

Synthesis and Electrochromism of Intermolecular Charge-Transfer Complex Dyes

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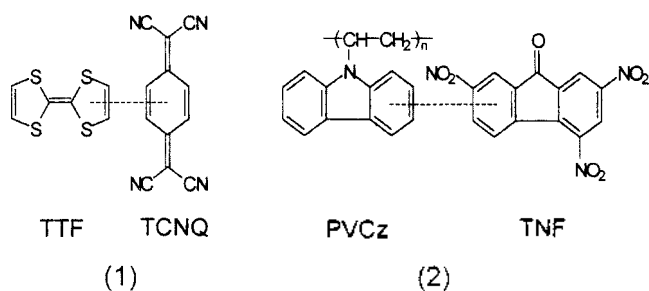
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The charge transfer (CT) complex dyes between electron donor phenothiazine and electron acceptors namely, 2,3-dichloro-1,4-naphthoquinone and 2,3-dichloro-5-nitro-1,4-naphthoquinone, were formed in the dichloromethane solution and electrochromic properties were studied using Bu_4NClO_4 as supporting electrolyte. A 1:1 correspondence between the donor and acceptor molecules in the CT complex was found.

Introduction

As the development of electronic industry, extensive studies of functional organic material have been reported. Especially, the roles of optics in the electronics field become more and more important in the form of the opto-electronics due to their potential applications in displays, imaging devices and energy conservation.¹⁻³ As a light absorbing material, dyes have been used in optical recording media and organic solar cells, on account of their special properties such as photoconductivity, sharp and intense absorption in the visible and/or near infrared regions. These dyes usually contain an intramolecular charge-transfer chromophore, involving a moiety (moieties) such as azo, quinone and cyanine.⁴⁻⁸ In contrast, the intermolecular charge-transfer complex has been studied in organic conductor and organic photoconductor fields. For instance, the intermolecular complex formed between tetrathiafulvalene (TTF) and tetracyano quinodimethane (TCNQ) (1) was found to be useful for organic conductor⁹ and that formed between poly-N-vinylcarbazole (PVCz) and 2,4,7-trinitrofluorenone (TNF) (2) was known for organic photo-conductor^{10,11} (Scheme 1). The examples of using this intermolecular charge transfer complex are rare because this property is not required for typical dyes and pigments.

Although the physical properties of intermolecular charge transfer complex has been studied,⁹⁻¹¹ the electrochromic properties have not been studied, in spite of its possible application as dyes and pigments. In this work, therefore, we synthesized the new type of the intermolecular charge transfer complexes and studied their electrochromic properties.



Scheme 1. The structure of the TTF-TCNQ complex and that of PVCz-TNF complex.

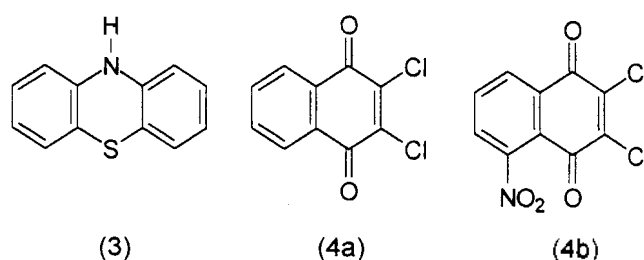
Experimental

Synthesis of 2,3-dichloro-5-nitro-1,4-naphthoquinone (acceptor).

