Formation of Specific Charge-transfer Complexes between Hyperbranched Polymer Viologen and Neutral Donors in Solid Films Depending on Donor Fraction

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Neutral donors and hyperbranched polymer with many viologen groups formed charge-transfer complexes in solutions and solid films. The charge-transfer absorption and fluorescence spectra showed red shifts with increasing donor fractions only in the case of polymer solid films, strongly suggesting solvatochromism in solid films and formation of multichromophore CT complex. These are unique microenvironmental effects of the present cationic polymer.

Viologen is a strong electron acceptor, and it forms charge-transfer (CT) complexes with various neutral and ionic donors in the solid state.[1–4] The CT excitation energy can be adjusted by using appropriate hosts such as Zeolite-Y and polycadmium–polycyanide crystal.[5,6] These studies revealed that CT excitation energy for a fixed donor–acceptor pair was drastically affected by the surrounding medium. We now report on the formation of CT complexes between hyperbranched polymer viologen HB-1 and various neutral donors as shown in Figure 1. CT absorption and fluorescence energy were found to depend on the donor fraction in solid films.

We synthesized a new hyperbranched polymer HB-1 with many viologen units which is highly soluble (>20 wt %) in polar organic solvents and can form amorphous film in the solid state. It is well known that the solubility of polymer viologens is low because they are bulky polyelectrolytes.[7] We successfully solved such problem by (i) using organic counter anion in the synthetic route, (ii) introducing adjusted alkoxy chain at each terminal unit, and (iii) introducing the hyperbranched structure. Elemental analysis and ^{1}H NMR supported that HB-1 had a viologen unit as a repeating unit (Figure S1).[8,9]

Mixtures of HB-1 and 9-methylanthracene (MeAnt) as a neutral aromatic donor in acetone solutions gave a new absorption with a peak at 517 nm, which was assigned to CT complex formation. Its stoichiometry was determined by a Job's plot (Figure S2) to clearly show the 1:1 complex formation.[9]

HB-1 and various donors as 1:1 mixtures were then cast on a glass substrate from acetone solutions. Naphthalene (vertical ionization potential $I_p = 8.15$ eV), fluorene (7.93 eV), pyrene (7.41 eV), MeAnt (7.24 eV), *p*-phenylenediamine (7.26 eV), and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (6.75 eV) were used as donors.[10] Figure 2a shows absorption spectra of HB-1 films doped with these donors. New absorption bands were observed in the visible region longer than 400 nm in all films. New shoulders or maxima were located at 419, 434, 485, 538, 595, and 717 nm for donors listed in the order as above. The colors of cast films were light yellow, yellow, orange, purple, deep blue, and green, respectively. CT excitation energy estimated from these absorption shoulders or maxima is plotted against I_p in Figure 2b. The observed CT excitation energy linearly depended on the ionization potential according to the following equation; $h\nu_{CT} = I_p(D) - 5.04$. The CT excitation energy is generally described by Mulliken's correlation; $h\nu_{CT} = I_p(D) - E_a(A) - e^2/R_{AD} - \Delta$,[11] where $h\nu_{CT}$ is the CT excitation energy, $I_p(D)$ is the vertical ionization potential of a donor, $E_a(A)$ is electron affinity of an acceptor, e is elementary charge, R_{AD} is distance between the donor and the acceptor, and Δ is steric repulsion. In the present films, an acceptor is cationic HB-1 and donors are neutral in all cases. Therefore, $E_a(A)$ is constant, and the third and fourth terms can be assumed to be constant. The linear correlation shown in Figure 2b indicates the formation of CT complexes between HB-1 and neutral donors in solid films.

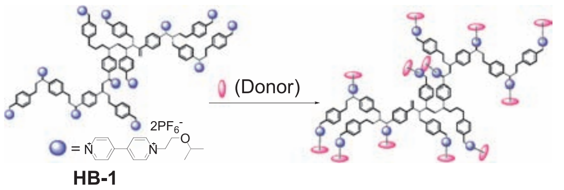

Figure 1. Schematic structure of HB-1 and schematic illustration of a CT complex film.

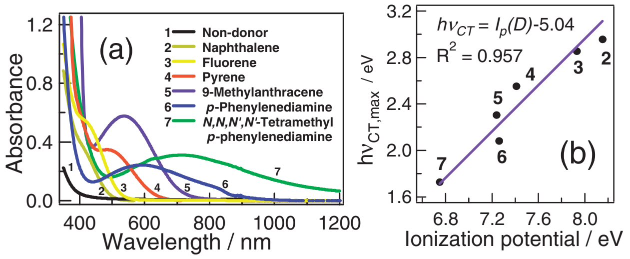

Figure 2. (a) Absorption spectra of HB-1 films doped with various donors. (b) Dependence of CT excitation energy on ionization potential of donors.

