



## HOMO-LUMO ENERGY GAP ANALYSIS OF ALKYL VIOLIGEN WITH A POSITIVELY CHARGED AROMATIC RING\*\*

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In order to confirm the effects of positive charges of alkyl viologens ( $C_nVC_n$ ,  $n = 3, 5, 7$  and  $9$ ) with aromatic rings, the changes in the HOMO-LUMO energy gap have been studied using the cyclic-voltammetry, the UV-visible spectra, and the calculations of the AM1 method. The electron transport across molecules has been explained by assuming that the incoming electron passes through the lowest unoccupied molecular orbital. The conduction barrier was determined from the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy states. The values of the HOMO-LUMO energy gap of alkyl viologen, which can be obtained from the cyclic-voltammogram characteristics, were found to be in the range of 5.02 ~ 4.86 eV. These values were similar to those obtained from the UV-visible spectra and the AM1 method. As the chain length of alkyl viologen increased, the HOMO-LUMO energy gap decreased. In addition, the positive charge on the aromatic ring lowered the energies of the  $\pi$  levels, while the effect of the positive charge on the alkyl chain decreased with increasing the alkyl chain length.

### INTRODUCTION

Viologens exist in three main oxidation states, namely,  $V^{2+} \leftrightarrow V^+ \leftrightarrow V^0$ . These redox reactions, especially for the first one ( $V^{2+} \leftrightarrow V^+$ ), are highly reversible and can be cycled many times without significant side reactions.<sup>1,2</sup> Mainly because of these desirable characteristics, viologen derivatives have been extensively investigated for applications such as the electron transfer mediation to various biological molecules,<sup>3-5</sup> the surface-enhanced Raman studies of adsorption at electrode surfaces,<sup>6</sup> the behavior of supramolecular assemblies at electrode surfaces,<sup>7-9</sup> and the electrochromic display devices.<sup>10</sup> Those previous studies used viologens with the random orientation or the well-defined molecular order. To clarify the electron transfer mechanism for an alternative approach for

practical applications, many systematic studies with the well-defined molecular arrangements have recently been designed using mainly the following techniques: the self-assembly, the immobilization and Langmuir-Blodgett (LB) transfer of viologen derivatives onto electrode surfaces, and the solubilization of viologens in vesicles.<sup>11</sup>

Viologen derivatives can be used as electron acceptors and mediators. Since L. Michaelis<sup>12</sup> first demonstrated the structure and properties of viologen in 1933, the synthesis procedure of viologen derivatives have been reported extensively elsewhere.<sup>13</sup> In our previous study,<sup>14,15</sup> the electrical (rectification) characteristics of viologen molecules having the thiol group were observed according to changes in energy gaps by the scanning tunneling microscopy (STM) and the cyclic-voltammetry, which have proven as some

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possibilities for a molecular device. These studies also indicated that the energy gaps of organic molecules would be very important in device applications. Under this direction, this study will focus on the investigation of the change in the HOMO-LUMO energy gap of alkyl viologens, ( $C_nVC_n$ ,  $n = 3, 5, 7$  and  $9$ ) with an aromatic ring on the HOMO-LUMO energy gap by comparing with previous experimental results in the literature.<sup>16</sup> In addition, the molecular HOMO-LUMO energy gaps are compared with the bulk properties using the UV-visible spectra, the AM1 calculations, and the cyclic-voltammetry, which is capable of rapidly observing the redox behavior of the molecules over a wide potential range.

## EXPERIMENTAL

### Cyclic-voltammetry

Cyclic voltammogram measurements were carried out using an EG&G PAR (Princeton Applied Research, Model 273) Basic Electrochemical System. The cyclic voltammograms for the solution of ca. 0.25 mM alkyl viologen in 20% dimethylformamide (DMF) and 0.1 M phosphate buffer (pH 7.3) as a supporting electrolyte were studied using a glassy-carbon (GC) working electrode.<sup>17</sup> The surface of the working electrode was polished with a 0.05  $\mu\text{m}$  alumina/water slurry on a felt surface and rinsed with purified water prior to electrochemical experiments. A saturated calomel electrode

(SCE) was chosen as a reference electrode, and a Pt wire was selected as a counter electrode. The solutions were purged using Argon for an hour before scanning the working electrode at a rate of 100 mV/s.