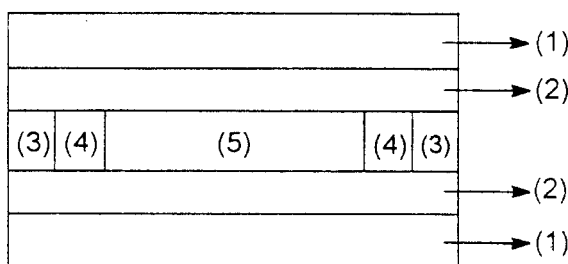
The structure of donor and acceptor are depicted in Scheme 2. The synthesis of the dye 4b was performed by the reported method,¹² which can be summarized as following. The mixture of 2,3-dichloro-1,4-naphthoquinone (0.125 mol), which was purchased from Sigma, and 98% H_2SO_4 (60 g) was mixed at 0 °C, and was stirred for 1 hour. The mixed acid of fuming HNO_3 (d=1.50) 90 g and 98% H_2SO_4 118 g was dropped in to above mixture while the temperature was maintained at 0 °C. After the mixed acid was added, the solution was stirred for 2 hour at 50 °C. Then the solution was poured into the iced-water followed by a precipitation by 10% (w/v) Na_2CO_3 aqueous solution. The precipitate was then washed several times with water and re-dissolved in methylene chlorid. At this stage the product is a mixture of the isomer in which nitro group is substituted at position 5 and 6. These isomer was separated by a Sephadex column using hexane/ethylacetate (3:1 v/v) as an eluate. The dried product was recrystallized by dissolving in the $CHCl_3$ solution and was identified by mass spectrometer (yield 47.6%. Anal: C, 43.85; H, 1.10; N, 5.46; $C_{10}H_3NO_4Cl_2$ requires: C, 44.15; H, 1.11; N, 5.15; mp 173 °C).

Synthesis of the Charge Transfer Complex. The charge transfer complex was prepared by mixing a pair of donor (3, Scheme 2) and acceptor (4a and 4b, Scheme 2), both were dissolved in the dichloromethane solution, then the mixture was stirred for 1 hour at the room temperature.

Continuous Variation Method. This method was



Scheme 2. Molecular structure of the donor and acceptors used in this work.



Scheme 3. ECD cell construction. (1) Slide glass, (2) ITO film, (3) Epoxy resin, (4) PET spacer, (5) Sample

used to find the stoichiometry of the complex formation. The total concentration of the mixture was fixed at 0.05 M (3-4a) and 0.025 M (3-4b) while the relative concentrations of donor and acceptor were varied. The maximum absorbance was observed for the 1:1 molar mixture, indicating one donor molecule forms the complex with an acceptor molecule, *i.e.*, a 1:1 complex was formed.

Preparation of the Electrochromic Display (ECD) Cell. The ECD cell, consisted of two glass sheets (2 cm × 2 cm), was separated by a 0.1 mm spacer of polyester film. The glass sheets were coated on one side with transparent conductive electrodes of indium-tin oxide (ITO) and these sides were placed so as to face each other on the inside of the cell and sealed with an insulating epoxide resin (Scheme 3).

Prior to the final sealing, the space between the electrodes was filled with a dichloromethane solution containing 0.196 mM phenothiazine (3) and the same concentration of either 2,3-dichloro-1,4-naphthoquinone (4a) or 2,3-dichloro-5-nitro-1,4-naphthoquinone (4b) and 1.5 mM of tetrabutylammonium perchlorate as electrolyte.

Electrochromism Measurements. The electrodes of ECD cell were connected to a D.C.-power supply (LG Co, Seoul). The ECD cell was fixed at UV/vis spectrophotometer and absorption was measured while various voltages were applied.

Results and Discussion

Intermolecular Charge Transfer Complex and Absorption Spectra. The absorption band in the visible region of intramolecular charge transfer complex was originated from the electronic transition between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of itself.¹³ In contrast, an electron transfer between the molecules is the reason for the absorption (usually in the visible region) in the intermolecular charge transfer complex. In this study we used the molecule (3) as a donor and (4a) or (4b) as an acceptor (Scheme 2). The reason to choose these sets of the donor-acceptor is that these molecules are known to form a well-behaving charge transfer complex.¹⁴ Furthermore, the molecule (3), (4a) and (4b) does not exhibit any color when are not formed the complex, thus enable us to observe the change in the color clearly (see below).

