

<Communication>

## Characteristics of HOMO and LUMO Potentials by Altering Substituents: Computational and Electrochemical Determination

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**Abstract**— Recently, computational calculation of molecular energy potentials and electrochemical reduction/oxidation behaviors are of very importance in view point of prediction of dye's properties such as energy levels and bandgaps of absorption. This can be influenced by their different constituents or substituents in chromogen molecules. Structural conformations and properties with computational modeling calculation are numerically simulated, which are fully or partly based on fundamental laws of physics. In addition, cyclic voltammetric measurement was used to obtain the experimental redox potential values, which were compared to the computed simulation values.

**Keywords:** cyclic voltammetry, HOMO, LUMO, computational calculation, anthraquinone dye, molecular modeling

### 1. Introduction

Anthraquinone and azo dyes have been the most widely used class of organic dyes. Two dye types, as the largest group of colorants and historically the most important categories, have been widely applied in chemistry, biochemistry and textile industry, especially as useful coloration dye stuff<sup>1-4</sup>). In addition, nowadays, these synthetic derivatives of anthraquinone and azo dyes<sup>4-6</sup>) have been enjoyed for other purposes as anticancer drug for anthraquinone and microfluidic dye synthesis for azo types. However, the widely used main target is the textile dyeing industries.

In this work, the effects of the chemical structures of six dyes were chosen with relation to the altering characteristics of dye substituents. Anthraquinone and azo dyes having different substituents were examined to determine their potential energy levels in ground and excited states, namely HOMO and LUMO.

All theoretically computational calculations for the energy potential and the electron distribution of HOMO/LUMO states were performed by means *Material Studio 4.3 package* program<sup>7-13</sup>).

HOMO/LUMO energy levels were concerned with the states of molecular orbital and the identifications of electron transition<sup>13,14</sup>). Thus, this theory is quite useful for the application of electron chemistry, because HOMO/LUMO potentials involve the functions of proton transfer or unshared pair/empty orbital interaction.

Futhermore, we have also considered cyclic voltammetric (CV) experiments to determine the energy potentials for the electrochemical reduction/oxidation potential of anthraquinone and azo dyes. These determined energy levels by electrochemical reduction were compared to the values of computational calculated ones. The effect of the structural properties of the dye molecules was studied by qualitative structure- zelectrochemistry relationship analysis.

All dyes were obtained from commercial sources. The dyes used were listed in Table 1. The computational calculation was used with *Material studio 4.3*.

The geometrical optimization and energy potential of HOMO/LUMO states were stabilized and calculated.

Electrochemical measurement was used by cyclic voltammetry (CV) electrode system utilizing a *Versa*

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STAT3 model. Cyclic voltammetry experiment was run in an acetonitrile solution containing tetrabutylammonium hexafluorophosphate electrolyte. The reference electrode, Ag/Ag<sup>+</sup> was directly immersed in the reaction cell. The working electrode was a glassy carbon. The counter electrode was a platinum wire. The scan rate was commonly 100mV/s. HPLC grade acetonitrile was used as purchased and used in the electrochemical redox potential measurements of all six dyes.

For the used dyes, namely three anthraquinone and azo dyes, respectively, the difference of HOMO/LUMO energy level was calculated using computational technique and measured using electrochemical cyclic voltammetric method. The obtained energy potentials of HOMO/LUMO states were compared. The geometrical conformation of molecular structures and electron density distributions were also computationally calculated.

These characteristics were useful to understand the electron distribution through the molecules in HOMO and LUMO energy potentials.

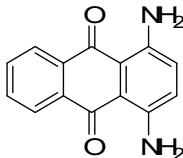
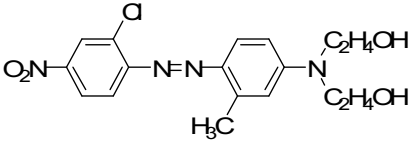
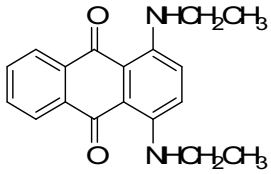
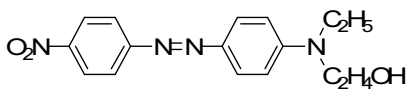
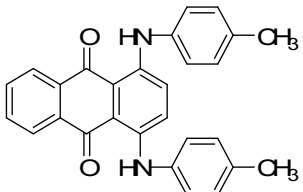
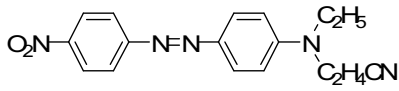
Fig. 1 and Fig. 2 show the computational calculations to expect the HOMO/LUMO energy potentials of anthraquinone and azo dyes. To obtain more detailed insight and information towards the intramolecular charge transfer process of six dyes, the computational

