



**SILESIAIAN UNIVERSITY OF TECHNOLOGY**

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**DOCTORAL DISSERTATION**

*The intermolecular and intramolecular donor-acceptor charge transfer behaviour as a way to control thermally activated delayed fluorescence emission.*

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## Summary

Luminescence of organic compounds originates from electronic transitions from one excited state back to the ground state, associated with the molecule in neutral conditions. The release of energy can undergo through radiative and non-radiative pathways, being one of the most common non-radiative decays the dispersal of thermal energy. Radiative deactivation processes may induce the emission of light and generally can be characterised as fluorescence or phosphorescence. The fluorescence mechanism consists of transitions from a singlet excited state to the singlet ground state, while phosphorescence is associated with transitions originating from triplet excited states. Due to the distinct spin nature of singlet and triplets, transitions from one to the other are considered forbidden and have a low probability of occurring, producing longer emission pathways, i.e., emissions originating from triplet states are characterised as long-lived mechanisms.

Charge recombination processes in Organic Light-Emitting Diodes (OLEDs) produce singlet and triplet excited states in a 1:3 ratio, limiting fluorescent OLED devices to 25% of Internal Quantum Efficiency (IQE), wasting most of the excitation energy (triplet excited states). Nevertheless, if the energy difference between singlet and triplet excited states is small enough, their interaction can increase OLED efficiency by harvesting the triplet excited states. Deriving from that effect, the Thermally Activated Delayed Fluorescence (TADF) process takes advantage of small singlet-triplet energy splits to achieve theoretically 100% of IQE.

A well-known approach to achieving a small singlet-triplet energy split is through the development of Donor-Acceptor (DA) structures, in which the donor and acceptor moieties are not strongly coupled, generating frontier orbitals minimally overlapped. The energy absorption in DA systems triggers the transfer of electron density from the donor to the acceptor part of the structure, a process known as Charge Transfer (CT). Through deeper investigation of photophysical parameters, excitons' energetic levels, CT processes, singlet-triplet interactions, emission mechanisms, etc. is possible to acquire a better comprehension of the TADF emission mechanism to develop more efficient lighting devices.

This work, divided into four sections of results, addresses the topic of intermolecular and intramolecular CT behaviour DA systems to understand better and control TADF emission. Through electrochemical measurements, the Ionization Potential (IP) and Electron Affinity (EA) values were determined, being related to the energies of frontier orbitals: Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO). Spectroscopic and electrochemical measurements combined allow us to investigate the charge carrier formation during oxidation and reduction processes by observing spectral changes while the potential difference is applied; it can also provide information about electrochemical stability and degradation of the materials. Furthermore, potentiostatic EPR measurements detect the presence of paramagnetic radicals, contributing to the characterisation of charge formation in molecular structures. Finally, the photoluminescence studies were performed in solution and solid-state samples by analysing emission spectra.

Determination of TADF behaviour was analysed by solvatochromism studies comparing emission spectra in solvents of different polarities; by degassing experiments examining the contrast in emission intensity between aired and degassed systems; and by time-resolved spectroscopic analysis using an iCCD-gated camera, able to detect emission in the nanosecond time regime.

The compilation of electrochemical, spectroelectrochemical and photophysical analysis of all the compounds in this study grant a better understanding of the relationship between delayed fluorescence mechanisms and molecular structures, which may induce and inspire the evolution of OLED technology.