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<Short running title>

**Color and constitution of anthraquinone dyes by theoretical
study using X-ray structure**

Ji-yong Hwang, Sunghoon Kim, Shinya Matsumoto***

Graduate School of Environment and Information Sciences,
Yokohama National University,
79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

*Corresponding author: matsumoto-shinya-py@ynu.ac.jp (S. Matsumoto)
<https://orcid.org/0000-0002-5796-1940>

**Corresponding author: kim-sunghoon-vn@ynu.ac.jp (S. Kim)
<https://orcid.org/0000-0001-7133-6183>

Comparison of semi-empirical and density functional approaches for the color and constitution of anthraquinone dyes using X-ray structure

Ji-yong Hwang, Sunghoon Kim**, Shinya Matsumoto*

Graduate School of Environment and Information Sciences,
Yokohama National University,
79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

*Corresponding author: matsumoto-shinya-py@ynu.ac.jp (S. Matsumoto)

<https://orcid.org/0000-0002-5796-1940>

**Corresponding author: kim-sunghoon-vn@ynu.ac.jp (S. Kim)

<https://orcid.org/0000-0001-7133-6183>

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Abstract

Theoretical calculations at the density functional theory (DFT) and semi-empirical PM5/RPA and ZINDO/CI have been carried out for some amino and hydroxy anthraquinones using X-ray structure data. Comparing quantum chemical calculation results based on X-ray structure, PM5/RPA method was the most promising for the prediction of λ_{max} of anthraquinone dyes among the

computational methods studied here.

From the results of calculated gross population p_z , it was found that the value of p_z in the TD-DFT method was greater than the value calculated by semi-empirical methods. Overestimation of p_z could be attributed to the incorrect DFT calculation results. The results of PM5/RPA-calculated oscillator strength and torsion angle showed reasonable agreement with the observed results for sterically hindered anthraquinone dyes.

1 INTRODUCTION

Theoretical prediction of absorption properties of organic dyes has been widely made not only for the pure scientific interest but also for the design of various organic functional dyes. The effective design of organic dyes is one area where experimental synthesis and theoretical prediction can effectively interact.¹⁻

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Molecular orbital (MO) calculation is therefore an essential tool for research and development of functional dyes. The main purpose of MO calculation in functional dye research is to examine optimized molecular structure and to predict and/or interpret the excited states with respect to absorption properties based on the optimized molecular structure.^{4,5} Various MO calculation methods have been proposed based on quantum chemistry. Usually, the main calculation of dyes and pigments has been carried out using the Pariser-Parr-Pople (PPP) MO method,^{6,7} which has been proved to be very useful. However, the PPP method was originally designed for planar π -electron system, neglecting all σ -electrons, and it is difficult to apply to non-planar systems, molecules containing hydrogen bonds, or to $n\text{-}\pi^*$ transitions. In order to calculate such molecules, semi-empirical methods, ab-initio method, and the method based on the density functional theory (DFT) have been developed and various applications of it have been presented.^{8,9}

Semiempirical methods can only be applied to molecules containing elements that have been parameterized, while DFT methods are generally applicable (apart from technical considerations such as basis set availability).

Recently calculation methods based on time-dependent density functional theory (TD-DFT) have been widely used for the same purpose and one of the most widely used methods in computational dye chemistry.^{10,11} On the other hand, the semi-empirical PM5/RPA and ZINDO/CI has already been applied for predicting molecular structures, reaction mechanism and electronic properties.¹²⁻

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Anthraquinone(AQ) dyes comprise the next most important dye class after azo dyes. Anthraquinones are typically present in the most common red natural colorants used extensively in textile dyeing, from many thousand years ago until the late 19th century.^{17,18} The introduction of synthetic fibers, such as polyester, polyamide, and polyacrylonitrile fibers, initiated a new phase in the development of anthraquinone dyes. This led to the number of substitution products of anthraquinone that were useful as disperse dyes or as basic dyes. Anthraquinone dyes showing brilliant colors with higher fastness properties are of great demand because of their suitability for various end-uses. Various numbers of anthraquinone chromophore have been investigated to achieve satisfactory characteristics in terms of functional applications and specialized uses.^{19,20} Common anthraquinone dyes, such as those used in the textile industry, are not suitable for displays. A quite surprising and more recent development is the discovery that suitably modified anthraquinones can be used as a dichroic dye in liquid crystal displays even though they can hardly be described as thin rodlike molecules.^{21,22}