To investigate the dependence of CT excitation energy on a molar fraction of donor, absorption spectra were measured by changing the donor fraction. As a model of donor, MeAnt was selected because it showed relatively sharp CT absorption spectrum as in Figure 2a. The molar fraction of donor was changed from 0.05 to 0.87. The results are shown in Figure 3a except the case of 0.87 in which macroscopic phase separation occurred to give an opaque film. The peak wavelength of CT absorption increased as shown in Figure 3b by black circles, i.e., CT excitation energy decreased with increasing molar fraction of MeAnt. To compare this result with those in solid CT complexes between methyl viologen and MeAnt formed in filter papers, reflection spectra were observed by changing the MeAnt fraction (Figure S3).[9] Reflection maxima were observed around 545 nm

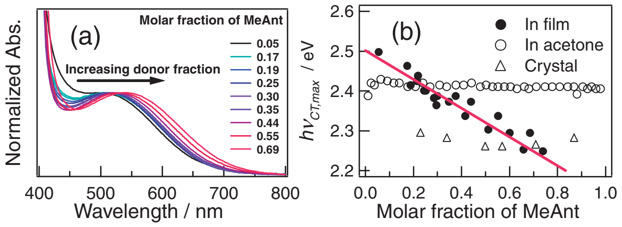

Figure 3. (a) Absorption spectra of MeAnt-doped HB-1 films at several molar fractions. (b) Dependence of CT excitation energy on molar fraction of MeAnt.

for all donor fractions as shown in Figure 3b by white triangles. The CT absorption peak was also constant in solutions of HB-1 (white circles). It should be noted that CT excitation energy decreased with increasing donor fraction only in the case of HB-1 solid polymer films.

IR spectra of HB-1 films doped with MeAnt were measured (Figure S4).[9] No additional peaks characteristic to radical cations of MeAnt were observed.[12] It clearly indicated that the extent of charge separation is very low at the CT ground state. Therefore, dipole moment of the complex in the ground state composed of neutral donor and dication acceptor is larger than those in the excited state.

Among various donors studied, only HB-1 films doped with fluorene showed new fluorescence by exciting the CT absorption band at 435 nm which became larger with increasing donor fractions. Absorption, fluorescence, and excitation spectra of HB-1 films doped with fluorene were measured by changing the donor fraction. Figure 4a shows the excitation and fluorescence spectra of the films. HB-1 alone showed weak fluorescence around 510 nm, which was probably due to thermally or photochemically formed bipyridone derivatives and was difficult to remove because it was a part of the polymer chain.[13] Fluorescence of HB-1 films doped with fluorene excited at 435 nm showed new peaks at 580–600 nm and was much stronger than that of HB-1 alone as shown in Figure 4a. Excitation spectra of fluorescence monitored at 590 nm corresponded well with the CT absorption band. These results strongly suggested that new fluorescence is assigned to CT fluorescence. By subtracting the excitation spectrum of nondoped HB-1 film from those of HB-1 doped with fluorene, CT excitation energy and Stokes shift were evaluated. They are plotted against molar fractions of fluorene in Figure 4b. With increasing donor fractions, CT excitation energy decreased in a similar manner as MeAnt, and the Stokes shift also decreased. The observed Stokes shift will reflect the change of microenvironmental polarity around CT complexes. For the molar fraction of 0.50, an additional shoulder was observed in CT fluorescence around 700 nm.

The following two explanations, i.e., solvatochromism in solid films and formation of multichromophore CT complex, are possible for the decrease of CT excitation energy and Stokes shift with increasing molar fraction of donors in solid films. These CT complexes which have larger dipole moment in the CT ground state show negative solvatochromism as ion-paired CT complexes.[4] The amount of Stokes shift reflects polarity of the surrounding medium. Therefore, decrease of Stokes shift equals decrease in polarity. We can then interpret that CT excitation energy decreased with decreasing polarity of surrounding medium. This behavior is negative solvatochromism in solid films, although the surroundings are not solvent. The negative solvatochromic property of the CT complexes in polar solvents was also confirmed by solvent effect (Figure S6).[9] CT fluorescence around 700 nm suggests formation of multichromophore CT complex between bipyridinium ions (A) and neutral donors (D) such as ADA or ADD types which have smaller CT band gap energy than AD type. CT polycomplex formation was reported for diphenylamine–CBr_4, for example.[14] In contrast to solid films, only the most stable AD type of CT complexes can exist almost independently from each other in solutions or in solid state of small molecules due to lack of confinement effects.

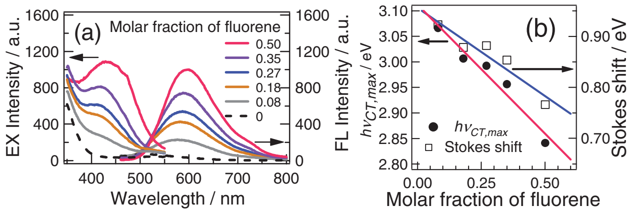

Figure 4. (a) Excitation and fluorescence spectra of fluorene-doped HB-1 films at several molar fractions, $\lambda_{EX} = 435$ nm and $\lambda_{FL} = 590$ nm. (b) Dependence of CT excitation energy and Stokes shift on molar fraction of fluorene in HB-1 films.

In conclusion, CT complexes between hyperbranched polymer viologen HB-1 and various neutral donors were formed in solid films. CT complexes with fluorene gave CT fluorescence. The CT excitation energy and Stokes shift decreased with increasing molar fraction of donor only in the solid films. These results are explained by negative solvatochromism in solid films and formation of multichromophore CT complex. The present results will contribute a great deal to elucidate the microenvironment of cationic polymer films.

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8 The synthesis of **HB-1** will be published elsewhere. **HB-1**; Elemental analysis Calcd(%) for $C_{24}H_{28}N_2OP_2F_{12}$: C 44.32, H 4.34, N 4.31; Found: C 44.05, H4.43, N4.16.
9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
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