Room-temperature phosphorescent coumarin derivatives: TDDFT assessment of the photophysical mechanism

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ABSTRACT

Coumarin derivatives have been widely explored in the fields of drug design and fluorescence sensing; the latest reports [1] revealed also that coumarins can exhibit room-temperature phosphorescence (RTP) in the polymer matrix, which paves the way for their potential applications in, e.g., information anti-counterfeiting. Recently, easily-measurable efficient RTP upon immobilization has been shown for 7-diethyloamino-4-hydroxycoumarin (7D4HC). [2]

In this contribution, (TD)DFT methodology, including spin-orbit coupling via perturbative approach to quantify intersystem crossing (ISC), is employed to rationalize experimental findings for 7D4HC and understand factors that determine an efficient ISC process in 4HC derivatives. The studies with a continuum solvation model indicate that 7D4HC likely exists in its two isomeric forms: diketo and enol, and the phosphorescence signal originates from the $S_1 \rightarrow T_2$ ISC and subsequent $T_2 \rightarrow T_1$ internal conversion (IC) in the S_1 diketo (see Fig. 1). Analysis of structural conversion processes for 7D4HC in both the ground and excited states, including explicitly solvated species, will also be presented.

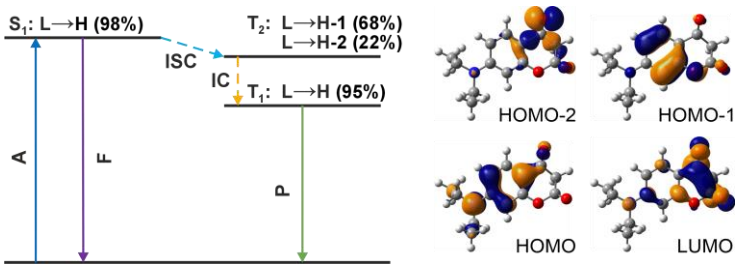

Figure 1: Postulated mechanism of photophysics for 7D4HC.

References

[1] Dong, M.; Liao, L.; Li, C.; Mu, Y.; Huo, Y.; Su, Z.-M. Su; Liang, F. Translating efficient fluorescence into persistent room-temperature phosphorescence by doping bipolar fluorophores into polar polymer matrix. *J. Mater. Chem. C.* **2024**, *12*, 443–448.

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