Fluorescence in Crystalline and Amorphous Phases of Molecular Systems: A Theoretical Perspective

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Amorphous-phase fluorescence presents a particularly challenging task for quantum mechanical approaches due to a large number of thermally-accessible molecular configurations. Sampling a representative number of these configurations represents a tremendous computational investment, particularly for excited state calculations, and thus prevents any attempt at the reproduction or prediction of amorphous-phase optical properties. In this contribution, we demonstrate that intelligent defect sampling of thermally accessible configurations using a recently developed embedding approach[1] in the crystalline phase coupled with an understanding of local, crystalline-like order in the amorphous phase leads to an impressive reproduction of experimental emission spectra and, in turn, provides vital understanding of the key processes behind mechanochromism and indeed the interpretation amorphous-phase optical properties in general.

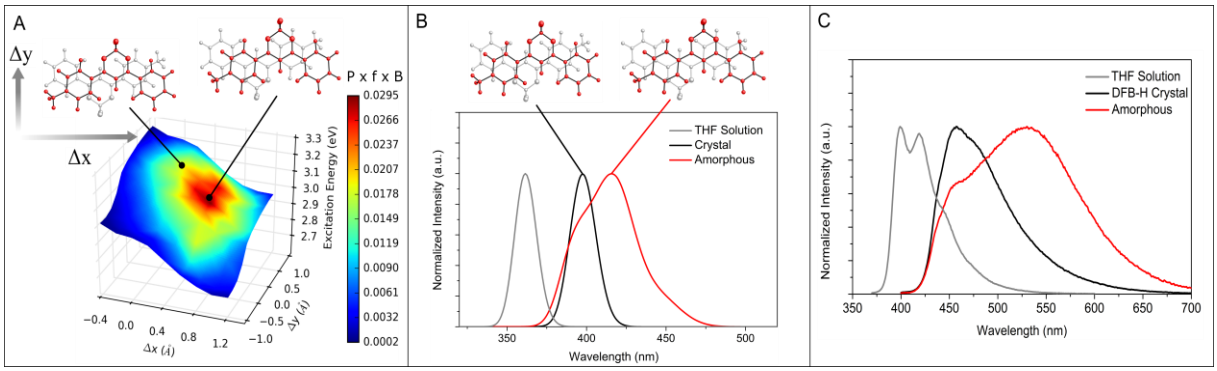

Figure 1. Surface plot of calculated emission energy with respect to scan coordinates. For a given pair of molecules in the crystalline phase, one molecule (highlighted in red) is displaced along its average plane in directions parallel (Δx) and perpendicular (Δy) to its long axis. A colour scheme is mapped onto this surface, representing the weighted emission signal for a given conformation (i.e. the weighted oscillator strength). Red (blue) regions represent a greater (lesser) contribution of a given scan coordinate to the overall computed emission spectrum in the amorphous phase. B) Computed and C) experimental emission spectra for solution (THF), crystalline and amorphous phases of DFB-H.

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References:

[1] L. Wilbraham, C. Adamo, F. Labat, I. Ciofini, *J. Chem. Theory Comput.*, **2016**, 12, 3316-3324