Anthraquinone itself does not exhibit a strong color, but the addition of electron-donating groups to the chromophore results in relatively strong visible absorption bands, attributable to $\pi \rightarrow \pi^*$ intramolecular charge-transfer transitions

between the substituent(s) and the carbonyl groups.²³ Amino- and hydroxy-substituted anthraquinones are a very important and interesting group of compounds that has been extensively studied during the last decade. Anthraquinone rings with amino and hydroxy groups are the main fragment in a large group of anthraquinone dyes and they have been used in anticancer drug design.²⁴⁻²⁶

The first attempts to explain the color and constitution of anthraquinone dyes were made by Peters in 1953²⁷ and by Labhart in 1957.²⁸ However, general studies of color-structure relationships in anthraquinone dyes have been relatively few in number, by comparison with similar studies on azo dyes. A systematic study of the relationship between the color and constitution of the anthraquinone dyes has been undertaken to investigate the synthetic design of dyes by PPP^{29,30} and TD-DFT method.³¹⁻³⁴

Geometry optimization is an important part of most quantum chemical calculations locating the minimum energy, i.e. the most stable form of a gas phase structure. However, most chemical processes are carried out not in the gas phase, but in solution and crystalline states. Even subtle changes in geometry can lead to significant changes in λ_{max} and other properties. X-ray crystal structure analysis has been a method for determining atomic positions in crystals. Therefore, the accurate experimental geometries such as X-ray crystallographic structures would seem to be better choice than automatically computed geometry optimized structure.

To the best of our knowledge, a systematic and comparative semi-empirical and density functional theory study of anthraquinone dyes using X-ray structure has not been reported. A series of 12 anthraquinone dyes had been selected from Cambridge Structural Database (CSD). They all have two types of structures, namely, mono- and disubstituted aminoanthraquinones (1-6) and hydroxyanthraquinones (7-12) (Figure 1).

<Figure 1>

In this present paper, we report the results of systematic calculations of the electronic and absorption properties for anthraquinone dyes by TD-DFT and semi-empirical PM5/RPA and ZINDO/CI method using X-ray structure.

2 COMPUTATIONAL METHOD

The deposited crystal structure data of mono- and di-substituted anthraquinone dyes were checked in the Cambridge Structural Database (CSD: version 5.41) using ConQuest³⁵ and 12 AQ dyes having donor substituent(s) were collected for the target in consideration of the quality of the X-ray analysis and geometrical parameters such as bond lengths, planarity and torsion angles.

Several anthraquinone dyes bearing different amino and hydroxy donor moieties were selected and their electronic properties were investigated experimentally and theoretically (PM5/RPA,^{13,14,36} ZINDO/CI^{37,38} and TD-DFT).³⁹ The positions of non-hydrogen atoms were based on the atomic coordinates from the obtained structural data and the positions of hydrogen atoms were normalized using Mercury 4.2.0⁴⁰ in all calculations. The calculations of absorption properties have been performed with semi-empirical methods (PM5/RPA and ZINDO/CI) and TD-DFT/B3LYP/6-31G(d,p) methods by using SCIGRESS V2.0 program package⁴¹ and Gaussian16 programs,⁴² respectively. In TD-DFT calculation, the excited states of the anthraquinone dyes have been calculated by using the Becke's three-parameter hybrid exchange functional, and Lee-Yang-Parr non-local correlation functional (B3LYP)⁴³ combined with 6-31G(d,p) basis set.⁴⁴ The conventional DFT functionals have several deficiencies, e.g., poor description of the weak interaction of van der Waals bonding, Rydberg excitation energies, oscillator strengths, and charge-transfer excitation

energies.^{45,46} Recently, there has been considerable interest toward the development and assessment of new functionals based on the long-range correction (LC) scheme.⁴⁶⁻⁴⁸ Long-range correction makes it applicable to general functionals, making it useful in quantum chemistry calculations.⁴⁹ Besides the original functionals, various long-range corrected functionals have been developed due to the high applicability of long-range correction.^{49,50} The CAM-B3LYP functional is a long-range corrected hybrid functional.^{47,51} The PBE0 functional is also known for producing optimized ground-state chemical geometries for most organic molecules.⁵²⁻⁵⁴ The Polarizable Continuum Model (PCM)⁵⁵ is a commonly used model to consider the solvent effects for excited states of organic compounds. On the basis of previous considerations, PCM/TD-B3LYP/6-31g(d,p), PCM/TD-CAM-B3LYP/6-31g(d,p), PCM/TD-PBE0/6-31g(d,p) methods were carried out to compare the reliability of absorption properties of anthraquinone dyes.