theoretical calculation was carried out using DMol3 program in the *Material Studio 4.3 package*<sup>15,16</sup>. Fig. 1 and Fig. 2 represent the electron distribution of HOMO/LUMO energy potential of anthraquinone and azo dyes, respectively. The potentials of HOMO/LUMO energy level of six dyes were computed and listed (Table 2 and Table 3). These results by theoretical calculation are in agreement with the obtained data using electrochemical redox measurement technique. Similar changing patterns of HOMO/LUMO energy levels were observed.

Comparison of the electron distribution in the frontier MOs displays the HOMO-LUMO excitation. Electron distribution for the anthraquinone dyes moved the central quinone ring and electron donating group substituted benzene ring at 1,4 position in HOMO state to the whole anthraquinone molecules in LUMO state. Three dyes showed the similar patterns for electron distribution. In the case of three azo dyes, similarly, The rich electron distribution was detected at the part of molecules, where electron donating amine groups are attached. However, these electrons were moved to the electron withdrawing nitro groups in LUMO state for three azo dyes.

In addition, the electrochemical reduction/oxidation behaviors of anthraquinone and azo dyes were determined by cyclic voltammetry (CV)<sup>17</sup> in dry CH<sub>3</sub>CN.

Table 1. dyes used

Anthraquinone dyes		Azo dyes	
C.I. Name (Dye No.)	Structure	C.I. Name (Dye No.)	Structure
Disperse Violet 1 (V01)		Disperse Red 5 (R05)	
Solvent Blue 59 (B59)		Disperse Red 1 (R01)	
Solvent Green 3 (G03)		Disperse Orange 25 (O25)	

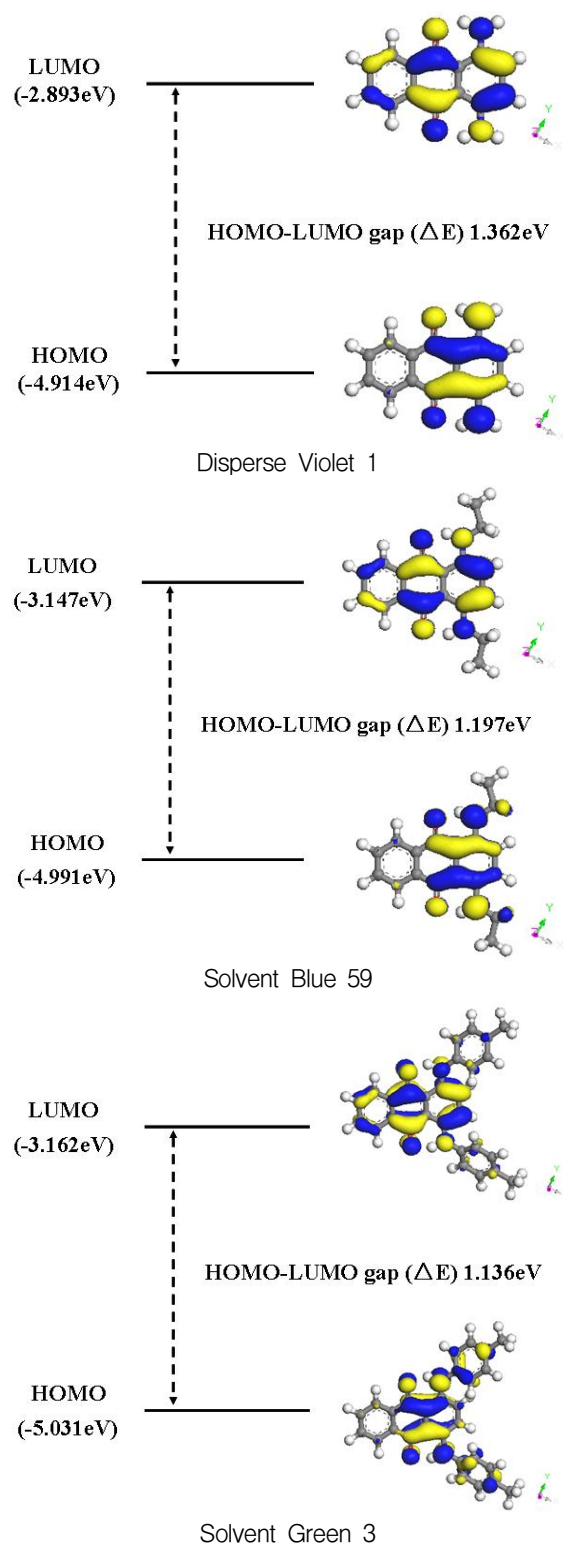


Fig. 1. Electron distribution of HOMO/LUMO energy potential of anthraquinone dyes.

