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〈Research Paper〉

Electrochemical Studies on Heptamethine Cyanine Dyes

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Abstract— Computational calculations of molecular orbital and electrochemical redox/oxidation potentials are of very importance to determine the compound properties. The energy levels of molecular orbital were calculated by the density function theory (DFT) with exchange correction functional of local density approximation (LSA) based on the Perdew-Wang (PWC) setting and cyclic voltammetry.

Keywords: *cyclic voltammetry, molecular modeling, heptamethinecyanine, electrochemical study, redox potential, oxidation potential*

1. Introduction

Recently, cyanines have received much attentions[1-4] to use because those compounds have wide application ranges such as photo-sensitizers, dye lasers, optical recordings and storage media. Herein, heptamethinecyanines being considered in this work are incorporating a cyclohexene ring in the polymethine chain.

This designed heptamethinecyanine compounds can be absorbed in near-infrared ranges as shown in this study[1-8].

The absorbing properties are related to the energy potential levels such as HOMO and LUMO. In this context, HOMO/LUMO energy levels were concerned with the molecular orbital and electron distribution[9,10]. These HOMO and LUMO values are useful for the study of electro-chemistry, because it can be estimated directly by quantum chemistry calculation or indirectly by the redox/oxidation potential determination[11,13]. Reduction potential relates with excited state (LUMO) compounds and oxidation potential relateswith ground state (HOMO).

Using the cyclic voltammetry measurement, we have determined the energy potential of the prepared heptamethinecyanine dyes[14,15]. In this work, we used different moeties of heptamethinecyanine dye molecules[16,22]. One is $(CH_3)_2$, and the other is sulfur atom in benz-X-oline parts and the synthesized dyes were then examined their electrochemical properties and computational calculations.

2. Experimental

2.1 Heptamethine Cyanine Chromophores

The prepared routes were referred to the part of our previous work[23]. This method was shown in Fig. 1.

2.2 Measurements

The spectroscopic characteristics were examined and determined using Agilent 8453 UV-Vis spectrophotometer. The electrochemistry properties of these dyes were examined with a Versa STAT 3 using a platinum wire served as a working electrode, an Ag/Ag^+ electrode served as a reference electrode

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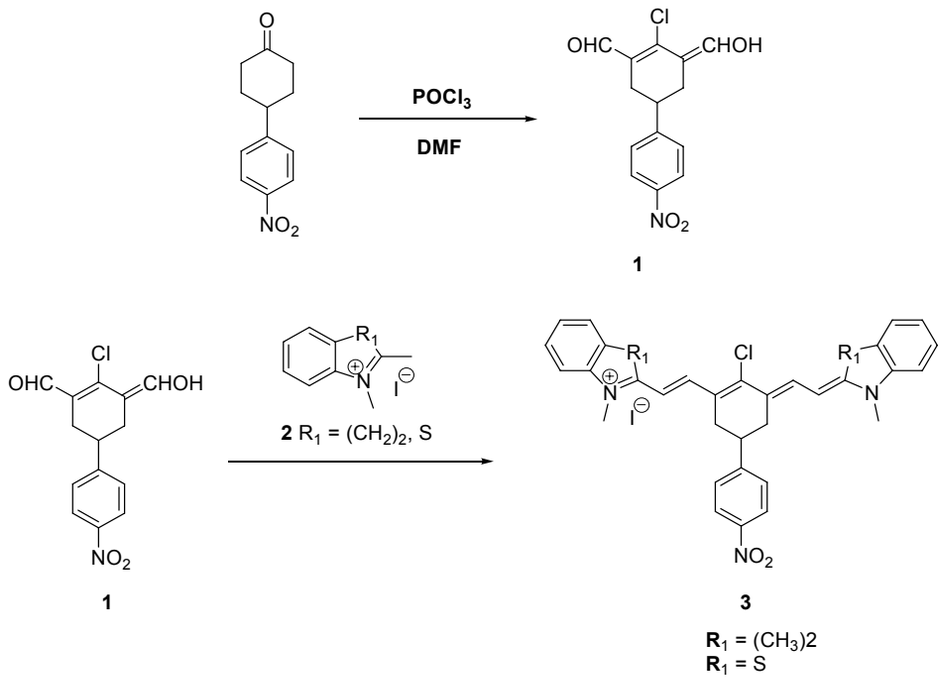


Fig. 1. Synthetic route[23] : Dye 1, R_1= $(CH_3)_2$; Dye 2, R_1= S.

and a carbon served as a counter electrode. The scan rate was 50mV/s. The optimized geometry structure and molecular energy potentials were calculated with Materials studio 4.2.

