Mechanistic origin of room-temperature phosphorescence in a coumarin derivative: role of tautomerism and spin–orbit coupling

Arkadiusz Paweł Matwijczuk[1,#], Dominika Jelonek[2,3], Lidia Ślusarczyk[1], Karolina Starzak[4], Alicja Matwijczuk[1], Ignacy Gryczynski[5], Karol Gryczynski[5], Monika Srebro-Hooper[2]

1. Department of Biophysics, Faculty of Environmental Biology, University of Life Sciences in Lublin, Akademicka 13, 20-950 Lublin, Poland.
2. Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Krakow, Poland,
3. Doctoral School of Exact and Natural Sciences, Jagiellonian University, Prof. St. Łojasiewicza St 11, 30-348 Krakow, Poland.
4. Department of Chemical Technology and Environmental Analytics (C1), Faculty of Chemical Engineering and Technology, Cracow University of Technology, 31-155 Krakow, Poland.
6. Department of Physics and Astronomy, Texas Christian University, Fort Worth, TX, 76129, USA.

Room-temperature phosphorescence (RTP) [1] in purely organic systems remains a challenging phenomenon due to inherently weak spin–orbit coupling and efficient non-radiative deactivation channels. Understanding the microscopic mechanisms governing population and decay of triplet states is therefore essential for rational design of efficient emitters. Here, we present a combined spectroscopic and theoretical study of excited-state processes in a 4-hydroxycoumarin derivative (16C [2]), focusing on the origin of its RTP emission. Steady-state and time-resolved measurements performed in liquids and in a rigid poly(vinyl alcohol) (PVA) matrix reveal a transition from dominant fluorescence in solution to long-lived phosphorescence in the immobilized system, with emission lifetimes reaching $\sim 10^{-1}$–10^{0} s and observable afterglow. To elucidate the underlying mechanism, quantum-chemical calculations (DFT and TD-DFT) were employed to analyze the electronic structure, excited-state energetics, and spin–orbit coupling between singlet and triplet states. The results indicate that efficient intersystem crossing occurs via coupling of the lowest singlet excited state of mixed ππ*/charge-transfer character with low-lying triplet states of nπ* nature, in agreement with the El-Sayed rule. Importantly, the accessibility of these pathways is strongly modulated by keto–enol tautomerism, with the diketo form providing favorable conditions for triplet-state population. The combined experimental and theoretical analysis demonstrates that RTP in this system arises from the interplay between electronic structure, tautomeric equilibrium, and environmental restriction of molecular motions.

These findings provide a mechanistic framework for understanding phosphorescence in metal-free systems and offer guidelines for tuning excited-state dynamics in organic luminophores.

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corresponding author: monika.srebro@uj.edu.pl, arkadiusz.matwijczuk@up.edu.pl