Fig. 3 shows the cyclic voltammogram of six dyes. Commonly, the HOMO energy level of these dye molecules can be estimated from its onset oxidation

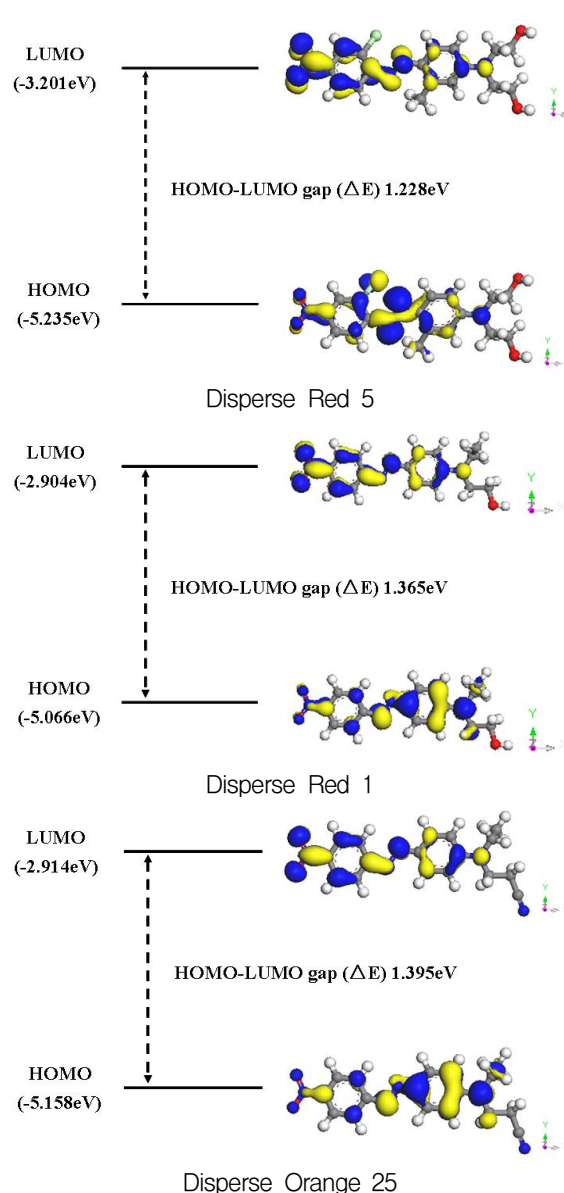


Fig. 2. Electron distribution of HOMO/LUMO energy potential of anthraquinone dyes.

potentials versus a saturated calomel electrode by adding 4.74 and LUMO energy level can be calculated by subtracting its optical bandgap from the HOMO energy level<sup>18,19</sup>, while the optical bandgap is deduced from the absorption edge.

In addition, the potentials of the highest oxidation peak and the lowest reduction peak can be used to calculate the HOMO/LUMO energy levels.

The following equation can be used at this method.