The absorption spectrum of (3), (4a), (4b) and a charge complex formed between them is compared in Figure 1. The donor (3) and acceptor (4a) do not show an absorption band in the visible region, but the charge transfer complex

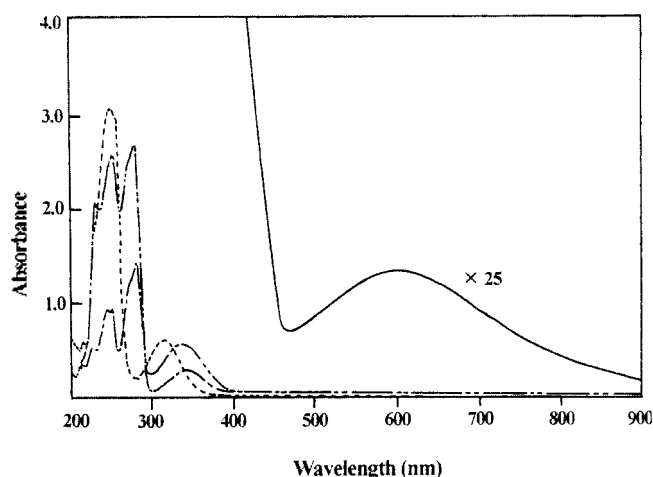


Figure 1. Absorption spectrum of donor (3) (.....), acceptor (4a) (—), (4b) (---) and the 1:1 mixture of (3) and (4a) (— · —). The optical path length was 10 mm.

showed a broad absorption band in the visible region centered about 605 nm, resulting in green color. When a charge transfer was formed between donor (3) and acceptor (4b), a broad absorption band (centered about 700 nm) was apparent and the solution showed a deep-green color (Figure 2). Compared with the complex formed between (3) and (4a), the maximum of the absorption band of the complex formed between (3) and (4b) was red-shifted about 100 nm and somewhat broadened. As it is shown in the above observations, intermolecular charge transfer complex can exhibit various absorption bands, implying a possibility of use of these molecules as pigments and dyes. However, it is worthy of noting that we were not able to obtain any precipitation of above charge transfer complex in spite of their beautiful color.

Stoichiometry of the Complex Formation. The stoichiometry of the complex formation was checked by continuous variation method. The intensities of the absorption band at 605 nm (for the donor (3) and (4a) combination) and 700 nm (for donor (3) and (4b) set) were followed for the mixture with various molar ratio of the respective set of the donor and acceptor, while the total concentrations were

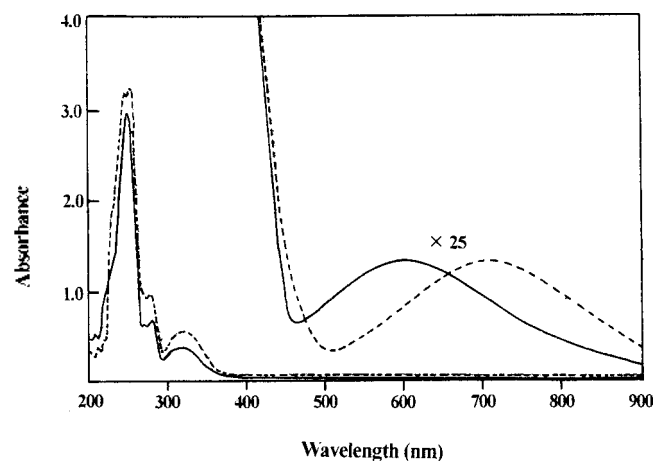


Figure 2. Absorption spectrum of the (3)-(4a) (—) and (3)-(4b) complex (---). The optical path length was 10 mm.

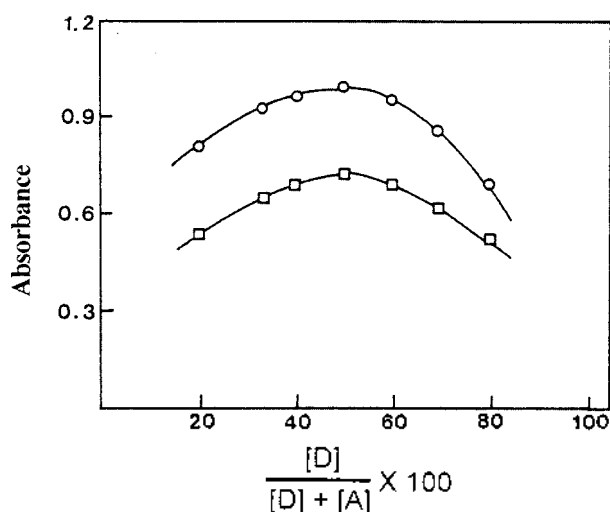


Figure 3. Variation of absorbance with molar percentage of donors. [D] and [A] denote the concentrations of the donor and acceptor. The circles represent the (3)-(4a) mixture and the squares the (3)-(4b) mixture. The total concentration of the former mixture was 0.05 M and latter 0.025 M.

kept constant (0.05 M for the (3) and (4a) set, and 0.025 M for the (3) and (4b) set). The resulting absorbance changes are depicted in Figure 3. Clear maxima in the variation method indicate that a 1 : 1 complex was formed in both cases.