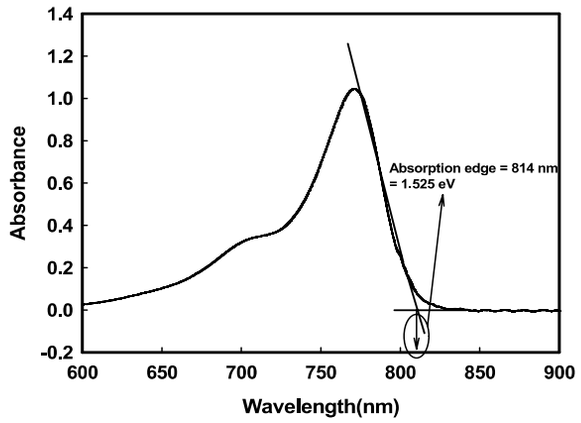
3. Results and Discussion

In this study, we have investigated the effects of different atoms and substituents within heptamethine cyanine dyes structures. We have used the methods of computational calculation and cyclic voltammetry toward the prepared cyanine dyes and compared the obtained data from each dyes. With electrochemical approaches, HOMO and LUMO energy level values were obtained.

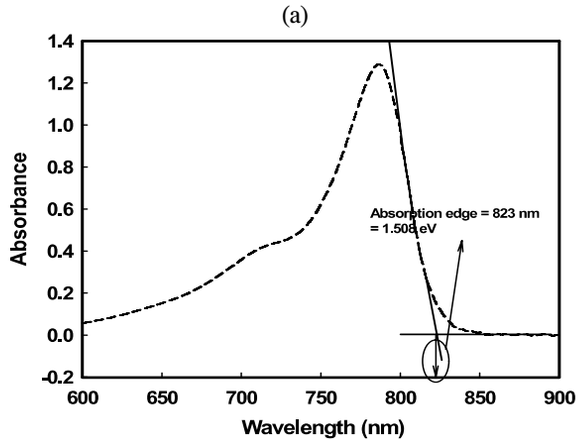
Using these values, we determined and compared the band-gap, Ip and Ea for each dyes. HOMO/LUMO energy levels were concerned with the states of molecular orbitals and electron transition. Thus, these measurements provided useful information and forecast of compounds about electrochemical properties. Band-gap shows the energy levels between HOMO and LUMO, which can be calculated by electrochemical method and UV-Vis absorbance[22] (Fig. 2).

In cyclic voltammetry, there are two consideration factors to determine the HOMO/LUMO energy levels. It can be proposed that one is peak potential and the other is onset potential. But, these two determinations showed a little different values. In this reason, we compared the data together between onset and peak potential, which were compared to the value of UV-Vis band-gap measurement. From the obtained data, onset potential calculation value is closer to the findings from UV-Vis band-gap measurement than peak potential value. This result can be concluded that onset potential calculation is more accurate than peak potential calculation.

Cyclic voltammogram for dye 1 and 2 shows the different potential positions (Fig. 3.). This data represents that different atoms and substituents may influence electrochemical reduction and oxidation behaviors. Using the data, we estimated HOMO /LUMO energy levels for dye 1 and 2. First oxidation (peak or onset potential) was related to HOMO and reduction (peak or onset potential) was related to LUMO. Due to the electro-donating strength, reduction potential was shifted. Weak donating group influenced reduction potential to be more negative values. In contrast, when the electro-donating strength increased, oxidation potential showed peak and onset potential values to be less positive values.

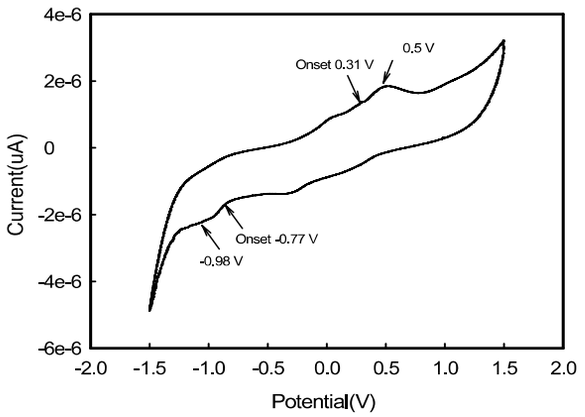


(a)

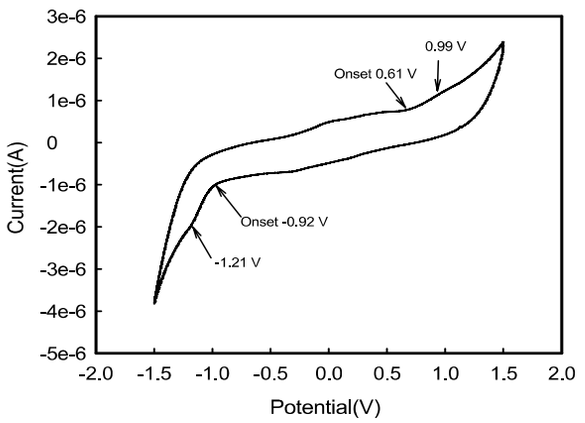


(b)

Fig. 2. UV-Vis band-gap measurements: (a) Dye 1; (b) Dye 2.



