PÔSTER - RESUMO - DISPOSITIVOS ELETRÔNICOS, ELETROQUÍMICOS, SUPERCAPACITORES E BATERIAS

HEAVY ELECTROCHEMICAL DOPING OF POLY(3-HEXYLTHIOPHENE-2,5-DIYL) (P3HT) WITH A CHLORIDE-BASED AQUEOUS ELECTROLYTE

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Electrolyte-gated organic transistors (EGOTs) have emerged as pivotal components in bioelectronics due to their low-voltage operation and high transconductance. While the choice of electrolyte is known to influence device performance, the underlying molecular mechanisms that dictate why specific anions facilitate electrochemical doping while others are limited to field-effect modulation remain poorly understood. This study provides a comprehensive investigation into the interaction between poly(3-hexylthiophene) (P3HT) and three common aqueous electrolytes: NaCl, Na2SO4, and NaClO4. Using a custom-built optoelectronic characterization setup, we simultaneously recorded transistor transfer curves and UV-Vis absorption spectra in situ. Our results reveal a dramatic dependence on the anion type: the perchlorate (ClO4-) electrolyte induced heavy electrochemical doping, characterized by a drain

current of 3 milliamperes and an 80 percent reduction in the pi-pi* absorption band at VG = -0.7 V. In contrast, sulfate (SO4 2-) and chloride (Cl-) exhibited significantly lower performance, with chloride restricted to a pure field-effect regime (1 microampere). To elucidate these discrepancies, we employed Density Functional Theory (DFT) and Molecular Dynamics (MD) simulations. TD-DFT calculations on T3HT:Anion clusters revealed that polymer oxidation efficiency is directly related to the net charge variation (delta e) on the backbone. For ClO4-, the removed charge originates almost entirely from the oligomer backbone, whereas for Cl- and SO4 2-, a significant portion is removed from the anion itself, hindering effective polymer doping. However, when simulating anion-water clusters, TD-DFT showed that water shielding inhibits this electron transfer from the anions, making all species theoretically capable of inducing similar polaronic states. This suggests that the experimental discrepancy is not purely electronic but transport-limited. MD simulations revealed distinct number density profiles at the P3HT-electrolyte interface. Although the hydrophobic nature of P3HT prevents water permeation, perchlorate ions demonstrate a higher surface concentration compared to chloride. Potential of Mean Force (PMF) profiles identify a thermodynamic entry barrier as the governing factor. The free-energy penalty for an ion to shed its hydration sphere -- which is significantly more structured for Cl- (three coordination shells) than for ClO4- (one shell) -- is much higher for chloride (around 15 to 17 kcal/mol) than for perchlorate (around 7 to 8 kcal/mol). These findings provide a predictive framework for organic electronics, emphasizing that ion processability into the polymer matrix, dictated by hydration energy and charge density, is the bottleneck for achieving high-performance electrochemical transistors.

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Palavras-chave: egots; p3ht; electrochemical doping; anion hydration shell.