Self-Complexation of a Poly-Conjugated Donor Molecule with a Cyclic Acceptor

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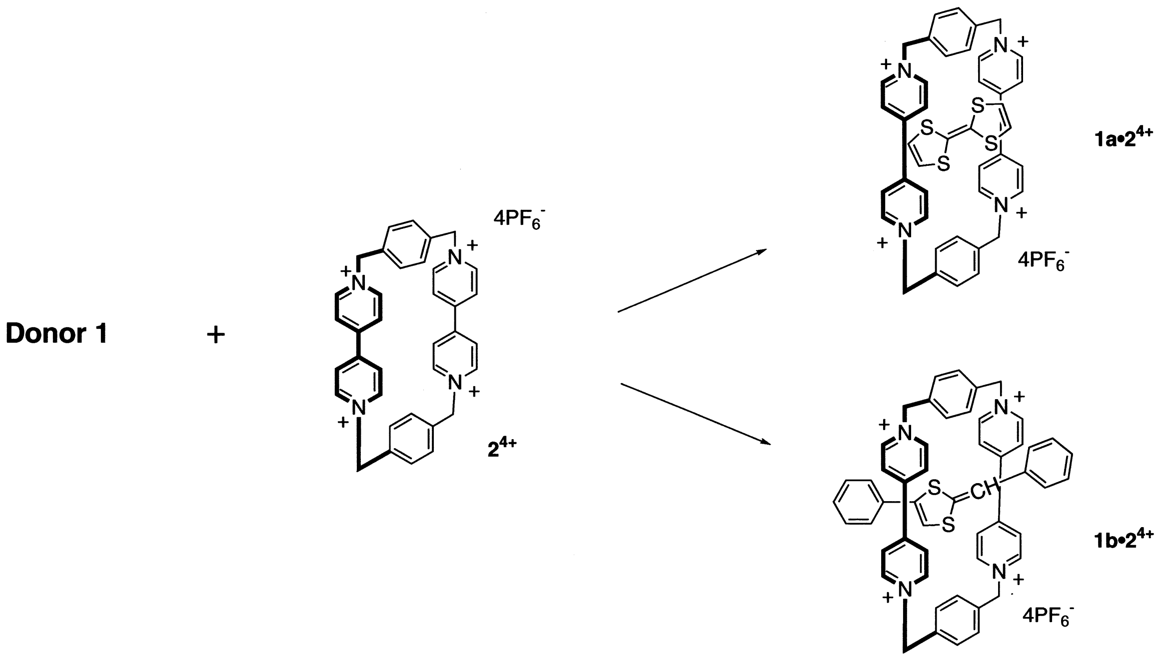
The mixing of 2-benzylidene-4-phenyl-1,3-dithiole and cyclobis[4,4′-bipyridinium-1,1′-diyl-1,4-phenylenebis(methylene)] as a cyclic acceptor in DMSO produced a green-brown solution, which showed a charge-transfer (CT) absorption band with a peak at 616 nm. The ^{1}H NMR spectrum of the dithiole, after adding the cyclic acceptor in DMSO-d_6, showed upfield shifts of the peaks for the dithiafulvene moiety. These facts indicated that an insertion of the dithiole into the cyclic acceptor by a CT interaction led to the formation of a pseudorotaxane. The self-assembly of π-conjugated dithiafulvene polymers and the cyclic acceptor by a CT interaction gave pseudopolyrotaxanes in DMSO. The UV-vis and ^{1}H NMR spectra of the pseudopolyrotaxanes suggest that the incorporation ratio of the cyclic acceptors into the polymers depends on the molecular weights of the polymers. The polymers with lower molecular weights seem to be more favorable for polyrotaxane formation. After self-complexation of the polymer with the cyclic acceptor, an anodic shift of the oxidation potential of the dithiafulvene unit was observed in the cyclic voltammogram. In addition, the effective CT interaction between the dithiafulvene unit and the cyclic acceptor afforded a high conductivity of the pseudopolyrotaxane.

