Excited State Kinetics of Ru(bpy)₂(PVP)₁₀²⁺ Lynn Dennany; Robert J. Forster; National Centre for Sensor Research (NCSR) School of Chemical Sciences, Dublin City University, Dublin 9, Ireland.

The creation of cascade processes, e.g., triggering the quenching of multiple luminescent centres in response to quenching at a single site, is an important amplification approach for sensing biomolecules with specificity and high sensitivity. Two processes can be important contributors to super quenching within luminescent polymers. First, a single acceptor may quench the fluorescence emission from an entire macromolecule in aqueous solution. Second, where the luminescent polymer is charged, a weakly bound complex between the polyelectrolyte and quencher may form enabling static super quenching. Polymers labelled with ruthenium polypyridyl complexes represent attractive systems for exploring super quenching because emission from the metal-to-ligand charge transfer (MLCT) excited states of Ru^{II} can be probed with great sensitivity.



Here, we report on quenching in solution and within thin films of $\text{Ru}(\text{bpy})_2(\text{PVP})_{10}^{2+}$. By combining solution phase cyclic voltammetry and the emission spectrum at cryogenic temperatures, the formal potentials for oxidation and reduction of the excited state were determined allowing the feasibility of quenching by electron transfer to be assessed. Also of importance is the transfer of excitation energy form the excited state molecule to another molecule or quencher, Q, in solution. Analysis of time resolved emission data indicates that the quenching constants for the polymeric system can be several orders of magnitude larger than those found for the corresponding monomers. The implications of these findings for analysis by fluorescence are considered.