Relaxation pathways in novel semicroconaine dyes probed by ultrafast spectroscopy

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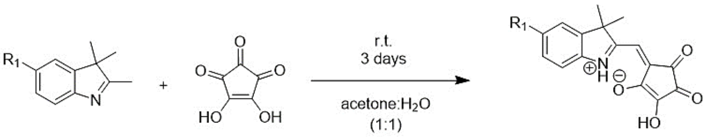
Semicroconaines represent a class of zwitterionic donor-acceptor (D-A) type of dyes within the polymethines family and are characterized by the presence of a five-membered ring, known as a croconic acid. Semicroconaines typically exhibit narrow absorption bands with high molar absorption coefficient in the visible that can be tuned by varying the donor moiety conjugated with the croconic acid core, as well as by introducing substituents on a given donor moiety.[1] These properties, together with good photo- and thermal stability, make semicroconaines interesting candidates for various applications, including bioimaging, photodynamic and photothermal therapy.[2]

Semicroconaines, similarly to croconaine dyes, are known for their remarkably low fluorescence quantum yield, a property which can be improved by synthetic modification of the semicroconaine skeleton. However, achieving an effective enhancement requires a thorough comprehension of the underlying causes of the low fluorescence yield. Therefore, delving into the photophysic of semicroconaine dyes provides crucial insights for refining the synthetic strategies for the development of superior fluorescence dyes. Additionally, this understanding might offer a broader perspective on potential relaxation pathways for NIR croconaine dyes.[3]

Our work focuses on resolving the ultrafast relaxation pathways of newly synthesized semicroconaine dyes (Scheme 1), and the influence of different substituents at the indolenine ring (-H, F, I and NO_2) on the excited-state dynamics. We hypothesize that the flexibility of the methine bridge may lead to de-excitation through the rotation of the donor moiety around the croconic acid core. To explore this hypothesis, we investigated the relaxation pathways of our dyes in solvent mixtures of increasing viscosity by means of steady-state and time-resolved femtosecond (transient absorption and fluorescence up-conversion) spectroscopies.



1a R_1 = H
1b R_1 = F
1c R_1 = I
1d R_1 = NO_2

2a R_1 = H
2b R_1 = F
2c R_1 = I
2d R_1 = NO_2

Scheme 1: Synthesis of the novel semicroconaines 2a-2d.

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