Electrochromic Properties. The electrochromic properties of acceptor (4a) was probed by absorption spectrum (Figure 4). A new absorption band was appeared at 480 nm as voltage of the system is increased to 3.2 volt. This observation led us to propose reduction of (4a). The color of the transparent electrochromic (EC) cell was changed to pale-yellow as voltage was applied. The current change of the EC cell was recorded as the 3.2V of the electricity was applied (Figure 5). It was increased sharply to reach 1500 μA then stabilized at 800 μA after 5 seconds. Figures 6 and 7 show the electrochromic properties and the current change of the $-\text{NO}_2$ which was substituted at acceptor (4b). The electrochromism of the (4a) and (4b)

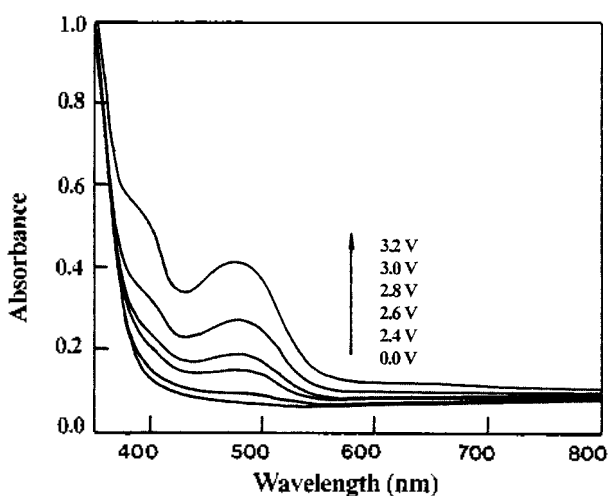


Figure 4. Absorption spectrum of 2,3 dichloro-1,4-naphthoquinone, (4a), as a function of the applied electric field. The concentration was 0.196 mM and the path length was 10 mm.

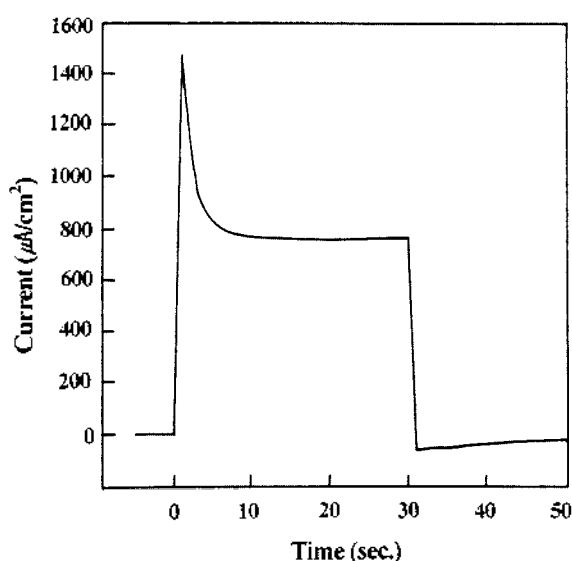


Figure 5. The change in the current with time for 2,3 dichloro-1,4-naphthoquinone, (4a). The 3.2V was applied at the time 0 and turned off at 30 seconds.

