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Electrochemical and Optical Properties of Aromatic Amine-Based Non-Conjugated Polymers and EC Cells using These Polymer Films

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Electrochemical and optical properties of two different aromatic-amine-based non-conjugated electrochromic polymers(DDP-P, DDB-P) are reported. These polymers have a band gap in a ultraviolet region, and are colorless transparent in their neutral states. DDP-P$^{\cdot +}$ and DDB-P$^{\cdot +}$ absorb light, respectively, in a visible region and in a near-infrared region, and are nitrogen-centered π -bridged mixed-valence compounds characterized by intervalence charge transfer (IV-CT) bands. The electrochemical and optical properties depend on the nitrogen-nitrogen distance correlating the electronic coupling of nitrogen redox centers. EC cells fabricated with these polymer films were confirmed to operate repeatedly by applying driving potentials.

Key words: aromatic-amine-based non-conjugated electrochromic polymers, spin-cast thin film, intervalence charge transfer band, electrochromic devices, conducting polymer-based electrode

1. INTRODUCTION

Electrically conducting polymers such as polythiophene, polypyrrole, polyaniline have been explored as elechtrochromic (EC) materials[1] for windows, antiglare car rear-view mirrors, and display panels, for example. Conducting polymers in their undoped states, however, are almost always colored due to their long conjugation lengths. For window application, the lower transparency in an undoped state turns out to be a drawback. One of the ways to solve the problem is then employing non-conjugated EC polymers with band gaps in a ultraviolet region, and then give an electrochemically-induced absorption in a visible and/or near-IR region.

We then focused attention on non-conjugated electrochromic polymers derived from aromatic amine chromophore units bridged by a non-conjugated unit like an alkyl chain.[2] In this paper, 1) non-conjugated polymers given in Fig.1 are reported, 2) an electrochemically induced absorption band originating from an intervalence charge transfer (IV-CT) are classified into the category suggested by Robin and Day[3], and 3) the polymers are cast to form a thin film on an ITO substrate and confirmed to work as an electrochromic electrode for an EC device.

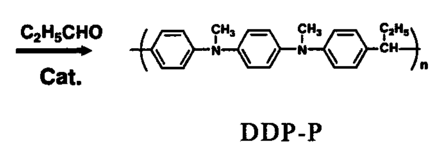
2. EXPERIMENTALS

DDP-P and DDB-P are obtained by polymerizing, respectively, *N,N'*-dimethyl-*N,N'*-diphenyl-1,4-phenylenediamine (DDP) and *N,N'*-dimethyl-*N,N'*-diphenylbenzidine (DDB) with propionaldehyde (P). The synthesis schemes of those polymers are given in Fig.1. The polymers thus synthesized were characterized by GPC and the figures of Mn, Mw, and the ratios of the figures are summarized in Table1.

1.7mass% polymer solution of CH_2Cl_2 was spin-coated to form a thin film on an ITO substrate. A spinning speed in coating was controlled to adjust a thickness of the film on the substrate. Typical film thickness is 500nm.

Table I Molecular weights of the polymers

	Mw	Mn	Mw/Mn
DDP-P	1381	4782	1.92
DDB-P	5578	10739	3.46



DDP-P

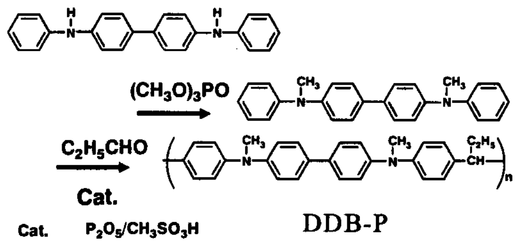


Fig. 1 Synthesis of DDB-P and DDP-P

Cyclic voltammograms of the polymers cast on an ITO substrate were measured in a solution of acetonitrile at a scanning rate of 20mV/s with a potentiostat(EG&G PAR 273). An Ag/Ag+ reference electrode and a platinum plate counter electrode are used in the measurement. Optical absorption spectra of the films were recorded using a spectrophotometer(HITACH U-3300). The spectral resolutions in a visible and near-IR region are 2nm and 8nm, respectively.

3. RESULTS AND DISCUSSION

Cyclic voltammogram(CV)s of DDP-P and DDB-P films are given in Fig. 2. The CV of DDP-P has two redox couple as indicated by "A" and "B" corresponding, respectively, to a reaction of DDP-P^0 → DDP-P$^{\cdot +}$ and DDP-P$^{\cdot +}$ → DDP-P^{++}. That of DDB-P has a similar CV except for a smaller difference in the oxidation potential splitting of the first(A') and second(B') peaks. The potential difference in DDP-P is 440mV, whereas that in DDB-P is 130mV: More energy is needed to extract a charge from the first oxidation state of the materials in which two redox nitrogen centers are more closely located. This fact leads to give a larger potential difference in DDP-P.