3 RESULTS AND DISCUSSION

3.1 TD-DFT, PM5/RPA and ZINDO/CI calculations of the absorption properties

Geometrical comparison was carried out for the bond lengths of some aminoanthraquinones such as 2-NMe₂AQ, 1-NMe₂AQ, 1,5-diNH₂AQ, 1,4-diNH₂AQ and 1,4-diNHEtAQ in unoptimized X-ray structure and optimized structure with AM1 and DFT (Figure S1). As a result, we found that there is a slight difference in bond distance of C=O and C-N bond depending on the geometry of anthraquinones. We have also compared the torsion angle between substituted amino group and anthraquinone moiety of 1,4-diNH₂AQ and 1-NMe₂AQ (Figure S2).

The torsion angle of C12-C1-N1-H3 in 1,4-diNH₂AQ: 3.9° (X-ray structure), 5.3° (DFT-optimized) and 22.0° (AM1-optimized), C11-C1-N1-C15 in 1-

NMe₂AQ: 32.8° (X-ray structure), 36.5° (DFT-optimized) and 64.4° (AM1-optimized). The results demonstrate that the conformational difference derived from steric hindrance can effectively affect the torsion angle between amino group and anthraquinone moiety. The torsion angles in these molecules are quite different between X-ray and calculated results. The conformational differences between the molecular geometry with X-ray conformation and those of fully optimized molecule can affect the energy of the electronic states and absorption properties.

The observed $\lambda_{\text{max}}(\text{EtOH})$ ⁵⁶ and values calculated by the PM5/RPA method of anthraquinone dyes are shown in Figure S3. The central line indicates a perfect theoretical/experimental match. The straight lines were evaluated by the least squares method. The correlation obtained with PM5/RPA-AM1 optimized method is not very good compared to other methods. In view of correlation between observed and calculated absorption maxima, the best method was found to be PM5/RPA with X-ray structure.

X-ray crystal structure analysis has been a method for determining atomic positions in crystals. It will be developed to that for determining electronic states in crystals. Therefore, the evaluation of absorption properties based on X-ray structure is highly accurate compared with the calculation methods including structural optimization process. For a reliable calculation, geometry of anthraquinone dyes were optimized at DFT and AM1 methods. Calculation result of PM5/RPA-X-ray and PM5/RPA-DFT optimized is show similar tendency, but the result of PM5/RPA-X-ray is closer to a perfect theory/experiment matching line than PM5/RPA-DFT optimized method.⁵⁷ The result suggested that the calculation with the X-ray structure is a fairly reliable method to interpret the UV/Vis spectra of anthraquinones.

To determine the adequate calculation method for predicting UV/Vis absorption

spectra of anthraquinone derivatives, λ_{\max} were calculated for amino- and hydroxyl anthraquinones using different methods such as PM5/RPA, ZINDO/CI and TD-DFT using X-ray structure (Figure 2). The observed and calculated λ_{\max} for anthraquinone dyes are given in Table S1. Numerous methods have been developed for absorption spectra and molecular design, but focus on practical methods that are well known and can be easily calculated. It has already been mentioned in the reference paper(9, 56a, 56c, 57) that B3LYP functional is a good calculation method for anthraquinone derivatives. The results of TD-DFT/6-31G(d,p) basis set and TD-DFT/6-311G++(d,p) are shown in Figure S4. The results of TD-DFT/6-311G++(d,p) were not superior to those of TD-DFT/6-31G(d,p).