Rotaxanes are molecules constructed by interlocked parts in the shape of one or more wheels that are trapped mechanically on the axle.[1–4] Recently, many of these interlocked compounds have been efficiently prepared as a consequence of the development of synthetic methods.[5–12] On the other hand, π-conjugated polymers have attracted great interest, and a large number of papers about the chemical and physical properties of these compounds have been published so far.[13–15] Nevertheless, the studies focusing on the hybrid systems between rotaxanes and π-conjugated polymers have been very limited.[16–19] The integration of these chemistries could open up new areas of unique and desirable materials, e.g. sensors, switches, molecular devices, and wires.[16,17,19]

The good π-electron donor tetrathiafulvalene (TTF, **1a**) enters the cavity of the cyclic acceptor, cyclobis[4,4′-bipyridinium-1,1′-diyl-1,4-phenylenebis(methylene)] (**2**), to form a strong complex in a pseudorotaxane manner by a charge-transfer (CT) interaction (Scheme 1).[20–23] By using this system in the self-assembly, a number of interlocked and intertwined compounds comprising TTF macrocycles and the cyclic acceptor **2** have been prepared.[24–31] Controllable molecular shuttles and switches based on **1a** and **2** by external stimuli were also reported.[21,28–30] Recently, we have reported π-conjugated polymers with an electron-donating dithiafulvene unit, which is a component of TTF, in the main chain.[32–35] Our poly(dithiafulvene)s could form CT complexes with organic acceptors, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ).[32,34,35] It is hence possible to create self-assembling systems between the poly(dithiafulvene)s and various organic acceptors by CT interaction. Here, we describe a self-complexation of the π-conjugated poly(dithiafulvene) **3** with **2**·4PF$_6^-$ by a CT interaction. There is no precedent for a π-conjugated polymer which can form polyrotaxane by a CT interaction. The construction of superstructures, such as catenanes, rotaxanes, double helixes, and knots, by a CT interaction should offer optical, magnetic, electric, and enhanced conducting properties.

Results and Discussion

Pseudorotaxane Formation of Model Compound. 2-Benzylidene-4-phenyl-1,3-dithiole[32,33](**1b**) was used as a model compound for the π-conjugated poly(dithiafulvene). An admixture of an equimolar proportion of **2**·4PF$_6^-$ and **1b** in DMSO-d_6 instantaneously produced a green-colored solution, which is diagnostic of charge-transfer complexation between the two components (Scheme 1). The ^{1}H NMR spectrum of this sample showed obvious changes in the chemical shifts relative to those for free **1b** and **2**·4PF$_6^-$. The signals for the dithiafulvene protons moved significantly upfield and small shifts of the peaks for **2** were observed (Table 1). In addition, no signals attributed to the free **1b** and **2**·4PF$_6^-$ were observed in this spectrum. These patterns of the chemical shift change indicated that the electron donor **1b** was inserted into the cavity of **2**, creating a 1 : 1 complex as a pseudorotaxane form.[20] The addition of methyl viologen (MV^{2+}·2PF$_6^-$) to the DMSO-d_6 solution of **1b** did not affect the chemical shift of **1b**. This result indicated that **1b** did not interact with the exterior of **2**. The complex [**1b**·**2**][PF$_6^-$]$_4$ in DMSO showed a CT absorption band centered at 616 nm in the UV-vis measurement (Fig. 1). A spectrophotometric dilution analysis[36] was performed on the solution at this wavelength at 25 °C yielded an association constant (K_a) of 51 M^{-1}. The obtained value was lower than that of [TTF(**1a**)·**2**][PF$_6^-$]$_4$ (K_a = 2600 M^{-1} in acetone at 21



Scheme 1.

