Absorption spectra of firefly oxyluciferin from first principle molecular dynamics simulations

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Abstract

The spectroscopic characteristics of oxyluciferin and its conjugate bases, the emitters of firefly bioluminescence, are the key to understanding the firefly bioluminescence. To elucidate the vibronic effect on the absorption and fluorescence spectra of the emitters, we have previously calculated the absorption and fluorescence spectra of the emitters within the Franck-Condon approximation taking the polarized continuum model (PCM) for the aqueous solution. The calculated spectral shapes well reproduced the experimental ones measured by Rebarz et al. (2013) and Ghose et al. (2015) except for the keto type of the oxyluciferin anion, where the theoretical peak was found significantly sharper than the experimental one (Hiyama et al. 2015). To see the reason, we carried out the first-principles molecular dynamics (FPMD) simulations of the keto-, enol-, and enolate-type of the oxyluciferin anion taking water molecules explicitly into account. The simulations showed that the hydrogen bonding network of solvents, overlooked by PCM, plays an important role (Noguchi et al. 2016). The anions were then picked up from the MD trajectory and were surrounded by a QM/MM solvation model to calculate the absorption spectra (Hiyama et al. 2017). The result reproduced well the experimental broad spectra, suggesting that the spectroscopic property can be reasonably well captured by our explicit solvation model.

Keywords: firefly oxyluciferin, the first, principles molecular dynamics simulations, absorption spectra, the hydrogen bonding network, the explicit solvation model

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