



Valentine I. Vullev ¹

¹ University of California, Riverside

**Electron-deficient photosensitizers:
How to make nitroaromatics fluoresce?**

Organic aromatic compounds are building blocks for a wide variety of p-type materials and potent photoreductants. Conversely, n-type organic conjugates are few and far between. The electron-withdrawing strength of nitro groups makes them promising substituents for attaining such n-type systems. Nitro groups induce positive shifts in the reduction potentials of polycyclic hydrocarbons, such as pyrene, that exceed 1 V. The shifts induced by nitrile and carbonyls range between 0.2 and 0.7 V. Optically excited states of most nitroorganics, however, undergo fast non-radiative decays. That is, nitro groups are efficient fluorescence quenchers, rendering these compounds unfeasible for a wide range of applications such as photosensitization and photooxidation. Therefore, understanding how to make nitroaromatics fluoresce is crucial for photonics, electronics and energy science. Nitro groups usually induce high densities of $\pi\pi^*$ and $n\pi^*$ states with different multiplicity, providing pathways for efficient intersystem crossing (ISC), i.e., triplet formation. Introducing a charge-transfer (CT) character in the singlet or triplet excited states can decrease the spin-orbit coupling (SOC) between them and reduce the ISC rates. Many of the fluorescent nitro compounds, indeed, carry electron-donating moieties. A nitro-induced strong CT character also leads to dark excited states with negligible overlaps between their natural transition orbitals (NTOs) resulting in slow radiative decay. Medium polarity stabilizes such CT states, bringing them close to the ground state, which favors internal conversion (IC) to it, and enhances the non-radiative decay rates. This conundrum of excited-state CT that reduces ISC, while augmenting IC deactivation, raises the question how much CT character is too much. This presentation will cover our latest advances in developing strategies for making nitroaromatics fluoresce. Suppressing the known pathways for quenching the fluorescence of nitrocompounds, however, leads to the emergence of previously unknown mechanisms for non-



radiative deactivation, involving, for example, aborted photochemistry. Engineering the alignments of the energy levels of the excited states of nitroaromatics allows to improve not only the fluorescence quantum yield to values above 0.1, but also the photostability. Despite the huge developments in the “traditional” or n-type dye sensitized solar cells (DSSCs), the p-type DSSCs still remain largely unexplored. Designing electron-deficient photostable sensitizers, such as fluorescent nitroaromatics, is essential for the realization of p-type DSSCs, where the electronically excited sensitizer has to efficiently inject holes in the photoelectrode. Combining p- and n-type DSSCs, while adding photocatalytic activity to their functionalities is an important path toward the realization of artificial photosynthesis.

Keywords: Abstract; language; scientific articles; congresses.