### Optical measurements

The UV-visible spectra of the alkyl viologen films on 1 cm glass substrates were recorded by the UV-visible spectrophotometer (Hewlett-Packard, Model 8453). The data acquisition between 150 and 600 nm was performed with the UV-visible ChemStation program (Agilent Technologies), running under Windows.<sup>18</sup>

### AM1 Calculation

The molecular orbital of alkyl viologen was calculated using the AM1 module. The AM1 is the semiempirical quantum calculation method based on the neglect of differential diatomic overlap integral approximation.<sup>19</sup>

## RESULTS AND DISCUSSION

Fig. 1 shows the molecular structures of the symmetric alkyl viologens ( $C_nVC_n$ ,  $n = 3, 5, 7$ , and  $9$ ) employed in this study. The alkyl chain-lengths of ( $C_3VC_3$ ), ( $C_5VC_5$ ), ( $C_7VC_7$ ), and ( $C_9VC_9$ ) were expected to be 3.85, 6.42, 9.0, and 11.6  $\text{\AA}$ , respectively. The cyclic voltammogram of symmetric alkyl viologens is shown in Fig. 2.

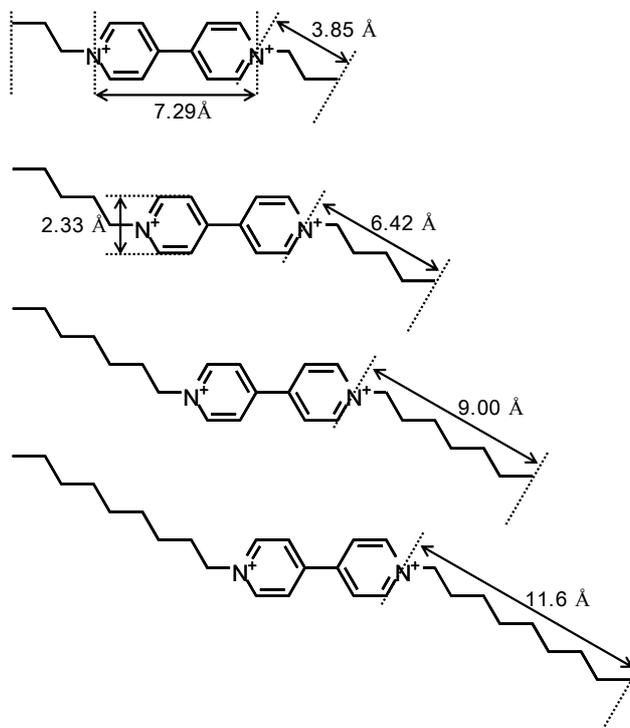


Fig. 1 – Alkyl viologen derivatives used in this study. The alkyl chain lengths of (a), (b), (c), and (d) were expected to be 3.85, 6.42, 9.0, and 11.6  $\text{\AA}$ , respectively.

