Semiconducting conjugated polymers have emerged as a promising cost-effective candidate for realising flexible transistors, solar cells, solid-state batteries and thermoelectric generators. In conjugated polymers, the dielectric constant and dc conductivity dominate power conversion efficiency and performance. Both arise from the chemical structure of the π-conjugated polymers that consist of a conjugated $sp^2$ hybridized backbone and, typically, an aliphatic side chain. The enhancement of the dielectric constant of the conjugated polymer results in a reduced exciton binding energy which is highly relevant in their application in solar cells, while the enhancement in conductivity of the polymers results in devices with faster response time. The dielectric constant is usually determined under time-varying small electric field conditions at relatively high frequencies. In contrast, the conductivity is usually determined under a steady-state electric field or DC conditions. Consequently, the efforts to tune the dielectric constant or conductivity in conjugated polymers have usually been carried out independent from each other.

The significant difference in electrical conductivity between different phases in heterogeneous materials gives rise to Maxwell-Wagner-Sillars interfacial polarization (IP) effect. The appearance of IP is characterized by a rise in the relative permittivity of the material at low frequencies, accompanied by a relaxation peak in the dielectric loss spectra. The existence of IP and the local build-ups of space-charge can significantly affect the dc conductivity, $\sigma_{dc}$, of the material. Therefore, understanding the IP process, its relation between dielectric permittivity and $\sigma_{dc}$ in conjugated polymers is highly relevant for further improving the performance of their optoelectronic devices. However, the IP process and establishing a direct correlation with $\sigma_{dc}$ have been overlooked so far in conjugated polymers because identification of the IP in dielectric loss, is usually masked by the conductivity of the samples at low frequencies, even at low temperatures.