Table 1. The Chemical Shift of ^{1}H NMR for **1b**, $\mathbf{2}^{4+}$ and [**1b**·**2**][PF_6^-]$_4$ in DMSO-d_6 at Ambient Temperature[a)]

Compound	Benzylidene	Dithiole	Bipyridinium	C_6H_4	$^+NCH_2$
1b	6.79	7.20	—	—	—
2·4PF_6^-	—	—	9.42, 8.63	7.69	5.80
[**1b**·**2**][PF_6^-]$_4$	6.47 (−0.32)	7.03 (−0.17)	9.44, 8.57 (+0.22), (−0.06)	7.76 (+0.07)	5.81 (+0.01)

a) The $\Delta\delta$ values caluculated using the equation, $\Delta\delta = \delta(\text{complex}) - \delta(\text{free})$, were indicated in parentheses.

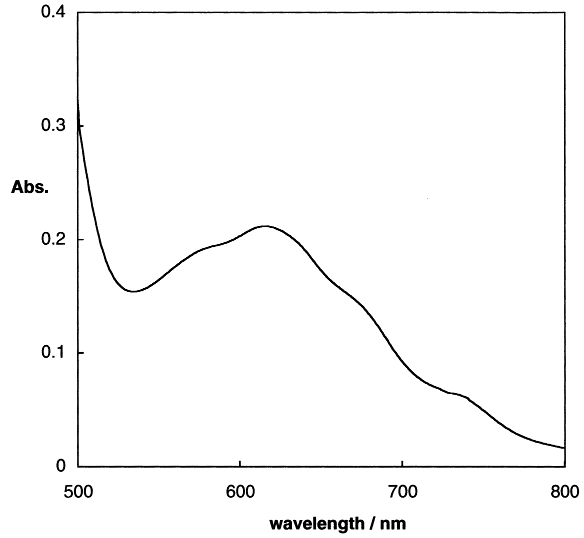
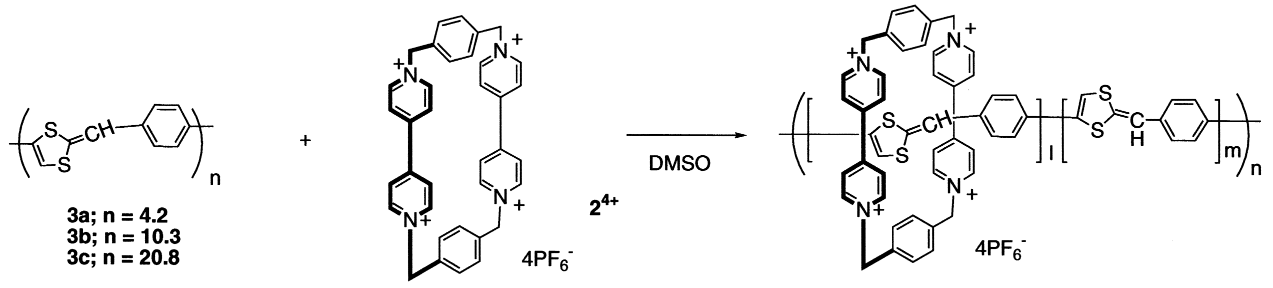


Fig. 1. UV-vis absorption of a pseudorotaxane [**1b**·**2**][PF_6^-]$_4$ (2.0×10^{-5} M) in DMSO.

°C[22]) due to the weaker electron-donating ability of **1b** than that of **1a**.[23]

Preparation of π-Conjugated Pseudopolyrotaxane. The π-conjugated poly(dithiafulvene)s **3** were synthesized by the cycloaddition polymerization of aldothioketene derived from 1,4-diethynylbenzene.[32,33] After the polymerizations were finished, terminal thioketenes were quenched by the addition of piperidine. Three kinds of polymers **3** having different degrees of polymerization (D.P.) were prepared by changing the polymerization times. In the ^{1}H NMR spectra of **3**, a broad signal for the benzylidene proton in the repeating dithiafulvene unit appeared at 6.7 ppm, as well as two broad signals at 4.2 and 3.6 ppm attributed to the terminal thioamide moiety. The D.P. for **3** employed in this system are **3a**; n = 4.2, **3b**; n = 10.3 and **3c**; n = 20.8, respectively, determined by comparisons of the peak intensities in their ^{1}H NMR spectroscopies.[32–35] We investigated the self-assembly of cyclic acceptors **2** and **3** (Scheme 2). When an excess of **2**·4PF_6^- was added to a DMSO-d_6 solution of **3**, an immediate formation of a green solution was observed, similar to the admixture of **1b** and **2**·4PF_6^-. The UV-vis spectrum of the resulting solution showed a CT absorption band ($\lambda_{\max}$ = 614 nm). In the ^{1}H NMR spectrum of the same solution, a new broad signal for the benzylidene proton due to the dithiafulvene unit complexed with **2** appeared at 6.6 ppm (Fig. 2). The signal for the benzylidene proton of the free dithiafulvene moiety remained at



