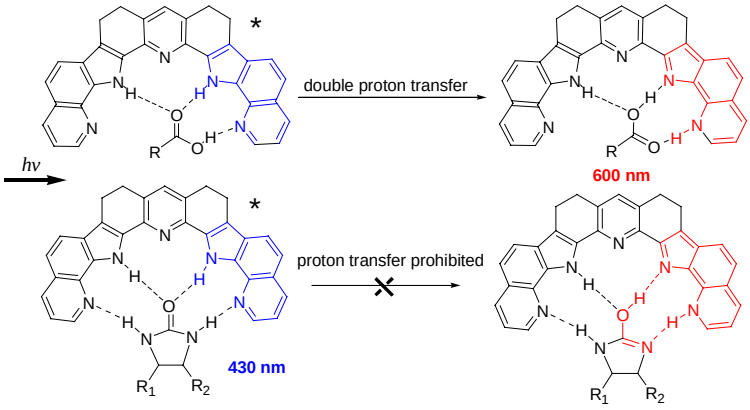
去年八月至今我們實驗室在多方面研究領域有所突破，依論論文的出版來區分各方向的成果則可以分為以下幾個重點來敘述:

(其中實在難以用中文表達的部分原諒不得不用英文)

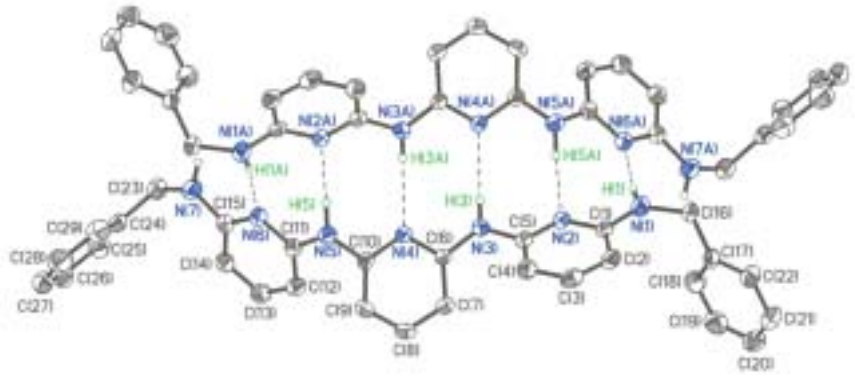
1. 我們在尋找高能態質子轉移系統方面有重大的突破，在六五環的內氫鍵系統我們發現 excited-state intramolecular proton transfer 需要在conformation 上做一個readjustment 致使能障增高，我們也由溫度效應導証了non-isotopic reaction kinetics，印證了我們的觀點. (C. C. Cheng, P. C. Wu, Y. H. Song, Y. Chi*, W. S. Yu and P. T. Chou*, ***J. Am. Chem. Soc.*** **2003,** *125(36)*, 10801.)



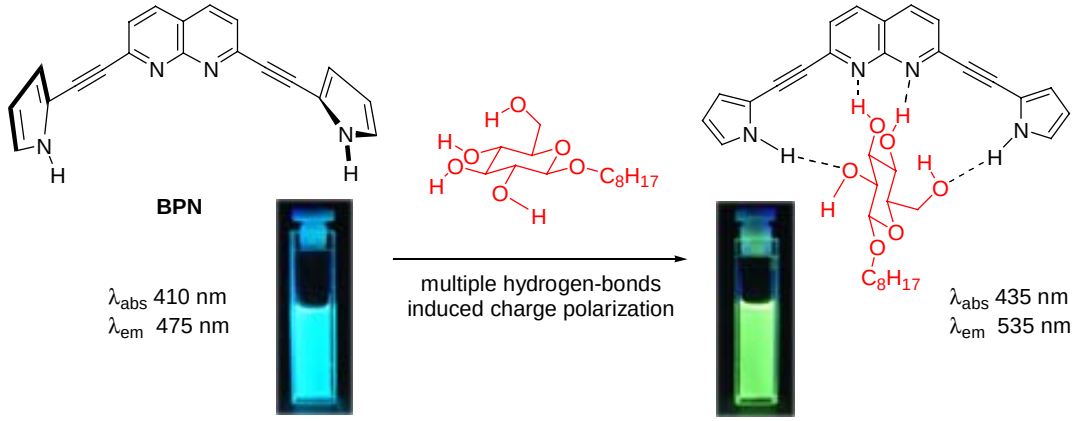
2. 我們也經由多重氫鍵效應的概念設計合成新一代的分子而達到分子辨識的目的(見下圖), 這化合物對於尿素具絕佳的辨識能力，並藉由catalyzed excited-state proton transfer 以及 non-catalyzed excited-state proton transfer 的概念成功的達到選擇性以及靈敏性的目的。(***J. Am. Chem. Soc.*** **2004,** *126*, 1650). 另外在同一概念下我們也可以經由設計另一型化合物，利用CD 的概念達到辨識glucose derivatives 的目的 (***J. Am. Chem. Soc.*** **2004**, *126*, 3559-3566).



