

COMMUNICATION

TD-DFT Study on the pH Related and Site-Specific Quenching Mechanism of 6-Formylpterin

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Abstract: In this communication, the pH related fluorescence quenching mechanism of 6-formylpterin (FPT) has been investigated by using time-dependent density functional theory (TD-DFT). The origin of fluorescence quenching of FPT in acid condition in the presence of acetate ion is originated from the site specific excited state proton transfer (ESPT) on the N1 site whereas the absence of ESPT in basic condition sustains FPT's fluorescence. This ESPT process is found to be modulated by hydrogen bonding patterns which not only controls the molecule's fluorescence but also coordinates its proton transfer site. Excitation process and relaxation process are further studied which give deeper insights into the origination of the proton transfer specificity.

AMS subject classifications: 65D18, 74E40, 78M50

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Pterins exist extensively in living creatures and absorb strongly in UV-A (320-420 nm) region which are generally believed to serve as photo-oxidants [1]. Abundant researches have been made to investigate their photophysical and photochemical properties, most of which focus on the electron transfer processes between triplet pterins and guest molecules [2]. Theoretical studies into the optic properties of singlet excited state pterins, especially the origin of fluorescence changes when they interact with guest molecules are still quite rare.

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Pterins have different structures in different pH regions which give strong fluorescence emissions [3]. As revealed by Thomas and co-workers, pterin as well as its non-conjugated pterin derivatives namely 6-formylpterin (FPT), neopterin (NPT) and bio-pterin (BPT) exhibit interesting pH-related fluorescence quenching towards hydrogen accepting anions [4]. In acid condition (pH region 4.9–5.5), pterins' fluorescence is significantly quenched by acetate and phosphate whereas in basic condition (pH region 10.0–10.5), pterins' fluorescence remains unchanged. As is known, fluorescence quenching is always a phenomenon generated by ESPT which plays important roles in pterins induced photo-damages. Thus, having a clear understanding of this pH related quenching mechanism would be of biological significances.

Hydrogen bonding interaction is a fundamental and widespread weak force which, as put forward by Han et al, varies in different electronic states and modulates fluorescence properties of chromophores [5]. With the aid of hydrogen bonds, electronic excitation frequently triggers proton transfer from the hydrogen donors to hydrogen acceptors which always lead to strong fluorescence quenching [6]. In the case of pterins, the fluorescence quenching in acid condition is likely to stem from proton transfer process as pterins have several hydrogen donating sites (**Scheme 1**) meanwhile acetate and phosphate can serve as good hydrogen acceptors. The absence of fluorescence quenching in basic condition may also closely related to hydrogen bonds which still remains unknown.

Herein, we perform a full investigation on the pH related fluorescence quenching mechanism of FPT in the presence of acetate by using quantum chemical calculations. In this communication, we first clarified the origin of the pH related fluorescence quenching. Then, excitation and relaxation processes of FPT are analyzed to further look into this pH related quenching mechanism. Density functional theory (DFT) and time-dependent functional theory (TD-DFT) approaches are applied to study the ground and excited state geometries as well as proton transfer potential energy curves. The ground and excited state geometry

Scheme 1: Molecule diagrams of 6-formylpterin and the acid-base equilibrium in aqueous solution.

