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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.

Theoretical 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 (intramolecular) 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.

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

Results and discussion

The lifetime measurement of TP showed that both crystal forms (the “plate” and the “needle” forms) have sub-nano second lifetimes in their S_1 state. This result 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 TP’s luminescence on-off switching was analyzed based on the following two hypothesis;

1. Different magnitude of Forster-type energy transfer driven by the absorption/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.

References