# COMMUNICATION

# Underestimation of Charge-Transfer Emission Energy Calculated by State-Specific Polarization Continuum Model

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**ABSTRACT** Charge-transfer (CT) emission energies of adenine-thymine dinucleotide are calculated by two commonly used polarized continuum models (PCM): linear-response PCM (LR-PCM) and state-specific PCM (SS-PCM). Time-dependent functional theory is used. The SS-PCM method is found to underestimate the CT emission energy relative to the LR-PCM method. The underestimation degree is more significant as the amount of transferred charges is larger. As a result, the SS-PCM method should be used with great caution when dealing with electronic transitions with significant CT characters.

In the photodynamics of DNA, Charge-transfer (CT) states are easily formed between two stacked bases and play an essential role in the photophysical and photochemical properties of DNA [1-3]. Time-resolved spectroscopy detects the evolutions of CT states and measures their lifetimes. Ab initio calculations can give deep insights into the nature of CT states, such as the amount of transferred charges and their energy profiles [4]. The reliability of the theoretical method is of primary importance when discussing the theoretical results. A simple and common criterion is to compare the calculated electronic excitation and emission energies with the experimental results. Because CT states are dark states and cannot be excited by UV light, their excitation energies cannot be measured by spectroscopy techniques [5]. On the

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other hand, the emissions of CT states are highly distinguishable in fluorescence spectra [3]. Therefore, the reliability of theoretical methods can be evaluated by comparing the calculated emission energies of CT states with experimental results.

Time-dependent density functional theory (TD-DFT) is commonly used in the excited-state calculations of DNA due to the large amount of atoms of DNA. Combined with linear-response polarized continuum model (LR-PCM) [6] or state-specific PCM (SS-PCM) [7], TDDFT is able to calculate the CT emission energies of DNA in aqueous solution. Generally, the geometry optimization of CT states is performed using LR-PCM due to the unavailable SS-PCM in excited-state optimizations in Gaussian 09 program [8]. Then, the minimum CT geometry is used to calculate the emission energy using SS-PCM because it is believed to be more accurate than LR-PCM owing to considering the dynamical effects [9, 10]. However, many previous studies using this combination method to calculate the CT emission energies of adenine-thymine (A-T) DNA systems find that the calculated values are significantly lower than experiment [9, 11]. Therefore, in order to provide a guideline for the future ab initio calculations on aqueous systems, it is necessary to evaluate the reliability of using SS-PCM when dealing with CT states.

In our recently published paper, we discuss the CT emission energy of T-A dinucleotide [12]. Nine water explicit molecules are included in the calculation model to consider the intermolecular hydrogen bonding interactions. The SS-PCM is found to severely underestimate the CT emission energy while LR-PCM gives reasonable results. As a result, the LR-PCM result can be used as a standard.
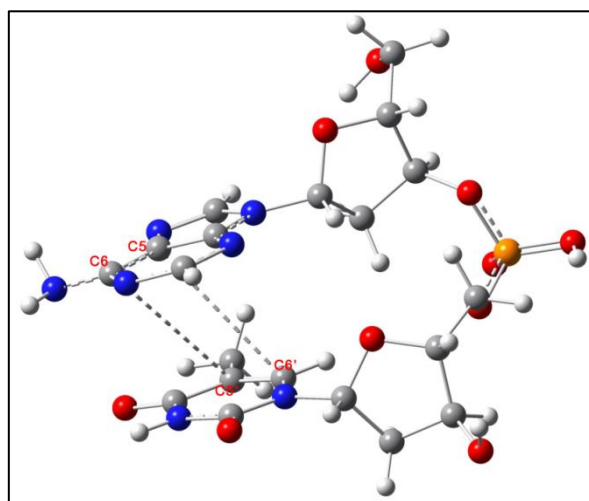


**Fig. 1**: Chemical structure of A-T dinucleotide.