Scheme 2.

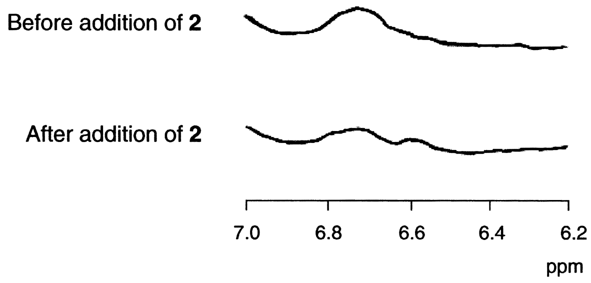


Fig. 2. Partial ^{1}H NMR spectra of **3b** in DMSO-d_6 before and after adding **2**•$4PF_6^-$.

6.7 ppm. These facts indicated a pseudopolyrotaxane formation by the self-assembly of **3** and the cyclic acceptor **2** by the CT interaction.

The UV-vis absorption study demonstrated that the formation of the pseudopolyrotaxane was strongly affected by the molecular weight of **3** at an early stage. Figure 3a shows the absorptions of the poly(dithiafulvene) **3a** with the lowest molecular weight before and 1 minute after the addition of the acceptor **2** in DMSO. The characteristic of the CT absorption band between the dithiafulvene units and **2** appeared clearly after the addition of **2**. However, a DMSO solution of **2** and the polymer **3c** showed a vague CT absorption under the same condition to **3a** (Fig. 3b). This result suggested that the incorporation ratios of the acceptor **2** depended on the molecular weights of **3** at the early stage of the complexing process. The polymers **3** with the lower molecular weights seem to be more favorable for complex formation.

^{1}H NMR was employed for estimations of the incorporation ratios of **2**. For this study, the cyclic acceptor **2**•$4PF_6^-$ (2 mg) and **3** (1 mg) were mixed in DMSO-d_6 (0.5 mL); the resultant solution was then examined by ^{1}H NMR immediately (1 minute after the mixing). Two broad peaks for the benzylidene proton, originated from the free and complexed dithiafulvene units, were observed as mentioned above. Comparisons of their peak areas suggests that the incorporation ratios of **2** in the dithiafulvene moiety of **3a**, **3b** and **3c** were found to be 34, 31, and 16%, respectively (aberrations are ±6%). This fact suggests that the incorporation ratio of **2** depends on the molecular weight of **3** and that low molecular weight polymers are kinetically preferable for the rotaxane formation. The easy 'threading' of **3a** and **3b** resulted from their higher proportion of terminal units compared with **3c**.

