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A DFT and TDDFT investigation of interactions between pyrene and amino acids with cyclic side chains

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ABSTRACT

A computational investigation of photoinduced charge transfer complex formation between pyrene (Py) and amino acids with cyclic side chains (Phenylalanine: Phe, Tyrosine: Tyr, Tryptophan: Trp, Histidine, His) has been carried out in gas phase and in water. Geometry optimizations were performed by density functional theory (DFT) at ωB97XD/6-311++G(d,p) level. Time-dependent density functional theory (TDDFT) was used to calculate the electronic transitions of molecules at B3LYP/6-311++G(d,p) level using the above ground-state geometries. Polarizable Continuum Model (PCM) and SMD are used for calculations in water. Analyses and comparisons have been performed for total electronic energies, complexation energies, free energy differences, solvation energies, excitation wavelengths, and HOMO–LUMO energy gaps of complexes in gas phase and in solution. The intermolecular distances between Py and amino acids increased in water compared to the gas phase for all studied with the exception of Py–Tyr system. The optimized complexes display an increasing complex stability in the order Trp > Tyr > Phe > His. Analyses of first excited singlet states have indicated charge transfers transitions between Py and amino acids His and Trp through π–π stacking in gas phase at 345 nm and 393 nm, respectively. Py–Trp system has also charge transfer (CT) in water at 389 nm. Py–Trp systems have the most significant charge transfer between HOMO and LUMO (full CT, 70%). However, S_0–S_1 transition (393 nm) has weaker dipole moment and oscillator strength than the other studied systems. Due to its charge transfer character, Py–Trp systems seem to be appropriate models to investigate and design bioorganic photosensitive materials.

1. Introduction

Photoinduced electron transfer processes play an important role in designing biomolecular light emitting materials. Polyaromatic hydrocarbons can form donor–acceptor complexes with similar molecules with π electrons by photoinduced electron transfer and display UV–Vis absorption and fluorescence properties because of their electronic structure.

Graphene has been subject to many studies recently because it is used as a potential candidate for developing new materials in different fields like molecular electronic sensors, energy production and conversion. Graphene has unique properties: fast electron transportation, high thermal conductivity, excellent mechanical stiffness and good biocompatibility [1]. These unique properties allow it to be used in a wide variety of applications in electronics, information, energy, materials and bio-medicine and other related fields. Use of thin graphene films as potential transparent electrodes for solar cells has also been reported [2–4]. Unfortunately, graphene and CNT are very large for quantum mechanical calculations; therefore, a smaller polycyclic hydrocarbon is used as a model system representing the former two molecules.

Pyrene is the polyaromatic hydrocarbon mostly chosen as the model compound due to its similarity to a graphene sheet and carbon nanotubes (CNTs). Because of electronic structure, it displays strong bands in UV–Vis absorption and emission spectra similar to graphene and CNT [5–7]. Thus, Pyrene–CNT interactions strongly resemble the interaction between CNTs themselves [8] at nanotube sidewalls by strong π electron coupling between the aromatic molecule and the nanotube [5,9,10].

Amino acids often possess particular properties that are very important in materials science [11,12]: weak van der Waals interactions, hydrogen bonds, wide transparency ranges in the visible regions and zwitterionic structures.

Aromatic amino acids which resemble aromatic amines may interact with aromatic hydrocarbons and form charge transfer

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complexes in the excited states upon excitation of their π-electronic systems [13–18]. They are able to form intra- and intermolecular charge transfer complexes in solution [19]. Thus, it is very important to determine their interactions with biologically important molecules. Interactions of pyrene with some selected amine systems have also been observed formerly in ground state [20].

Intercations of pyrene derivatives with proteins and nucleic acids [21–23] have also been studied in order to develop emitting and charge transporting materials [24–27]. Pyrene and its derivatives have been frequently used as emitting materials in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaic cells (OPVs) [28–36] as they emit blue light strongly. Studies related to the use of pyrene derivatives as oxygen sensors, DNA intercalators and solar cell components have also been reported [37–39]. The design and modification of these structures require accurate knowledge of the electronic properties of the Pyrene moiety induced by the substituents. Quantum mechanical methods can provide useful information about the correlation between the structural and electronic properties [16,40–42].

In this study, the intermolecular interactions and the complex formation between donor and acceptor molecules will be investigated. Amino acids with cyclic side chains (histidine-His, phenylalanine-Phe, tyrosine-Tyr, tryptophan-Trp) have been chosen as they naturally occur in biological systems and display donor characteristics due to presence of nitrogen atom (donor modification). Pyrene will used as the acceptor and its properties will be determined upon formation of donor–acceptor complex formation with selected amino acids.