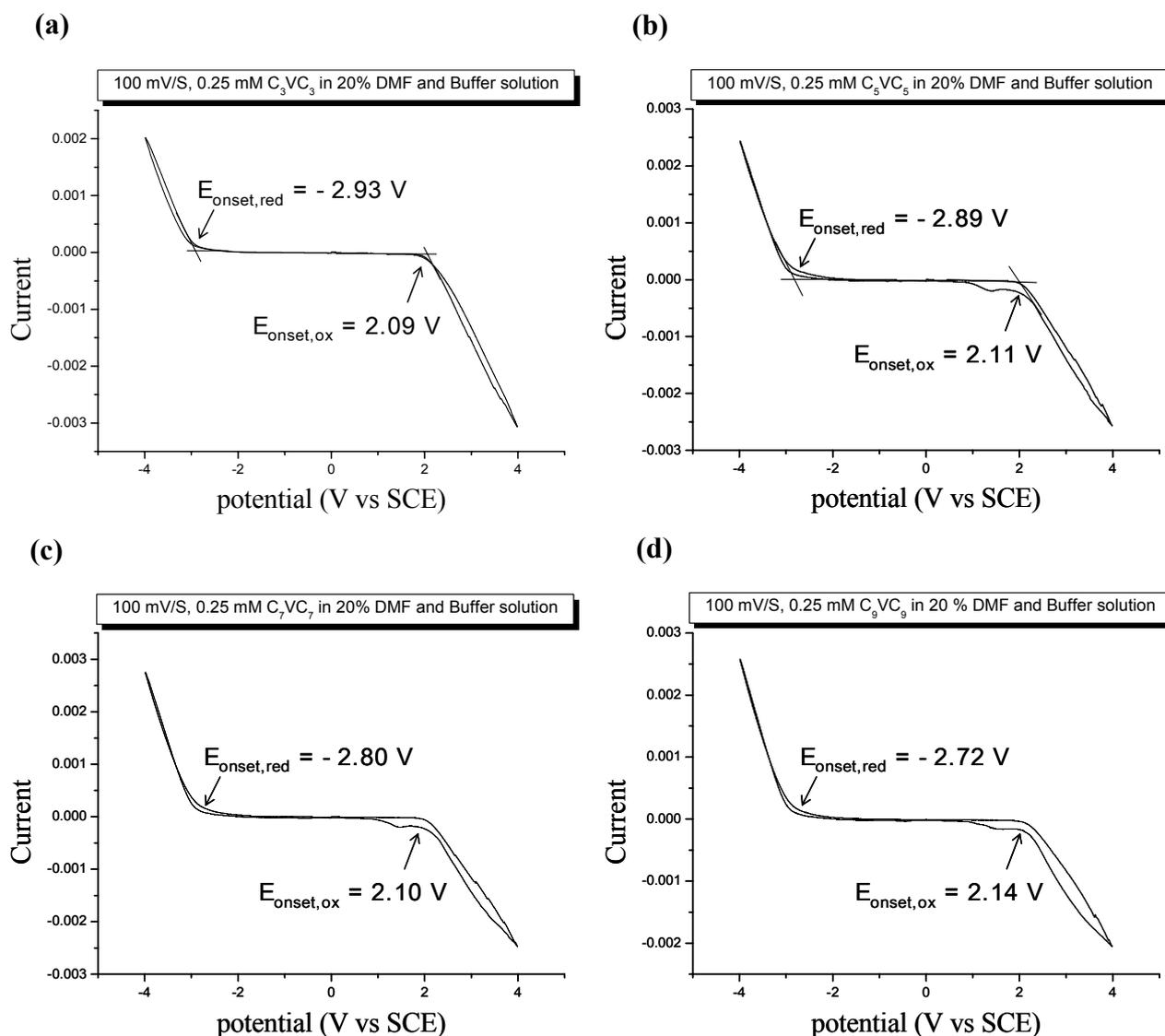


Fig. 2 – The cyclic voltammograms of the symmetrical alkyl viologens. The oxidation (reduction) onset potentials of  $C_3VC_3$ ,  $C_5VC_5$ ,  $C_7VC_7$ , and  $C_9VC_9$  were 2.09 V(-2.93 V), 2.11 V(-2.89 V), 2.10 V(-2.80 V), and 2.14 V(-2.72 V), respectively.

The oxidation and reduction onset potentials of  $C_3VC_3$ , respectively, were 2.09 V and -2.93 V for the SCE standard electrode. In this case the ionization potential and electron affinity obtained from the Hamiltonian calculation and electrochemical method can be expressed as the following equations:

$$I_p = (E_{\text{onset,ox}} + 4.4) \text{ (eV)}, \quad (1)$$

$$E_a = (E_{\text{onset,red}} + 4.4) \text{ (eV)}, \quad (2)$$

where  $I_p$  is the ionization potential,  $E_a$  is electron affinity,  $E_{\text{onset,ox}}$  is the onset potential of oxidation, and  $E_{\text{onset,red}}$  is the onset potential of reduction. In this study, we defined the point where the baseline meets an adjoint line as onset potential as represented in Fig. 2 (a) and (b).<sup>20</sup> The 4.4 eV

constant in the relation between  $I_p$ ,  $E_a$ , and redox potentials arises from the difference in gas phase ionization potentials and electrochemical oxidation potentials of solid films and the solid state polarization energy.<sup>21</sup> Therefore, the HOMO-LUMO energy gap can be calculated by substituting the measured onset potential into Eqs. (1) and (2).<sup>22-25</sup> The HOMO-LUMO energy gap of  $C_3VC_3$ ,  $C_5VC_5$ ,  $C_7VC_7$ , and  $C_9VC_9$  were 5.02, 5.0, 4.9, and 4.86 eV, respectively.

