

Fluorescence quenching revisited from first principles: Dark-state quenching or photoinduced electron transfer?

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Photoinduced electron transfer (PET) plays relevant roles in many areas of chemistry, including charge separation processes in photovoltaics, natural and artificial photosynthesis, as well as in photoluminescence sensors and switches. As in many other photochemical scenarios, the structural and energetic factors play relevant roles in determining the rates and efficiencies of PET and its competitive photodeactivation processes. Particularly, in the field of fluorescent sensors and switches, intramolecular PET is believed (in many cases without compelling experimental proof) to be responsible of the quench of fluorescence. In this contribution,^[1] I revise the origins of the fluorescence quenching in some of these systems with state-of-the-art quantum chemical tools. These studies go beyond the common strategy of analyzing frontier orbital energy diagrams. Instead, the potential energy surfaces (PESs) of the lowest-lying excited states are explored and the radiative and nonradiative decay rates from the involved excited states are computed from first-principles. With such a strategy, this work reveals the real origins of the fluorescence quenching, herein entitled as dark-state quenching. The success of the dark-state quenching mechanism is demonstrated for a wide variety of fluorescent probes, including proton, cation and anion targets. Furthermore, this mechanism provides a general picture of the fluorescence quenching which englobes intramolecular charge-transfer (ICT), ratiometric quenching, and those radiationless mechanisms believed to be originated by PET.

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References:

[1] D. Escudero, *Acc. Chem. Res.*, **2016**, 49, 1816-1824.