Perylene Diimide Dyes: Modeling the Molecular Motion of Supra-molecular Aggregates in solution

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The optoelectronic properties of perylene diimide (PDI) dyes, coupled with their relatively low production costs, have attracted considerable interest in recent years for various applications, ranging from solar cell devices and electronic displays to cancer treatment[1,2]. The PDI molecules have the capacity to spontaneously self-assemble into ordered one-dimensional nanostructures in solution, resulting in aggregates of modulable size and shape[3,4]. This self-assembly process is influenced by a delicate balance of non-covalent interactions, including hydrophilic, hydrophobic, and π-stacking. In particular, the nature of the core substituents, either in bay or imide position (see Figure1a), influence the structural and physicochemical properties of the self-assembled nanostructures[2]. In turn, the differences induced in the supramolecular arrangments by the modulated inter-molecular interactions have a strong impact on the optical properties and the photophysical response. This makes computational investigations of such multi-level systems much more challenging than those designed for single molecules. The relationship between the aggregate's structures and their photophysical responses may lead to establish design guidelines in developing innovative materials and technology.
In this framework, the present work aims to delve into the fundamental principles governing the self-assembly of PDI molecules in solution, providing insights into the model of the motion of these $\pi-$stacked aggregates and their interaction with the surrounding environment. Extensive Molecular Dynamics simulations were conducted for systems comprising two to twelve layers of PDIs in solution, employing a highly accurate QMD-FF[3], previously derived from specific QM data, and developed to represent both PDI's flexibility and its intermolecular interaction patterns. A post-processing protocol was implemented to examine the structural properties and dynamics of $\pi-$stacked systems in solution. The PDIs' motion along the MD trajectories was characterised by designing geometrical supramolecular descriptors. In addition, the rotation of the pendant chains resulted in the interconversion of the two possible isomers (syn/anti), at a monomeric level. The anti/syn transition of every PDI unit within the various aggregates underwent a comprehensive analysis. Moreover, the interaction energies between solute-solute/solute-solvent were studied in detail. The latter was widely investigated by computing pair correlation functions and three-dimensional density distributions. This approach could be employed as a general protocol to conduct in-depth structural analyses of different supramolecular systems that share similar properties with PDI's dyes.

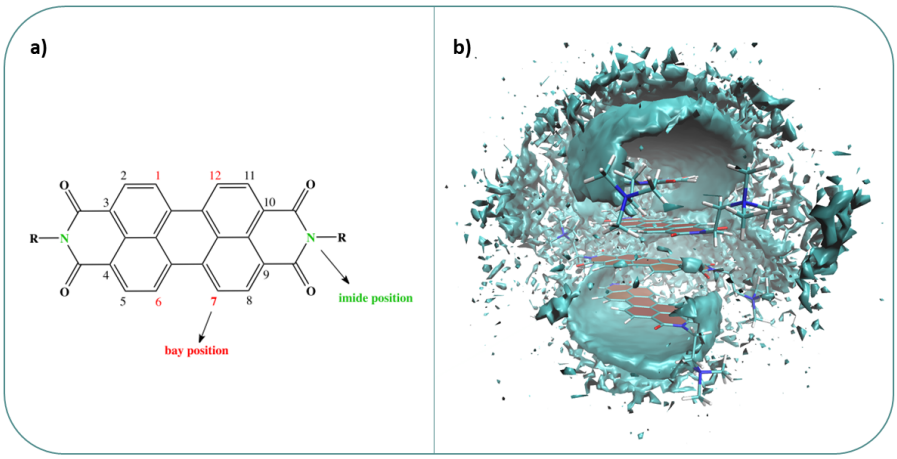

Figure 1: a) PDI molecular structure, highlighted in red and green the key substitution positions. b) showing the tetramer aggregate in the solution.

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3.Alekos Segalina, et al. J. Chem. Theory Comput. 2022, 18, 3718- 3736.
4.Alekos Segalina, et al. J. Chem. Theory Comput. 2019, 123, 64276437.