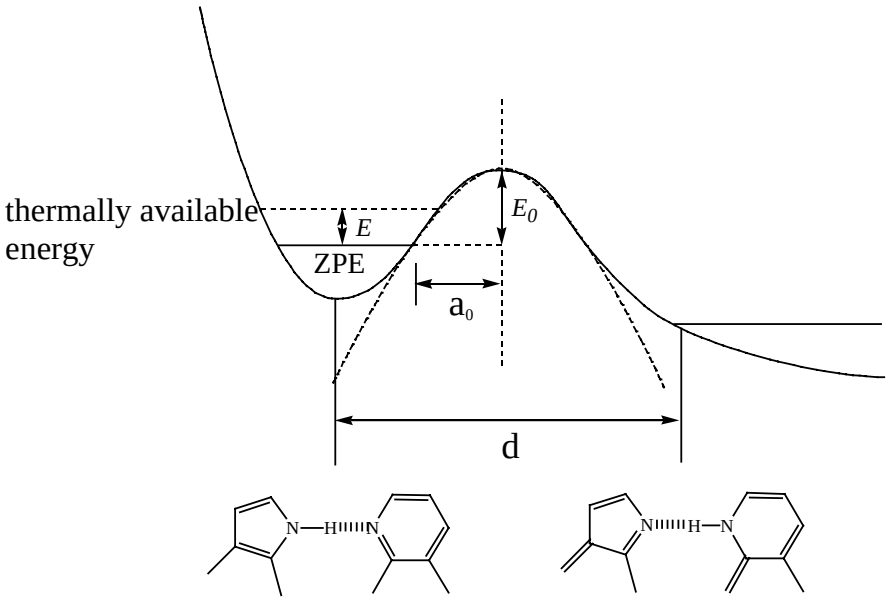
3. 我們在經過多年的努力後，已經可以generalized許多azaindoles以及adenine衍生物的質子轉移機制實際上是和amino-imino tautomerism在本質上是相同的。實驗上我們在2000年獲得許多直接的證據（***J. Phys. Chem. B* 2000**, *104*, 7818, ***J. Phys. Chem. A* 2000**, *104*, 8863）。這個機制亦引發我們和系上彭旭明老師合作設計一系列多環aminopyridine衍生物，利用自身proton donor/acceptor 的雙性，得到多氫鍵複體，並藉由各種的光譜動力學來解析出環數和複體形成之間的熱力學對應關係（***J. Am. Chem. Soc.* 2002**, *124*, 4287）。



這結果在多氫鍵基礎研究上是一大突破，主因是一般氫鍵的結合並不太考慮entropy 的影響，但在多氫鍵的自組結合上當氫鍵數超過n = 4 後即變成主要的影響因素. 我們根據這原理進一步應用到多氫鍵辨識上利用設計合成的分子2,7-Bis-(1*H*-pyrrol-2-yl)ethynyl-1,8-naphthyridine 成功的達到高靈敏具選擇性辨識glucose的效能 (*Org. Lett.* **2002**, *4*, 3107).

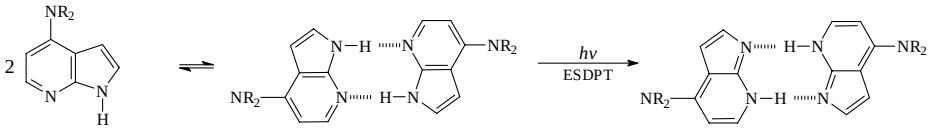


4. 在一系列的研究當中，我們也在國際間首次利用3-取代基的影響將azaindoles雙體的單晶解析出。一般azaindoles的單晶皆是tetramer的形式，故在固態無法進行雙質子轉移。我們利用3-methyl-7-azaindoles的雙體單晶做變溫(298-8 K)的steady-state 以及相對的時間解析動力學在國際上第一個成功的解出激發態雙質子轉移對azaindoles而言確實有能障在3-methyl-7-azaindole 氘取代中由質子穿遂的理論中求出約為1.76 kcal/mol （***J. Phys. Chem. A* 2002**, *106*, 8006），更重要的是雙質子轉移機制應為one-step reaction， 這結果也平息了近十年對7-azaindole雙體質子轉移動力學的爭執。