Figure 2 shows the correlations between the calculated and observed λ_{\max} at TD-DFT, PM5/RPA and ZINDO/CI. The ZINDO/CI method does not seem to be suitable for the calculation of absorption spectra of anthraquinones. In general, ZINDO/CI's λ_{\max} are under-estimated by ~ 40 -80 nm with respect to TD-DFT λ_{\max} .^{56(b),58} To check the consistency between calculated and experimental data, simple linear regression (SLR) was applied for each of the three data set obtained with the above calculation methods.^{33,56(b)} The resulting equations read:

$$\lambda_{\max,\text{nm}} = -22.296 + 1.0390\lambda_{\max,\text{nm}}(\text{PM5/RPA})$$

$$\lambda_{\max,\text{nm}} = -219.6034 + 1.5565\lambda_{\max,\text{nm}}(\text{TD-DFT/B3LYP/6-31G(d,p)})$$

$$\lambda_{\max,\text{nm}} = -132.2304 + 1.5953\lambda_{\max,\text{nm}}(\text{ZINDO/CI})$$

with R^2 of 93.29% (PM5/RPA), 96.00% (TD-DFT) and 94.84% (ZINDO/CI), respectively. Although the correlations obtained with TD-DFT ($R^2 = 96.00\%$) and ZINDO/CI ($R^2 = 94.84\%$) are higher than that of PM5/RPA results, calculated λ_{\max} of anthraquinone dyes are far from the perfect theory/experiment matching line, making it less reproducible. It turned out that PM5/RPA is computationally efficient method and it produces results that are comparable in accuracy with the

results from much more computationally intensive TD-DFT method. In order to make a fair comparison to the PM5 method, we have chosen to use the PCM/TD-B3LYP/6-31g(d,p), PCM/TD-CAM-B3LYP/6-31g(d,p), PCM/TD-PBE0/6-31g(d,p) methods for the calculation of UV/Vis absorption spectra of anthraquinone derivatives. All the calculations have been performed in the same solvent (EtOH) as used for the experiment. In view of correlation between observed and calculated absorption maxima, the best method was found to be PM5/RPA with X-ray structure (Figure 3). To predict the λ_{max} of anthraquinone dyes with strong electron donating and withdrawing substituents, we investigated the observed and calculated λ_{max} of 1-OCH₃AQ and 1-NO₂AQ: 328 nm(ZINDO/CI), 408 nm(PM5/RPA), 376 nm(TD-DFT/6-31G(d,p)) and 385 nm(TD-DFT/6-311G++(d,p)) for 1-OCH₃AQ(378 in MeOH)⁵⁹: 302 nm(ZINDO/CI), 368 nm(PM5/RPA), 337 nm(TD-DFT/6-31G(d,p)) and 338 nm(TD-DFT/6-311G++(d,p)) for 1-NO₂AQ(325 in MeOH).⁵⁹

<Figure 2>

<Figure 3>

The introduction of electron-accepting substituents do not appreciably alter the anthraquinone absorption properties. However, electron donor substituents can affect the electronic state of anthraquinone cause spectral changes. When powerful electron-donor groups are present in the anthraquinone ring (hydroxyl or amino groups for example), a relatively intense π - π^* absorption band appears in the visible region and is assigned to a charge-transfer (CT) transition, and it is this band which is responsible for the color of anthraquinone dyes.^{23,60} This CT transition is associated with the transfer of an electron from the electron-donating substituent to the anthraquinone moiety including carbonyl groups.^{60,61} The

relative position of this CT band is the result of the conjugation of the $2p_z$ orbital of the O or N atom with the anthraquinone π -electronic system.⁶²

For quantitative analysis of the CT character and electron-releasing tendency of donating substituent, the electron density of p_z orbital of hetero atom such as N and O was calculated using TD-DFT, PM5/RPA and ZINDO/CI using X-ray structure.

The majority of colored organic compounds are based on a donor-acceptor chromogen, the characteristic feature of which is that the donor group is linked to the acceptor group by an unsaturated bridge. The longest wavelength of absorption band is normally dependent on the excitation from the HOMO to LUMO, which gives rise to the π - π^* transition. The primary peaks of anthraquinone dyes are mostly attributed to the electronic excitation from HOMO to LUMO.^{32,63}

Figure 4 shows the gross populations of p_z orbitals of HOMO and LUMO of 1,4-diNH₂AQ. According to the gross population changes, p_z , accompanying the first transition from HOMO to LUMO, decrease of p_z at the N atoms and increase of those at carbonyl O atoms were observed. As the gross population changes of p_z of 1,4-diNH₂AQ was found to be caused by the intermolecular CT of the transition, the introduction of electron-donating group to anthraquinone ring may produce a bathochromic shift of λ_{\max} . From the results of calculated p_z , it was found that the value of the gross populations of p_z in the TD-DFT method was greater than the value calculated by semiempirical PM5/RPA and ZINDO/CI methods. The cause of the overestimating p_z value ($|2p_z|+|3p_z|$) is the addition of Rydberg $3p_z$ orbital in TD-DFT method. A similar results were observed for 1,4-diOHAQ (Figure S5). This method is based on the electron density difference between the ground state and excited state.

