

PÔSTER - SÍNTESE E CARACTERIZAÇÃO DE MATERIAIS

**EFFECT OF THE SIDE CHAIN IN DIKETOPYRROLOPYRROLE
COPOLYMERS: A COMPARATIVE STUDY BETWEEN HYDROPHOBIC
ALKYL AND HYDROPHILIC TRIETHYLENE GLYCOL CHAINS**

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Organic materials, and particularly conjugated polymers, have played an essential role in optoelectronics and have been applied in a wide variety of devices, such as organic solar cells (OSCs), organic field-effect transistors (OFETs), light emitting diodes (LEDs), electrochromic windows, supercapacitors, and recently, in Li-ion batteries. In recent years, considerable attention has been devoted to organic dyes, such as diketopyrrolopyrrole (DPP). In this molecule, changes in the chemical structure can easily modulate their electronic and optical properties. Moreover, functional groups such as C=O, N-H, S-H, and -NO₂ can directly be coupled to the conjugated backbone, influencing inter- and intramolecular interactions. This has been a valuable tool for controlling the supramolecular structure of the material. Also, in contrast to the great efforts to

develop new conjugated polymer backbones, there are few studies involving the structure-properties correlation of conjugated polymers containing polar side chains, mainly involving electrochemical techniques. The glycol chain is a widely-used solubilizing moiety, which is well-known for its hydrophilicity. Compared with typical alkyl side chains, polymers with branched glycol side chains show a smaller p-p stacking distance, higher hole mobility, smaller optical band gap, higher dielectric constant, and larger surface energy. In this work, the effect of the DPP side chain (triethylene glycol - TEG or hexyl - Hex) on the electronic and electrochemical properties of a donor-acceptor (D-A) copolymer containing fluorene (F) and DPP units, connected through thiophene (Th) rings, is being studied. The optical features of the copolymer containing alkyl side chains linked to DPP (PFTThDPPHexTh) show two distinct bands. First, the one located in the high-energy region (between ~300 and 470 nm) shows three main peaks, with the most intense peak centered at 370 nm. The other band is extended from 480 to 700 nm, with a peak at 650 nm and a shoulder at 602 nm. The electronic spectra obtained in the thin film are quite similar to those obtained in the solution. The cyclic voltammetry technique was further employed to investigate the electrochemical behavior and to estimate the energy values of the ionization potential (IP) and electron affinity (EA). In a potential window between -1.3 and 1.6 V (vs NHE), four quasi-reversible redox peaks were observed at 1.37 V/1.06 V, 1.56 V/1.34 V, 0.90 V/-0.67 V, and - 1.29 V/-1.16 V, which are associated with the p and n doping. The EA and IP were estimated at - 3.83 and -5.54 eV, respectively. In addition to the previous investigation, understanding the stability and ion transport in conjugated polymers is an important aspect of organic electronic devices. The doping/dedoping processes at anodic potentials (p-doping) did not show a significant drop in the current peak response of the copolymer even after 410 cycles. This result can be associated with fast charge transport in the polymer or that the electroactive sites remain unchanged during the cycling in the region of applied potentials. By contrast, the reduction process (n-doping) in a wide potential window was seen to be quite unstable, and the loss of electrochemical activity occurs already in the 10th cycle. The sluggish diffusion of the counter anion and its interaction with the aliphatic ester side chain in the copolymer leads to the trapping of NBu₄⁺, deactivating the reduction of active sites. Concerning the copolymer with TEG

side chain, we finished the synthesis and started the chemical characterization. We expected the glycolated side chain would improve the electrochemical stability due to its ability to effectively take up ions from aqueous solutions at a relatively fast rate, allowing the application of these materials in energy storage devices, for example.