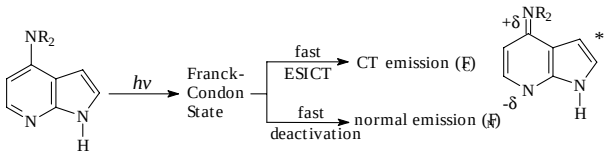


ΔE ~ 0.58 kcal/mol for 3MAI-h
~ 1.73 kcal/mol for 3MAI-d

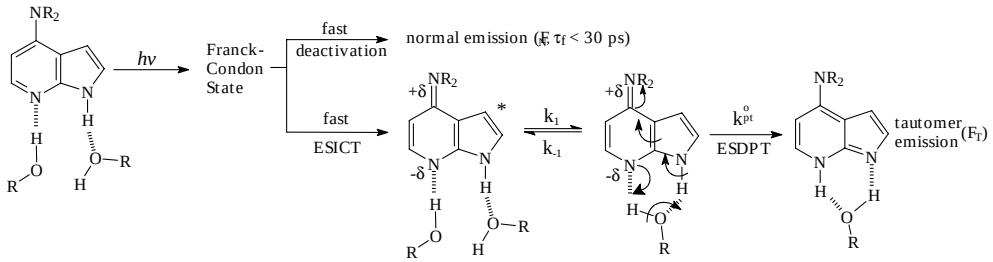
5. 我們也繼續既定的目標在 proton/charge transfer coupled reaction 上做更精準的研究, 我們發現生化重要分子 4-(dimethylamino)-1H-pyrrolo[2,3-b]pyridine (DPP)（見下圖）具雙重的物性。 In cyclohexane, DPP dimer and/or dual hydrogen-bonded complex are formed with association constants K_a as high as ~ 4.2×10^3 and 5.2×10^4 M^{-1} (e.g. the DPP/acetic acid complex) at 298 K, respectively, which upon electronic excitation undergo ultrafast rate (>> 6.7×10^{10} s^{-1}) of double proton transfer, resulting in a unique tautomer emission. Dual fluorescence was observed in polar, aprotic solvents, in which the large Stokes shifted emission band originates from the charge-transfer species incorporating a dimethylamine and pyridine ring as electron donor and acceptor, respectively. Detailed solvent-polarity and temperature dependent studies in combination with theoretical approaches have been performed to determine the excited-state charge transfer properties such as dipole moment, orbital configuration, etc. Supplementary support for the dual charge/proton transfer behavior was provided by the comparative spectroscopy and dynamics of various DPP related derivatives. Further time-resolved measurements conclude that dual emissions share a common Franck-Condon excited state but undergo two independent relaxation channels. In protic solvents such as in ethanol, following fast solvent relaxation dynamics, the excited charge-transfer state further undergoes a solvent (i.e. alcohol) assisted proton transfer reaction. The charge versus proton transfer emission can be distinguished via the temporal spectral evolution. The results demonstrate DPP to be a unique model among 7-azaindole analogues in which the interplay between charge and proton transfer reactions is operative in the excited state. 這個研究凸顯了 charge transfer 和 proton transfer 的相關性。相信未來將是理論計算的重點研究方向。 研究成果已在今年發表在 ***J. Phys. Chem. A*** **2003,** *107,* 1459-1471 上.



in nonpolar solvents (**a**)

