

Comparison of TD-DFT and semi-empirical methods for description of spectral properties of anthraquinone dyes using X-ray crystal structure

(¹*Graduate School of Environment and Information Sciences, Yokohama National University*)
○Ji-Yong Hwang,¹ Sunghoon Kim,¹ Shinya Matsumoto¹

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Various molecular orbital calculation methods are used in the study of the electronic states of organic dyes. Although the time-dependent density functional theory (TD-DFT) is also often used for the calculation of absorption spectrum, the cases which consider not only the quantitative properties of the absorption wavelength, but also the molecular orbitals related to the transition state and etc., are extremely limited.¹ In this research, we made an attempt to evaluate the applicability of several MO calculation methods to characterize absorption properties of anthraquinone dyes (AQ) by using the X-ray structure analysis.

Among many organic dyes, AQ chromophore was selected in this research considering the industrial importance of organic dyes. From the Cambridge Structural Database (CSD), 12 AQ dyes having donor substituent such as OH and NH₂ were selected. The calculations of absorption properties of the AQ dyes were performed with semi-empirical methods (PM5/RPA and ZINDO/CI) and TD-DFT/B3LYP/6-31G (d, p) method.

Among three methods, there are slight differences in the calculated λ_{max} for AQ dyes depending on the position or torsion angle of the substituent. From the calculation results, it is confirmed that PM5/RPA method is the most suitable to reproduce the experimental λ_{max} .

Furthermore, through the calculation of gross populations of p_z orbital of all atoms in the AQ molecule, the TD-DFT method was found to be overvalued compared to the two semi-empirical methods. These results are also known to be attributed to the states of Rydberg character in TD-DFT method.² The change in the value of the gross populations of N_{pz} due to the rotation angle between the AQ moiety and amino substituents was confirmed in PM5/RPA method. In addition, it was shown that the values of N_{pz} and oscillator strength (f) in HOMO and LUMO states decreased as rotation angles increased.

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