Generally, DFT methods predict highly accurate molecular geometries, absorption properties and reaction energies. Nevertheless, there are many

situations in which the currently used approximate density functional fail.^{64,65} The practical use of DFT typically involves employing some of over-delocalization approximations. Over-delocalization and overestimation lead to delocalization error such as incorrect electron densities, molecular properties, band gaps and absorption properties.^{66,67} Rydberg orbitals are formed by the atomic wavefunctions with the principal quantum numbers higher than those of the valence-shell levels.⁶⁸⁻⁷⁰

Due to the spatial expansion of Rydberg $3p_z$ orbitals in HOMO and LUMO of 1,4-diNH₂AQ and 1,4-diOHAQ, the result of $2p_z+3p_z$ of TD-DFT leads to overestimation of gross population of p_z compared to the other two methods (Figure 4 and Figure S5). A large deviation between experimental and calculated λ_{\max} by TD-DFT could be explained by overestimation of gross population p_z . The HOMO and LUMO of 1,4-diNH₂AQ and 1,4-diOHAQ are shown in Figure 4 and Figure S5. In the ZINDO/CI and PM5/RPA method, HOMO and LUMO is mainly localized at the electron-donating amino and hydroxy group and electron-accepting carbonyl moieties. However, the TD-DFT results showed that the HOMO and LUMO is widely delocalized at whole molecule (i.e. overestimation of delocalization). The same phenomenon is also observed for all other anthraquinone dyes. Such investigation provided new insight into the dye structures and quantum chemical methods which are of key importance for accurate prediction of λ_{\max} .

A similar results are observed for the gross populations of p_z orbitals of HOMO and LUMO of 1,4-diNH₂AQ and 1,4-diOHAQ in PCM/TD-B3LYP/6-31g(d,p), PCM/TD-CAM-B3LYP/6-31g(d,p), PCM/TD-PBE0/6-31g(d,p) methods (Figure S6 and Figure S7). From the calculated results of HOMO-LUMO gap of the anthraquinone dyes, the energy gap for the TD-DFT method are much lower than other semi-empirical methods(Figure 4, S5 and Figure S6 and S7).

<Figure 4>

3.2. Applications and performance of PM5/RPA in steric hindrance and λ_{\max}

The introduction of electron-accepting substituents do not appreciably alter the anthraquinone absorption spectrum. However, electron donor substituents can affect the electronic state of anthraquinone cause spectral changes. Maximum bathochromic shift is found in the 1,4-disubstituted anthraquinone: indeed, the majority of commercial anthraquinone dyes are based on 1,4-di-donor-substituted anthraquinone. According to the traditional resonance and valence bond explanation, the charge separation structure for 1,4-disubstituted anthraquinones are predicted to be largely stable because they contain a fully aromatic naphthalene nucleus (Figure S8).^{60,71,72} Resonance, valence bond theory and several quantum chemical calculations predict the following order of bathochromicity for the donor substituted anthraquinone dyes: 1 < 1,5 < 1,2 < 1,4.

The absorption properties of anthraquinone dyes were characterized by PM5/RPA with X-ray structure which indicates the superiority for the calculation of anthraquinone series. The origin of the absorption spectral feature of anthraquinone dyes can be rationalized by means of molecular orbital (MO) analysis. The absorption bands observed for the anthraquinones can be assigned to the HOMO-LUMO transition. The maximum absorption peaks are mostly attributed to the transitions from the HOMO to LUMO: contribution of the HOMO-LUMO transition in 78% (1-NH₂AQ), 81% (1,5-diNH₂AQ), 91% (1,4-diNH₂AQ) and 70% (1-OHAQ), 76% (1,5-diOHAQ), 71% (1,2-diOHAQ), 77% (1,4-diOHAQ), respectively.

The results of the amino- and hydroxyanthraquinone dyes are shown in Figure S9. As consequence of the variation of MO energies using PM5/RPA, the HOMO-LUMO gap of amino AQ decreases when going from 1-NH₂AQ (6.91

eV) to 1,5-diNH₂AQ (6.56 eV), 1,4-diNH₂AQ (6.16 eV), the latter anthraquinones being expected to absorb lower energy.