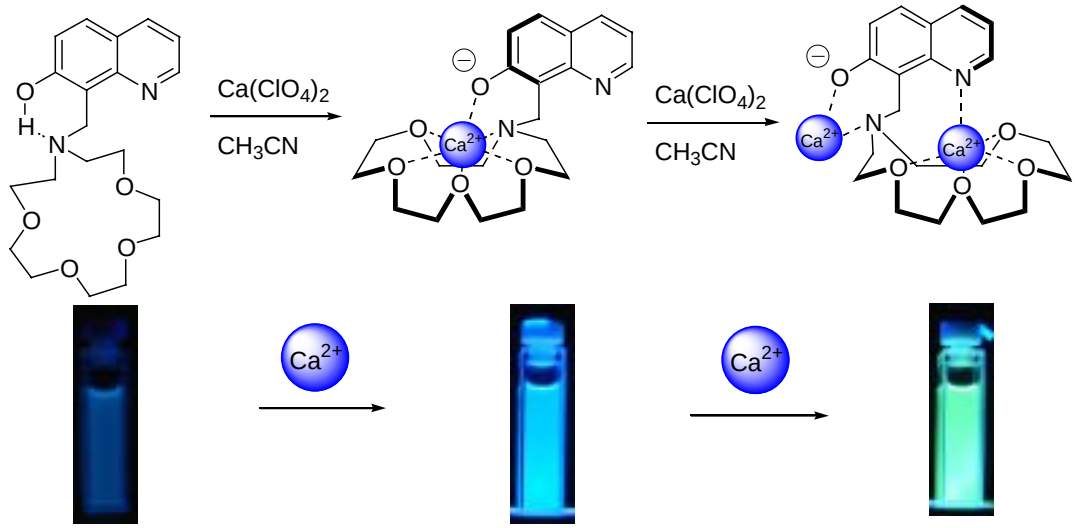


in polar, aprotic solvents (**b**)



in protic solvents (**c**)

6. 我們今年在分子辨識的發展上也更上一層樓，利用7-hydroxyquinoline 在激發態經過介質傳遞質子的特性，我們設計了冠醚夾在其中當作傳導層的架構。實驗結果得知當鹼金屬及鹼土金屬加入時，其螢光的變化非常的顯著。而利用激發態質子轉移 的基理來設計分子辨識架構是個非常新穎的領域，未來仍有非常寬廣的發展空間。我們的結果也在寄 Chem. Commun. 審核時於一個星期內即獲三位審查人的認同而同意登錄. (***Chem. Commun.* 2003,** 890-891)，足見其前瞻性之一般。



我們另一個突破研究方向是利用超快速飛秒(femtosecond)雷射系統，並且利用fluorescence upconversion的技術解析出β-carboline 的激發態內質子轉移動力學，在常溫其質子轉移速率約~1.2 ps^{-1}，並結論β-carboline 激發態雙質子轉移能障約是1.5 kcal/mol左右，而反應是由一些in-plane，large amplitude的振動模式所觸發。這方面結果已送至J. Phys. Chem. 發表。

有關2003-2004 年成果的詳細內容請參見以下發表.

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91 "Excited-State Intramolecular Proton Transfer in 5-Member Ring Intramolecular Hydrogen Bonding Systems, 2-Pyrazole-Pyridines" C. C. Cheng, P. C. Wu, Y. H. Song, Y. Chi*, W. S. Yu and P. T. Chou*, ***J. Am. Chem. Soc.*** **2003,** *125(36)*, 10801.

92 "Comprehensive Studies on Dual Excitation Behavior of Double Proton versus Charge Transfer in 4-(N-Substituted amino)-1H-pyrrolo[2,3-b]pyridines, C. C. Cheng, C. P. Chang, W. S. Yu, F. T. Hung, Y. I. Liu, G. R. Wu and P. T. Chou*, ***J. Phys. Chem. A*** **2003**, *107*, 1459-1471.

93 "On the Evidence Obtained by Exciting 7-Azaindole at 320 nm in 10^{-2} M Solutions" P. T. Chou,* Y. M. Cheng, W. S. Yu and S. C. Pu**,** ***J. Phys. Chem. A*** **2003,** *107*, 5640.

94 "Dynamics of Ground-State Reverse Proton Transfer in the 7-Azaindole/Carboxylic acid System" W. P. Hu*,[1], R. M. You,[1] S. Y. Yen,[1] F. T. Hung[2], W. S. Yu[3] and P. T. Chou*,[3] ***Chem. Phys. Lett.*** **2003**, *370*, 139-146.

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97 "Time-Resolved Thermal Lensing Studies of Metastable Species" P. T. Chou*, G. R. Wu, J. K. Yu, C. S. Chiou, ***J. Chin. Chem. Soc.*** **2003,** *50*, 31-39**.**

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99 "8-(1,4,7,10-Tetraoxa-13-azacyclopentadec-13-ylmethyl)quinolin-7-ol: Its Synthesis and Use as a Highly Sensitive Metal Cation Probe" K. C. Wu, M. O. Ahmed, C. Y. Chen, G. W. Huang, Y. S. Hon* and P. T. Chou* ***Chem. Commun.*** **2003**, 890-891.

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