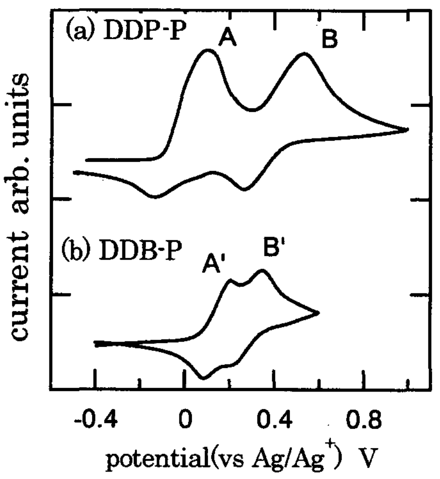


Fig. 2 CVs of DDP-P and DDB-P

Both DDP-P and DDB-P have a band gap in a ultraviolet region, and are colorless transparent in a visible region. Fig.3 shows optical absorption spectra of DDP-P$^{\cdot +}$(blue) and DDB-P$^{\cdot +}$(yellow). The transition wavelength at maximum molar extinction coefficients in the spectra of DDP-P$^{\cdot +}$ and DDB-P$^{\cdot +}$ are 14880 cm^{-1} (672 nm) and, 9058 cm^{-1} (1104 nm), respectively. In one-electron oxidation states, DDP-P$^{\cdot +}$ absorbs light mainly in a visible region, whereas DDB-P$^{\cdot +}$ absorbs light in a near-IR region.

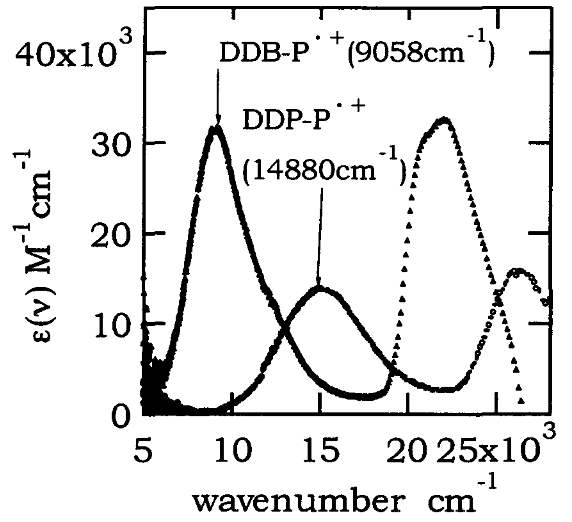


Fig. 3 Absorption spectra of DDP-P$^{\cdot +}$ and DDB-P$^{\cdot +}$

DDP-P$^{\cdot +}$ and DDB-P$^{\cdot +}$ are nitrogen-centered π-bridged mixed-valence compounds showing intervalence charge transfer (IV-CT) bands. The mixed-valence compounds with two redox centers of two nitrogen atoms are classified into three categories, depending on the nitrogen-nitrogen distance closely relating to an electronic coupling strength of redox centers[3].

Class I:	The redox centers are completely localized.
Class II:	The redox centers are intermediately coupled and the electron is partially delocalized.
Class III:	The coupling between the redox centers is strong enough to delocalized the electron completely.

The absorption band shape is well understood by the Hush theory.[4] The parameters characterizing the absorption spectra were estimated using the following equation.

$$V = \frac{0.09584}{er}\sqrt{\nu_{\max}\int \varepsilon(\nu)\, d\nu}$$

The definition of the parameters are shown in Fig.4,where λ is Marcus reorganization energy, V is Hush electronic coupling matrix element, and $\nu_{\max}$ is the wavenumber giving a maximum absorption. The parameters thus obtained are tabulated in Table2. λs are larger than 2Vs in DDP-P and DDB-P, which indicates that these compounds are classified to class II and that DDP-P is located closer at class III than DDB-P.

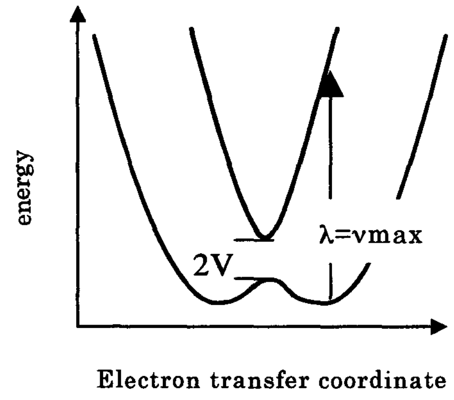


Fig. 4 Potential energy surface for the mixed-valence compounds with two redox centers of two nitrogen atoms.