$$HOMO(\text{or } LUMO) (eV) = -4.8 - (E_{peak} - E_{1/2}(\text{Ferrocene}))$$

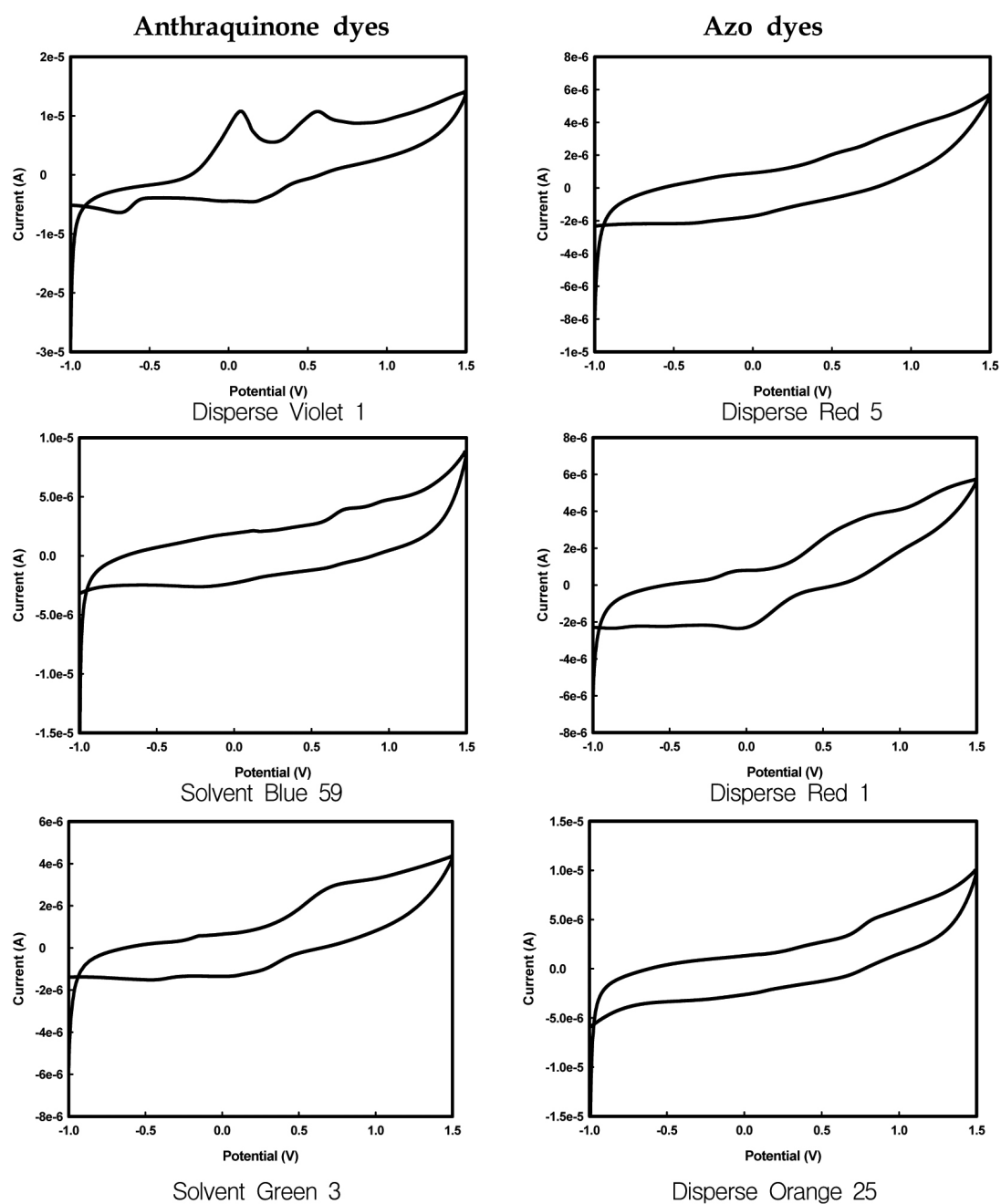


Fig. 3. Cyclic voltammograms of six dyes used.

Table 2. HOMO/LUMO and bandgap energy potential for anthraquinone dyes

Anthraquinone dyes	Computational calculation			Cyclic Voltammetry		
	HOMO	LUMO	$\Delta E$	HOMO	LUMO	$\Delta E$
Disperse Violet 1	-4.866eV	-3.504eV	1.362eV	-4.914eV	-2.893eV	2.021eV
Solvent Blue 59	-4.742eV	-3.545eV	1.197eV	-4.991eV	-3.147eV	1.884eV
Solvent Green 3	-4.776eV	-3.640eV	1.136eV	-5.031eV	-3.162eV	1.869eV

**Table 3.** HOMO/LUMO and bandgap energy potential for azo dyes

Azo dyes	Computational calculation			Cyclic Voltammetry		
	HOMO	LUMO	$\Delta E$	HOMO	LUMO	$\Delta E$
Disperse Red 5	-5.063eV	-3.835eV	1.228eV	-5.235eV	-3.201eV	2.034eV
Disperse Red 1	-5.220eV	-3.855eV	1.365eV	-5.066eV	-2.904eV	2.162eV
Disperse Orange 25	-5.272eV	-3.877eV	1.395eV	-5.158eV	-2.914eV	2.244eV

Table 2 and Table 3 show the HOMO/LUMO energy levels for the six dyes, where the potential energy values for the computationally calculated levels and the electrochemically determined levels are shown. For each dyes, the potential energy levels showed the similar characteristic patterns from the values of computational calculation and electrochemical measurement.

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