Fig. 3 shows the UV-visible spectra of the symmetric alkyl viologens used in this study. Inset shows the magnified curve of the solid square. The energy gap obtained from the absorption edge of  $C_3VC_3$  is 4.17 eV ( $=1240/\text{onset}$  in eV), which is similar to the value obtained using the

electrochemical method. The HOMO-LUMO energy gaps of  $C_5VC_5$ ,  $C_7VC_7$ , and  $C_9VC_9$  obtained

by the UV-visible spectra were 4.112, 4.07, and 4.05 eV, respectively.

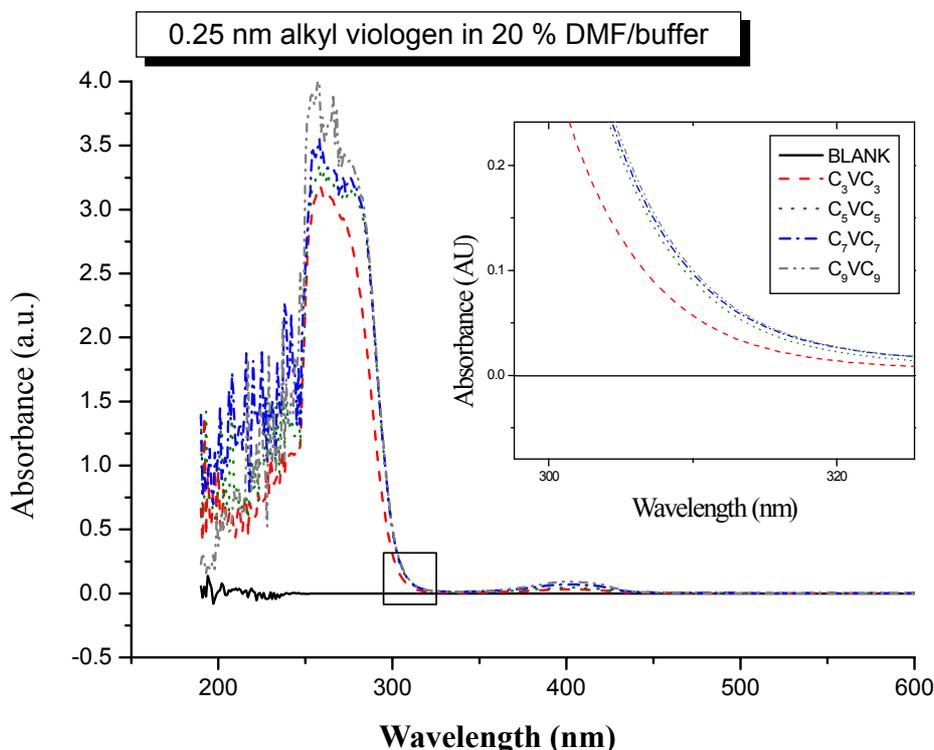


Fig. 3 – The UV-visible spectra of symmetrical alkyl viologens. The energy gaps obtained from the absorption edges of  $C_3VC_3$ ,  $C_5VC_5$ ,  $C_7VC_7$ , and  $C_9VC_9$  were 4.17, 4.112, 4.07, and 4.05 eV, respectively. Inset shows the magnified curve of the solid square.

Fig. 4 illustrates the calculated molecular orbital determined by the AM1 module. The molecular orbitals were measured within the range from HOMO-4 to LUMO+4. The HOMO-LUMO energy gaps of  $C_3VC_3$ ,  $C_5VC_5$ ,  $C_7VC_7$ , and  $C_9VC_9$  were 8.38, 6.78, 5.75, and 5.11 eV, respectively, as calculated by the AM1 module. The HOMO-LUMO energy gap calculated using the AM1 method is slightly higher than the values obtained from the cyclic-voltammetry and the UV-visible spectra. Although the AM1 method marginally overestimate the HOMO-LUMO energy gap in comparison with the experimental values obtained from the cyclic-voltammetry and the UV-visible spectra, these estimates are widely used for qualitative estimations.<sup>26</sup> Table 1 lists the HOMO-LUMO energy gaps measured using three different methods. As the chain length of the alkyl viologen increased, the HOMO-LUMO energy gap decreased. In practice, in the case of the alkane, this gap is known to remain constant at about

~8 eV regardless of the chain length.<sup>27-29</sup> In the case of the alkyl viologen, this suggests that the change in the HOMO-LUMO energy gap can be detected due to the influence of positive charges on the aromatic ring rather than to the influence of the chain length.

