

Impact of Side Alkyl Chain Geometry on Diketopyrrolopyrrole Derivatives: Spectroscopic Properties, Aggregation, and Thin Film Organization

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Diketopyrrolopyrroles (DPP), a family of organic dyes featuring a π -conjugated dilactam core, are known for their rich structural modification capabilities, leading to various property changes. The impact of the spatial structure of side alkyl chains (branched and straight) on the properties of oligothiophene derivatives of DPP in solution and thin layers was explored. In order to control the process of creating thin films at the air-water interface, the Langmuir technique was employed. The process of layer compression was analyzed in detail, where, aside from surface pressure, changes in surface potential and absorption spectra were examined. Thin layers were transferred onto the solid substrate using the Langmuir-Schaefer technique and were studied with confocal microscopy and absorption spectroscopy. Additional conclusions enhancing our understanding of molecular arrangement in thin layers were obtained by combining experimental techniques with DFT calculation results.

Results revealed significant differences in the isotherm during Langmuir layer compression, particularly for the branched alkyl side chain dye, where an additional compression stage was observed. Interestingly, the layer formation process was initiated at a value of 1/3 area per molecule as obtained from DFT geometry optimization calculation, suggesting an elaborate structure of formed layers. It was shown by confocal microscopy that the Langmuir layers transferred onto a solid substrate are not monomolecular but are composed of three different structures. Complexity in the absorption spectra of both materials in solution and significant changes between their spectroscopic properties in the thin film were revealed by spectroscopic study analysis, although minimal differences were observed in their spectra in solution. The appearance of three absorption bands in the red region was revealed by the deconvolution of absorption spectra, in the spectra of the material in every form (solution, In-situ, thin layer). By combining information obtained with Langmuir, spectroscopic and microscopic studies, and DFT calculations, it was concluded that three forms of aggregations - monomer, dimer, and higher aggregation structure (most likely tetramer) - are present already in materials in solution, which translates into their molecular arrangement in thin films. Moreover, the pathways of formation and the ratio of aggregation forms in thin films are influenced by the spatial structure of the side alkyl chain.

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