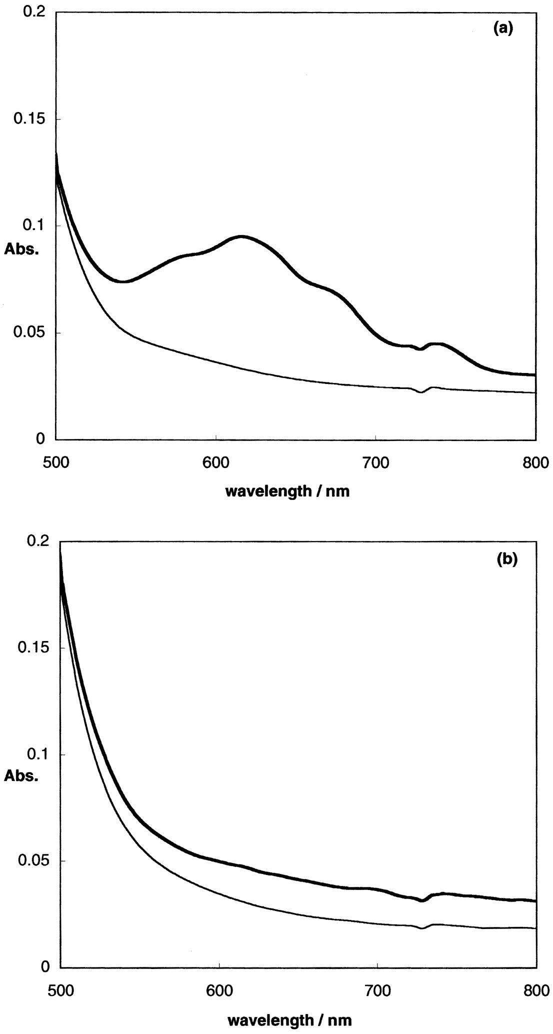


Fig. 3. (a) UV-vis absorptions of free **3a** (1.1×10^{-4} M of the dithiafulvene unit, solid line) and **3a** just after addition of 10 fold excess amount of **2**•$4PF_6^-$ against the dithiafulvene unit of **3a** (time = 1 min, bold line) in DMSO. (b) UV-vis absorptions of **3c** (1.3×10^{-4} M of the dithiafulvene unit, solid line) and **3c** just after addition of 10 fold excess amount of **2**•$4PF_6^-$ against the dithiafulvene unit of **3c** (time = 1 min, bold line) in DMSO.

After mixtures of **2**•$4PF_6^-$ and **3a**–**c** in DMSO were left for 15 minutes, the intensities of the CT absorptions decreased significantly and green precipitates were deposited. The precipitates were characterized by IR and elemental analysis. The IR spectra of the obtained precipitates showed a peak for the dithiafulvene unit in **3a**–**c** at 1575 cm^{-1} as well as a peak for

2·$4PF_6^-$ at 1634 cm^{-1}, indicating that the precipitates were composed of **2** and **3** as rotaxane manners. An elemental analysis of all three precipitates revealed that 24–29% of the repeating dithiafulvene units complexed with **2**. These values were independent of the molecular weight of **3**, suggesting that the settled incorporation ratio of **2** in the precipitated pseudopolyrotaxane was determined thermodynamically.

Properties of the Pseudopolyrotaxane. A pseudopolyrotaxane consisted of **2** and **3b** in a ratio of **2** to the dithiafulvene unit of **3b** = 1:5 was prepared by the accurate addition of **2**·$4PF_6^-$ into a polymer solution in DMSO and continuous evaporation. The redox property of the obtained pseudopolyrotaxane was examined by cyclic voltammetry (CV). In the cyclic voltammogram of the uncomplexed **3b**, an oxidation peak for the dithiafulvene unit appeared at 0.61 V vs Ag/Ag^+.[33] After complexation of **3b** with **2**, the oxidation peak moved to 0.83 V vs Ag/Ag^+ (Fig. 4). A drastic shift of the oxidation potential for the pseudopolyrotaxane originated from the strong electron-withdrawing character of **2**. A shoulder peak appeared at around 0.6 V, resulting from the uncomplexed dithiafulvene moiety of **3b**. Polymer **3b**, containing MV^{2+} (ratio of MV^{2+} to the dithiafulvene unit of **3b** = 1:5), was prepared by the same way as the above-mentioned pseudopolyrotaxane, which showed an oxidation peak at a lower potential (0.72 V vs Ag/Ag^+) than the major peak of the pseudopolyrotaxane (Fig. 4). This indicates that the stronger electron-withdrawing property of **2** than that of MV^{2+} led to the effective CT interaction between **3b** and **2** in the rotaxane formation. The electrical conductivities were measured by the conventional two-probe technique. The pseudopolyrotaxane, consisted of **2** and **3b** (dithiafulvene unit of **3b**:**2** = 5:1), had a conductivity of 7.6×10^{-4} S/cm, while the uncomplexed polymer **3b** and the mixture of **3b** and MV^{2+} (ratio of MV^{2+} to the dithiafulvene unit of **3b** = 1:5) exhibited electrical conductivities of 3.4×10^{-7} and 2.6×10^{-4} S/cm, respectively. The cyclic acceptor **2** itself showed a conductivity of 9.3×10^{-5} S/cm. These results indicated that not only the addition of the ionic compound, such as **2**, but also the effective CT interaction between the dithiafulvene unit of **3b** and **2** afforded the highly improved conductivity of the pseudopolyrotaxane.