Table II The parameters of the spectra

	ε_{max}($M^{-1}cm^{-1}$)	λ(cm^{-1})	V(cm^{-1})
DDP-P	13694	4880	4086
DDB-P	31231	9058	2237

Hence, DDP-P $^{\cdot +}$ gives an additional absorption band in a visible region, and DDB-P$^{\cdot +}$ in turn can attenuate light mainly in a near-IR region. These results show that we can tune a position of the absorption band in non-conjugated polymers by selecting appropriate amine derivatives as a unit monomer.

The cross sectional structure of the cell is depicted in Fig. 5. EC cell is composed of the polymer film(500nm) formed on the ITO substrate together with the conducting polymer(CP)-based counter electrode[6], and the gel polymer electrolyte sandwiched in between. The gel polymer electrolyte is a cross-linked methacrylated PEG(20mass%) containing 0.5M Bu_4NBF_4 / γ -GBL(80mass%). The conducting polymer used to form the counter electrode is an electrochemically synthesized poly-3-methylthiophene. The mixture of conducting polymer and a thermal curable binder was screen-printed on a transparent electrical conductive substrate, and then treated at 120℃.

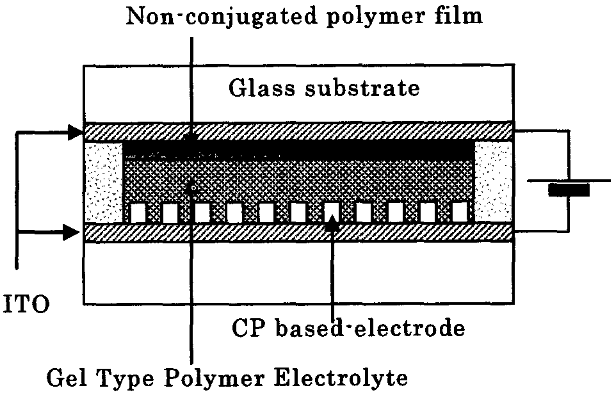


Fig.5 Cross-sectional view of EC

We have confirmed the EC cell to be operated cyclically by applying driving potentials of 1.9V and 0V, respectively, for coloration and bleaching. Fig.6 shows transmittance spectra of the EC cell at two different coloration states.

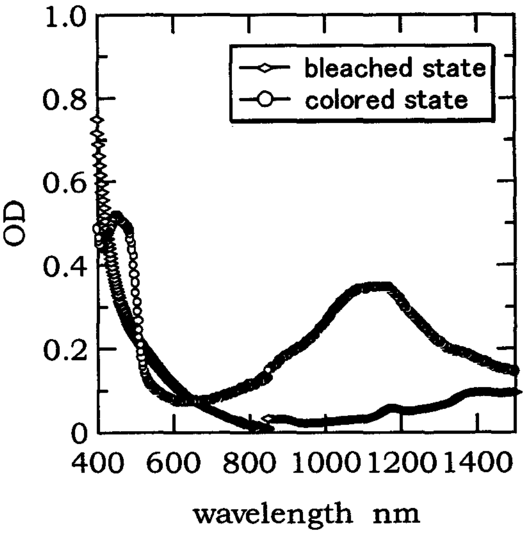


Fig.6 Transmittance spectra of the cell

A large optical modulation in a near-IR region is obtained in the colored state. Differential OD change at 1150nm as a function of operating time is given in Fig.7. The slower switching speed for coloration is due probably to a lower ion diffusion coefficient in the DDB-P film. The switching speed is one of the key parameters of the cell for a display application. For a architectural application, on the other hand, a faster switching speed is desirable but not indispensable.

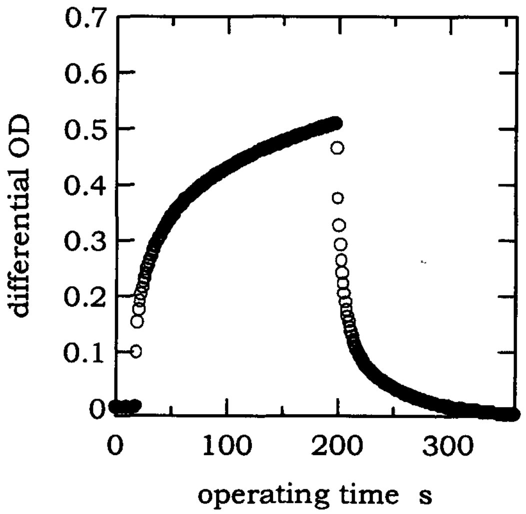


Fig.7 Differential OD change in the cell

λ=1150nm

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