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

A FIRST-PRINCIPLES STUDY ON THE ABSORPTION CHARACTERISTICS OF CHARGE-TRANSFER STATES IN A-SEXITHIOPHENE:FULLERENE SYSTEMS

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The interconversion dynamics between charge-transfer-state charges (CTCs) and separated charges (SCs) is still an unresolved issue in the field of organic photovoltaics and has therefore remained highly debated in literature.[1] Although, ultrafast techniques, such as transient absorption spectroscopy (TAS), bring invaluable insights, the attribution of the obtained absorption characteristics to the charged species often require knowledge about the photophysical properties of the system and its components. [2,3] Such information can be obtained from time-dependent density functional theory (TD-DFT). In this work, a case study on a-sexithiophene:fullerene (a6T:C60) systems will be presented, for which TAS measurements revealed two charge species with distinct absorption characteristics and different dynamics.[4] Two hypotheses were formulated, which could give rise to this experimental observation. The first assumes the formation of two different charge transfer states with different absorption characteristics, related to different positioning of the C60 anion with respect to the corresponding a6T cation. The second hypothesis attributed the two species as charge-transfer-states and separated charges. Modelling different charge transfer configurations that occur in system

with different morphological structures, TD-DFT simulations were performed to assess the absorption characteristics compared to that of the cationic state. It is found that the spectral differences arise from broken symmetry in the charge transfer state that turns forbidden transitions into allowed ones. This symmetry breaking occur similarly independent of whether the anion was position face-on, tip-on or edge-on reproofing hypothesis 1. On the other hand, the absorption characteristics obtained from averaging over several CT configurations yielded good agreement with one of the experimentally obtained signatures while the properties of the isolated cationic state agreed to the other. This confirmed hypothesis 2 and allowed to identify the two species as CTCs and SCs. Based on this assignment, a kinetic model could be formulated allowing the characterization of the charge generation, separation, and recombination mechanisms.[4]

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References

[1] Shivhare, R. et al. Adv. Mater 2022, 34 (22), 2101784.

[2] Moore, G. J. et al. J. Phys.Chem. Lett. 2020, 11 (14), 5610-5617.

[3] Zhong, Y. et al. Nat. Com. 2020, 11 (1), 833.

[4] Moore, G. J. et al. Nature Communications. 2024, 15 (1), 9851.

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