

# 有機分子與有機奈米粒子在溶液中之飛秒螢光動力學研究

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## 摘 要

在本篇論文中，我們利用時間解析螢光光譜對於有機奈米粒子(PPB) 和有機奈米帶 (CNDSB) 的激發態動力學以及螢光增益現象作一深入的探討。在水和 THF 的混合溶液中，我們藉由控制水和 THF 比例生成不同大小的奈米粒子。研究結果顯示，在 PPB 奈米粒子中的螢光增益效應主要是由於在奈米粒子中分子的平面化以及在聚集體(aggregate)中分子和分子間的交互作用所造成。我們利用時間解析螢光光譜以及粉末 X 光繞射 (powder XRD)的量測，發現在 PPB 奈米粒子中，其晶體的排列具有兩種不同的構型。對於 CNDSB 分子，藉由比較 CNDSB 在 THF 和 PMMA 薄膜中的時間解析螢光光譜，我們發現在結構上的限制僅能造成部分的螢光增益效應。然而在 CNDSB 奈米帶中，我們觀測到一十分有趣的超快能量傳遞過程，其時間小於 150 飛秒。由於在 PPB 奈米粒子中，我們並沒觀測到此一現象，因此我們認為此一超快的能量傳遞過程應該由於 CNDSB 的一維奈米結構所造成，而其反映了能量在奈米帶的長軸方向的傳遞速度。

在第二部份的研究方面，我們針對了一新合成的咪唑(carbazole) 衍生物: BMVC，分別對其在有機溶劑中以及 DNA 錯合物中的激發態及水合動力學做一探討。當 BMVC 溶解於 tris-buffer (PH=7.5)時，其激發態的緩解主要是經由 C=C 雙鍵旋轉所造成的內轉換(internal conversion) 或是 C-C 單鍵旋轉所造成的系統間跨越(intersystem crossing)。也因此當我們將 BMVC 溶解在甘油(glycerol)時，由於分子的轉動受到了限制，其螢光強度以及生命期均大幅的增加。在水合動力學(solvation dynamics)方面，在甘油中由於分子的高黏滯性，因此使得水合時間大幅度的減緩。而當 BMVC 雙股螺旋(duplex)及四股螺旋(quadruplex) DNA 作用時，由於 BMVC 和 DNA 間的作用限制了分子內運動，因此其螢光強度和在甘油中一樣均有大幅度的增加。藉由水合動力學的測量，我們認為在 DNA 表面的水可分為兩種，其中之一是屬於自由的水分子，而另一種則屬於和表面有部份結合的水分子。藉由分析此兩種水分子的水合時間，我們認為 BMVC 在雙股螺旋 DNA 中的結合位置是位於大溝(major groove)以及小溝(minor groove)之間。而當 BMVC 和四股螺旋 DNA 結合時，其水合作用中和表面有部份結合水分子所佔的比例和 BMVC 在雙股螺旋 DNA 中相較有顯著的增加。因此我們認為在四股螺旋中 BMVC 是更加深埋在 DNA 分子之中。

# Femtosecond fluorescence Dynamics of Organic Molecules and Organic Nanoparticles in Solutions

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## Abstract

With the application of time-resolve fluorescence spectroscopy, Field Emission Scanning Electron Microscopy (FESEM), single crystal X-ray Diffraction (XRD) and powder XRD; the excited state dynamics and origin of the fluorescence enhancement of organic nanoparticle (1,4-di[(E)-2-phenyl-1-propenyl] benzene, PPB) and nanobelts((Z)-3-{4-[(Z)-2-cyano-2-phenyl-1-ethenyl] phenyl }-2-phenyl-2-propenenitrile, CNDSB) was investigated. Through the reprecipitation method, organic nanostructure of those two compounds was formed in water/ THF solution, and the size increases with the water percentage. The crystal structure of PPB nanoparticles and single crystal was also determined. For PPB nanoparticles, the origin of this fluorescence enhancement was contributed from both the conformational planarization, and the herringbone-type aggregate. The time-resolved fluorescence spectroscopy and powder XRD reveal that two different packing structures involved in the PPB nanoparticles. For CNDSB, the role of intramolecular motion was tested by measuring the time-resolved transient of CNDSB/PMMA film. The result reveals that the structure confinement only contributes parts of the fluorescence enhancement of the CNDSB nanobelts. In CNDSB nanobelts, a unique ultrafast energy transfer

process along the long axis of crystal was observed ( $\sim 150$  fs), which was absent in PPB nanoparticle.

For 3,6-bis(1-methyl-4-vinylpyridium) carbazole diiodide (BMVC) molecules, by comparing the time-resolved transient of BMVC in tris-HCl buffer and glycerol, the excited-state and solvation dynamics has been investigated. The results indicated that the rotational induced internal conversion and intersystem crossing process is an important nonradiative process for excited BMVC molecules. The solvation dynamics of BMVC in glycerol is significant decelerated due to the high viscosity of solvent. As BMVC interacted with linear duplex DNA (LD) and quadruplex DNA (Hum24), significant fluorescence enhancement was observed, which accompany with the hypsochromic shift of absorbance. The fluorescence enhancement was attributed to the specific interaction between BMVC and DNA macromolecule, which suppress the intramolecular motion of the molecules. The solvation dynamic of BMVC/LD and BMVC/Hum 24 complexes reveal that there are two types of water on DNA surface: bulk like and weakly bound water, and the solvation time is  $\sim 1$  ps and  $\sim 9$  ps, respectively. The result indicated that in BMVC/LD, BMVC is buried between the major and minor grooves. For BMVC/Hum 24, the fraction of the solvation caused by weakly bound water is increased, which indicated that BMVC is further buried into the DNA surface.