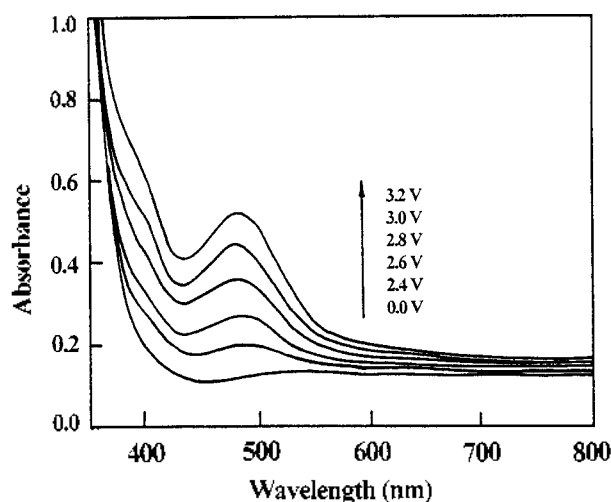


Figure 6. Absorption spectrum of 2,3 dichloro-5-nitro-1,4-naphthoquinone, (4b). The conditions are the same as in Figure 4.

appeared to be similar except for the initial maximum in the current, which was 2000 μA for (4b). Increase in the initial maximum suggests that substituted nitro group of (4b) result in stronger acceptor property compared to (4a). Electrochromism and change in the current was similarly depicted in Figures 8 and 9 for donor phenothiazine ((3), Scheme 2). The initial current reached to 276 μA as applied voltage was 1.9V. The electrochromism and the current change for the charge transfer complex (3)-(4a) and (3)-(4b) are summarized in Figures 10 and 11, respectively. As the voltage was applied, a new absorption band of the complexes (3)-(4a), (3)-(4b) was found in the 400-500 nm region.

In a previous study Lim¹⁵ reported the appearance of similar new absorption band in the 500 nm region for polyvinyl phenothiazine film due to the electric oxidation of the film. Bodea and Silberg¹⁶ suggested that the new absorption band was the results of absorption of methyl phenothiazine radical cation.

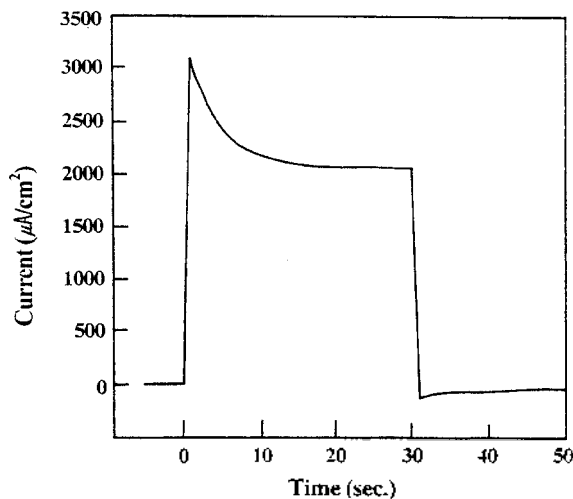


Figure 7. The change in the current with time for 2,3-dichloro-5-nitro-1,4-naphthoquinone, (4b). The 3.2V was applied at the time 0 and turned off at 30 seconds.

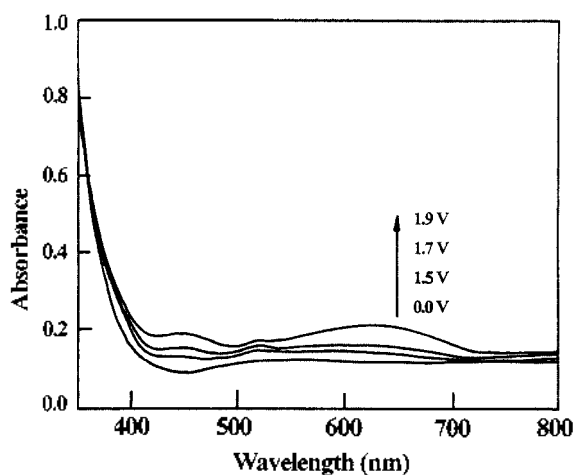


Figure 8. Absorption spectrum of phenothiazine, (3). The conditions are the same as in Figure 4, except for the applied voltage.