It should be worth noting here that the aromatic ring in the alkyl viologen was ionized by +2. In our case of the alkyl viologen molecule, the HOMO and LUMO were located at the side of the alkyl chain and the aromatic ring, respectively. The increasing in the alkyl chain length lessens the decreasing in the energy level of the HOMO, which is caused by the positive charge of the aromatic ring in the alkyl viologen. On the other hands, this effect relatively increases the energy level of the HOMO. Such observations indicate that the HOMO-LUMO gap decreases as the length of the chain increases due to the positive charge in the aromatic ring.

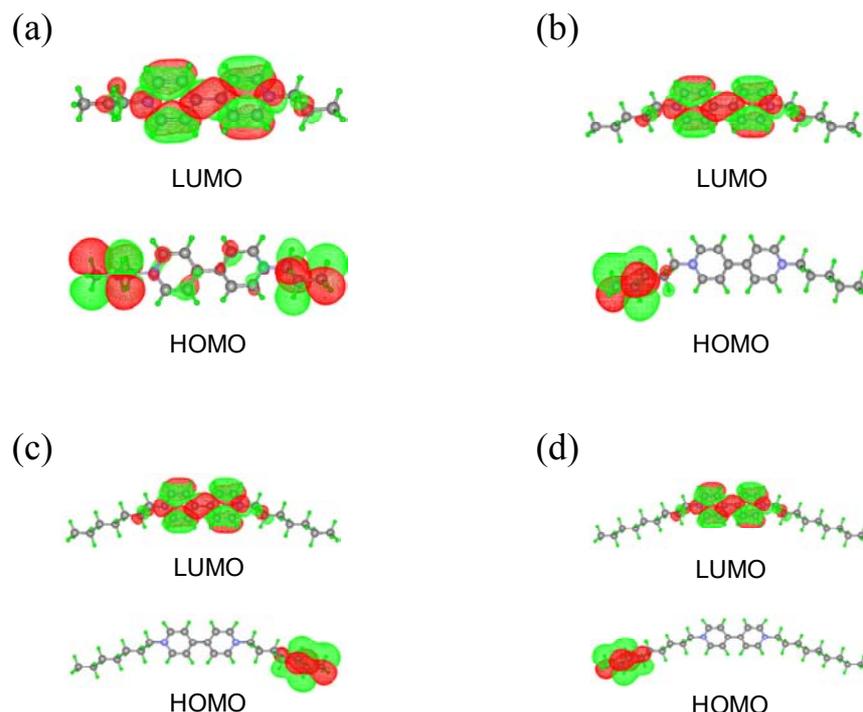


Fig. 4 – Molecular orbitals calculated using the AM1 module. (a)  $C_3VC_3$ , (b)  $C_5VC_5$ , (c)  $C_7VC_7$ , and (d)  $C_9VC_9$ .

Table 1

List of the HOMO-LUMO energy gaps using three different methods

	$C_3VC_3$	$C_5VC_5$	$C_7VC_7$	$C_9VC_9$
cyclic voltammogram	5.02 eV	5.0 eV	4.9 eV	4.86 eV
UV-visible spectra	4.17 eV	4.112 eV	4.07 eV	4.05 eV
AM1	8.38 eV	6.78 eV	5.75 eV	5.11 eV

## CONCLUSION

In this study we report the change in the HOMO-LUMO energy gap with respect to the chain length of alkyl viologens ( $C_nVC_n$ ,  $n = 3, 5, 7$  and  $9$ ) using the cyclic-voltammetry, the UV-visible spectra, and the AM1 calculations. The HOMO-LUMO energy gap values of  $C_3VC_3$ ,  $C_5VC_5$ ,  $C_7VC_7$ , and  $C_9VC_9$  obtained by the cyclic-voltammetry were 5.02, 5.0, 4.9, and 4.86 eV, respectively. The HOMO-LUMO energy gaps of  $C_3VC_3$ ,  $C_5VC_5$ ,  $C_7VC_7$ , and  $C_9VC_9$  obtained using the UV-visible spectra and the AM1 calculation were 4.17(AM1; 8.38), 4.112(AM1; 6.78), 4.07(AM1; 5.75), and 4.05(AM1; 5.11) eV, respectively. The positive charge of the aromatic ring in the alkyl viologen has played an important role in decreasing the HOMO energy level. This effect decreases as the alkyl viologen chain length increases, and the HOMO-LUMO energy gap decreases as the alkyl viologen chain length increases.

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