Quantum chemical study on the excitation and optical properties of pi-stack aggregates of open-shell polycyclic aromatic hydrocarbons

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Geometric features and physical properties of the pi-stack type one-dimensional aggregates of polycyclic aromatic hydrocarbons (PAHs) incorporated in carbon nanotubes have been investigated intensely as novel multi-functional materials. On the other hand, several PAHs and their related molecules having unpaired electron(s), i.e., open-shell PAHs, have attracted much attention since they are expected to show unique covalent-like interactions between the monomers in solution and/or in crystal phase. In this study, we investigate the relationship between the structures and electronic excitation properties of molecular aggregates composed of open-shell PAHs, and then discuss the open-shell character dependence of their static and dynamic optical response properties. We here employ several PAHs, such as a phenalenyl, as the monomer unit, and then we evaluate the excitation properties of several pi-dimers and -tetramers with different inter-monomer distances and orientations by using the quantum chemical calculations. The linear and third-order nonlinear optical response properties of these systems are evaluated by the sum-over-states method, and then we discuss the structural dependences of open-shell characters and optical response properties of molecular aggregates composed of open-shell PAHs.