Spectroelectrochemistry methods have gained considerable attention as a powerful tool to evaluate the synergy between kinetic and thermodynamic information and molecular vibrational processes. In particular, *in situ* UV–vis–NIR spectroelectrochemistry has been intensively used to evaluate the electronic transitions during the charging/discharging process of π-conjugated polymers. Such simultaneous monitoring allows obtaining important information about the type of charge carrier and the mechanism of charge carrier transport. In this work, we present the coupling between UV–vis–NIR spectroscopy and *in situ* electrochemical-conductance measurements to compare the doping process of three different thiophene-based conducting polymers. The simultaneous monitoring of electrical and absorption properties, associated with low energy electronic transitions, characteristic for polarons and bipolarons, was achieved. In addition, this method allows evaluating the reversible charge trapping mechanism of poly-3,4-α-xylendioxythiophene (PXDOT), caused by the formation of α-dimers, making it a very useful tool to determine relevant physicochemical properties of conductive materials, such as conductivity, electrode potential and energy transitions.

**Figure 1.** (Top) Generalized chemical structures of neutral and non-mobile charged species formed during the electrochemical doping process. (Bottom) Change of the optical density (ΔOD) (blue lines, left axis) at 600 and 800 nm, and of conductivity (green line, right axis) during charging/discharging cycles.

**References**