(a)



(b)

Fig. 3. Cyclic voltammograms: (a) Dye 1; (b) Dye 2.

Table 1. HOMO/LUMO and band-gap energy potential

	Onset			Peak			Computataional Calculation		
	HOMO	LUMO	△E	HOMO	LUMO	△E	HOMO	LUMO	△E
Dye 1	-4.69 eV	-3.61 eV	1.08 eV	-4.9 eV	-3.4 eV	1.5 eV	-4.927 eV	-3.778 eV	1.149 eV
Dye 2	-4.99 eV	-3.46 eV	1.53 eV	-5.37 eV	-3.17 eV	2.2 eV	-4.880 eV	-3.854 eV	1.026 eV

The following peak potential and onset potential can be calculated by HOMO/LUMO energy levels[22].

HOMO(or LUMO) (eV)

$$= -4.8 - (E_{peak/onset} - E_{1/2(Ferrocene)}) \quad (1)$$

From the calculation, it can be proposed that when compared to the computer simulated calculations, the values from onset potential are closer than the obtaining from peak potential. It gives more clear evidence from onset potential measurement than the data from peak potential method. However, both methods are useful for determination and analysis of electrochemical properties of the prepared dyes.

Table 1 shows HOMO/ LUMO energy levels of the heptamethinecyanine dyes, where the potential energy values by the computationally calculated levels and the electrochemically determined levels are shown. The onset potential energy showed the similar values with the findings of computational calculation and cyclic voltammogram.

Further electrochemical behaviors were calculated using these oxidation and reduction values, namely Ionization potential (I_p, HOMO level) and electron affinity (E_a, LUMO level).

This empirical relationship result has been reported by Bredasetal[24].

Table 2. Electrochemical properties between the Ip and Ea

	E_{red}^{peak}	E_{red}^{onset}	E_a(eV)	E_{ox}^{peak}	Eo_x^{onset}	I_p(eV)
Dye 1	-0.98	-0.77	3.63	0.52	0.23	4.63
Dye 2	-1.21	-0.92	3.48	0.99	0.61	5.01

This report[12] compared the method between valence effective Hamiltonian calculations and experimental electrochemical measurements using formula (2), (3).

$$I_p = (E_{onset.ox} + 4.4)\ eV \quad (2)$$

$$E_a = (E_{onset.red} + 4.4)\ eV \quad (3)$$

Table 2 shows these electrochemical data. Ip and Ea levels were determined from the onset potentials being compared to ferrocene (4.4 eV).

Table 2 shows the relationship between Ip and Ea. Each Ip and Ea values reveals that dye 2 provided stronger electro-donating effect than the structure of dye 1. In this reason, reduction potential of dye 2 was shifted to negative values, and oxidation potential of dye 2 was shifted to positive values.

Fig. 4 shows HOMO/LUMO energy levels and electron distributions of dye 1 and 2. he computational calculations of dye 1 and 2 showed that the electron density distributions were T differently delocalized delocalized from HOMO levels to LUMO levels. The electron populations of methine conjugation bridge in HOMO were moved to nitrophenyl moiety in LUMO for both dye 1 and 2.

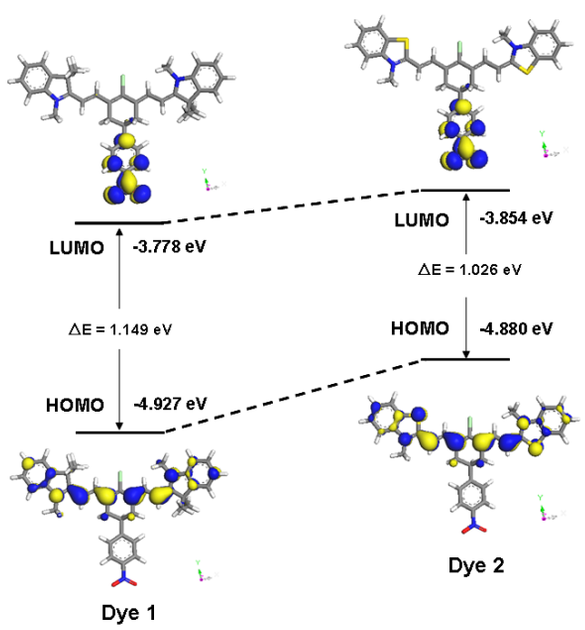


Fig. 4. HOMO/LUMO energy levels and electron distributions.

4. Conclusions

In this study, we investigated the electrochemical properties based on the effects of atoms and substituents in heptamethine dye structure. Herein, one is $(CH_3)_2$, and the other is sulfur atom in benz-X-oline parts and the synthesized dyes were then examined their electrochemical properties and computational calculations. From the findings, experimental data and theoretical calculation values were obtained and its effective approaches were compared to consider more detailed characteristics of the designed dye molecules.

Acknowledgments

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