One of the challenges of computational chemistry is the excitation of chromophoric systems. Additionally, subsequent photochemical processes are also difficult to predict and to treat theoretically, especially when they occur in liquid phase. Most of the studies mainly focused on intramolecular photoinduced charge transfer [41–43] and only a few studies on intermolecular photoinduced charge transfer is reported [20,41,44–46].

This study aims to investigate all possible intermolecular interactions in donor–acceptor complexes formed between pyrene and amino acids with cyclic side chains, and their ground-state and excited-state electronic properties using density functional theory (DFT) and time dependent density functional theory (TDDFT).

Current study will provide detailed information on donor–acceptor systems composed of organic–biological hybrid components which have potential use in many related fields including health, electronics and materials science.

2. Computational details

The calculations were performed with Gaussian09 [47], Gaussview5.0 [48] and Spartan08 [49] programs. Initial structures for the monomers have been determined by conformational analyses using Spartan 08. The ground state geometries were optimized using density functional theory (DFT) [50]. To improve the description of the van der Waals interactions, we employed the empirical van der Waals correction proposed by Grimme as implemented in ωB97XD functional in conjunction with 6-311++G(d,p) basis set [51]. The initial complex structures were obtained by using different orientations of the donor and acceptor molecules with variable donor–acceptor distances and they were optimized in gas phase. The calculations were repeated in water. All optimized geometries have been verified as minima by frequency analysis.

The hybrid DFT Becke's three-parameter nonlocal exchange functional [52,53], with a correlation function similar to Lee–Yang–Parr (B3LYP) [54] was used for excited state calculations with time-dependent (TD) formalism in conjunction with the 6-311++G(d,p) basis set which is determined to be reliable in our former study for similar systems [46]. Additional TD-DFT calculations were performed with ωB97XD [51] and CAM-B3LYP (Coulomb-Attenuating Method) [55] which both include long-range corrections using the same basis set to verify the chosen level of calculation. 40 lowest singlet excited states were calculated for each molecule. Molecular orbital energies and the UV–Vis spectra of the studied molecules were illustrated by the Gaussview program

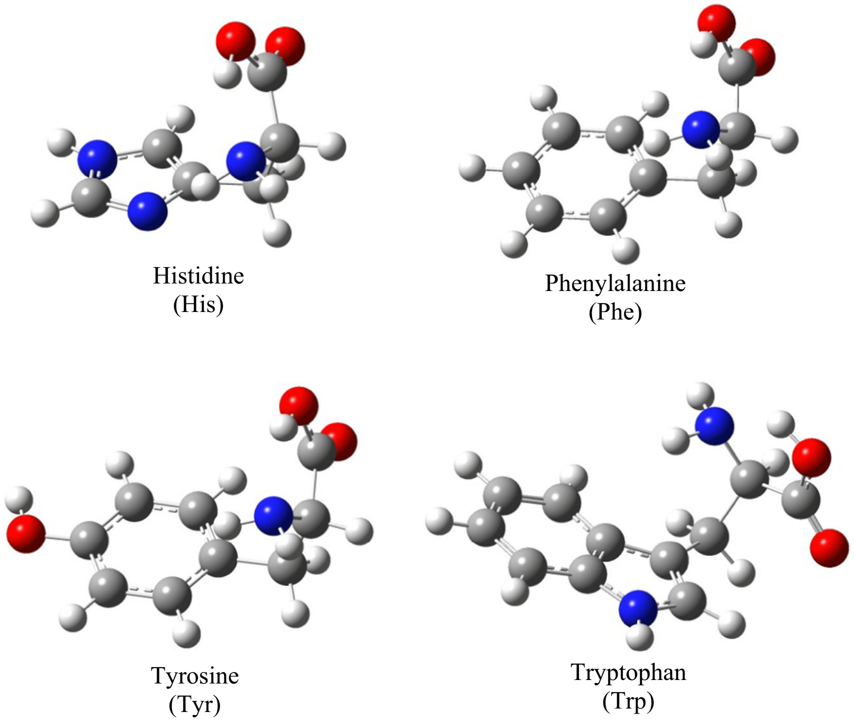

Fig. 1. Optimized molecular structures of amino acids with cyclic side chains, Histidine (His), Phenylalanine (Phe), Tyrosine (Tyr) and Tryptophan (Trp) in gas phase.