Solid-state luminescence of terpyridine : A theoretical analysis on the non-radiative decay kinetics.

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Introduction

Organic luminescent materials are attracting interests in various fields of photofunctional applications such as nonlinear optics, organic light-emitting diode, and fluorescent biosensors.

We previously reported that 2,2':6',2"-terpyridine(TP), practically non-luminescent in the form of amorphous solid or the "needle" crystal, shows strong blue luminescence upon formation of the "plate" crystal [1], where the efficient and reproducible on–off switching of solid-state luminescence was demonstrated by heat-mode interconversion between the two lattice forms (the "plate" and the "needle" forms). The objective of this study is to theoretically elucidate the solid state–specific fluorescent on/off switching.

Thoretical model and computational details

The Bixon-Jorter model was employed in the Marcus inverted region [2], where the Franck-Condon factor is governed by the reorganization energy and the Gibbs free energy variation during non-radiative decay. The reorganization energy, derived from electron-vibration coupling, is decomposed further into the contribution of inner (intramoelcular) high frequency modes and outer (intermolecular) low frequency modes. The ground states and the lowest singlet excited states (S_1) were geometrically optimized with DFT(B3LYP)/6-31+G(d,p) and CIS/6-31G+(d,p) level of theory, respectively. All calculations were done using Gaussian 03 program.

$$k = \frac{2\pi}{\hbar} |V_{if}|^2 \sqrt{\frac{1}{4\pi\lambda k_B T}} \exp[-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T}]$$

Results and discussion

The lifetime measurement of TPs showed that both crystal forms (the "plate" and the "needle" forms) have sub-nano second lifetimes in their S_1 state. This results mean that the non-radiative dynamics of is governed by the slow process induced by the interaction of S_1/S_0 PES, not by the ultrafast deactivation process via the Conical Intersection.

So that, the TPs luminescence on–off switching was analyzed based on the following two hypothesis;

(1) Different magnitude of Forster-type energy transfer driven by the abosorption/emission spectral overlap (Stokes shift)

(2) Different magnitude of outer-reorganization energies between the two crystal shapes.
, indicated by the different pai-pai intermolecular distances.

These hypothesis were rationalized by theoretical estimations of non-radiative decay rate based on the series of quantum chemistry calculations.
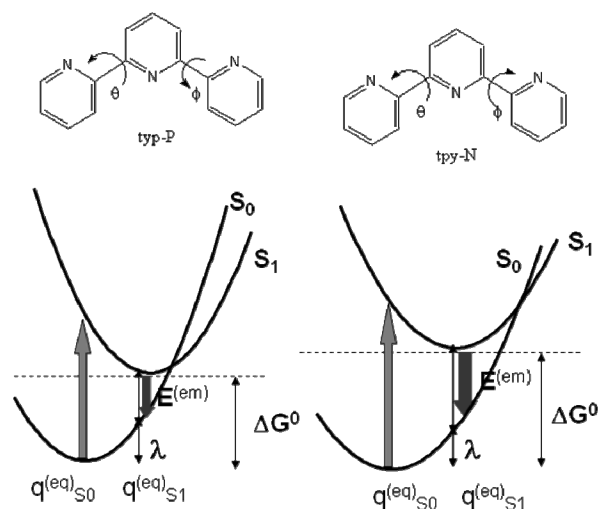
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