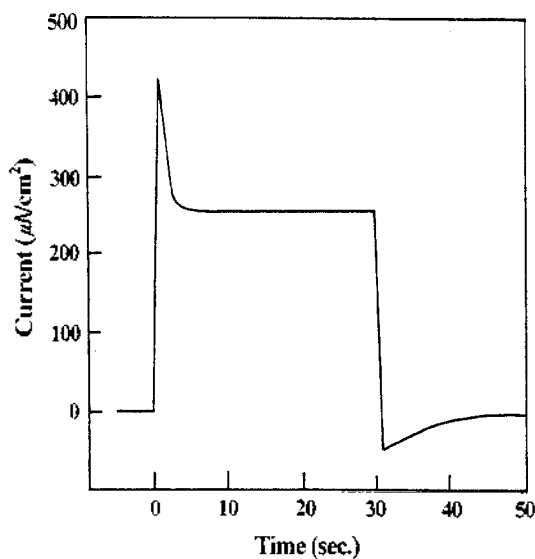


Figure 9. The change in the current with time for phenothiazine, (3). The 1.9V was applied at the time 0 and turned off at 30 seconds.

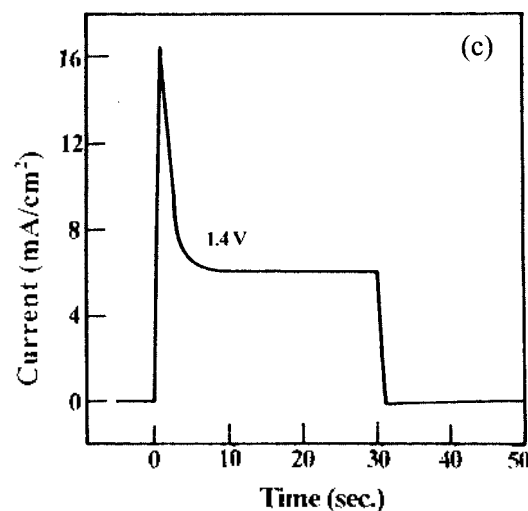
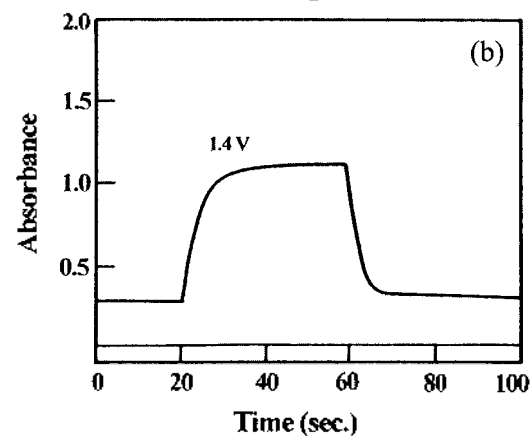
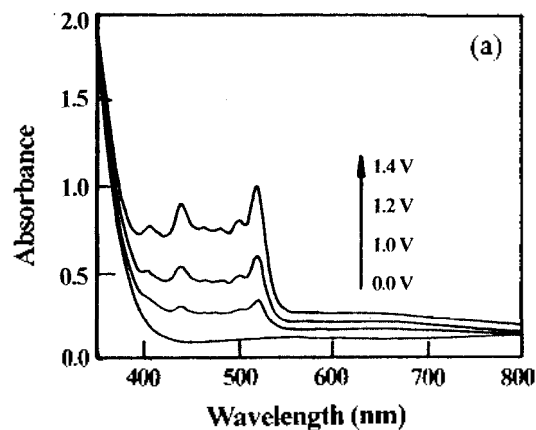


Figure 10. Effect of applied voltage in the absorption pattern (a), change in the absorbance at 510 nm (b), and the current (c). The complex was 1:1 mixture of the 0.098 mM of (3) and (4a).

Similarly, we suggest that the new absorption band appeared in 400-500 nm for both charge transfer complex is due to the formation of radical cation of phenothiazine donor. The formation of phenothiazine cation radical due to the transferring of one electron from donor (3) to one of acceptor with an applying voltage in the charge transfer complex was reported.^{1,8} As a result of applied voltage, the complexes exhibit the change in color in several ten seconds. Furthermore, these opto-electric properties were reproducible after several ten times of electricity application, indicating