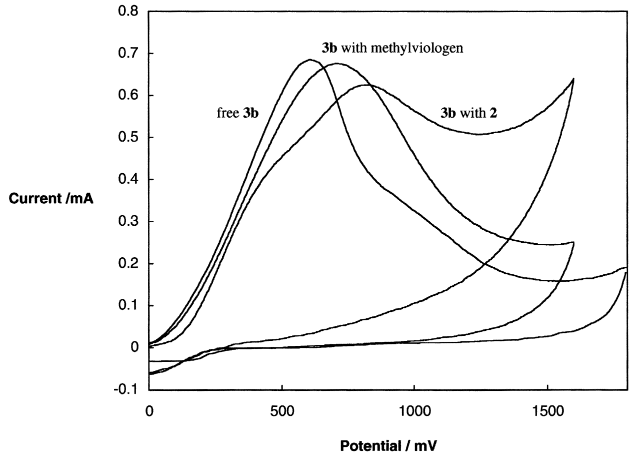


Fig. 4. Cyclic voltammograms of free **3b**, **3b** after the 20% incorporation of methylviologen (MV^{2+}·$2PF_6^-$) against the dithiafulvene unit, and **3b** after the 20% incorporation of **2**·$4PF_6^-$ against the dithiafulvene unit.

Conclusion

We have demonstrated that the electron donating dithiafulvene was inserted into the cavity of the cyclic acceptor **2** creating a 1:1 complex as a pseudorotaxane formation and have created the first pseudopolyrotaxane consisted of the π-conjugated polymer and the macrocycle by the CT interaction. The incorporation ratio of **2** in the polydithiafulvene **3** depended on the molecular weight of **3**. The self-complexation of the polymers **3** and **2** gave rise to the anodic shift of the oxidation potential and the high conductivity of **3**. This system, which is regarded as a semi-conducting pseudopolyrotaxane, will find applications in the macromolecular, supramolecular, and material fields of chemistry.

Experimental

Materials. Unless otherwise stated, all of the reagents and chemicals were obtained from commercial sources and used without further purification. The solvents were dried and distilled under N_2. The synthesis of the dithiafulvene **1b** is described in a previous paper.[33] Cyclobis[4,4′-bipyridinium-1,1′-diyl-1,4-phenylenebis(methylene)] (**2**·$4PF_6^-$) was synthesized according to the literature.[37]

Measurements. ^{1}H NMR spectra were recorded on a JEOL JNM-EX270 spectrometer. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer. For cyclic voltammetry studies, thin polymer films were deposited on an indium-tin-oxide (ITO) coated glass electrode by casting from a DMSO solution. The electrodes were dried under a vacuum. Cyclic voltammetry was carried out with a BAS CV-50W Electrochemical Analyzer. A platinum wire auxiliary electrode and a Ag/AgCl RE-5 reference electrode were used in the CV measurements. The electrical conductivity was measured at room temperature by the two-probe technique using a Keithley 2400 source meter. The polymer films were prepared by dropping DMSO solutions onto glass plates equipped with platinum electrodes, followed by drying in vacuo.

Polymerization. π-Conjugated poly(dithiafulvene)s **3** were synthesized by cycloaddition polymerization.[33] The polymerization reactions were conducted for 0.5 h, 1 h and 3 h to prepare **3a**, **3b** and **3c**, respectively.

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