

## Photoinitiating Hole Transfer for Harvesting Energy From the Sun

Eli M. Espinoza and Valentine I. Vullev

University of California, Riverside

Molecular-level control of charge transfer is paramount for organic electronics and solar-energy conversion. Electromagnetic interactions, originating from the second strongest fundamental force in the universe, occur between charged particles. As electrostatic analogues of magnets, molecular electrets are dielectrics that contain ordered electric dipoles. We have demonstrated the utility of anthranilamides as suitable candidates for the bioinspired approach in the design of molecular electrets. Much like protein helices, anthranilamides, composed of non-native beta amino acids, possess intrinsic dipole moments originating from ordered amide and hydrogen bonds. Unlike the protein helices, however, anthranilamides have a backbone of directly linked aromatic moieties comprising pathways for highly efficient electron and hole transfer. The distal sites, i.e., the fourth and fifth position in the aromatic rings, provide a means for tuning the electronic properties of the electrets via chemical modifications. The dipole-generated local fields of the bioinspired molecular electrets rectify the kinetics of charge separation and charge recombination. That is, the rates of electron transfer along the dipole are different from the rates against the dipole. Because our focus is on hole-transfer electrets, we need a suitable electron acceptor for photoinitiating long-range charge transfer, providing the motivation for the design and development of such light sensitizers. To be able to harvest the energy from the sun, we choose sensitizers that absorb in the red, green and blue region of the spectrum, i.e., corroles, diketopyrrolopyrrole and fluorescent nitropyrenes. Such broad use of the light across the visible region of the electromagnetic spectrum will open avenues toward tandem light harvesting devices. In this presentation I will focus on our newly discovered fluorescence from nitropyrenes. Pyrenes are the most used organic photoprobes. Upon nitration, pyrene exhibits a shift in its absorption to the visible spectral region. While the nitro group makes it a better electron acceptor, the nitropyrene is non-fluorescent due to efficient triplet formation. Amidating the nitropyrene to produce  $\text{NO}_2\text{-Py-C(O)-NH-R}$  did not eliminate the intersystem crossing. Recently, we discovered that inversion of the amides suppresses triplet formation and makes nitropyrene fluorescent. Reorienting the amide bond with the nitrogen adjacent to the pyrene ( $\text{NO}_2\text{-Py-NH-C(O)-R}$ ) elevates the energy levels of the  $T_2$  and  $T_3$  states above that of the  $S_1$  state, resulting in the suppression of intersystem crossing. It results in fluorescence quantum yields as high as 0.26. This approach for modifying energy levels of excited states via relatively straight forward chemical changes sets an important precedent not only for energy science, but also for organic electronics and photonics.