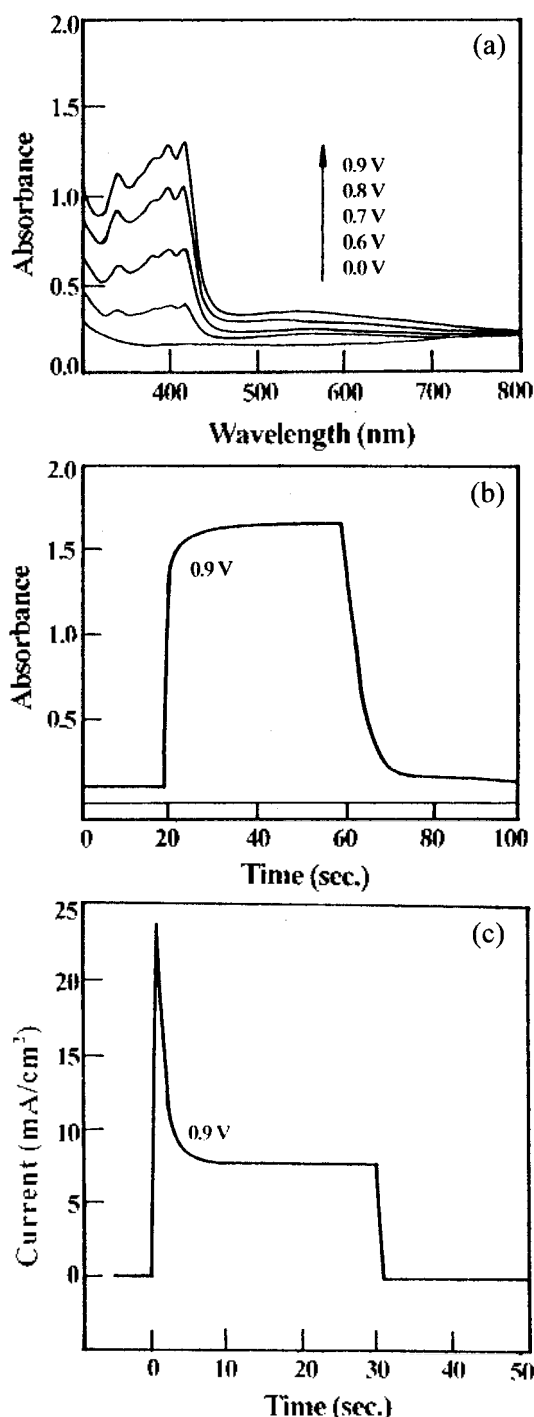


Figure 11. Effect of applied voltage in the absorption pattern (a), change in the absorbance at 510 nm (b), and the current (c). The complex was 1:1 mixture of the 0.098 mM of (3) and (4b).

that the complex is very stable. For the complex formed between (3) and (4a), absorption band of phenothiazine appeared at 400-500 nm with an applying voltage 1.4 volt and disappeared as the voltage was turned off. When the voltage was increased above 1.4V, the absorption band start to decreased and further increasing in the electricy results in the disappearance of the absorption band, indicating the complex was distorted. No reversibility for the complex (3)-(4a) system was observed when the voltage higher than 1.4

volt was applied.

Figure 10(b) shows the change in the absorption intensity at 510 nm with time as the 1.4V of electricity was applied. When the voltage was applied, it represented full color in 15 seconds and the absorption was reduced back to its original state in several seconds. Figure 10(c) shows that the current change with applied voltage of 0.9V for the complex (3)-(4b). After applying the voltage, surprisingly, the current reached at as high as 16 mA/cm² in 5 seconds and reached to 7 mA/cm² afterward. This value is about 10³ times higher compared to that observed from the donor (3) or acceptor (4a) and (4b). The electrochromism of (3)-(4b) (Figure 11) was basically similar to electrochromism of the complex (3)-(4a). The highest voltage of 0.9V, initial maximum of 24 mA/cm² and reversibility of 8 mA/cm² for this complex was observed. The observed 10-100 times higher current upon complex formation in the similar applied voltage indicate that a very small amount of the electricity is required for the similar color effect. This phenomenon can be ascribed to the formation of the charge transfer complex in the solution which enhances the current of the electrons compared to the solutions in which the donor or acceptor exist independently.

Conclusion

The donor and acceptor set, we synthesized here, exhibits an absorption band in the visible region by applying relatively low voltage, resulting in the rich and noble green color. When this color appears, the current of the donor-acceptor mixture was 10-100 times higher compared to donor or acceptor alone, indicating the formation of the charge transfer complex.

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