Furthermore, comparing the computed HOMO-LUMO energy gap of hydroxyanthraquinones, it can easily be seen that energy gap decreases in the following order; 1-OHAQ (7.42 eV), 1,5-diOHAQ (7.34 eV), 1,2-diOHAQ (7.24 eV), 1,4-diOHAQ (7.06 eV), these are in excellent agreement with order of bathochromicity explained by resonance and valence bond theory. The HOMO-LUMO gap is decreased mainly due to stabilization of LUMO level, while the destabilization of the HOMO is modest.

Steric crowding in colored system has a pronounced effect on the absorption properties. Bond rotation gives a non-planar structure, and also causes a reduction in the overlap between adjacent p orbitals. The effects of steric hindrance on the absorption intensity have been reported only by qualitative explanations and have not yet been reported in detail. The PM5/RPA-calculated torsion angle, oscillator strength and λ_{max} of 1-NH₂AQ, 1-NMe₂AQ and 1-NPhMeAQ are shown in Figure 5. Steric hindrance in anthraquinone dyes always lowers the tinctorial strength (oscillator strength), f , and may cause a hypsochromic or bathochromic shift of λ_{max} . The 1-NMe₂AQ and 1-NPhMeAQ groups are significantly twisted out of the anthraquinone molecular plane. 1-NH₂AQ, 1-NMe₂AQ and 1-NPhMeAQ dyes exhibit maximum absorption (λ_{max}) at 465, 504 and 527 nm in EtOH, and their corresponding extinction coefficients (ϵ) are 6300, 5370 and 3300 mol⁻¹cm⁻¹ in EtOH, respectively. We have also compared the torsion angle of C13-C1-N1-H1 of 1-NH₂AQ, C13-C1-N1-C15 of 1-NMe₂AQ and C13-C1-N1-C15 of 1-NPhMeAQ. The torsion angles are 0.8° for 1-NH₂AQ, 32.8° for 1-NMe₂AQ and 58.1° for 1-NPhMeAQ based on the X-ray structure. The DFT- and AM1-optimized structure also showed the same tendency of the torsion angle difference.

Intramolecular hydrogen-bonding holds the NH₂ group coplanar with the anthraquinone nucleus. Replacing the hydrogen atom by the more bulky group

destroys both the intramolecular hydrogen-bonding and the coplanarity because of steric hindrance between the NMe₂, NPhMe group and the adjacent C=O group.

From the conformational point of view, the large torsion angle between sterically hindered 1-NPhMe and anthraquinone moieties could greatly relieve the steric crowding, thus diminishing the orbital overlap between the 2p_z orbital of N atom and the anthraquinone π -system. Consequently, the oscillator strength (*f*) of 1-NPhMeAQ was significantly decreased by the increase of the torsion angle.

<Figure 5>

It is useful to relate the gross population p_z to the oscillator strength and molar extinction coefficient corresponding to the first transition. As a PM5/RPA-calculation result of the gross population of Np_z of 1-NH₂AQ, 1-NMe₂AQ and 1-NPhMeAQ is shown in Figure 6, the value of Np_z in the HOMO and LUMO states decreases as the bond torsion angle increases.

<Figure 6>

4 CONCLUSION

The purpose of this work was to compare the reliability of calculated absorption maxima, λ_{max} , using X-ray structure and geometry optimized structure of some amino and hydroxy anthraquinones. The results demonstrated that the conformational differences between the molecular geometry with X-ray conformation and those of fully optimized molecule can affect the energy of the electronic states and absorption properties. Then, λ_{max} for anthraquinone dyes were calculated using PM5/RPA, ZINDO/CI and TD-DFT. The DFT deviation from approximate functionals causes excess charge delocalization, which leads to incorrect densities, molecular properties, absorption properties, and excitation energies. From the results of calculated gross population p_z , it was found that Rydberg 3p_z orbital of TD-DFT lead to overestimation of p_z compared to the

semi-empirical methods. We found that semi-empirical PM5/RPA with X-ray structure is the most promising for the prediction/explanation of λ_{max} of the anthraquinone dyes among the computation methods studied here and will be available for practical applications to a wide variety of dyes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRedit authorship contribution statement

Ji-yong Hwang: Calculation, Methodology, Writing - Original Draft, Formal Analysis

Sunghoon Kim: Writing – Original Draft Preparation, Conceptualization and Supervision

Shinya Matsumoto: Conceptualization and Supervision, Writing - Review & Editing

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.